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The effects of calcium and potassium on CO_2 gasification of birch wood in a fluidized bed

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HIGHLIGHTS

- Fluidized bed gasification of raw, leached, Ca doped and K doped wood.
- Effects of Ca and K on pyrolysis and char behavior.
- Char characterization using SEM-EDS, BET surface area and ICP-OES.

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ABSTRACT

Birch wood was leached of its naturally occurring ash forming elements and doped with three concentrations of calcium or potassium before being gasified in a laboratory bubbling fluidized bed reactor. The wood samples were pelletized and inserted into a fluidized bed reactor where they were first pyrolyzed with N_2 and then gasified with CO_2. In addition to tracking the gas concentration of the exit gas, char samples were taken from the fluidized bed and analyzed to study the char properties. The presence of potassium in the biomass was found to have a significant influence on the structure of the resulting char, however potassium did not have an observable catalytic effect on the overall gasification reaction rate with CO_2 due to the formation of a unreactive coke layer on the char surface. In contrast, calcium did increase the char conversion rate and is likely the primary active catalyst in gasification of birch wood with CO_2.

1. Introduction

Biomass naturally contains between 0.1–35% ash forming elements by weight, depending on the type of biomass and the environment in which it grew, and waste derived fuels can reach nearly 50% ash [1]. While the composition of these inorganics can vary greatly, it is common that potassium and calcium are two elements which can be found in significant quantities in woody biomass [1–4].

The presence of ash forming elements has been shown to influence the thermochemical conversion of biomass in different ways. For example, it has been shown that K, Na and Mn increase mass loss during torrefaction of wood [5]. The mineral content of biomass has been shown to have a number of effects on the pyrolysis behavior of the fuel [6], and potassium in particular has been identified as having effects on char and gas yields during pyrolysis [7–9]. The presence of some inorganics in chars has been shown to increase the reactivity of the char during gasification [10–18].

Much of the work done to investigate the role of inorganics in gasification reactions has been done on small scales, using only a few milligrams of sample in a thermogravimetic analysis (TGA) device or fixed bed reactor (for example, [12–17] for TGA measurements and [18] for fixed bed). In many cases the chars are created first and then have metals added [13,15,18], rather than adding the metals to the parent material [16,17]. The method of char preparation is important as Suzuki et al. reported that adding K and Ca to leached wood produces higher char reactivity than adding K or Ca to leached char when gasifying in CO_2 [19]. While adding the metals to pre-made chars removes the complicating factor of the effect of the metals on char formation and guarantees that the initial char

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structure is uniform for all samples, it does not reflect the reality of fuel behavior in actual gasification processes.

In the present work birch wood was leached of its naturally occurring ash forming elements and then doped with different concentrations of potassium or calcium. The wood samples were pelletized and inserted into a fluidized bed reactor where they were first pyrolyzed with N_2 and then gasified with CO_2. This experimental technique allows the measurements to be more representative of industrial processes in a number of important ways: the added inorganics are present in the wood during pyrolysis; the samples undergo high heating rates in the fluidized bed; the sample sizes and resulting char amounts are larger; and the char is not cooled after pyrolysis but is instead gasified immediately once pyrolysis has ended. Char samples were collected from the fluidized for further analysis to better understand the causes for the observed changes in char reactivity. The char analysis techniques include: SEM-EDS, BET surface area measurements, and ICP-OES analysis.

2. Experimental methods

2.1. Sample preparation

Wood chips made from Finnish birch wood (Betula pendula) were milled to particle sizes of less than 2 mm. The ultimate and proximate analysis of the birch wood powder is given in Table 1. The wood powder was then leached of ash forming elements by following the method used by Kharzraie Shoulaifar et el. [20,5]. This procedure involves first adding the wood to a sodium EDTA solution for two hours. After this, the wood was rinsed with ultra pure water, added to a 0.01 M HCl solution for two hours, and finally rinsed again with ultra pure water.

The leached wood was then doped with two concentrations of potassium or three concentrations of calcium following the process described by Perander et al. [17]. The doping was done by adding the leached wood powder to either a KNO_3 or $Ca(NO_3)_2$ solution. This method dopes the metal to organic functional groups through ion-exchange, mimicking how K and Ca can be naturally found in the wood [17,21,22]. The concentration of K and Ca in the final wood was adjusted by changing the concentration of the K and Ca nitrates in the solution.

