Fast pyrolysis of cellulose in vacuum: The effect of potassium salts on the primary reactions

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HIGHLIGHTS

- Primary products of cellulose fast pyrolysis in a screen-heater.
- AAEMs catalysed reactions are extremely fast (millisecond).
- Destructive catalytic effects of AAEMs on anhydrosugars.
- Vacuum improves oil and anhydro-sugar yield for low AAEMs content cellulose.

ARTICLE INFO

ABSTRACT

In this work we investigated the effects of K_2CO_3 (1, 100, 1000 and 10,000 mg kg^{-1}), KOH (1000 mg kg^{-1}) and KCl (1000 mg kg^{-1}) on the primary products of cellulose fast pyrolysis in vacuum (5 mbar) and at atmospheric pressure (1000 mbar) using a dedicated screen-heater set-up. The screen-heater combines fast heating of the cellulose sample with very fast (milliseconds) removal (high escape rate) and quenching of the reaction products. The solid residue, condensed product, non-condensable gas, levoglucosan and glucose yields obtained from the screen-heater experiments are compared with the product yields from the fluidized bed reactor to elucidate potassium catalysed reactions in the hot vapour phase. Potassium was found to be catalytically active even when the escape rate (milliseconds) of the product was extremely high. Consequently, significantly lower condensed product and sugar yields were obtained. The production of non-condensable gas could almost completely be ascribed to thermal reactions in the vapour phase when the potassium content is low but was predominately produced at the hot reacting particle when the potassium content is high. It was found that in the case of levoglucosan the anions were active in potassium the following order $Cl^- > OH^- > CO_3^{2-}$. The activity in reducing the hydrolysable anhydro-sugars (levoglucosan and oligomers), expressed as glucose recovery, shows the following order, $OH^- > Cl^- > CO_3^{2-}$. Vacuum could help to improve the oil and sugar yield by fast removal of the products from the hot reacting sample. However, this only holds for cellulose with a low potassium (<100 mg kg^{-1}) content.

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1. Introduction

One of the promising routes to renewable energy and chemicals is via fast pyrolysis of lignocellulosic biomass to produce a bio-oil also known as pyrolysis oil. Fast pyrolysis is a process in which the biomass thermally decomposes, in the absence of oxygen, at temperatures around 500 °C. The generated pyrolysis vapours are condensed to obtain the pyrolysis oil. This oil is a complex mixture of water and many different organic compounds, which are often present at low concentration [1]. Nowadays, the majority of the research focuses on the production of targeted compounds (e.g. mono-phenols, sugars) at high yields. Especially the production of anhydrosugars from lignocellulosic biomass seems to be a promising route. Sugar yields (e.g. levoglucosan, xylose and mannose) up to 30 wt% have been reported [2]. These sugars are interesting building blocks for the production of chemicals such as levulinic esters, acids (e.g. levulinic, citric) and can be fermented to produce bio-ethanol [3]. The pyrolysis of cellulose, being one of the major building blocks of biomass and a precursor of sugars, is therefore often studied [4,5]. The underlying mechanism of cellulose pyrolysis is a complex network of reactions which is largely affected by heat and mass transfer.

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The true primary reaction products from cellulose pyrolysis are levoglucosan and anhydro-sugar oligomers built-up from levoglucosan units. These oligomers have varied degrees of polymerization (e.g. levoglucosan, cellobiosan, cellotetrasan, etc.) [6–9]. In almost all of these studies these primary products (anhydro-sugars) were extracted from a partially converted cellulose particle by a solvent [6–8]. In our previous paper the potential of producing anhydrosugars from very pure cellulose, containing only 1 mg kg^{-1} of AAEMs, under various process conditions was studied [10]. It was found that 70 wt% of hydrolysable anhydro-sugar can be obtained when high heating rates are combined with high escape and quenching rates of the volatile products. Sugars with a DP up to 12 were identified in the condensed product. Reducing the escape rate of volatile products thereby increasing the time of the molecules on the pyrolyzing particle, accomplished by increasing the pressure from 5 mbar to atmospheric, reduced the hydrolysable sugar yield to 50 wt%. Increasing the hot vapour residence time did not affect the sugar yield but significantly more gas is produced. It is well known that the presence of AAEMs reduces the anhydro-sugar production at particle level and in the vapour phase under typical fast pyrolysis conditions. Several methods exist to remove the AAEMs from biomass; however, complete removal of the AAEMs will not be realistic in practice. Currently it is unknown to which extent the effects of low concentration of AAEMs can be minimized by the means of process conditions, such as very high heating rates, vacuum and short hot vapour residence times. Therefore, the goal of the work is to investigate the effects of small amounts of potassium in cellulose under various pyrolysis process conditions.

In order to study the effects of potassium on the primary products of cellulose pyrolysis a screen-heater set-up is used that provides fast heating rates, minimal mass transfer limitations (vacuum, small sample size), minimal vapour residence times and fast freezing of the condensed product. This study is an extended work of our previous publication on the interplay between chemistry and mass/heat transfer limitations for AAEMs free cellulose [10]. Potassium carbonate was chosen as model compound for the AAEMs because it is naturally presented in biomass [2]. In this work it was shown that impregnating carbonate salts in acid leached biomass gave identical pyrolysis results as obtained from native biomass. The following concentrations were chosen: 1 mg kg^{-1}– 100 mg kg^{-1} was selected as lower boundary and 1000 mg kg^{-1} because it is typically achieved after acid leaching and 10,000 mg kg^{-1} as concentration typical in untreated biomass. It is worth to mention that 100 mg kg^{-1} corresponds to a single potassium molecule per ~2500 sugar monomers and 1000 mg kg^{-1} to a single potassium molecule per ~250 sugar monomers. In addition, the catalyzing effects of different anions (i.e. potassium connected with CO_3^{2-}, Cl^-, or OH^-) on cellulose fast pyrolysis will be studied. In this set of experiments the potassium concentration in cellulose is kept constant at 1000 mg kg^{-1}. The effect of pressure will be studied by comparing the results of cellulose pyrolysis at 5 mbar and 1000 mbar. In addition, the effect of vapour residence time on the pyrolysis products will be studied by comparing the results from the screen-heater experiments (minimal vapour residence time) with fluidized bed experiments (1.6 s hot vapour residence time). Not only GC–MS/FID detectable compounds (e.g. levoglucosenone and acetol) and levoglucosan (HPLC) will be analysed but also larger hydrolysable anhydro-sugars lumped as glucose.

