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# A molar basis comparison of calcium hydroxide, sodium hydroxide, and potassium hydroxide on the pretreatment of switchgrass and miscanthus under high solids conditions

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ABSTRACT

Pretreatment is an essential step in the formation of liquid biofuels. Switchgrass and miscanthus were pretreated using calcium hydroxide, potassium hydroxide, and sodium hydroxide at an equivalent hydroxyl concentration (0.46 g $OH^-$/g dry biomass), at a solids content of 40%, and two temperatures (25 and 50 °C) for seven days. The cellulose, hemicellulose, and lignin composition before and after pretreatment were quantified according to the standard procedures developed by the National Renewable Energy Laboratory. After pretreatment, enzyme hydrolysis was performed at 50 °C in a shaking incubator with an enzyme loading of 60 FPU/g cellulose. Potassium and sodium hydroxide led to the largest reduction in lignin of between 30–47% with the two feedstocks and two temperature levels. Calcium hydroxide had a significantly lower amount of delignification of between 13–21%. Sodium and potassium hydroxide had a similar maximum reaction rate, except for switchgrass pretreated at 50 °C where the reaction rate was lower for potassium hydroxide. Cellulose conversion was the highest for sodium and potassium hydroxide and varied between 56.1 and 80.5% for both feedstocks at the two pretreatment temperatures investigated. Calcium hydroxide demonstrated a significantly lower cellulose conversion that varied between 23.0 and 44.9%. The results indicated that with an equivalent molar basis of $OH^-$, potassium and sodium hydroxide had superior performance relative to calcium hydroxide in a high solids environment.


## 1. Introduction

Lignocellulose biomass pretreatment is a fundamental step in the production of renewable fuels as the conversion of cellulose into fermentable monomers is enhanced by the cleavage of lignin and hemicellulose (Kumar et al., 2009). A number of different pretreatment methods exist, but alkaline pretreatment demonstrates many desirable qualities with low energy and temperature requirements for reactions which makes alkaline pretreatment desirable as a potential low-severity, pretreatment option. The alkalinity of sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide ($Ca(OH)_2$) weakens the intermolecular hydrogen bonds between cellulose, and this creates swelling (Baral et al., 2013). The swelling allows for more accessibility to the cellulose structure by increasing the surface area while reducing cellulose crystallinity and the degree of polymerization. Furthermore, the lignin, hemicellulose, and silica are dissolved by hydrolyzing the acetyl moieties attached to hemicellulose (Jackson, 1977). The rate of delignifcation is influenced by the concentration of hydroxide ions and overall pH (Dolk et al., 1989).

Numerous hydroxides have been studied for alkaline biomass pretreatment, but sodium hydroxide (Nlewem and Thrash, 2010; Silverstein et al., 2007; Varga et al., 2002), potassium hydroxide (Bales et al., 1979; Ong et al., 2010; Sharma et al., 2013), and calcium hydroxide (Kaar and Holtzapple, 2000; Sirohi and Rai, 1998; Xu et al., 2010a) are the most common with sodium hydroxide being the most extensively studied. For the differing alkaline pretreatment options, the physical/chemical composition of the biomass and pretreatment conditions (chemical used, chemical concentration, moisture content, temperature, pH, and duration of pretreatment) are influential in determining the final yields of glucose available to be transformed into products (Chen et al., 2013).

The physical and compositional characteristics of biomass varies with the crop. The use of dedicated biomass crops such as

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**Table 1**
Comparison of sodium, potassium, and calcium hydroxide based on% OH concentration by mass[a], pH of 1% solution[a], and estimated cost.

| Property | Sodium hydroxide | Potassium hydroxide | Calcium hydroxide |
|---|---|---|---|
| Molecular Formula | NaOH | KOH | $Ca(OH)_2$ |
| Molecular Weight (g/mol) | 39.998 | 56.106 | 74.092 |
| % OH by mass | 42.5% | 30.4% | 45.9% |
| pH (1% solution) | 12.7 | 13.7 | 12.4 |
| Cost ($/Mg) | $507[b] | $1100[c] | $385[d] |

[a] Developed from MSDS from Santa Cruz Biotechnology, Inc. Santa Cruz, CA 95060 USA and PubChem http://pubchem.ncbi.nlm.nih.gov.
[b] http://www.alibaba.com/showroom/bulk-sodium-hydroxide.html.
[c] http://www.alibaba.com/trade/potassium+hydroxide+price.
[d] http://magissues.farmprogress.com/BeefProducer/BP11Nov12/bp04.pdf.

*Miscanthus x giganteus* and *Panicum virgatum* (generically referred to as miscanthus and switchgrass in this study) is becoming ever more important as these crops manifest high yields, resilience in production on marginal land and at various climates, and low fertilizer/pesticide inputs (Heaton et al., 2008; Samuel et al., 2011). For these crops, hemicellulose and lignin can make up 45% of the weight on a dry basis (Brown, 2003). Therefore, the solubilization of these polymers is important to increase the cellulose available to the degrading enzymes. Solubilization is directly related to lignin and hemicellulose removal from the lignocellulosic matrix.