The success of the leaching and doping process was determined by measuring the elemental composition of the wood samples. This was done using inductively coupled plasma optical emission spectrometry (ICP-OES) and the results are shown in Table 2.

2.2. Fluidized bed reactor

Char reactivity was measured using a laboratory bubbling fluidized bed (FB) reactor. This reactor has been used in previous studies [25–27] and is constructed from stainless steel. The FB section of the reactor has an internal diameter of 51 mm and height of 200 mm. The freeboard has an internal diameter of 81 mm and height of 250 mm. The reactor is externally heated by a 10 kW electrical oven. Gases are preheated and fed into the reactor through the distribution plate at the bottom of the FB. Fuel is added batchwise through the top of the reactor. Gases exit the reactor and pass through a system to remove tar and condensable species before being analyzed for CO, CO_2, H_2, and CH_4 concentration with an accuracy of 0.01%.

Table 1
Ultimate and proximate analysis for raw birch wood used in the fluidized bed tests.

	Weight % (dry basis)
Moisture (wet)	1.99
Ash	0.35
Volatiles	89.46
Fixed carbon	10.19
Carbon	48.94
Hydrogen	6.16
Nitrogen	<0.05
Sulphur	<0.05
Oxygen	44.90

2.3. Fluidized bed experimental procedure

To prevent immediate entrainment out of the fluidized bed, the wood powder was pressed into pellets of approximately one gram using a pellet press. The pellet diameter was 1 cm and the length approximately 2 cm. The FB reactor was preheated to the desired temperature and the gas flow was switched to N_2. Two pellets were added to the reactor through the fuel feel valve at the top of the freeboard and the resulting pyrolysis gas composition measured. Because only CO_2, CO, CH_4 and H_2 could be measured by the gas analyzer, some of the sample will leave the reactor without being detected, typically as tars or light hydrocarbons which are removed from the exit gas before reaching the analyzer. The amount of these undetected products was calculated by subtracting the mass of the measured gas flow from the sample input mass. Pyrolysis was considered to be complete once the gas analyzer indicated that no CO, CO_2, H_2 or CH_4 were present in the exit gas from the reactor, at which point the gas flow was changed to 20% CO_2 and 80% N_2. Typically the time to complete pyrolysis was 10 min. Initial tests were conducted in which the bed and char were removed from the reactor after pyrolysis to inspect the resulting char. These tests indicated that the pellets broke apart during pyrolysis and the resulting char particles were approximately of the same size as the original wood particles.

The bed material used in most of the tests was olivine, although some tests were also carried out using bauxite as the bed material. In all cases the bed mass was 500 g. In order to minimize elutriation of the wood particles the gas velocity into the reactor was kept relatively low at 0.2 m/s, which was still over the minimum fluidization velocity for the olivine bed of 0.18 m/s.

Char conversion, is defined as

$$X_{ch} = \frac{m_0 - m}{m_0}, \quad (1)$$

where m_0 and m are the initial mass of char and char mass at time t, was calculated from the CO concentration measured in the product gas assuming CO is generated through the Boudouard reaction given by Eq. (R1),

$$C + CO_2 \rightarrow 2CO. \quad (R1)$$

Once the CO concentration became too low to measure reliably (i.e. below 0.01%) the gas flow into the reactor was switched to air and the remaining char was combusted. The amount of char combusted was calculated from the CO_2 concentration in the exit gas during the combustion stage. Tracking the char carbon in this way achieved and average char balance of 93% of the char predicted from the fixed carbon value given in Table 1. Char conversion rate and instantaneous reaction rate are defined by Eqs. (2) and (3) respectively,

$$r = \frac{dX_{ch}}{dt}, \quad (2)$$

$$k = -\frac{1}{m}\frac{dm}{dt} = \frac{1}{1 - X_{ch}}\frac{dX_{ch}}{dt}. \quad (3)$$

The term reactivity is used in a general way in this work, and refers to the tendency of the char to react with CO_2.