2. Materials and methods

2.1. Materials

Avicel Cellulose PH101 (Sigma Aldrich; particle size ~50 μm, 60.5% crystallinity [11], ash content 0.005 wt%, AAEMs content 1 mg kg^{-1}, degree of polymerization specified <350, average 220 [12]) and levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth Ltd., purity > 98) were used as a feedstocks. Potassium carbonate (K_2CO_3, Sigma Aldrich, purity > 99%), potassium chloride (KCl, Sigma Aldrich, purity > 99%) and potassium hydroxide (KOH, Sigma Aldrich, purity > 98%) were used as a source for potassium.

The screens (25 mm × 50 mm) were tailored from a large metal mesh (Dinxperlo, Wire Weaving Co. Ltd., mesh 200 wire thickness 0.06 mm × 0.06 mm, twilled weave, AISI 316). The screens were washed with Milli-Q water followed by Acetone (Merck, LC LiChrosolv®, purity > 99.8%) and dried at 105 °C for 24 h.

The condensed product was recovered by rinsing the reactor vessel with Methanol (Merck, LC-MS LiChrosolv®, purity > 99.9%) or Milli-Q water for GC/MS or HPLC analysis respectively. Sulfuric acid (H_2SO_4, Sigma Aldrich, purity > 99.99%) was used for hydrolysis of the condensed product and barium carbonate ($BaCO_3$, Sigma Aldrich, purity > 99%) to neutralize the sample prior to HPLC analysis.

Levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth Ltd., purity > 98%) and glucose (Sigma Aldrich, purity > 99.99%) were used as standards for the HPLC calibration.

Acetol (1-Hydroxy-2-propanone, Sigma Aldrich, purity > 89%), Levoglucosenone (1,6-anhydro-3,4-dideoxyhex-3-enopyran-2-ulose, Carbosynth Ltd., >95%) were used for calibration of the GS-MS/FID.

2.2. Methods

2.2.1. Impregnation of potassium in cellulose

K_2CO_3, KCl or KOH was dissolved in the Milli-Q water and then mixed with dry cellulose. The potassium (K_2CO_3) concentration in cellulose was varied between 1 mg kg^{-1} and 10,000 mg kg^{-1}. For KCl and KOH the concentration of potassium was 1000 mg kg^{-1}. The mixture was thoroughly mixed (T = 20 °C) in a round bottom flask for 1 h. After mixing the Milli-Q water was removed using a rotary evaporator (BÜCHI Rotavapour R-200, T = 65 °C, P = 100 mbar, ~1 h). Next, impregnated cellulose samples were dried for 24 h using a vacuum oven (Heraeus FVT420, T = 20 °C, P = 1 mbar). A similar procedure was applied to levoglucosan impregnation (potassium (K_2CO_3) concentration 1000 mg kg^{-1}). Levoglucosan and potassium carbonate readily dissolve in an aqueous solution. Potassium carbonate was added to the levoglucosan/ water solution (with excess water). The water was slowly removed using a Rotavapour set-up. The mixture was constantly stirred to ensure uniform distribution of salt in the solution. As water evaporated from aqueous mixture, the solution became saturated. Gradual precipitation of sugar and salt, from the saturated aqueous solution, ensured a homogeneous distribution of potassium covering the levoglucosan.

2.2.2. Fast pyrolysis in a screen-heater set-up

In current work, the screen-heater set-up was used to study the effects of potassium on the early stages of cellulose fast pyrolysis [13]. The screen-heater set-up is shown in Fig. 1. The screen-heater set-up, operating procedure, characteristics and a detailed experimental validation of the screen-heater has been explained in detail in our previous work [10]. Briefly described as follows: The feedstock was pressed between two screens (#2). The pressed screens were clamped between the two copper electrodes with bolts (#5). The electrodes and clamps with bolts (#5) were covered with tape (#6). A glass vessel (#1, Duran 250 ml centrifuge tube, round bottom, 147 mm × 56 mm) was installed around the copper electrodes (#5) and screens (#2) as shown in the Fig. 1. The reactor vessel was placed in a liquid nitrogen bath (#4) to achieve quick quenching of the produced vapours/aerosols.
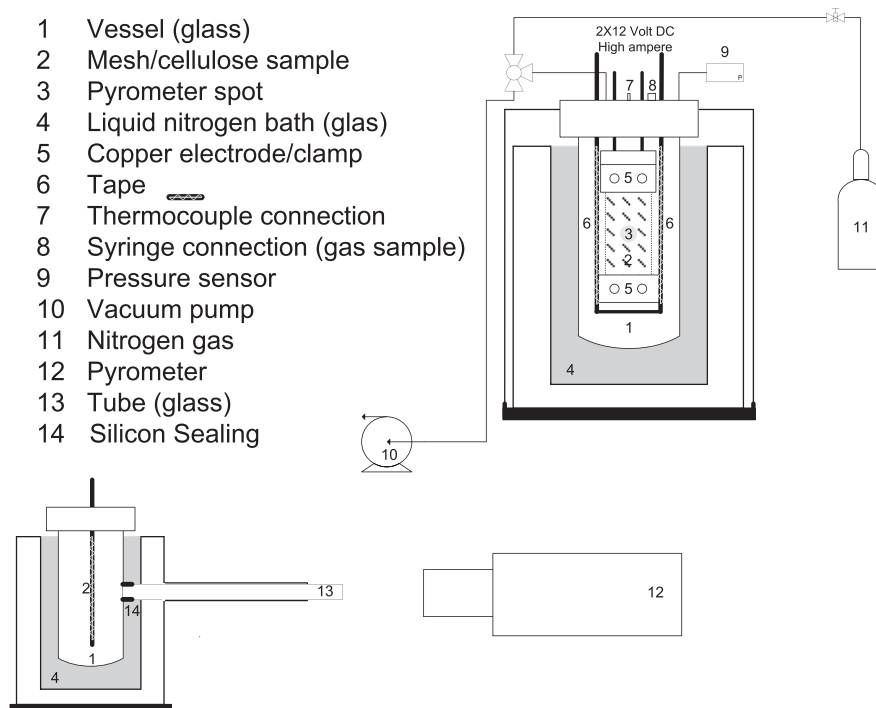
1 Vessel (glass)
2 Mesh/cellulose sample
3 Pyrometer spot
4 Liquid nitrogen bath (glas)
5 Copper electrode/clamp
6 Tape
7 Thermocouple connection
8 Syringe connection (gas sample)
9 Pressure sensor
10 Vacuum pump
11 Nitrogen gas
12 Pyrometer
13 Tube (glass)
14 Silicon Sealing

Fig. 1. Schematics of the screen-heater reactor.

