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

Jason Kramb[a], Alberto Gómez-Barea[b], Nikolai DeMartini[c], Henrik Romar[d], Tharaka Rama K C Doddapaneni[a], Jukka Konttinen[a]

[a]*Department of Chemistry and Bioengineering, Tampere University of Technology, PO Box 541, FI-33720 Tampere, Finland*
[b]*Chemical and Environmental Engineering Department, Escuela Técnica Superior de Ingeniería, University of Seville, Camino de los Descubrimientos s/n. 41092 Seville, Spain*
[c]*Johan Gadolin Process Chemistry Centre, Åbo Akademi University, FI-20500 Turku, Finland*
[d]*University of Oulu, Research Unit of Sustainable Chemistry, P.O.Box 3000, FI-90014 University of Oulu, Finland*

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.

Keywords: biomass, gasification, fluidized bed, catalysts, char

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 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. Char samples were collected 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. [5, 20]. 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.

Email address: jason.kramb@tut.fi (Jason Kramb)

	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

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

Sample	Concentration (mg/kg)							
	Ca	K	Mg	P	Mn	Zn	Ba	Fe
Raw birch	760	570	210	91	50	22	10	5.4
Leached	44							
Ca low	460			29				26
Ca med	545			23		12		
Ca high	600			22		11		
K med	84	491		24		6		
K high	39	568		20				

Table 2: Elemental composition for the raw birch wood, leached wood, Ca doped and K doped samples as determined by ICP-OES. If no value is present then the concentration was below the detection limit.

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 [23–25] 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%.

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 minutes. 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

$$X_{ch} = \frac{m_0 - m}{m_0}, \tag{1}$$

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 Equation R1,

$$\mathrm{C} + \mathrm{CO_2} \longrightarrow 2\,\mathrm{CO}. \tag{R1}$$

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. Char conversion rate and instantaneous reaction rate are defined by Equations 2 and 3 respectively,

$$r = \frac{dX_{ch}}{dt}, \tag{2}$$

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

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.

In order to study char gasification kinetics, the gasification must occur in the kinetically controlled regime (i.e. Regime I). Ensuring that the gasification is kinetically controlled is typically done by using small particle and low enough temperatures. Preliminary tests in which the bed was removed after

devolatilization showed that the pellets had broken apart during devolatilization and the char particles were of similar size to the original wood particles (less than 2 mm). The transition temperature between the kinetic and combined kinetic/diffusion regime (Regime II) is typically identified by the temperature at which a rapid change in the slope of the Arrhenius plot occurs.Char reactivity measurements were first conducted at 750°C, 800°C, 850°C and 900°C and the Arrhenius plot of the natural log of the instantaneous reactivity vs temperature was plotted. From this plot, which is shown in Figure 7, it was determined that 900°C was likely no longer kinetically controlled for the most reactive samples, but 850°C remained in Regime I. Measurements using the same reactor on olive tree pruning of approximately the same particle size reached a similar conculsion [23]. Based on this, 850°C was selected as the temperature for the majority of the char gasification tests.

Char samples were collected from the fluidized bed by increasing the gas velocity into the reactor which pushed the low density char particles into the cyclone where they were collected. For the leached wood and Ca doped wood it was not possible to collect chars using this method as the chars would not entrain from the bed, even at very high gas velocities. To collect the char in these tests, the entire bed, containing the char and olivine, was removed from the reactor and the char was recovered by screening. The reasons for this behavior are discussed in more detail in Section 3.3.

A complete list of fluidized bed tests conducted is included given in Table A.6 in Appendix A.

2.4. Char characterization

Chars collected from the fluidized bed were analyzed in a number of ways to better understand the relationship between the calcium and potassium content of the biomass and the char reactivity.

First, the char samples were analyzed by scanning electron microscopy with X-ray microanalysis (SEM-EDS) which gives some indication of the char structure and distribution of the metals on the char surface. Surface areas and pore distributions were measured on a Micromeritics ASAP 2020 by physisorption of nitrogen (N_2). For the adsorption tests 100 mg of each sample was weight into a quartz tube. Prior to measurement the samples were evacuated at 10 μm Hg at an elevated temperature (160°C) in order to remove any contaminating gases from the samples. Surface areas were measured under isothermal conditions obtained by immersing the sample container into liquid nitrogen by the addition of small portions of N_2. The surface areas were calculated using the BET (Brunauer-Emmerson-Teller) model [26]. Pore size distributions were calculated from the adsorption isotherms according to the BJH (Barret-Joyner-Halenda) model [27]. Finally the char samples were analyzed with ICP-OES to determine the total metal content which remains in the char.

