Controlled Batch Leaching Conditions for Optimal Upgrading of Agricultural Biomass

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ABSTRACT

Agricultural biomass presents a promising feedstock, which may contribute to a transition to low carbon fuels. A significant amount of research has identified a number of challenges when combusting agricultural feedstock, related primarily to energy value, ash, emissions, corrosion and combustion characteristics. The mitigation of such challenges can be addressed more cost effectively when dealing with large or utility scale combustion. The costs associated with harvesting, conversion, transportation and ultimately, market development all create additional roadblocks for the creation of an agricultural biomass industry. Nova Scotia, an Eastern Canadian province, has significant land resources, however it is prone to wet spring and as yet does not have a supply chain established for such an industry. The main components of supply, processing and conversion and demand simply do not yet exist. This research addresses one aspect of this supply chain by attempting to develop a fuel suitable for a) existing markets (local residential wood and wood pellet stoves and b) a scale that will support industry engagement. The outcomes of this research have determined that such a venture is possible and presents empirical preprocessing conditions to achieve a competitive agricultural fuel.

Keywords: Optimal Leaching; Agricultural Biomass; Fuel Design; Ash Reduction

1. Introduction

The drive to reduce Green House Gas (GHG) emissions and increase renewable energy has created an opportunity for alternative sources of biomass fuel or bioenergy, particularly for residual applications [1,2]. The term biomass has historically been used to describe wood based fuel, in either raw or densified form. One common example is the wood pellet, compacted biomass, which results in a homogeneous fuel with better handling and transportation characteristics than wood logs. Most pellets are made from by-products, such as sawdust and ground wood chips, inherent in many primary wood processing operations which help reduce the costs associated with waste disposal. The global pellet industry had an estimated 6 million tons production capacity in 2006, 50% of which originated from Sweden and North America with an additional 1.2 million tons from Canada [3]. This industry has seen steady growth in recent years reaching 28 million tons [4] by 2010.

Agricultural crops and crop residue are relatively untapped energy sources which present an attractive low cost local fuel with potential to augment wood based biomass and to some degree replace a portion of fossil fuels for the production of heat and power [5,6]. In addition, the combustion of agricultural biomass is generally regarded as carbon neutral [7,8] with annual growing cycles. The presence of alkali metals and other inorganic elements inherent in agricultural biomass when combusted creates elevated ash content, 10 to 20 times that of wood pellets, corrosion, slag formation and emissions, all of which may have significant economic or environmental impact and ultimately limit the combustion potential of agricultural biomass [9]. These limitations arise primarily from inorganic elements such as potassium (K) and chlorine (Cl) present in the raw material. K is the largest contributor to ash and slag formation, however alkali metals such as sodium (Na) can also lower the melting temperature of the ash, which causes a greater formation of fused ash known as clinkers [10]. Research conducted by the National Renewable Energy Laboratory (NREL) reports that essentially all biologically occurring alkali material has high mobility, where mobility is defined as the ability of a material to come in contact with other material [11]. This applies especially to K, whose mobility is facilitated by Cl, which acts as a shuttle
transporting K to the surface of the material where the ash compounds are formed. The presence of K and Cl also increases its potential for corrosion [12]. When K is transported to the surface by Cl it tends to form chlorides, hydroxides and sulfates, all of which are significant in the corrosion mechanism [13]. Ca is also commonly found in biomass which forms oxides, and to a lesser extent carbonates, but is less volatile than K and lacks similar corrosion potential [14]. Paulrud et al. also suggested a link between high Si concentrations and ash formation [15]. Combustion of the material comprised of metal oxides and silicon dioxide at temperatures typically in excess of 800°C causes K to react with the silicon-rich substance and form alkali-silicate compounds known as slag [16,17], the composition and strength of which is dependent on the fuel ash composition [18]. Fuels rich in Si and K also contribute to higher levels of deposits on furnace heat exchanger tubes [19], resulting in an increase requirement for boiler maintenance. Fuels with little alkali/silica are reported to produce fewer and more manageable deposits [20,21], however Ogden et al. determined that K will form oxides, hydroxides, chlorides and sulfates which also contribute to slagging and fouling of furnaces [22].