Nitrogen gas (#11) was used to remove air from the vessel before each experiment. Vacuum (≤5 mbar) was achieved by an inline vacuum pump (#10). In case of an atmospheric pressure experiments (referred to as 1000 mbar experiment) a nitrogen atmosphere was maintained after flushing the air out. The pressure inside the glass vessel was 5 mbar or 1000 mbar and was monitored by two high speed pressure sensors (#9, Heise DXD3765 and Druck PTX 520). The vapour phase temperature was recorded by using a K-type thermocouple (#7, diameter 0.025 mm connected to a Weidmuller MAS K-type thermocouple signal conditioner, recording every 16 ms) placed at 15 mm distance from the screens. The temperature of the screen was measured with a pyrometer (#12, Kleiber KGA 730). The detailed calibration procedure of the pyrometer is described elsewhere [10]. The optical beam of pyrometer was focused at the centre of the screens (#3) via a glass tube (#13) and silicon sealing (#14) to avoid the disturbance of the temperature measurement by the liquid nitrogen. The temperature measured at the pyrometer spot is termed final mesh temperature (T_{FS}). The heating pulse was given via copper electrodes by two Varta Silver Dynamic batteries (12 V/225 Ah, 830A). The energy required during the reaction i.e. to maintain constant T_{FS}, was supplied by two Varta Pro Motive batteries (12 V/100 Ah/1150). A Pyrolysis experiment was performed by giving a heating pulse using a LabVIEW program which contained a PID routine to control T_{FS}. The holding time at 530 °C was set at 5 s. The pressure and temperature data was recorded by using a DAQ card (NI PCI-6281) and is processed by a LabVIEW program (running at 2000 Hz on a computer). At the end of the experiment, the set-up was removed from the liquid nitrogen bath. The gas sample was taken after each experiment (at room temperature) with a 10 ml syringe (#8) mounted on top of the reactor.

2.2.3. Product recovery screen-heater

To recover the pyrolysis products after the experiments and to obtain the mass balance the following procedure was applied. After the experiment was performed and the reactor reached ambient temperature, it was filled with dry nitrogen gas, in the case of

5 mbar vacuum, until the pressure in the reactor reached 950 mbar. A gas sample was taken from the reactor using a 10 ml syringe. In case of an atmospheric pressure experiments, gas was allowed to expand in a gas bag from which a sample was taken using a 10 ml syringe. The total gas volume was determined as the summation of the reactor vessel volume and gas bag volume. The volume of gas bag was estimated by volume displacement. Gas samples were analysed using gas chromatography. The gas yield was calculated as followed (Eq. (1)):

$$Y_{gas} = \sum_{i=1}^{n} \frac{\frac{P_{sample} \; Vol\%_i \; (V_{vessel}+V_{bag})}{RT_{ambient}} MW_i}{M_{feedstock}} \tag{1}$$

where, $M_{feedstock}$ is the mass of dry cellulose feedstock. Where, i is the number components detected in the gas sample; P_{sample} is the pressure at which sample is taken; $Vol\%_i$ is the volume percentage of component i in the gas sample; V_{vessel} is the volume of vessel; V_{bag} is the volume of the gas bag, for vacuum experiment V_{bag} was neglected; MW_i is the molecular weight of component i; $T_{ambient}$ was the temperature at which sample was taken; R is the universal gas constant.

The weight of the screens (#2) was measured with and without feedstock before the start of the experiment. After the experiment the screens are weighed again. Note, the solid residue is not corrected for salts. The yield of solid residue can be calculated as followed (Eq. (2)):

$$Y_{solid\ residue} = \frac{M_{screens+residue} - M_{screens}}{M_{feedstock}} \tag{2}$$

where, $M_{screens+residue}$, $M_{screens}$ are the mass of the screens with and without the solid residue, respectively.

Tape (#6) was wrapped around the electrodes, clamps and bolts to allow for recovery of the condensed product. Before and after every experiment the glass vessel (#1), copper clamps with bolts (#5) and tape (#6) were all weighed. After the experiment, the glass vessel (#1) was removed and immediately weighed. After that, the glass vessel was sealed with parafilm to prevent evapora-

tion of volatile compounds. The tape (#6) was removed from the electrodes, clamps and bolts (#5) and weighed together. The yield of condensed product is calculated by the following equation (Eq. (3)):

$$Y_{condensed\ product} = \frac{(M_{vessel+CP} - M_{vessel}) + (M_{c+b+t+CP} - M_{c+b+t})}{M_{feedstock}} \quad (3)$$

where, $M_{vessel+CP}$, M_{vessel} are the mass of the vessel with and without the condensed product, respectively. Similar, $M_{c+b+t+CP}$, M_{c+b+t} are the mass of the clamps, bolts and tape with and without condensed product. The mass balance closure is calculated as follows (Eq. (4)):

$$Y_{total} = Y_{gas} + Y_{solid\ residue} + Y_{condensed\ product} \quad (4)$$

In our previous work we found that above 500 °C, optimal yield of condensed product can be achieved with less than 1 wt% of solid residue, and gas yield [10]. Therefore, in current work all experiments were performed at 530 °C.

2.2.4. Fluidized bed pyrolysis

In this research cellulose was also pyrolyzed in a bench scale fluidized bed reactor at a temperature of 530 °C. Potassium carbonate was impregnated in cellulose. The potassium concentration in cellulose was varied between 1 mg kg^{-1} and 1000 mg kg^{-1}. Details of the set-up can be found elsewhere [14]. Short recap, silica sand (220 μm) was used as bed material and preheated nitrogen as the fluidization gas. During each experiment, ~100 g of cellulose was fed manually to the reactor in batches of 2 g–5 g together with 4 g–8 g of sand. The feeding system consists of two valves which function as a gas lock. The experimental time was 25 min. Produced solid residue was separated from outgoing gas/vapour stream leaving the reactor by using a wire-mesh filter (pore size 9 μm). Almost all solid residue, including potassium, was collected on the filter. This filter cake with varying amounts of potassium was used as tool to study the secondary vapour phase reactions. The estimated vapour residence time in the hot zone of the set-up, including reactor and tubing, was always kept around 1.6 s. About 95% of the produced vapours were condensed by an electrostatic precipitator (ESP) operated at 20 °C (outgoing gas temperature). The remaining vapours were condensed in a double walled glass condenser operated at −5 °C (outgoing gas temperature). Both fractions were considered for the mass balance. The solid residue yield was determined by weighting the solid residue/sand mixture and solid residue/filter after the experiment and subtracting the initial weight of the sand and filter plus the sand fed during the experiment. The gas yield was determined by difference.