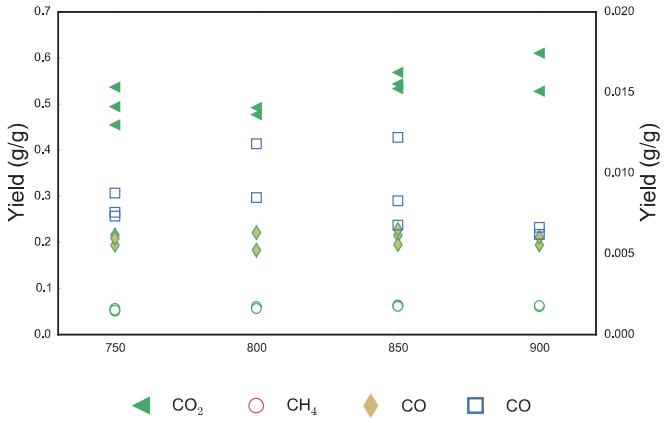

Figure 1: Pyrolysis gas yields as a function of pyrolysis temperature for raw birch wood. The yields were calculated on a dry biomass basis.

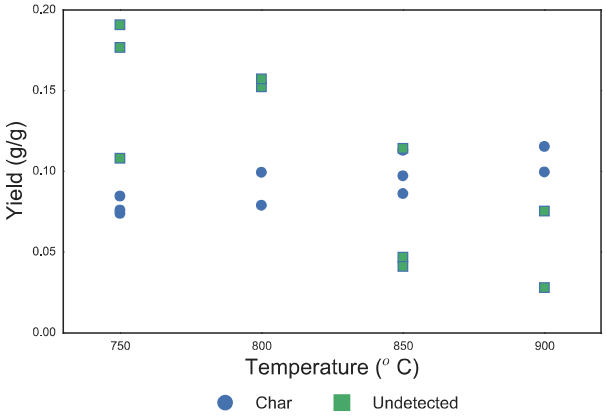

Figure 2: Char and undetected (condensable) fraction as a function of pyrolysis temperature for raw birch wood. The yields were calculated on a dry biomass basis.

3. Results and discussion

3.1. Pyrolysis gas and char yields

Pyrolysis yields were measured for each fluidized bed test. The pyrolysis gas composition for raw birch wood varied little at temperatures between 750°C and 900°C, as seen in Figure 1. The char (carbon only) and undetected fraction yields are shown in Figure 2. Carbon dioxide was the primary pyrolysis gas component, typically over 50%. The undetected fraction decreased as the pyrolysis temperature increased, which likely signifies a decrease in tar production at higher temperatures. The char yield was largely unaffected by increasing pyrolysis temperature, remaining around 9% by mass for all temperatures. This is in contrast to the widely reported observation of a decrease in char yield with increasing pyrolysis temperature over similar temperature ranges [28–30].

The measured yield of CO_2 at approximately 0.5 g/g fuel was much higher than what is commonly reported for this temperature range while the CO yield was low [28, 31]. In addi-

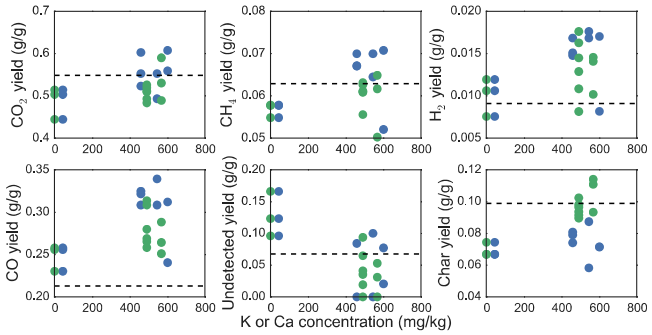

Figure 3: Pyrolysis gas yields and char yields as a function of K and Ca doping concentration. Green points indicate K concentration and blue points indicate Ca concentration. The black dashed line indicates the averaged yield of the raw birch wood. The yields were calculated on a dry biomass basis.

