



Research paper

Calcium oxide as an additive for both conservation and improvement of the combustion properties of energy grass: A preliminary study



Shaojun Xiong^{a,*}, Marjan Bozaghian^a, Torbjörn A. Lestander^a, Robert Samuelsson^a, Sven Hellqvist^a, Marcus Öhman^b

^a Swedish University of Agricultural Sciences, Department of Forest Biomaterials and Technology, SE-901 83, Umeå, Sweden

^b Luleå University of Technology, Energy Engineering, Division of Energy Science, SE-971 87, Lulea, Sweden

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ABSTRACT

Degradation of biomass is one of the major reasons for high costs of feedstock collection, transport, and storage, which is largely associated with biomass moisture and microbial activities. Our concept is to add calcium oxide (CaO) to the biomass already when it is collected and in its natural (wet) condition. When a suitable quantity of CaO is added to moistened biomass, an alkali microenvironment will be formed with a pH exceeding 9, based on the reaction $\text{CaO} + \text{H}_2\text{O} \leftrightarrow \text{Ca}(\text{OH})_2$. As a consequence, microbial activities are largely inhibited. The $\text{Ca}(\text{OH})_2$ will then successively react with CO_2 , following the reaction $\text{Ca}(\text{OH})_2 + \text{CO}_2 \leftrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$. The CaCO_3 will reside in the feedstock throughout the entire production chain and end up as an additive/sorbent to improve combustion by decreasing slagging. Two experiments were conducted and proved the concept works for at least reed canary grass, but, as expected, the strength of the effect was dependent on the CaO dosage and initial biomass moisture.

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1. Introduction

Agriculture-based biomass (mostly herbaceous, including conventional crop residues and energy grasses) is an important potential bioenergy resource worldwide [1]. Studying the potential uses of this agro-biomass for energy production in the context of sustainable development is therefore crucial, in particular as the use of energy crops from marginal lands as well as surplus food crop residues will increase the value and security of food production. However, effective technologies for energy conversion and feedstock handling systems, including quality control, have to be further developed.

Degradation of biomass, i.e. substance and energy losses caused by microbial action, is one of the major reasons for high feedstock costs [2]. In the sequence of collection, transport, and storage, this degradation may occur under scenarios where biomass moisture is sufficient for microbial growth. In practice, biomass moisture is often not low enough to stably inhabit microbial growth. Even if the moisture level may not be high enough to allow general microbial

attacks, water in the feedstock (“water activity”) might exist in some spots, causing damage and, subsequently, heterogeneity in the fuel quality. Microbes react more to “water activity” than to the bulk percentage of moisture in the biomass [2–5], attacking structural sugars which may cause decreases in feedstock mass and energy content. There are also risks of overheating and self-ignition of biomass during storage, which are often induced by the activities of thermophilic microbes [6].

Delayed harvest may help to reduce drying costs and obtain better quality biofuel feedstock from different energy crops [7–10] as well as conventional crop residues such as corn stovers [11]. However, the success of delayed harvest depends on the climate and on local agricultural practices; in some cases, delayed harvest may lead to a greater harvest loss (up to 40–50% in weight) than traditional autumn harvest [12]. On the other hand, silage is considered a way to store biomass of 0.50–0.70 moisture mass fraction [13,14], but dry mass losses of up to 30% have been reported. Thus, efforts to develop cost-effective technologies to reduce microbial activities need to be undertaken. The high costs of artificially drying biomass and keeping it dry emphasize that other techniques must be developed to keep feedstock quality stable during transport and storage, without large substance losses or contamination by hazardous matter.

* Corresponding author.

E-mail address: Shaojun.Xiong@slu.se (S. Xiong).

In regards to the emergence of ash-related operational problems during combustion, agro-biomass is often characterized as a more problematic biofuel for combustion in comparison to woody biofuels. Slagging, for example, is mostly caused by the ash composition that decreases the ash melting temperature [15]. For example, high ratios of silica and alkali metals, such as potassium, can result in forming alkali silicates at melting temperatures as low as below 700 °C.

Lime is a well-known material used for hygienic purposes, among others. When lime meets water, an alkali calcium-hydroxide is formed, based on the reaction $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$. When lime is applied to moisten biomass in sufficient quantity to create an alkali microenvironment with a pH of around 9, most microbial growth is unsustainable [16]. The $\text{Ca}(\text{OH})_2$ will successively react with CO_2 by way of $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightleftharpoons \text{CaCO}_3 (+\text{H}_2\text{O})$. Studies have demonstrated that slagging can be greatly reduced by blending Ca-based compounds, such as lime and CaCO_3 , in biofuels [8,17]; in addition, Ca compounds can be sorbents and react with, e.g., sulphur-bearing gases (such as SO_2 , H_2S , etc.), forming stable salts of calcium (CaSO_4) at high temperatures and reducing acid-gas emissions [18,19].