Increasing environmental restrictions mean that combustion analysis of fuels should also consider flue gas and particulate emissions. Biomass combustion releases CO, NO, NO 2 and SO 2 . The presence of N and S create NOx and SOx oxides released through the flue which are classified as harmful emissions [23]. NOx (NO, NO 2 and other oxides of nitrogen) and SOx (SO 2 and other oxides of Sulfur) primarily depend on the nitrogen and sulfur content of the fuel [6]. While wheat straw fuel has relatively low emissions during combustion, wood fuel is typically lower [24]. The vapors from incomplete combustion and fly ash inorganic materials resulting from potassium, sulfur, chlorine and oxygen [25] particles condense to form particulate matter [21], which has been associated with various respiratory and cardiovascular issues [11,26]. It is therefore necessary to reduce the presence of K and Cl in biomass prior to combustion before agricultural biomass can be used as a fuel for residential combustion appliances. While concentrations of carbon, hydrogen and oxygen remain relatively constant in grass biomass, the grasses vary with respect to their ash forming constituents [27]. Biomass composition can be influenced by the management of fertilizers, harvesting techniques, time of harvest and climate, all of which affect the end-composition of the raw material and thus its combustion suitability. Literature suggests that the main mitigation option relates to the solubility of the alkali metals and the potential to avoid the use of Industrial chemicals or complicated processes and simply remove the inorganic materials by in-field leaching.

Leaching periods can range from as little as one week up to a few months, depending on the grass species [22]. Switchgrass performs considerably well if cut in early fall and left over winter to leach, resulting in low ash content and a similar concentration of potassium to that found in wood pellets. Allowing the crop to stand over winter can have similar results, and has proved promising for reed canary grass [27], however in both cases a reduction in biomass yield is experienced, especially in geographical locations that experience wet springs. Hadders and Olsson [19] reported an average loss of 25% in yield due to delayed harvesting.

To avoid yield loss, the biomass could be harvested in fall and the inorganic elements leached in a controlled manner by submerging biomass in water [23,28]. Jenkins et al. [17] showed that soaking or flushing in water has similar effects of in-field leaching, but requires additional drying before it could be milled and further densified. This technique should have less contamination and higher yields than that experienced with in-field leaching. The results of research on leaching of various types of grass biomass strongly support the removal of K and Cl. Si was typically found to increase or decrease slightly, but with high removal of K the slagging tendency will fall accordingly. Tonn et al. [29] investigated the efficacy of leaching of two types of biomass: dry calcareous grass (Mesobromium) and hay meadow (Arrhenatherion). Their work reported an average 63% reduction for K and 82% for Cl after 120 min of leaching, while Si was found to increase by 10% over the same period. Skoulou et al. [30] performed leaching on raw olive kernel biomass and found that alkali and chlorine were “significantly” reduced. Turn et al. [31] leached banagrass for only three (3) minutes, and reported a 90% and approximately 100% reduction of K and Cl respectively. This study also found Si to be the most persistent, with reductions of less than 15%. Jenkins et al. [32] reduced K and Cl concentrations in wheat straw by 81% and 92% respectively, with only 65 mm of natural precipitation. There are potential applications for regions like Nova Scotia to implement controlled leaching. Nova Scotia has sufficient land which could be utilized for energy crop production. The region however typically experiences mild and wet springs which cause significant damage to crops that have not been harvested in the fall or winter. Producers have reported wide variability in crop quality and in some cases lost the harvest completely by delaying harvest until spring. This region would benefit from a process whereby the biomass material is harvested in late fall early winter and a controlled preprocessing leaching method developed that can be implemented over the winter. This paper presents the results of a study to develop such a process. The study investigates the impact of several variables on the modification of four feed-
stocks native to Nova Scotia, which include reed canary grass, barley straw, switchgrass and wheat straw. The input variables include water temperature and residence time with the objective of identifying the optimal conditions for creating an upgraded agricultural biomass feedstock suitable for combustion in residential wood burning appliances.

2. Materials and Methods

2.1. Feedstock for the Experiments

The following experiments were carried out using four feedstock (reed canary and switch grass that represent energy crops, and barley and wheat straw that represent commonly available crop residue). Reed canary grass (Phalaris arundinacea) was collected form a dairy farm near Truro, NS (+45°22'46.3", −63°27'38.6"). Switch grass (Panicum virgatum) was bought from a commercial energy crop grower located in Antigonish, NS (+45°33'40.6", −61°51'9.6"). Wheat (Triticum spp.) and Barley (Hordeum vulgare) were collected from the experimental farm plot of Dalhousie University, Faculty of Agriculture in Truro, NS (+45°22'23.2", −63°15'17.2").

2.2. Experimental Design

A 2 × 3 full factorial design was used for the design of experiments. Leaching experiments were designed to investigate the potential impact of water temperature and residence time in controlled batch leaching or washing of agricultural biomass. Two (2) different residence times and three (3) different water temperatures were selected as experimental variables, to yield six (6) experiments per feedstock for a total of 24 experiments and the experiments have been replicated three times.