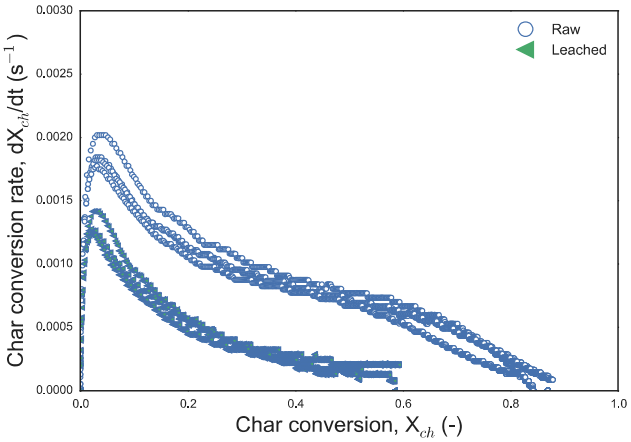

Figure 4: Conversion rate measurements of chars from raw birch wood and leached birch wood at 850°C in 20% CO_2 and 80% N_2. Multiple measurements for each sample are shown to demonstrate the repeatability of the measurement.

tion, the undetected fraction of pyrolysis products, consisting primarily of condensable tars and water vapor, is slightly below the level which is generally reported. In many cases the oxygen in the pyrolysis gas exceeded the oxygen in the original sample, indicating that some air has entered the reactor during fuel feeding. While air penetration during fuel feeding will affect the pyroylsis gas composition, creating additional CO_2, it was unlikely to influence the main purpose of the work, which was the char behavior. The distribution of pyrolysis products is likely further affected by a combination of two additional factors: the low gas velocity into the reactor which resulted in longer than normal gas residence times of approximately 2.5-3.5 seconds; and the use of olivine as a bed material, which has been shown to promote the water-gas shift reaction [32] in addition to reducing tar yields through promoting tar decomposition (see, e.g., [33]).

Pyrolysis gas composition for the doped samples at 850°C showed few significant trends, as can be seen in Figure 3. Both calcium and potassium doping slightly increased the measured gas yields while reducing the undetected fraction. Potassium doping also clearly increased the char yield.

Leached wood has been reported to have decreased char and gas (CO and CO_2) yield compared with unleached wood when pyrolyzed in a fluidized bed at 400°C [9]. Addition of potassium to the leached wood increased char and gas yields while calcium had little effect in that study. Eom et al. [8] also reported that potassium doping increased char yields and affect pyrolysis product formation while calcium had little effect. The behavior of the potassium doped samples in the present work is largely consistent with the reported effects of potassium on biomass pyrolysis. The observed influence of calcium on pyrolysis gas composition is in contrast to previous studies which did not report such an effect [8, 9], but the large differences in pyrolysis conditions (peak temperature, applied heating rate and fuel particle size) make comparisons difficult.

3.2. *Char reactivity*

Char conversion rate measurements showed high repeatability between multiple tests at a given operating condition. To show this, the conversion rate curves from multiple runs of raw birch wood and leached wood are given in Figure 4. The averaged conversion rate curve for all the samples are given in Figures 5 and 6 which show conversion rate measurements for all the wood samples at 850°C. The leached wood char was clearly less reactive than the raw birch wood char throughout the measured conversion range. The calcium doped wood chars show higher conversion rate peaks with increased Ca doping concentration, as can be seen in Figure 5. All the Ca doped wood chars have a higher conversion rate peak than the raw birch wood char despite having lower Ca concentrations. This high initial peak in the Ca doped samples compared with the raw wood may result from other inorganics (e.g. Mg, P) which are present in the raw wood but not in the Ca doped wood. In addition the Ca doped wood shows significant structural differences compared to the raw, as shown in 3.3, which may affect char reactivity. All the wood chars show decreasing conversion rates throughout the conversion process, and between approximately 50-80% char conversion the raw birch wood is faster than the Ca doped woods.

Potassium doped wood chars exhibited very low reactivity and after an initial peak were similar to the leached wood chars, as shown in Figure 6. The initial conversion rate of potassium doped wood char was generally higher than the leached wood, nearly at the same level as the raw birch wood char. However the conversion rate quickly dropped off to the level of the leached wood. The reactivity of the potassium doped wood chars was also not dependent on the potassium concentration in the wood, as all samples were equally unreactive (see Figure 6).