2.2.5. Hydrolysis

The total amount of hydrolysable anhydro-sugars (including oligomers) were determined, after hydrolysis, as glucose. The NREL LAP method "Determination of sugars, by-products, and degradation products in liquid fraction process samples" was used. In short, 30 mg–50 mg of condensed product was dissolved in Milli-Q water. Concentrated H$_2$SO$_4$ was added to the diluted condensed product to obtain a concentration of 3.5 vol.%. The condensed product is heated in a glass autoclave at 120 °C for 1 h. After hydrolysis the condensed product was neutralized by adding BaCO$_3$. The condensed product is then filtered to remove the formed precipitates. The glucose concentration was determined using HPLC. Glucose is a representative of all hydrolysable sugars including levoglucosan, cellobiosan, cellotetrasan, etc. The yield of hydrolysable anhydrosugars is therefore expressed as the ratio of carbon in glucose to carbon in cellulose.

2.3. Analytical techniques

2.3.1. Gas chromatography (GC)

A micro-GC (Varian MicroGC CP4900, 2 analytical columns, 10 m Molsieve 5A, 10 m PPQ, Carrier gas: Helium) was calibrated for N$_2$, O$_2$, CO, CO$_2$, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, C$_3$H$_6$, C$_3$H$_8$. The gas samples taken after the screen-heater pyrolysis experiments were analysed twice to ensure reproducibility.

2.3.2. Gas chromatography mass spectrometry (GC-MS/FID)

The amount of acetol and levoglucosenone in the condensed product was obtained using GC–MS/FID (GC 7890A Ms 5975C Agilent Technologies) analysis. The GC–MS/FID was equipped with a capillary column (Agilent HP-5Ms, HP19091S-433) and helium was used as carrier gas. The samples were prepared by rinsing the screen-heater reactor vessel with methanol (~2 ml) and were filtered with 0.45 μm Whatman RC Agilent filter.

2.3.3. Ion chromatography (IC)

The potassium impregnated cellulose was added to the Milli-Q water and mixed for 30 min. The samples were filtered (Whatman RC Agilent 0.2 μm filter) prior to ion chromatography (IC) analysis. The IC (Metrosep 850 Professional IC) is equipped with a cation column (Metrosep C6 – 150/4.0) and Metrohm 732 IC detector coupled to a IC Separation Centre. The analysis was performed at room temperature and with eluent (1.7 mM nitric acid + 1.7 mM dipicolinic acid) flow rate of 1 ml min^{-1}. The amount of potassium was quantified by using five point calibration.

2.3.4. High pressure liquid chromatography (HPLC)

Levoglucosan and glucose in the condensed product were analysed using HPLC (Agilent 1200 series, column: Hi-Plex-Pb maintained at 70 °C, mobile phase: Milli-Q water, 0.6 ml min^{-1}). All samples were filtered (Whatman RC Agilent 0.2 μm filter) prior to analysis. The quantification of levoglucosan and glucose in the condensed product was done by using a four point calibration.

3. Results and discussion

3.1. Screen-heater and fluidized bed characteristics

The characteristics of the screen-heater have been discussed in detail in our previous papers [10,15]. In this work, the characteristics are briefly discussed and summarized in Table 1. The cellulose sample is distributed evenly between the two screens. The heating rate of the screens is ~5000 °C s^{-1}. A nearly uniform heating of the thin cellulose layer (50 μm) was achieved [10]. The temperature difference over the screen was ±15 °C. The cooling rate of the screens was 100 °C s^{-1}. A detailed validation of the temperature profiles and measurement can be found elsewhere [10]. Previously it was found that the pyrolysis time (time to reach full conversion) at 610 °C and at 5 mbar is around 121 ms for cellulose with

Table 1
Summary of experimental conditions.

	Screen-heater	Screen-heater	Fluidized bed
Temperature (°C)	530	530	530
Pressure (mbar)	5	1000	1000
Heating rate (°C s^{-1})	5000	5000	5000
Hot vapour residence time (s)	0.02	~0.02	1.6
Vapour temperature (°C)	N.A.	80[*]	530
Levoglucosan evaporation time (s)	0.03	<0.3	<0.3

[*] Temperature measured 1.5 cm distance from the screen.

1 mg kg^{-1} AAEMs. The pyrolysis time is also checked for cellulose impregnated with potassium at 530 °C and at 5 mbar, see Fig. 2. This figure shows screenshots of a movie recorded with a high speed camera. After 79 ms the pyrolysis reactions are finished because the shape of the black material between the screens and the appearance of the condensed product (see arrows) on the glass reactor wall did not change anymore between 79 ms and 304 ms.

The time difference between the escape of vapours/aerosols from the reacting particle till quenching, is defined as the hot vapour residence time. At 5 mbar, the vapours/aerosols are rapidly quenched at the reactor wall (−100 °C) which was surrounded by liquid nitrogen. The hot vapour residence time was calculated and verified by visual inspection and was ∼20 ms [10]. Also at 1000 mbar the escaped products cool very rapidly to temperatures below 80 °C. This was measured by a thermocouple positioned 1.5 cm from the screens. The vapours were cooled by the cold nitrogen in the reactor vessel. This nitrogen gas is cooled by the liquid nitrogen bath surrounding the reactor vessel. The biggest difference between the screen-heater set-up and the fluidized bed set-up is the hot vapour residence time (∼20 ms [10] versus 1.6 s [14]), see Table 1.

When vacuum (5 mbar) is applied in the screen-heater experiments the escape rate of the products is a factor 10 higher compared to 1000 mbar experiments in the screen-heater [10]. As a consequence, the residence time of the products on the hot reacting particle is considerably lower in the case of vacuum (lower mass transfer limitations).

3.2. Effect of K$_2$CO$_3$ concentration on condensed product, gas and solid residue

In this part of the work the concentration of potassium (K$_2$CO$_3$) in cellulose has been varied between 1 mg kg^{-1} and 10,000 mg kg^{-1}. The predetermined amount of added potassium to the cellulose and the actual amount potassium in cellulose after impregnation can be seen in Table 2. The amount of impregnated potassium was measured by IC. As can be seen these values nicely match each other for all three concentrations.

The obtained mass balance closure of our experiments was between 77 wt% and 96 wt%. The reason for the lower mass balance closure is that water and some of the light oxygenates are lost during dismantling of the set-up. The mass balance closure was the lowest for the high potassium concentrations. For pyrolysis experiments with a higher concentration of potassium higher production of water can be expected [2]. Indeed, the fluidized bed experiments showed that the water production increases from 11 wt% to 14 wt% when potassium concentration increased from 1 mg kg^{-1} to 1000 mg kg^{-1}, respectively. The number of experiments in the screen-heater performed, for each potassium concentration, was at least 6 at 5 mbar and 2 at 1000 mbar. As can be seen, the reproducibility of the experiments was satisfactory, see Figs. 3, 4 and 6.

