Feasibility and Concurrent Remediation of Red Mud as an *in situ* Pyrolysis Catalyst

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Catalytic pyrolysis may serve as an alternative production strategy to petroleum-derived fuels and chemicals. Furthermore, red mud, a toxic industrial bauxite byproduct, could serve as a sustainable catalyst and overcome the need for more robust catalysts. To test this, *in situ* catalytic pyrolysis was run on a semi-pilot scale reactor with various ratios of red mud and switchgrass (*Panicum virgatum*). Authors hypothesized that the coking process would render red mud environmentally friendly, improve soil quality, and yield for bioenergy crop production, like biochar. Therefore, this work investigated red mud's capability to enhance bio-oil quality, as well as, how the modified biochar produced from *in situ* pyrolysis affected switchgrass seedling vigor, and root/shoot mass. The results indicated that red mud was effective at increasing soil pH and biochar and bio-oil yields, while reducing the total acid number in bio-oil. While a high loading of reacted red mud had a negative impact on plant yield, the addition of uncatalyzed biochar to pure red mud considerably improved the seedling yield in marginal soils. These results suggest that this technology has potential for valorizing a waste stream and creating a soil amendment from red mud that closes nutrient and bioenergy production cycles while potentially reducing soil pollution.

**Keywords:** Bioremediation; Red mud; Pyrolysis; In situ catalyst; Bauxite; Bioenergy

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**INTRODUCTION**

Concerns of national security and global climate change pressure scientists, engineers, and policymakers to develop economically viable and ecological renewable fuels. A bio-derived oil that can directly replace gasoline and diesel must have nearly identical chemical and physical properties to conventional oil. These requirements include, but are not limited to, its boiling point, energy density, corrosivity, viscosity, toxicity, and cost (Wahyudi et al. 2017). The magnitude of fuel production, compounded with these strict requirements, defines one of the greatest challenges of today.

Red mud, or bauxite residue, is a well-known industrial waste product generated by the Bayer process during the production of aluminum. This waste stream is generated at a massive scale; for every 1 kg of aluminum produced, there are 2.5 kg to 3.0 kg of red mud created. This equates to 44 million tons of red mud annually produced around the world (Hammond et al. 2013). It is estimated that there are currently 3 billion tons of red mud created annually.
stockpiled worldwide (Elham et al. 2013). Currently, red mud slurries are spread over large fields to dry. Red mud is a highly basic mixture of metal oxides; however, the specific composition varies greatly with the bauxite mineral’s geographic origin. Large scale applications for red mud have been limited, but applications such as utilization as a concrete additive and as a sorbent show promise (Sutar et al. 2014). Furthermore, reserves of red mud are ecologically hazardous, and developing its use as a catalyst could turn this waste into a value-added material.

Pyrolysis, the thermal conversion of biomass under anaerobic conditions, could prove to be a viable strategy to produce fuels and chemicals from non-food crops or lignocellulosic biomass (Sadaka et al. 2014). However, there are many challenges to convert biomass into a petroleum alternative. Bio-oils are typically corrosive, viscous, and unstable, mainly due to oxygenated species such as carboxylic acids, alcohols, and esters. Developing catalysts that are both active towards deoxygenation and selective against carbon-carbon cleavage is a significant challenge when considering the harsh reaction conditions and the complexity of the many possible reaction pathways Catalysts employed today experience rapid deactivation and must constantly be regenerated and replaced, making production costly. To create an economically viable bio-oil, novel catalysts must be very inexpensive and be able to withstand the harsh pyrolysis environment. Recently, researchers have shown red mud to be an effective post-pyrolysis bio-oil (Karimi et al. 2010) and an in situ catalyst (Yathavan and Agblevor, 2014). This technology has the potential to generate revenue from unwanted materials such as both crop and bauxite residues (Liu et al. 2013). However, red mud’s toxicity must be neutralized during pyrolysis for use downstream as a soil amendment.