Comparison of conversion rate curves for char gasification between studies is difficult because pyrolysis conditions have a large effect on the resulting char reactivity [34]. As most studies with K or Ca doped chars have been performed in TGA devices with much different heating rates and gasification conditions than the fluidized bed reactor used in the present work, and doping is often done to chars directly rather than the parent biomass, the resulting conversion rate curves will be different

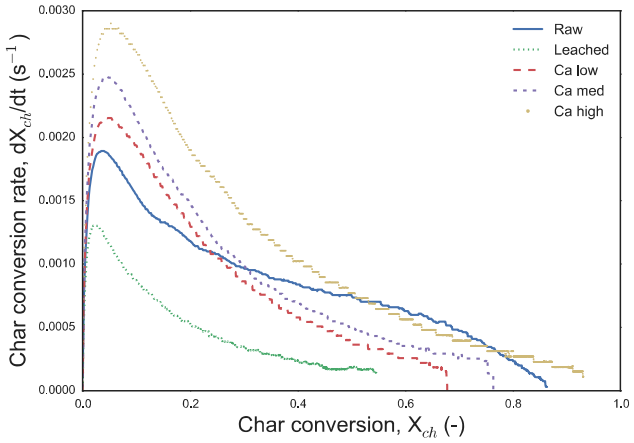

Figure 5: Conversion rate measurements of chars from raw birch wood, leached birch wood and Ca doped birch wood at 850°C in 20% CO_2 and 80% N_2. The lines are an average result from multiple measurements using each sample.

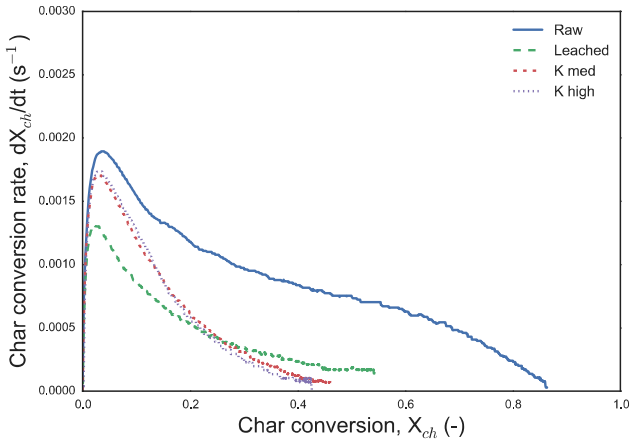

Figure 6: Conversion rate measurements of chars from raw birch wood, leached birch wood and K doped birch wood at 850°C in 20% CO_2 and 80% N_2. The lines are an average result from multiple measurements using each sample.

even for similar doping concentrations. In work using a similar wood and a similar leaching/doping method but at much higher K and Ca concentrations the wood was gasified in a TGA [17, 35]. In that work the wood was lowered in a sample holder into a preheated reactor with 100% CO_2 flow. The resulting heating rates were lower than the current work (approximately 50°C/s) and the devolatilization occurred in a CO_2 atmosphere. Both calcium and potassium doped samples showed increased reactivity compared to the leached wood, but the lowest doping level for the K doped wood was four times greater than the maximum doping in the present work. The catalytic effects of potassium were observed slightly later in the char conversion process than with calcium

Suzuki et al. [19] loaded Ca and K to leached cedar wood, which was then gasified in a TGA. While the metal loading process used in that study was different than in the present work, it has been shown that potassium loaded wood will be-

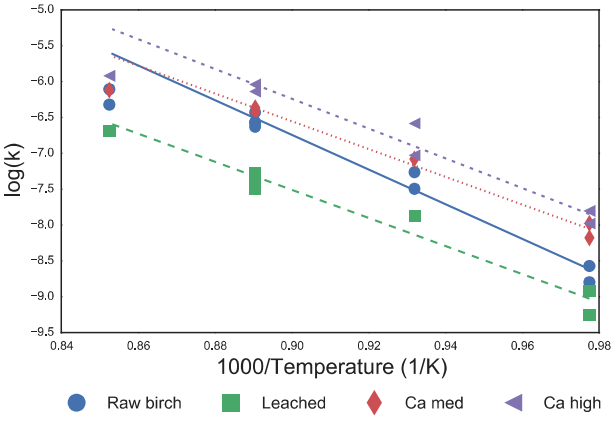

Figure 7: Arrhenius plot of log(k) vs 1000/T for raw birch, leached, Ca med and Ca high chars. The instantaneous reactivity was taken at 20% char conversion. The dashed lines indicated the linear regression line for the 750-850°C temperatures. It can be seen that for the raw wood, Ca med and Ca high samples the reactivity at 900°C falls well under the regression line.