The objectives of this study were therefore to mix one type of additive, such as lime (CaO), in a quantity with moist biomass. We hypothesized that this would have two effects: (1) the biomass will be less degraded or better conserved during storage and (2) the slagging problems during combustion will be reduced. By adding this mineral compound of sufficient quantity to the moist biomass, an alkaline (pH \approx 9) microenvironment will be formed, inhibiting microbial growth. The resulting product (CaCO_3) will remain in the feedstock throughout the entire production chain until combustion and increase the ash melting temperature. In addition, the ash composition will be changed, which may facilitate reuse of the ashes due to less slag. The purpose of the current study was therefore to test our hypothesis and evaluate the consequences of adding CaO to the microenvironment in terms of biomass fuel characteristics and ash melting behavior during combustion.

2. Material and method

Laboratory experiments with reed canary grass (RCG) (*Phalaris arundinacea* L.) as biomass material were carried out at the Swedish University of Agriculture, using CaO as a model additive.

2.1. Experimental settings

Two major laboratory experiments were conducted, using CaO and initial moisture mass fraction (IMC or MC = (mass of water / (mass of water + mass of dry biomass))) as major factors. The purposes of the experiments were to examine the consequences of applying CaO to the biomass with different IMC values in terms of changes in (1) biomass remaining after a certain period of storage, (2) biomass pH and mold degree, and (3) ash behavior during combustion. Experiment A was composed of nine treatments (three levels of IMC \times three CaO mass ratios, Table 1) in 2008–2009. Experiment B was composed of three treatments, one level IMC \times three CaO mass ratios in 2009–2010. It was designed for three replicates for each treatment. The designed mass ratios of CaO to dry fuel mass were 0, 4, and 8 g per 100 g of the mixture (biomass and added CaO).

Prior to any treatment, pilot experiments were conducted using the same RCG biomass as in the main experiments to examine the water contents and settle the moisture gradients. In addition, we tested the correlation between CaO mass ratios (1–10 g/100 g dry mass mixture) and initial biomass pH.

2.1.1. Experiment A

Freshly harvested RCG biomass (cultivar Palaton) with a moisture mass fraction of 0.71 was used for the experiment, originating from an SLU field station in Röbackdalen, Umeå, Sweden (63°48'N, 20°14'E). The crop was in its 8th season and harvested around 20 November 2008 (at the end of season). Harvesting was carried out by hand and the entire aboveground part, 5 cm above the soil, was collected. The plants were cut into pieces <5 cm long and spread on the ground of a greenhouse to reduce moisture mass fraction (MC) to the targeted levels (0.65, 0.55, and 0.45). A curve of MC against drying time derived from a pilot test was then used to manage the MC levels. The materials were put in large (205 L) plastic bags and stored in a cool room at 5 °C for 1–3 days prior to treatment. Samples were taken to control MC. The CaO powder (grade 98%, Sigma Aldrich) was manually added and mixed into the biomass in a box; the biomass corresponded to about 400–500 g of dry mass and was designed for each of the replicates of each treatment. The mixed materials with different combinations of IMC and doses of CaO were arranged among 27 buckets, with three replicates (buckets) per treatment. Care was taken to maintain a homogeneous mixture of CaO and biomass. After mixing CaO, a part of the mixed material, corresponding to 50–100 g of dry mass, was immediately used to determine the achieved MC. To measure temperature changes during storage, mini loggers (Tinytag Plus2, INTAB Interface-Teknik AB, Sweden) were immediately buried in the buckets, one for each treatment, about 7–8 cm below the surface.

All buckets were randomly arranged in a greenhouse with a temperature of around 18 °C during the two-month period. The room was equipped with a normal ventilation system.

For the treatments of IMC 0.65 and 0.55, around 1/3 of the biomass of each bucket was taken as a sample on day 45, while the remaining biomass was sampled on day 60. For the treatments of IMC 0.45, the entire biomass was taken on day 45 after establishing the experiment. All samples, including the initial sample (prior to treatment), were used to determine MC, pH value, and fuel characteristics.

2.1.2. Experiment B

For Experiment B, we used the same RCG cultivar but grown in a field outside Umeå and harvested in November 2009. The biomass (MC = 0.73) was stored for one month after collection and room-dried to the desired levels of (MC = 0.35) for experimental use. All the materials were cut smaller than 1.5 cm. Mixing the CaO powder with the RCG material was achieved manually in a large plastic bag by carefully shaking and rolling the temporary closed bag. The mixed materials, corresponding to about 15 kg of dry mass each, were then placed in chicken-net cages 60 cm in diameter. The nine cages were randomly distributed inside a room with a temperature of 18–20 °C.

An additional test was performed to attest for differences in biomass weight and fuel characteristics between low (75 kg m⁻³) and high (120 kg m⁻³) bulk densities. The desired low bulk density was achieved by simply measuring to the reached height of the biomass in the cages, whereas the high level was created by means of a hydraulic press from a tractor.

Biomass samplings were performed on day 1, 45, and 90 after establishing the experiment. Three samples were randomly taken from the same cage.

2.2. Estimation of mold degree

Degrees of mold, i.e., the extent of mold fungus contamination as an indication of microbial activity in the biomass, were determined on day 45 after the start of the experiment. The degree of

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