Red mud’s catalytic ability is not completely understood (Karimi et al. 2010). One study found that the impregnation of acid pre-treated red mud into biomass increased bio-oil yield from 39 to 52 wt% in a fixed bed reactor (Lim et al. 2014). Another study, using a fluidized bed reactor, compared HZSM-5, red mud, and sand as in situ pyrolysis catalysts. The study found that bio-oil created using red mud was seven times less viscous than oil created with sand, while oil created with HZSM-5 was only three times less viscous. Furthermore, previous work suggests that red mud favored the production of CO2 over CO, whereas HZSM-5, a more active catalyst, favored CO production (Yathavan and Agblevor 2014). This result led to greater carbon retention in red mud catalyzed bio-oil. Physicochemical properties suggest red mud outperforms HZSM-5, indicating that utilizing red mud as an in situ catalyst deserves further exploration.

While bio-oil has the potential to be a valuable source of energy, biochar, a coproduct of pyrolysis, is also potentially valuable. Biochar has been shown to improve soil quality, sequester carbon, and act as a sorbent for environmental toxins (Mohan et al. 2007; Sadaka et al. 2014). Specifically, red mud could be rendered less toxic due to carbonization. Considering that it has been proposed that the coking process lowers the red mud pH and makes potentially harmful metals (such as sodium and heavy metals) less bioavailable. This modified biochar could enhance soil properties for agricultural production such as cation exchange capacity, as seen in many agronomic biochar studies (Ashworth et al. 2014). For this novel catalytic reaction to be industrially viable, red mud should be rendered environmentally benign. If this modified biochar is valuable, then two revenue streams could be realized from remediating an immense waste stream. Hence, this study investigated red mud as an in situ catalyst on a semi-pilot-scale pyrolysis reactor. Switchgrass, the biomass feedstock, was pre-mixed with various loadings of red mud to investigate its catalytic effect. The resulting biochars were tested as soil additives to
evaluate the potential plant toxicity that occurred in pyrolyzed red mud and determine its potential end-use as a soil amendment.

**EXPERIMENTAL**

**Materials**

The bauxite residue used in this study was generously supplied by Alcoa Inc. (Point Comfort, TX, USA). Red mud is a highly basic mixture of metal oxides; however, the specific composition varies greatly with the bauxite mineral’s geographic origin. The most abundant metals present in our material in approximate weight ration were as follows: 45 Fe$_3$O$_4$ : 25 Al$_2$O$_3$ : 11 SiO$_2$ : 8 TiO$_2$ : 5 CaO : 5 NaOH. The material was dried for 24 h at 106 °C, and then crushed with a Wiley soil crusher (Thomas Scientific, Swedesboro, NJ, USA) and sieved to a particle size between 180 μm and 850 μm. The switchgrass (*Panicum virgatum*) biomass was supplied by Genera Energy Inc. (Vonore, TN, USA) and was air-dried, ground to a particle size of less than 2 mm, and had a moisture content of approximately 16 wt%.

**Methods**

*In-situ* catalytic pyrolysis of switchgrass

*In-situ* catalytic pyrolysis was conducted at the Center for Renewable Carbon in Knoxville, TN, USA. The semi-pilot-scale auger pyrolysis system used in the study was equipped with a feeding system, an auger pyrolysis reactor, a biochar collector, a particle-precipitating chamber, and a condensation section (Fig. 1). A detailed description of the pyrolysis system is provided in Kim et al. (2011). Four loadings of red mud were used in this study, and the red mud (RM): switchgrass (SG) mass-based ratios were as follows: 0:1, 1:5, 1:1, and 3:1. Uncatalyzed pyrolysis (0:1) was used as a control. Feedstock mixtures were subjected to the same continuous operation conditions in the auger pyrolysis reactor. Feedstock mixtures were transported from the feeding hopper to the auger by a single screw auger with a feeding rate of approximately 8.5 kg/h. The auger reactor (250 cm × 10 cm × 10 cm) contained internal dual augers. The auger speed controlled the residence time of feedstock at 72 s. The heated zone comprised of a 200-cm-long electrical resistance furnace system with an operating temperature of 500 °C. The sweeping gas (nitrogen gas, 20 L/min) was introduced to the auger reactor and moved with evolving vapors to the condensation section. Before vapors entered the condensers, the particle chamber (20 cm in diameter and 100 cm in length) precipitated fine particles from the vapors. The biochar produced from the feedstock was collected into the biochar drum. The condensation section was comprised of three condensers (10 cm in diameter and 200 cm in length) (Fig. 1). Before pyrolysis, all condensers were cooled to 10 °C to 15 °C using a circulation water cooling system. Bio-oils collected from the three condensers were immediately combined and mixed for homogeneity and frozen at -20 °C until their characterization. The methods used for calculating the aqueous modified total acid number (AMTAN) and the component analysis are reported in Connatser et al. (2014).
Germination and growth of switchgrass from biochar amended soil