In order to obtain a homogeneous sample, for each of the four raw feedstocks, the following process was used. Each feedstock was milled separately using a New Holland 358 hammer mill fitted with a 1/8-inch screen. A few hundred grams of each feedstock was dried in a Fisher Scientific - isotemp programmable muffle furnace at 105°C for 24 hours.

Fifteen (15) grams of each oven-dried feedstock sample was then added to one (1) liter of millipore water in a hot water bath, which was heated to the three experimental temperatures of 20°C, 50°C and 80°C. The temperature was maintained using a Julabo refrigerated and heating circulator. The feedstock samples were manually agitated for five (5) minutes and a circular steel mesh pushed through the top of the beaker to submerge the sample thoroughly in the water. Samples of each feedstock were taken after the two experimental residence times of 6 hours and 24 hours and filtered through whatmann 2 filter paper. The filter samples were oven-dried again at 105°C for 24 hours.

2.3. Analytical Methods

The leached and unleached feedstock once oven-dried, were then ground in a mini-willy mill with a 40 mesh. These ground samples were analyzed for ash, alkali metals (K, Na, Ca, Mg), nitrogen and sulfur. The ash content of each feedstock was analyzed using ASTM E1755-01 (Standard Test Method for Ash in Biomass). Ash content is represented as the mass percentage of residue remaining after dry oxidation at 575°C ± 25°C of the oven-dried sample.

Atomic Absorption Spectroscopy was performed using a Varian SpectrAA 200FS to analyze Potassium (K), Calcium (Ca), Sodium (Na) and Magnesium (Mg). One (1) gram of each feedstock was placed in a porcelain dish and preheated in an electric furnace for approximately 20 minutes. After which the samples were ignited in a muffle furnace at 550°C for at least 6 hours. The ash samples were cooled in a desiccator for at least one (1) hour and 10 ml of 5% HCl added to the dishes. Ten (10) minutes later the dishes were rinsed into a 50 ml volumetric flask through a whatmann 1 filter in a conical funnel. The extracted feedstock samples were then analyzed for alkali metals with the concentration represented in mg/g.

ASTM D4208-13 (Standard Test Method for Total Chlorine in Coal by the Oxygen Bomb Combustion/Ion Selective Electrode Method) was used to analyze total chlorine for each feedstock sample. Total chlorine content in the sample was presented in ppm. LECO-3000 CNS was used to analyze total nitrogen and sulfur, approximately 0.2 grams of each feedstock sample was placed in tin foil, wrapped and loaded in the auto-sampler. The sampler was loaded initially with three blanks and three standards. Additionally, a standard was loaded with a blank every tenth sample.

2.4. Statistical Analysis

The results of the leached feedstock representing each of the experimental variables (time and temperature) were compared to the unleached control feedstock samples presented as % x-reduction, which can be defined as,

\[ \% x \text{ reduction} = \left( \frac{X_{\text{leached}} - X_{\text{unleached}}}{X_{\text{unleached}}} \right) \times 100 \]

% reduction in ash and other elemental concentration was analyzed using central composite full factorial design.

The influence of residence time and water temperature was assessed separately for each feedstock using ANOVA in a full factorial design. Since the analysis contains two factors and one of those factors is time, repeated statement in MIXED procedure of SAS 9.3 (SAS Institute Inc.) was implemented. The following model was used for analysis,
\[ Y_{ijk} = \mu + \alpha_i + \beta_j + \alpha\beta_{ij} + \epsilon_{ijk} \]

where, \( \mu \) = overall mean; \( \alpha_i \) = effect of temperature factor; \( \beta_j \) = effect of time factor; \( \alpha\beta_{ij} \) = interaction effect of temperature and time factor; \( \epsilon_{ijk} \) = overall experimental error.

The statistical assumptions are checked to validate the ANOVA results. When the ANOVA results are significant (if P-value is less than 0.05) for the interaction effect, Tukey’s test (\( \alpha = 0.05 \)) were used to compare the means for different resident time and water temperature combinations. If and only if, the interaction is not significant the significance of the main effect is considered for means comparison.

3. Results

Ash, nitrogen, sulfurs, chlorine and other alkali metals such as potassium, sodium, magnesium and calcium are some of the potential elements that contribute to higher emissions (NO\(_x\), SO\(_2\), and particulate) and other boiler issues (slagging, clinkering and corrosion of boiler heating surfaces). Ultimate analysis and ash analysis on a per oxide basis were carried out on the four unmodified feedstock used for the experiment, the results of which are reported in Tables 1 and 2. These results provide a benchmark from which to determine the relative changes due to the leaching experiment.