With regard to pretreatment conditions, inherent tradeoffs exist for the differing hydroxide pretreatments with each possessing positive and negative attributes related to hydrolysis effectiveness, cost, ability to recover/recycle, caustic nature, and environmental impact (Chen et al., 2013). When the pretreatment effectiveness of potassium and sodium hydroxide were compared, opinions varied. Bales et al. (1979) reported that NaOH applied at 0.05 g/g DM on milo stalks appeared superior to potassium hydroxide at the equivalent concentration, despite disadvantages associated with sodium related to animal and soil toxicity. Ong et al. (2010), on the other hand, showed that higher cellulase production was achieved with rice straw treated with potassium hydroxide than with samples treated with sodium hydroxide after solid state fermentation with $1 \times 10^{-7}$ $ml^{-1}$ spores of *Aspergillus niger*.

Many researchers have concluded that calcium hydroxide is not as effective of a pretreatment agent as other alkalis such as sodium and potassium hydroxide (Chang et al., 1997). Nonetheless, calcium hydroxide possess many desirable qualities for pretreatment from many aspects. Firstly, the cost of calcium hydroxide is the lowest of the hydroxides typically used for biomass pretreatment $0.10/kg $Ca(OH)_2$ versus $0.36/kg sodium hydroxide and $3.78/kg potassium hydroxide (Kaar and Holtzapple, 2000). Furthermore, the calcium can be recovered by adding $CO_2$ to the solution and precipitating calcium carbonate ($CaCO_3$) out of solution. Compared to the other alkalis, calcium hydroxide is safer to handle (Davidson, 1927) whereas sodium and potassium hydroxide possess a more caustic nature (Davidson, 1927).

In a direct comparison of sodium, potassium, and calcium hydroxide, Yang (2009) showed that after 24 h of pretreatment, NaOH at a 10% concentration was the most effective pretreatment for the production of biogas. In this trial, NaOH removed the most lignin overall, and at each concentration level (5%, 10%, and 15%), NaOH removed more lignin than the other hydroxide treatments. However, the short pretreatment time period (24 h) favors NaOH compared to $Ca(OH)_2$ which performed the poorest. Calcium hydroxide would need more time for delignification and increased sugar yield to take place. With a 24 h pretreatment duration, the in vitro dry matter digestibility of corn cobs was demonstrated to be equivalent (~75%) for sodium and potassium hydroxide at 0.05 g/g DM but $Ca(OH)_2$ was deemed to be ineffective at ~62% (Rounds et al., 1976).

Most of these comparisons were made considering a combination of treatments using calcium, sodium and potassium hydroxides under the same conditions, specifically using the same amount of chemical on a weight basis. However, this is an imbalanced comparison as sodium, potassium, and calcium hydroxide possess differing% OH concentrations as shown in Table 1. Furthermore, calcium hydroxide is a weaker base and to achieve an equivalent alkalinity requires eight times as much calcium hydroxide as sodium hydroxide (Winugroho et al., 1984). For potential on-farm processing, a moderate temperature range (25–50 °C) would be desirable and similar temperature ranges have been used in other trials (Kim and Holtzapple, 2005).

Another complicating issue is the solids content during pretreatment. Most studies have utilized a low solids loading rate that aids pretreatment; however, there are numerous advantages to high solids systems including higher sugar yields and lower costs (Modenbach and Nokes, 2012). Chen et al. (2013) investigated the lignin removal from corn stover pretreated at solids loadings of 5, 10, and 15% and found minimal differences. A proposed on-farm solid-state conversion system would utilize high density, baled biomass feedstocks in a modified bunker system (Nokes et al., 2014). Pretreatment under high solids contents (greater than 30%) that could be expected using baled biomass has not been extensively studied, although pretreatment studies of crop residues with solid-state anaerobic digesters would be similar. Ge et al. (2016) reviewed solid-state anaerobic digestion and reported that alkaline pretreatments of crop residues was effective at increasing the biogas yield at solids contents greater than 20%.

Undigested solid biomass and byproducts of pretreatment could be reapplied to the land and utilized for the production of additional lignocellulosic materials. The disposal of the undigested biomass would be complicated by the formation of salts resulting from alkaline pretreatment (Zheng et al., 2009). This project is focused on investigating techniques that could be applicable to distributed, on-farm processing. With regard to pretreatment with sodium, potassium, and calcium hydroxide, calcium and potassium are macronutrients required for soil fertility and land application of these nutrients for crop production is common. Whereas, the land application of residual sodium would result in the accumulation of salts.

An experiment comparing calcium, sodium, and potassium hydroxides on a molar basis would contribute to a better understanding of their pretreatment effectiveness. For this reason, this study aimed to develop comparative technical information on the alkaline pretreatment of miscanthus and switchgrass and the subsequent enzyme hydrolysis of sodium, potassium, and calcium hydroxide on a constant molar basis under high solids conditions.

## 2. Materials and methods

### 2.1. Biomass preparation

Harvesting, storage, and grinding of Alamo switchgrass (*Panicum virgatum* L.) and miscanthus (*Miscanthus x giganteus*) was conducted as described by Jackson et al. (2016) with some mod-