A switchgrass establishment and growth study were conducted over six weeks at the East Tennessee AgResearch and Education Center in Knoxville, TN, USA. Switchgrass cv. Alamo was planted into a local soil (Etowah series; Fine-loamy, siliceous, semiactive, and thermic Typic Paleudults) of a known texture (silt loam) that had been autoclaved to 250 °C for 48 h to kill any pathogens, or beneficial bacteria. Biochars produced from the pyrolysis experiment were mixed into the aforementioned marginal soil at two rates (10 wt% and 20 wt%). Germination was counted every week. After the sixth week, the shoots and roots were harvested. The plant material was washed, weighed, and oven-dried for 4 h at 105 °C, and then re-weighed. The dried root and shoot material was sent to The University of Tennessee Soil, Plant and Pest Center (Nashville, TN, USA) for elemental plant tissue analysis to investigate the uptake of various elements.

Scanning electron microscopy (SEM) images

Scanning electron microscopy images were collected of the pyrolyzed biochar with different loadings of red mud. The samples were adsorbed to adhesive carbon tape on an aluminum stub. Micromorphology images of the biochar samples were observed by using a SEM system (Zeiss Auriga; Carl Zeiss NTS, Oberkochen, Germany). Morphology images were taken at a 250× magnification and 100 µm distance from the imaging sensor.

Statistical analysis

The germination and yield data were analyzed using two separate analyses to determine the soil amendment treatment (i.e., biochar and red mud combinations) impact on seedling emergence and vigor. The first analysis assessed week-4 germination results in a one-factor randomized complete block design. In this analysis, soil amendment was considered a fixed effect with replication assumed to be random. The second analysis tested dependent variables (i.e., root and shoot yield (pot⁻¹), root and shoot yield (plant⁻¹), and the root/shoot ratio) in a one-factor randomized complete block design, with replication at a random effect. Analysis of variance tests were performed using the Mixed program (SAS v.9.3, SAS Institute, Cary, NC, USA) for both of the aforementioned models. When the main effect differences were found, mean separations were performed by the SAS macro.
‘pdmix800’ (Saxton 1998) utilizing Fisher’s least significant difference with a Type I error rate of 5%. For all models, the Shapiro-Wilks test was used to test for normally distributed residuals, and the Levene’s F-test was used to test the homogeneity of the variances.

RESULTS AND DISCUSSION

**In-situ Catalytic Pyrolysis of Switchgrass**

The addition of red mud to switchgrass feedstock had dramatic effects on the yield of biochar, oil, and gas (Fig. 2). Generally, bio-oil and biochar yields were enhanced with an increased loading of red mud. The mass of the char does not include the mass of the red mud; however, the oil may contain some fine particles of red mud that were not accounted for in the mass yield. Gas wt% was estimated by the difference in total mass (i.e., 100 - oil wt% - char wt% = gas wt%). In general, as the ratio of red mud to switchgrass increased, less of the paracrystalline visible secondary cell wall was present along with greater degradation. This observation was likely due to a greater presence of heavy metals (Fig. 3). Porous structures and spaces between agglomerates were similar to previous SEM images evaluating red mud as a catalyst for biodiesel production (Wahyudi et al. 2017).