The results reported in Tables 1 and 2 show that the overall ash content was lower in switchgrass than the other three feedstock and the potassium (K) and chlorine (Cl) were significantly higher in wheat, barley and reed canary grass than found in switch grass.

3.1. Energy Crop

Switch grass and reed canary grass are purpose-grown.

Table 1. Ultimate analysis for the samples used, expressed as percentage of initial dry mass and chlorine expressed in parts per million (ppm).

<table>
<thead>
<tr>
<th></th>
<th>C %</th>
<th>H %</th>
<th>O %</th>
<th>S %</th>
<th>N %</th>
<th>Cl, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barley</td>
<td>46.50</td>
<td>6.15</td>
<td>45.79</td>
<td>0.24</td>
<td>1.32</td>
<td>2446.2</td>
</tr>
<tr>
<td>Switch Grass</td>
<td>46.00</td>
<td>6.1</td>
<td>46.41</td>
<td>0.28</td>
<td>1.21</td>
<td>888.1</td>
</tr>
<tr>
<td>Wheat</td>
<td>45.53</td>
<td>6.07</td>
<td>47.38</td>
<td>0.3</td>
<td>0.72</td>
<td>5528.5</td>
</tr>
<tr>
<td>Reed Canary</td>
<td>45.00</td>
<td>5.9</td>
<td>47.15</td>
<td>0.31</td>
<td>1.64</td>
<td>2295.5</td>
</tr>
</tbody>
</table>

Table 2. Ash analysis and alkali metal composition for the samples, expressed in milligram per gram of dry sample.

<table>
<thead>
<tr>
<th></th>
<th>Ash</th>
<th>Mg</th>
<th>Ca</th>
<th>K</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/g</td>
<td>mg/g</td>
<td>mg/g</td>
<td>mg/g</td>
<td>mg/g</td>
</tr>
<tr>
<td>Barley</td>
<td>56.63</td>
<td>0.93</td>
<td>3.38</td>
<td>12.14</td>
<td>0.595</td>
</tr>
<tr>
<td>Switch Grass</td>
<td>30.5</td>
<td>1.22</td>
<td>2.6</td>
<td>2.03</td>
<td>0.248</td>
</tr>
<tr>
<td>Wheat</td>
<td>68.73</td>
<td>0.98</td>
<td>2.47</td>
<td>9.76</td>
<td>0.994</td>
</tr>
<tr>
<td>Reed Canary</td>
<td>73.17</td>
<td>1.07</td>
<td>2.47</td>
<td>8.5</td>
<td>0.081</td>
</tr>
</tbody>
</table>

crops used for the production of bio renewable energy. Improving the quality of biomass produced by these energy crops is a key for these to be predominantly used in the energy sector. Leached switch grass and reed canary grass were tested for ash, nitrogen, sulphur and other alkali metals and the data is presented in Table 3.

3.1.1. Switch Grass

Potassium, chlorine, sodium and sulfur had a reduction of 90%, 93%, 75% and 27% respectively, when subjected to a water temperature of 80°C for 24 hours. Whereas, in the case of magnesium and calcium the average reduction of 57% occured at each of the following three conditions of 80°C for 6hours, 50°C for 24hours and 80°C for 24hours residence time.

Nitrogen content in switch grass was reduced by an average 30% with no significant difference between 50°C and 80°C at both 6 and 24 hours resident time. Whereas, the overall ash content reduced by an average 49% at 80°C at both 6hours and 24 hours residence time.

3.1.2. Reed Canary Grass

Reed canary grass had a maximum chlorine reduction of 97% and there was no significant difference between the time and temperature combination. Similarly, the interaction between the two factors was not significantly different for sodium and potassium, which indicates that there was a consistent decrease to a maximum of 92% and 48% respectively in potassium and sodium with increase in temperature and time. When magnesium, calcium, nitrogen and overall ash are considered, reduction was inconsistent. For example, nitrogen decreases with an increase in temperature at 6 hours, whereas nitrogen increased with increase in temperature at 24 hours residence time. However, in the case of sulfur there was a consistent percentage reduction up to a maximum of 28% with time and temperature.

3.2. Agricultural Residue

Abundantly available agricultural residue such as wheat and barley straw could substantially servebioenergy market demands. Unlike energy crops, wheat and barley are primarily grown for their grain yield. This demands the use of fertilizers, which could potentially increase the inorganic element accumulation in these agricultural residues. The fuel properties of leached wheat and barley straw are reported in Table 4.