have similarly whether the potassium is added as K_2CO_3 or doped through ion-exchange [17]. Suzuki et al. reported that at potassium loading levels approximately twice what was used in the present work there was an increase in reactivity compared with leached wood char. However, the influence of potassium was greatest at the end of the conversion process, and at low loading levels it was most significant at char conversion greater than 90%.

Numerous other studies report an increase in char reactivity with potassium doping [16, 18, 36, 37], though the char preparation and gasification methods tend to differ significantly from the present work. As potassium has been shown to deactivate as a catalyst by reacting with silicon in chars [38, 39], to rule out the possibility the potassium was reacting with the silicon in the bed material the olivine bed was replaced with bauxite. However, reactivity tests with raw birch wood and K doped wood using bauxite gave the same result as with the olivine bed.

In order to determine the effect of calcium on the activation energy of the char gasification reaction, char conversion rate measurements were conducted at 750°C, 800°C, 850°C, and 900°C for the raw birch wood, leached wood, Ca med and Ca high wood samples. The instantaneous reactivity at 20% was taken as the reference char conversion in order to calculate the apparent activation energy for the gasification reaction, according to Equation 4,

$$k = A \exp\left(\frac{-E_a}{RT}\right). \quad (4)$$

The instantaneous reaction rates are shown in the Arrhenius plot given in Figure 7. The calculated activation energies are given in Table 3. The activation energy for the raw birch wood is largely consistent with published activation energies for CO_2 gasification [40], which is typically in the range of 200-250 kJ/mol. The leached and Ca doped woods were found to have lower activation energies than the raw birch wood char, how-

Sample	Ea (kJ/mol)	R^2
Raw birch	197	0.9797
Leached	159	0.9563
Ca med	157	0.9883
Ca high	169	0.9571

Table 3: Activation energies for raw birch, leached, Ca med and Ca high chars and the R^2 for the linear regression.

ever there was no clear dependence of the activation energy on the calcium concentration in the wood. This is consistent with previous studies which report no significant dependence of activation on inorganic content [41, 42]. There is some disagreement on this issue, as other studies have reported both increases [43] and decreases [14, 44] in activation energy with catalyst loading and it is not understood what causes the conflicting results.

3.3. Char characterization

Three types of characterization were performed on the char samples collected from the fluidized bed. First, SEM images were taken including SEM-EDS analysis. The SEM gave a qualitative understanding of the char structure and and the EDS analysis showed the composition of the char surface. Next, BET surface area was measured to understand the effect of the doping on the total surface area of the char. Finally, ICP-OES analysis was done to measure the inorganic contents of the chars.

SEM images were taken of chars from the raw birch wood, leached wood, K doped wood and Ca doped wood and are shown in Figure 8. The chars which were imaged were collected from the reactor immediately after pyrolysis was finished. The raw birch wood char (Figure 8A) and K doped wood char (Figure 8B) were taken from the fluidized bed cyclone. The wood structure in these chars has been preserved and is clearly visible in the images. Significant amounts of K and Ca were detected on the surface of the raw birch wood char using EDS, however for the K doped wood char only a small amount of K was present, possibly indicating that potassium is no longer present on the char due to vaporization or that the potassium has been covered, such as by condensed tar or char during a melted char-precursor phase [45], and was no longer exposed to the char surface.

The leached wood char (Figure 8C) and Ca doped wood char (Figure 8D) were obtained by manually separating the char from the bed. These chars show similar features, in that the wood structure has largely been lost and the surface of the char shows significant plastic deformation. In both images it can be seen that bed particles have become attached to the char, and this is likely the reason that the char could not be removed to the cyclone even at high gas velocities. This is shown more clearly in Figure 9 which shows a close up image of a bed particle embedded in a Ca med wood char particle.