Fig. 3 (see Tables S1 and S2) shows the condensed product yield as function of the potassium concentration (on logarithmic scale) at 5 mbar and at 1000 mbar pressure. The figure includes the data from the screen-heater and fluidized bed experiments. It can be seen that, as an effect of increasing potassium concentration, the condensed product yield decreases from 0.86 to 0.57 kg kg^{-1} at 1000 mbar. At 5 mbar the condensed product yield decreases from 0.96 to 0.52 kg kg^{-1}.

A clear difference in condensed product yield can be observed between vacuum and atmospheric pressure experiments at low concentration of potassium i.e. up to 1000 mg kg^{-1}. In this range, the condensed product yield was higher at 5 mbar compared to at 1000 mbar experiments. A plausible explanation is that under vacuum the escape rate of pyrolysis products from the hot reacting particle is faster resulting in a shorter contact time, or even no contact at all, between the hot products and the potassium. The pyrolysis time at 5 mbar is ∼79 ms. which implies a very high product escape rates from the hot reacting particle. Moreover, even in this short pyrolysis time, potassium causes the oil yield to decrease dramatically. When the potassium concentration is further increased to 10,000 mg kg^{-1} the yield of condensed product becomes almost equal at both pressures. It is worthwhile to mention that during pyrolysis in the screen-heater some water insoluble compounds (<12 wt% of the cellulose) were ejected from the screens. In case of cellulose with 1 mg kg^{-1} AAEMs, the insoluble fraction turned out to be unconverted white cellulose whereas in presence of potassium in cellulose the ejected material had a dark brown colour, indicating that it has been (partially) converted [10].

For the fluidized bed experiments comparable reduction in condensed product can be observed when the potassium concentration in cellulose increases. The condensed product yields in the fluidized bed are always lower compared to the screen-heater
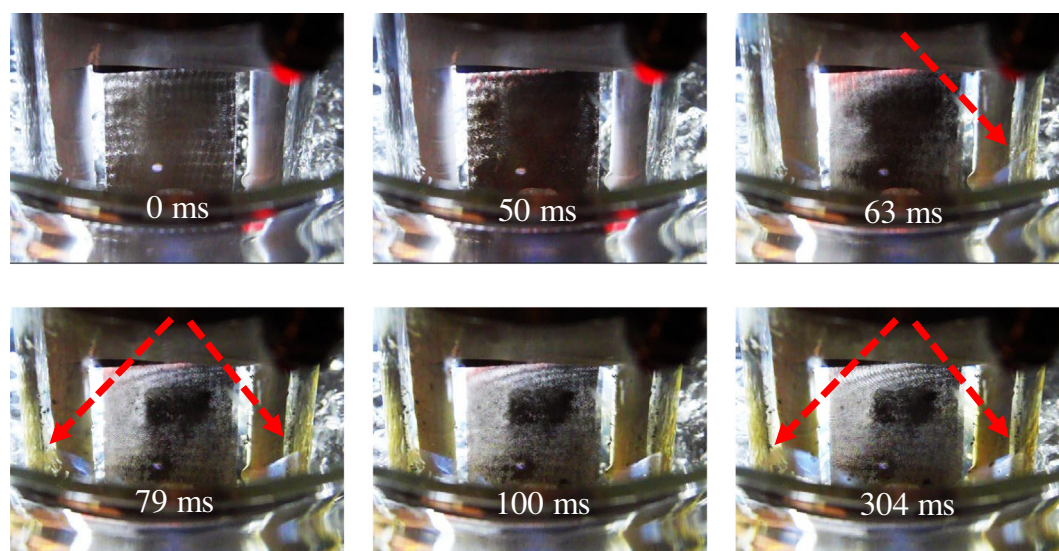

Fig. 2. Screen shots extracted from a high speed camera movie of potassium impregnated cellulose (10,000 mg kg^{-1}) pyrolysis. Pressure 5 mbar, T$_{FS}$ = 530.

Table 2
Potassium content added and detected by IC.

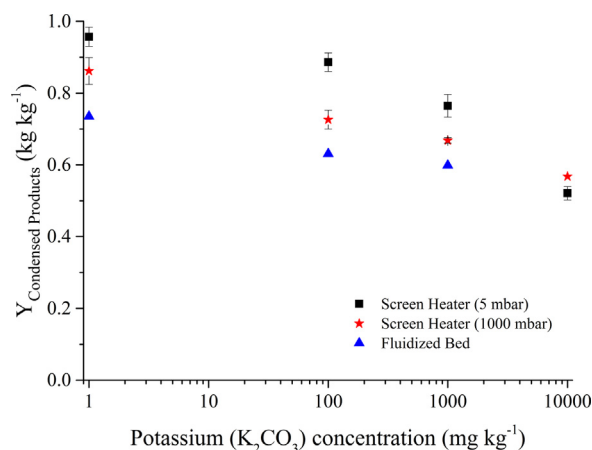| Added potassium ($mg\,kg^{-1}$)	Potassium impregnated in cellulose ($mg\,kg^{-1}$)	Error (%)
100	98	2.5
1000	962	3.8
10000	9982	0.3

Fig. 3. Condensed product yield as a function of potassium concentration in cellulose; in screen-heater and fluidized bed. T_{FS} = 530 °C.
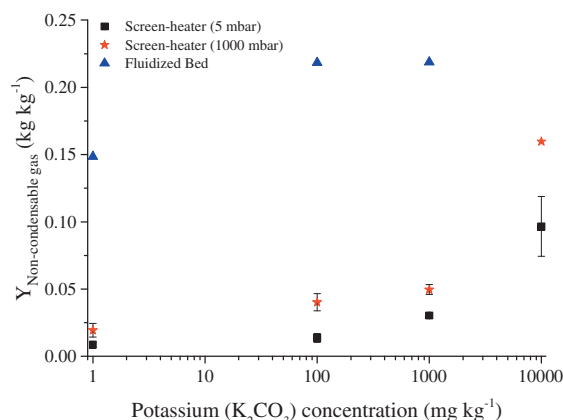