![Graph showing yield of biochar, oil, and gas](image)

**Fig. 2.** The proportion of biochar, liquid, and gas yield using various red mud (RM) loadings in the switchgrass (SG) feedstock, determined by mass; *Gas was derived by difference.*
Fig. 3. SEM images of switchgrass biochar particles taken at approximately $85\times$ and $250\times$ magnification; the material was pyrolyzed under an auger style pyrolysis reactor and mixed at various red mud to switchgrass ratios: 0:1 (a), 1:1 (b), 3:1 (c), and 5:1 (d).

Biochar analytical results are shown in Table 1. The chemical and physical properties of the bio-oil were affected by the red mud’s presence during pyrolysis. The pH of bio-oil increased from 2.7 to 4.3 as well as the AMTAN from 75 to 39 when comparing the uncatalyzed to the catalyzed reaction with the highest loading (3:1; RM:SG). This reflected a greater reaction with the presence of red mud. This trend was similar to acetol, as greater loadings resulted in reduced levels compared to the ‘no catalyst’ (Fig. 4). Bio-oil water content dramatically increased with the addition of red mud, which was likely due to the decarboxylation of oxygenate species (Fig. 4). This was also observed in a batch laboratory-scale pressure reactor, wherein the use of red mud as a catalyst created bio-oil with fewer carbonyl-containing and oxygenated compounds, but more saturated hydrocarbons (Karimi et al. 2010). This was related to its ability to catalyze both deoxygenation and cracking reactions (Karimi et al. 2010).

The C/H ratio decreased as a result of the presence of red mud. The bio-oil heat of combustion was not severely changed by the addition of red mud, but was actually lowered due to its addition (Table 1). The heat of combustion has been corrected to account for the higher water content. These results illustrate no compelling trends that point to a specific activity level and/or mechanism of red mud as a catalyst. However, the results do suggest similarities between low red mud to switchgrass ratios (0:1 and 1:5 RM:SG) and their marked contrast with higher red mud to switchgrass ratios (1:1 and 3:1 RM:SG). Previous work suggests that the main cause of red mud catalyst deactivation is from obstruction of activation sites by contaminants, which can effectively improve the properties and increase catalytic activity (Wahyudi et al. 2017).
Fig. 4. Component analysis of acetol (A) and other oxygenates (B) of bio-oils produced from the different red mud and switchgrass loadings.
Table 1. Bio-oil Properties and Composition with Respect to RM Loading in SG Feedstock

<table>
<thead>
<tr>
<th>RM:SG</th>
<th>AMTAN</th>
<th>pH</th>
<th>C (%)</th>
<th>H (%)</th>
<th>C/H</th>
<th>O (%)*</th>
<th>H₂O (%)</th>
<th>Ash (%)</th>
<th>Heat of Combustion (Kj/Kg)†</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Catalyst</td>
<td>75</td>
<td>2.7</td>
<td>38.2</td>
<td>7.5</td>
<td>5.1</td>
<td>8.1</td>
<td>46.2</td>
<td>N/A</td>
<td>23.1</td>
</tr>
<tr>
<td>1:5</td>
<td>83</td>
<td>3.8</td>
<td>21.0</td>
<td>8.2</td>
<td>2.6</td>
<td>9.8</td>
<td>61</td>
<td>N/A</td>
<td>21.0</td>
</tr>
<tr>
<td>1:1</td>
<td>54</td>
<td>3.7</td>
<td>13.7</td>
<td>8.7</td>
<td>1.6</td>
<td>5.6</td>
<td>72</td>
<td>N/A</td>
<td>19.9</td>
</tr>
<tr>
<td>3:1</td>
<td>39</td>
<td>4.3</td>
<td>8.4</td>
<td>7.2</td>
<td>1.2</td>
<td>2.5</td>
<td>81</td>
<td>0.88</td>
<td>18.8</td>
</tr>
</tbody>
</table>

Aqueous modified total acid number; N/A- not applicable
* Determined by mass difference
†- Based on hydrocarbons