It has been observed in many previous studies that wood chars will tend to retain the fibrous structure of the parent material at low heating rates, appearing similar to the raw and K doped wood chars in this work, but lose those structures and show signs of plastic deformation at high heating rates, resembling the leached and Ca doped wood chars [34, 46, 47]. Guerrero et al. [48] compared eucalyptus chars formed in a slow heating TGA and fast heating fluidized bed. While the chars formed in the fluidized bed did show larger pores and increased surface area due to the rapid release of volatiles, the chars did not exhibit significant plastic deformation or loss of structure and so resembled the raw and K doped wood chars in the current work. There has been some evidence that the presence of inorganics will cause changes in char structure despite equal heating rates, but the mechanism of this is not well understood. Perander et al. observed plastic deformation in chars from wood which was leached of ash forming elements and impregnated with CaC_2O_4, but not in chars impregnated with K_2CO_3 or doped with Ca or K [17]. Jones et al. also observed melting during devolatilization of leached wood but not potassium impregnated wood [49].

BET surface area measurements were conducted on the raw birch wood char and K doped wood char which were collected from the cyclone of the fluidized bed reactor. Acid washed wood and Ca doped wood chars could not be separated from the bed in large enough quantities to perform the BET surface area measurement. The results of the measurement is shown in Table 4. The specific surface area for the raw birch wood char is consistent with surface area values for biomass chars reported in literature [19, 48, 50–56] and the observed increase with conversion also agrees with commonly observed char behavior. While the specific surface area of the raw birch wood char increases with char conversion, the instantaneous reaction rate, as given by Equation 3, remains largely constant until approximately 80% char conversion. As such, the BET surface area measurement does not correspond to the reactive surface area of the char in this case. The inability of the BET surface area measurements to explain the char reactivity is consistent with other studies [19, 57], although there is no consensus on this as some work has shown a correlation may exist [50, 53].

Despite the similarities in appearance between the K doped and raw birch wood chars, the potassium doped chars have a much smaller specific surface area when compared to the raw birch wood char. Low surface area measurements for chars have been reported previously [30, 58], however typically such low surface area is a sign of incomplete pyrolysis which is not the case in the present work. The specific surface area of the K doped wood chars does not change during the conversion process to the same extent as the raw birch wood char, but the low surface area of the K doped wood char corresponds to the comparatively low reactivity of the chars. It is generally thought that inorganics on the char surface will block some meso- and micropores causing a decrease in the surface area of the char and is the reason why chars produced from leached materials will have higher surface areas [59]. In some it has also been reported that doped chars will have decreased reactivity due to surface particles hindering gas diffusion to the carbon atoms [16, 17], but this is typically seen for Ca gasification at high temperatures or high Ca concentration.

Poor surface contact between the catalyst and the char or uneven dispersion on the char surface can also lead to ineffec-