Fig. 4. Non-condensable gas yield as a function of potassium concentration in cellulose; in screen-heater and fluidized bed. T_{FS} = 530 °C.
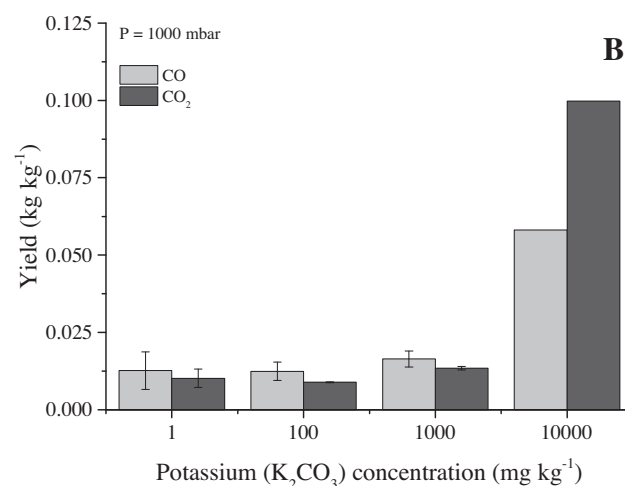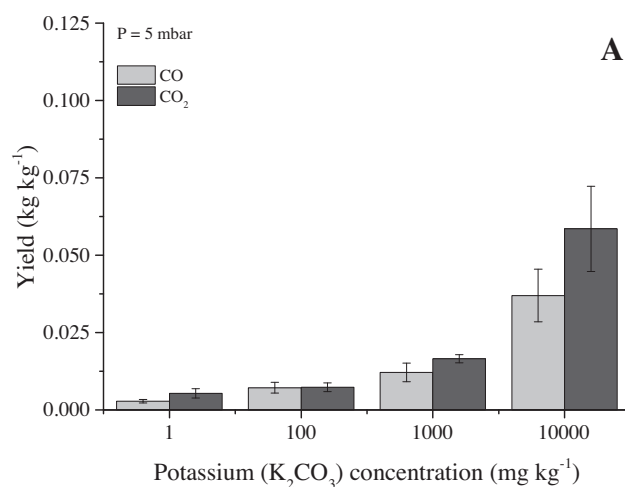

Fig. 5. CO and CO_2 yield as a function of potassium concentration in cellulose in screen-heater. A) 5 mbar B) 1000 mbar, T_{FS} = 530 °C.
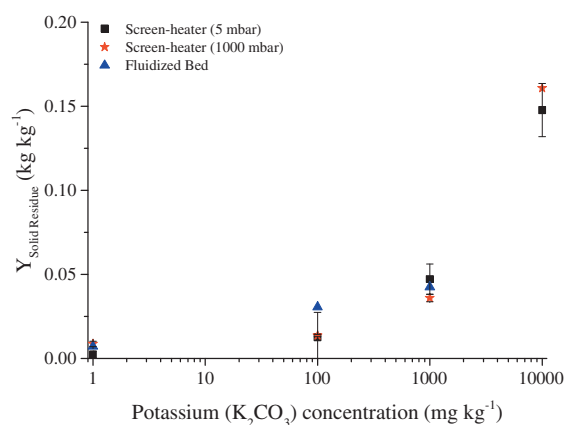

Fig. 6. Solid residue yield as a function of potassium concentration in cellulose; in screen-heater and fluidized bed. T_{FS} = 530 °C.

due to extensive vapour phase cracking reactions. Concluding, a significant higher yield of condensable product could be obtained when vacuum is applied and the vapour phase residence time is minimized as long as the concentration of potassium (K_2CO_3) in cellulose is low. At higher AAEMs concentrations, (partly) removing or passivation of the AAEMs prior to pyrolysis is mandatory to prevent AAEMs catalysed reactions that lead to low oil and sugar yields.

The effect of potassium (K_2CO_3) concentration on non-condensable gas yield, at two different pressures in the screen-heater, and fluidized bed experiments is shown in Fig. 4 (see Table S1 and S2). It can be seen that in the case of the screen-heater more non-condensable gas is formed at higher potassium concentration. However, at both pressures until a potassium concentration of 1000 $mg\,kg^{-1}$ the gas yield remains below 5 wt% and is even close to zero when the potassium concentration is 1 $mg\,kg^{-1}$. At higher potassium concentration (10,000 $mg\,kg^{-1}$)

the gas yield increases up to 10 wt% and 15 wt% at 5 mbar and at 1000 mbar, respectively. Reactions at particle level catalysed by potassium salt are responsible for the non-condensable gas production since the vapour phase reactions are largely suppressed in the screen-heater.

The fluidized bed experiments revealed that a large amount of the non-condensable gas is already produced at very low potas-

sium concentration (1 mg kg^{-1}). This non-condensable gas is produced by vapour phase reactions induced by the long hot vapour residence time (1.6 s). However, even at very low potassium concentration (1 mg kg^{-1}) most of the non-condensable gas is already produced. This non-condensable gas is produced in the gas phase by thermal effects. At higher concentrations of potassium (K$_2$CO$_3$), the additional amount of non-condensable gas produced is small and can be explained by potassium catalysed intra-particle reactions or reactions in the vapour phase catalysed by potassium present in the entrained solid residue particles.

Fig. 5 (see Table S3) shows the CO and CO$_2$ production for the screen-heater experiments. Other non-condensable gasses like CH$_4$ and H$_2$ and higher hydrocarbons, which are typically found in pyrolysis with significant vapour residence times [10], were not observed. It can be seen that the yields of CO and CO$_2$ are quite comparable at low potassium concentrations. At higher potassium concentrations the CO$_2$ production becomes dominant. Because the vapour phase residence time is very small in the screen-heater it can be concluded that CO and CO$_2$ are produced by reactions occurring on the hot reacting particle and is accelerated by the presence of potassium.

Fig. 6 (see Tables S1 and S2) shows the solid residue yield as function of potassium (K$_2$CO$_3$) concentration in cellulose, at 5 mbar and at 1000 mbar. It was found in our previous paper that in case of cellulose with 1 mg kg^{-1} AAEMs, virtually no solid residue was observed on the mesh for both pressures. At 100 mg kg^{-1} potassium in cellulose the solid residue yield is still very low. A general trend is that when the potassium concentration increases the solid residue yield increases. This trend is comparable to the trend observed for the gas yield. The solid residue yield remained below 5 wt% until 1000 mg kg^{-1} potassium concentration at both pressures (5 mbar and 1000 mbar) and increased steeply to 15 wt% for 10,000 mg kg^{-1} potassium concentration. The insignificant difference in char yield (in screen-heater) at 5 mbar and 1000 mbar point towards the conclusion that the composition of the pool of decay products on the reacting sample does not influence the production rate of char. Moreover, the different products can escape fast enough from the reacting particle in either cases preventing or supressing the formation of char. No significant differences can be observed between the fluidized bed and screen-heater experiments. At this high potassium concentration, carbonaceous material, black in colour, was found between the meshes after the experiment.