Germination and Growth of Switchgrass from Biochar Amended Soils

The addition of modified biochar affected switchgrass growth over the 6-week study period ($P < 0.05$). High loadings of modified red mud were used to test the upper limit of its application in marginal soils. Considering this, those treated with the higher loading (20 wt%) typically resulted in a reduced biomass yield. The highest root and shoot yields were seen for the uncatalyzed biochar at 10 wt% loading. The soils treated with 10 wt% red mud resulted in equivalent biomass yields in comparison to the control. However, the addition of modified biochar from the 3:1 (RM:SG) pyrolysis reduced both the root and shoot yield at both high and low loadings ($P < 0.05$; Fig. 5). These trends could potentially be explained by the bioavailability of sodium, considering that a significantly negative relationship was observed between the plant growth (root and shoot yield per plant pot) and the bioaccumulated sodium (Fig. 6). It was hypothesized that the biochar present in the post-catalytic pyrolysis would help sequester sodium along with other elements present in red mud; however, it appears that at high red mud to switchgrass loadings, biochar helped facilitate ion exchange in the case of sodium. Therefore, metal oxides comprising of red mud increased as expected in the catalyzed biochars.
In previous work by Ruyters et al. (2011), increasing red mud applications by 5% and 25% increased the soil pH and negatively impacted the shoot yield of barley (*Hordeum vulgare*) and increased the shoot metal uptake; although neither of the rates exceeded toxic limits. In addition, this study suggested that NaOH was one of the main drivers of adverse growth effects from red mud (Ruyters et al. 2011). Therefore, it appeared that a higher red mud dosage results in a salt injury in plants, which has implications for bioremediation and may be one of the major limitations for the use of red mud in closing bioenergy nutrient cycles. Further research is needed to test additional soil amendment combinations, such as gypsum, to improve red mud structure and composition. Similarly, a study investigating the ability of red mud to act as a catalyst for biodiesel synthesis found that red mud can not only recycle this waste product but can reduce the price of biodiesel production (Liu et al. 2013).

Fig. 5. Root and shoot yield per pot based on dry mass with various soil treatments. Loading of RM to SG was pre-pyrolysis. The resulting biochar was added on a weight basis into the oil; different letters denote significant differences within a 5% confidence interval. Uncatalyzed pyrolysis (1:0) was used as a control.
Pyrolysis of biomass may be one viable pathway to create renewable fuels and chemicals while minimizing soil pollution. However, many technological challenges remain for replacing the whole barrel. Though the catalytic pyrolysis process has proven to produce higher quality bio-oil, stability and cost must be considered when evaluating the overall process. This technology hinges on valorizing a waste stream; hence, the exploration of creating a soil amendment from red mud. The application of this technology could exist under two circumstances, either a localized or delocalized model. Biomass is not a dense material and thus requires a large volume to generate a small amount of oil. This has shifted the general consensus away from centralized processing and towards a distributive model. Small distributed reactors will need to be large enough to handle thousands of pounds of biomass during harvest seasons. However, a smaller, reproducible design for the system will allow for regional processing. In this scenario, red mud would need to be shipped from the aluminum manufacturer to pyrolysis units. This would demand low catalytic loading and multiple regeneration cycles. Alternatively, in a localized model, the biomass would need to be transported to the red mud reservoir. In this situation, a high catalyst to biomass ratio would be advantageous with fewer regeneration cycles. Using biomass readily available near the refinery would lower transportation costs. This model’s main objective may be to neutralize red mud instead of producing oil. The ultimate fate of this technology will be decided based on overall process economics and whether or not red mud is remediated or valorized. However, future investigation of red mud’s catalytic ability and its presence in the soil, post-reaction, needs further investigation.

CONCLUSIONS

1. Red mud pyrolysis produced a bio-oil with a greater pH and a higher H/C ratio, while producing a higher proportion of biochar and bio-oil. However, the loading of the catalyst must be considered when using this approach. In addition, red mud is effective at increasing soil pH and reducing the total acid number in bio-oil.
2. The use of modified biochar as a soil amendment on marginal soil may enhance its fertility; although, this is highly dependent on the nature of the soil and the extent of the loading.

3. This technology has the potential to create multiple revenue streams from long-standing waste materials, thus mitigating soil pollution during post-aluminum manufacturing.

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