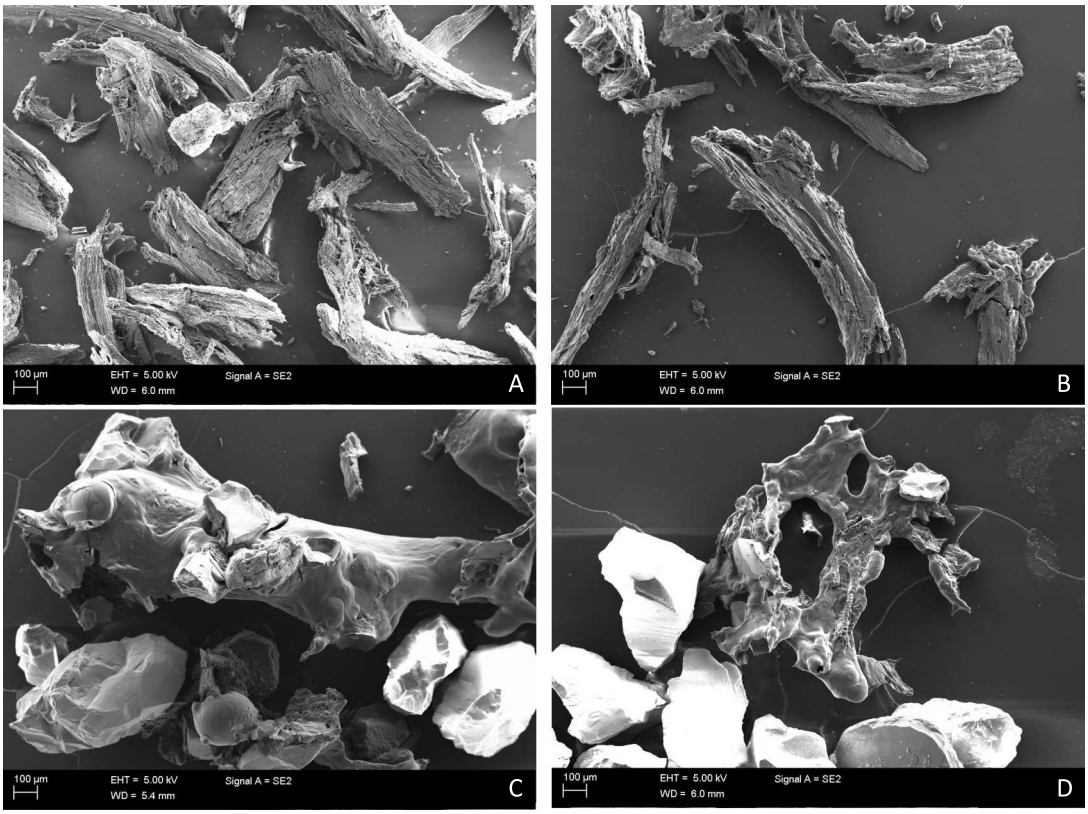

Figure 8: SEM images of char samples taken immediately after pyrolysis. The chars are: A) Raw birch, B) K med, C) Leached wood, D) Ca med.

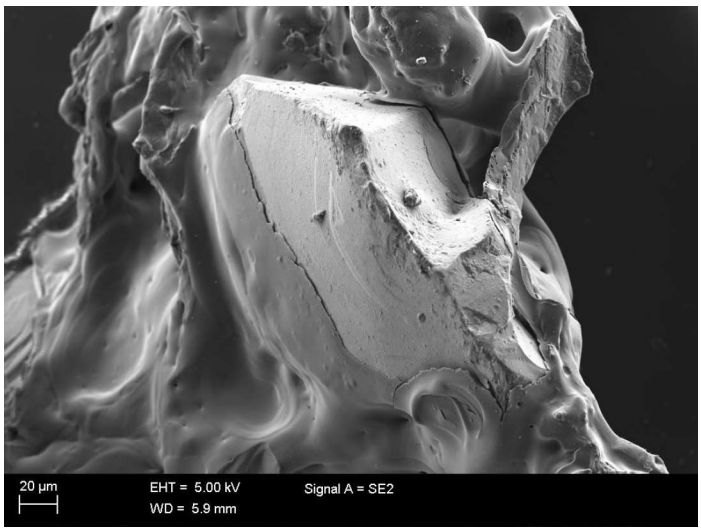

Figure 9: Close up image of bed particle embedded in Ca doped wood char.

tive catalysts during gasification. This has been seen, for example, with CaC_2O_4 impregnated wood when gasified in CO_2 [17]. This is unlikely to be the case for the doping process used in the present work, as the potassium and calcium are loaded to organic functional groups in the same way that most metals are naturally found in the wood [22]. It is likely that cause of the low reactivity and low surface area of the chars from K doped wood is due to coke formation on the char surface which blocks the char pores and prevents diffusion of the gasifying gas into the char. Interactions between coal volatiles and coal char have been shown to affect char reactivity and is dependent on the presence of inorganics in the char [60], while coke formation on char has been shown to block pores on char surfaces [61, 62]. It has been shown that potassium not only increases primary char formation but also catalyzes secondary reactions with volatiles to form char [63], and longer gas residence times allow these secondary reactions to happen. While the raw birch wood has approximately the same potassium concentration as the K high doped wood the raw birch wood char did not show signs of significant coke formation on the char surface. Because the only difference between the wood samples was the concentration of ash elements, it is possible the presence of calcium or other inorganics in the raw wood inhibited the formation of the coke layer on the char surface which resulted in lower char yield, higher surface area, and increased reactivity compared to the K doped wood char.

Sample	Gasification time (s)	Approximate char conv. (%)	BET surface (m^2/g)
Raw birch	0	0	104
Raw birch	120	10	370
Raw birch	200	20	553
K med	0	0	0.08
K med	120	10	7.8
K med	400	20	1.3
K high	0	0	0.20

Table 4: BET surface area measurements using N_2 for raw birch wood and K doped wood chars taken from the fluidized bed reactor.