3.2.1. Condensed product composition

Fig. 7(A) (see Table S4) shows the levoglucosan yield and Fig. 7 (B) (see Table S4) shows the glucose recovery as a function of the potassium (K$_2$CO$_3$) concentration in cellulose. Glucose was obtained after hydrolysis of levoglucosan and oligomeric anhydro-sugars present in the condensed product. The glucose recovery is expressed as the ratio between the carbon in glucose and carbon in cellulose, see Fig. 7(B). The following observation can be made from the data – i) Levoglucosan was found to be the major product in fluidized bed experiments and for the screen-heater experiments when operated at 1000 mbar for a potassium concentration below 1000 mg kg^{-1}. When the potassium concentration was 1000 mg kg^{-1} or higher no differences in levoglucosan yield was found at 5 mbar and 1000 mbar experiments in the screen-heater. Moreover, when the concentration of potassium in the cellulose sample increases the levoglucosan production decreases, ii) When vacuum is applied, in the screen-heater experiments, the glucose recovery is the highest due to the production of more anhydro-sugars with higher degree of polymerization (e.g. cellobiosan, cellotriosan, etc.). The higher production can be explained by the higher escape rates from the hot reacting particle compared to the 1000 mbar experiments resulting in less time for
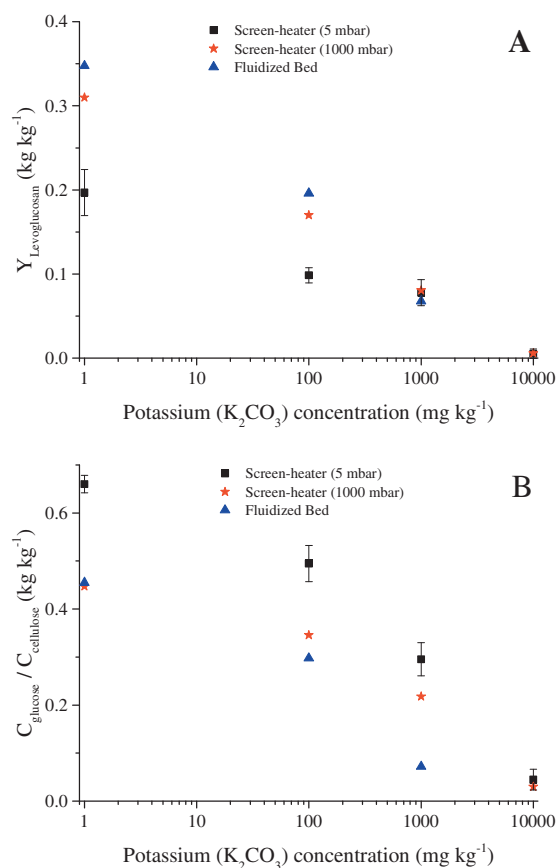

Fig. 7. (A): Levoglucosan yield as a function of potassium concentration in cellulose; in screen-heater and fluidized bed. T$_{FS}$ = 530 °C. (B): Glucose recovery after hydrolysis of condensed product as function of potassium concentration in cellulose; in screen-heater and fluidized bed, T$_{FS}$ = 530 °C.

them to crack further to for example levoglucosan. Just like levoglucosan, the recovery of glucose decreases with increasing potassium concentration in the cellulose sample and eventually approaches zero even under the extreme conditions applied to the screen-heater.

It is remarkable how fast the potassium catalysed reactions are (milliseconds) and the low concentrations at which those reactions become destructive to sugars. Literature shows that with increasing AAEM concentrations in cellulose the yield of levoglucosan decreases sharply. For example, the levoglucosan yields decreased from 25 wt% (400 mg kg^{-1} ash) to 2 wt% (2200 mg kg^{-1} ash) at 500 °C and 1000 mbar [7,16]. Patwardhan reported constant concentration (not yield) of levoglucosan when the potassium concentration increased from 3000 mg kg^{-1} to 11,800 mg kg^{-1} [17]. Taking into account the oil yield, it is also likely that the levoglucosan yield decreases further as the potassium concentration increases. When translating these findings to the real biomass, it can be concluded that it is impossible to produce high yields of anhydro-sugars from untreated biomass which has typically 10,000 mg kg^{-1} AAEM content. Removing of AAEMs from the biomass or passivation of AAEMs in the biomass is therefore mandatory.

3.2.2. Levoglucosan pyrolysis

It was previously shown that levoglucosan could be completely evaporated at vacuum [15] and atmospheric pressure [18]. To obtain more information on the reaction mechanism of this important compound, it was pyrolyzed using the screen-heater operated at 5 mbar and 1000 mbar, see Fig. 8 (see Table S5) & Fig. 9 (see

Table S6). The potassium concentration in the levoglucosan feed-stock was 1 mg kg^{-1} and 1000 mg kg^{-1}. Indeed, both at 5 mbar and at 1000 mbar levoglucosan without potassium could be completely recovered (R$_{Levoglucosan}$). When potassium is added, only a small amount of non-condensable gas and solid residue were produced at 5 mbar and the liquid contained solely levoglucosan. When the pressure is increase to 1000 mbar and the potassium concentration was 1000 mg kg^{-1}, only half of the levoglucosan was recovered and significant amounts of solid residue and gas were produced. This can again be explained by the faster escape rate of levoglucosan from the hot reacting particle at 5 mbar compared to at 1000 mbar (factor 10, see Table 1). In other words, levoglucosan is already evaporated before the potassium became catalytically active. Even though levoglucosan could be completely evaporated at 1000 mbar in the nearly absence of potassium, only half of the levoglucosan was recovered at potassium (K$_2$CO$_3$) concentration of 1000 mg kg^{-1}, pointing again towards very fast catalytic reactions. Note, in the nearly absence of vapour phase reactions, destruction of levoglucosan at 1000 mbar can solely be ascribed to intra-particle (catalytic) reactions.