3.2.1. Barley

Barley had a maximum ash reduction of 75% at 80°C for 24 hour residence time. A consistent reduction of 93% and 92% was observed for potassium and chlorine at 80°C and 24 hours residence time. Whereas, magnesium and calcium had a maximum reduction of 65% and 57%
at 50°C with 24 hours residence time. Sodium and sulfur had a maximum reduction of 77% and 17% at 80°C with both 6 hours and 24 hours residence time. Furthermore, nitrogen reduced by an average 35% at 50°C and 80°C with both 6 hours and 24 hours residence time.

### 3.2.2. Wheat
Similar to barley, the overall ash content reduced to an average of 63% with no significant difference between 80°C at 24 hours, 50°C at 24 hours and 80°C at 6 hours. There was an inconsistent reduction in nitrogen with increase in time and temperature. Whereas, with magnesium and calcium a reduction of 40% was observed for a temperature of 50°C and 24 hours residence time. Unlike other feedstocks, chlorine reduced by up to 93% at 80°C with 6 hours residence time. A reduction of 35% was observed when wheat was subjected to 80°C and 24 hours residence time.

### 3.3. Statistical Interpretation of the Results
Analysis of Variance (ANOVA) was performed on each response (% reduction in Ash, K, Na, Ca, Mg, Cl, N and S) separately for each of the four feedstocks. If the results were significant at 5% (P-value < 0.05), multiple means comparison was performed on the significant interaction else on the main factors. Multiple means comparison is a technique widely used to determine the differences and similarities between the means. A range of means comparison are available, few methods that are predominantly used for are LSD, Tukey-Kramer, Duncan, Scheffe’s method, etc. Tukey-Kramer method at 5% level of significance was used for analyzing the results.

Letter groups (a, b, c, d and so on) at the top of each column in Figure 1 will be used to represent all possible similarities and differences between means. Letter “a”
Figure 1. % reduction in Ash and other inorganic elements with respect to resident time and temperature factor. Treatments within a feedstock with same letters are not significantly different.
may represent a treatment combination or a group of treatment combination with largest mean. Likewise, letter “b” may represent a treatment combination or a group of treatment combination with the second largest mean. The treatment combination with letter group “a” is different for the combination that received a letter group “b”. However, if there is a group of treatment combinations that received the same letter, there is no significant difference between those combinations. If the treatment combination can be further grouped, those means would be grouped with the letters “c”, “d” and so on. A treatment combination may sometime be represented by more than one letter (say “ab”). In such cases, “ab” treatment combination is not significantly different form the treatment combination or a group of treatment combination that received a letter group “a” or “b”.

For example, Figure 1(a) presents a graph—% ash reduction vs. feedstock—resident time with letters grouping for each feedstock.

Let us consider reed canary, which is represented as RC 6 for 6 hours and RC 24 for 24 hours with three columns indicating temperatures. The letters for each treatment combination is given at the top if each column. Treatment combination of 80°C at 6 hours gets letter “a” indicating that it has the largest % reductions in ash. Further, 50°C and 80°C at 24 hours group receives a letter “ab”. Since, all of these treatment combinations has letter “a” there is no significant difference between them (all three treatments combinations reduces ash to the maximum). If the best treatment that offers maximum ash reduction for reed canary was to be chosen among these three treatment combinations mentioned above, other factors such as energy used to subject the feedstock to each treatment combination and the cost associated with it may be considered (i.e. treatment combination that reduces ash to a maximum with low energy use or cost).

4. Conclusions

The research presented in this paper has proven the most efficient method for batch leaching of inorganic material, particularly K and Cl, in switchgrass and wheat straw to be at 50°C for 24 hours. This temperature and time are the most effective, however more moderate conditions may be used depending on the ash content of the unleached material. Previous literature has identified the leaching potential for reduction of these properties, but has not yet determined the effective conditions for performing this leaching. Using the method established in this research, switchgrass and wheat straw can be prepared for combustion with the assurance that inorganic material content has been reduced sufficiently to safeguard against ash production, corrosion, slagging and harmful emissions in residential pellet stoves.

The implications of this knowledge can be used to develop a biomass fuel that, once processed and pelletized or briquetted, can be sold and combusted in residential appliances. This will give farmers an opportunity to assess the value in their natural grasses by either autonomous energy generation (oil and gas independence) or the commercial application of their natural resource. The simplicity of the leaching process lends itself to the possibility of creating a natural grass biomass value chain, with farmers investing in the harvesting, leaching and pelletizing/briquetting of their materials.

REFERENCES


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