Sample	Ca (mg/kg char C)	K (mg/kg char C)
Raw birch	8840	6130
K med	3220	5480
K high	2150	6160

Table 5: ICP-OES results for raw birch wood and K med chars showing the concentration of calcium and potassium in the char.

To determine to what extent the calcium and potassium remain on the char after pyrolysis, the char samples were analyzed using ICP-OES and the results are shown in Table 5. If a fixed carbon amount of 9% is assumed for all samples these concentrations in the char correspond to 790 mg Ca/kg biomass and 550 mg K/kg biomass for the raw sample. For the K med sample, assuming again 9% fixed carbon, the values are 290 mg Ca/kg biomass and 490 mg K/kg biomass. And finally for K high, 190 mg Ca/kg biomass and 550 mg K/kg biomass. These values correspond well to the initial biomass concentrations shown in Table 2 and indicate that a significant amount of the calcium and potassium remain in the char. While the concentration of calcium in the K med sample is slightly higher than expected, it still shows a significant decrease from the amount in the raw birch wood as a result of the leaching. The potassium concentration in the K med and K high chars are close to the potassium concentration in the raw birch wood, indicating that the low reactivity of the K doped wood chars is not a result of volatilization of the potassium. This supports the conclusion that the K doped chars were covered with a unreactive coke layer which prevented the potassium from catalyzing the char gasification.

4. Conclusion

Four types of birch wood samples (raw, leached, Ca doped, and K doped birch wood) were gasified in a laboratory scale fluidized bed reactor. Each sample exhibited different behavior in the fluidized bed as a result of the varying amounts of inorganics in the wood. The leached wood, containing very little inorganics, showed significantly lower char conversion rate than the raw birch wood. When the leached wood was doped with calcium, the conversion rate of the resulting char increased as the calcium concentration increased. The leached wood and Ca doped wood chars both showed signs of large amounts of plastic deformation on the char surface and had bed particles embedded into the char. The embedded bed particles made the char particles heavier and prevented elutriation out of the bed.

Doping the leached wood with potassium, even up to approximately the same level as in the raw birch wood, did not result in a significant increase in char conversion rates compared with the leached wood char. The low conversion rates measured for the K doped wood chars were due to the formation of an unreactive coke layer on the char surface which blocked the char pores. The formation of the coke layer is indicated by the increased char yield and low BET surface area of the K doped wood chars.

These results suggest that calcium is the primary active element in birch wood gasification. However, neither the presence of potassium or calcium alone explained the behavior of the raw birch wood. It is therefore likely that there is some interaction between the inorganics during pyrolysis and char gasification.

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Appendix A. Complete test list

The complete list of fluidized bed tests is shown in Table A.6. The test conditions and whether char was collected and through what method is given.

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Sample	Temperature °C	Gasification	No. of tests	Char collected
Raw birch	750	Complete	3	-
Raw birch	800	Complete	2	-
Raw birch	850	Complete	4	-
Raw birch	900	Complete	2	-
Raw birch	850	0 s	2	Cyclone
Raw birch	850	65 s	2	Cyclone
Raw birch	850	210 s	2	Cyclone
Leached	750	Complete	2	-
Leached	800	Complete	1	-
Leached	850	Complete	4	-
Leached	900	Complete	1	-
Leached	850	0 s	2	Bed removal
Ca low	850	Complete	3	-
Ca med	750	Complete	2	-
Ca med	800	Complete	1	-
Ca med	850	Complete	3	-
Ca med	900	Complete	1	-
Ca high	750	Complete	2	-
Ca high	800	Complete	2	-
Ca high	850	Complete	2	-
Ca high	900	Complete	2	-
Ca high	850	0 s	2	Bed removal
K med	850	Complete	4	-
K high	850	Complete	2	-
K med	850	0 s	2	Cyclone
K med	850	120 s	2	Cyclone
K med	850	400 s	2	Cyclone
K high	850	0 s	2	Cyclone

Table A.6: Complete list of fluidized bed measurements, test conditions and method of char collection. All gasification was done using 80% N_2/20% CO_2. 'Complete' gasification refers to tests where the char sample was fully converted in the bed (i.e. gasified until no more CO could be measured, then combusted) and no char was extracted for analysis.

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