3.2.3. Levoglucosenone and acetol production (screen-heater, 5 mbar)

An important effect of AAEMs on cellulose pyrolysis is the ability to catalyze dehydration and ring fragmentation reactions of the anhydro-sugar molecules. Levoglucosenone was chosen to be able to identify dehydration reactions and the products of fragmentation reactions are represented by acetol in this study [11,19]. Fig. 10 (see Table S7) shows the yield of levoglucosenone against the potassium (K$_2$CO$_3$) concentration in cellulose. Furthermore, each data point is at least three measurements. It can be observed that with increase potassium concentration up to 1000 mg kg^{-1} the yield of levoglucosenone increases from 0.25 wt% to 1 wt%. At 10,000 mg kg^{-1} potassium concentration no levoglucosenone was detected. Similar levoglucosenone yields (0.25 wt% to 0.38 wt%) were obtained for pyrolysis of pure cellulose (Sigmacell 50), between 400 °C and 600 °C, [20] compared to our yields. It is also reported that the levoglucosenone yield is inversely proportional to the chain length of the pyrolyzing cellulose sample and it may not be formed via the dehydration of levoglucosan [21]. Levoglucosenone has probably reacted away to form solid residue and/or other compounds like water, gas and light oxygenates. It is worthwhile to mention that, in the case of levoglucosan pyrolysis, no levoglucossenone production was observed.

Fig. 11 (see Table S8) shows the yield of acetol plotted against the potassium concentration in cellulose, at 5 mbar. In the range
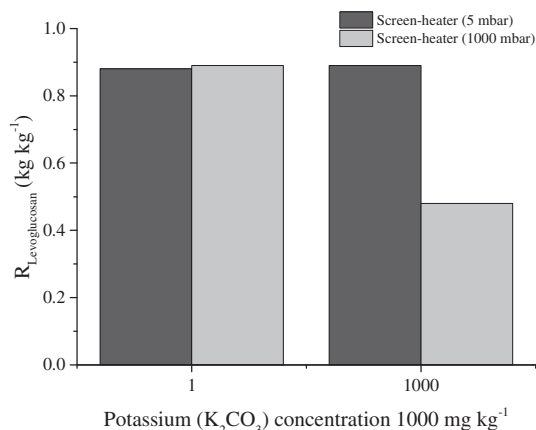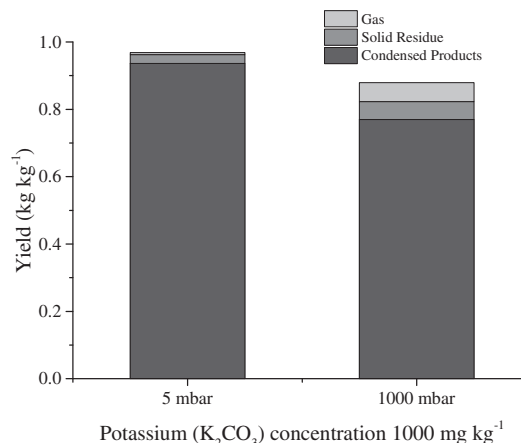

Fig. 9. Effect of pressure on condensed product, solid residue and gas yields at constant potassium concentration in levoglucosan; in screen-heater. T$_{FS}$ = 530 °C.

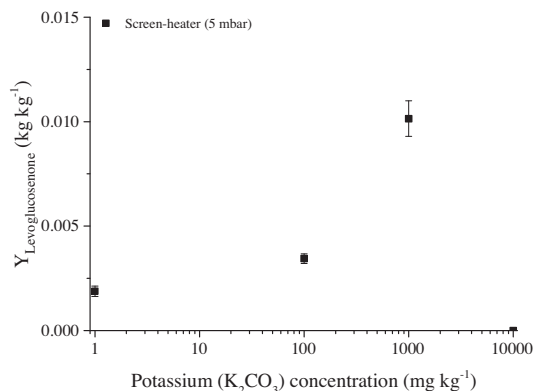**Fig. 10.** Levoglucosenone yield as a function of potassium concentration in cellulose; in screen-heater. Pressure 5 mbar, T$_{FS}$ = 530 °C.

of 1 mg kg^{-1} to 1000 mg kg^{-1} of potassium concentration the acetol yield is constantly low. The acetol yield increases rapidly to 2.3 wt% in the presence of 10,000 mg kg^{-1} of potassium in cellulose. Piskorz performed cellulose (400 mg kg^{-1} ash) pyrolysis experiments in a fluidized bed at 500 °C. The acetol yield was 0.7 wt%. They also found for cellulose with relatively high ash content (2200 mg kg^{-1} ash) that the acetol yield increased to 3.2 wt%
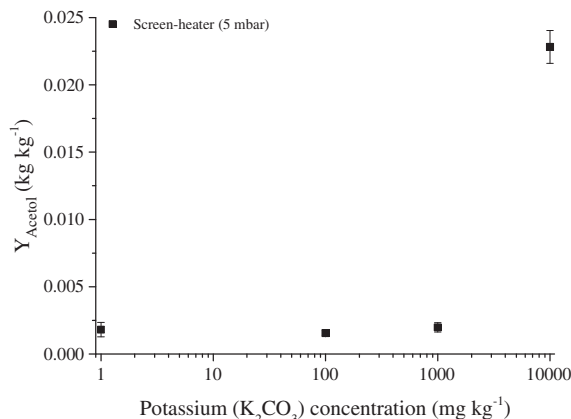

Fig. 8. Levoglucosan recovery as a function of potassium concentration in levoglucosan and pressure in screen-heater. T$_{FS}$ = 530 °C.

Fig. 11. Acetol yield as a function of potassium concentration in cellulose; in screen-heater. Pressure 5 mbar, T$_{FS}$ = 530 °C.

[7]. In summary, based on the production of levoglucosenone and also char, dehydration reactions of anhydro-sugars are more pronounced at higher potassium concentrations. Ring fragmentation reactions leading to non-condensable gasses and acetol unequivocally increases with increasing potassium concentration.

3.3. Influence of different anions – by keeping the potassium concentration constant

Cellulose was impregnated with K_2CO_3, KCl or KOH. The potassium concentration was kept constant (1000 mg kg^{-1}) for all samples. All cellulose samples were pyrolyzed at 530 °C and at a pressure of 5 mbar or 1000 mbar to study the effect of different anions on the pyrolysis products. Fig. 12 (see Table S9) shows the yield of condensed product, solid residue and gas, at 5 mbar and at 1000 mbar, as a function of the different anions. The potassium concentration was kept constant. The reported standard deviation is on mean and is based on at least 3 measurements at 1000 mbar and 6 measurements at 5 mbar.

At 5 mbar, comparable mass balance closures of 84 wt% were obtained. However, at 1000 mbar the mass balance closure decreased by 10 wt%–15 wt% of the cellulose. The solid residue and gas yield did not differ much between the experiments performed at 5 mbar and 1000 mbar for all three anions. The condensed product yield decreases when the pressure is increased to 1000 mbar, this can mainly be attributed to the increasing loss of water and light oxygenates. The obtained condensed product was
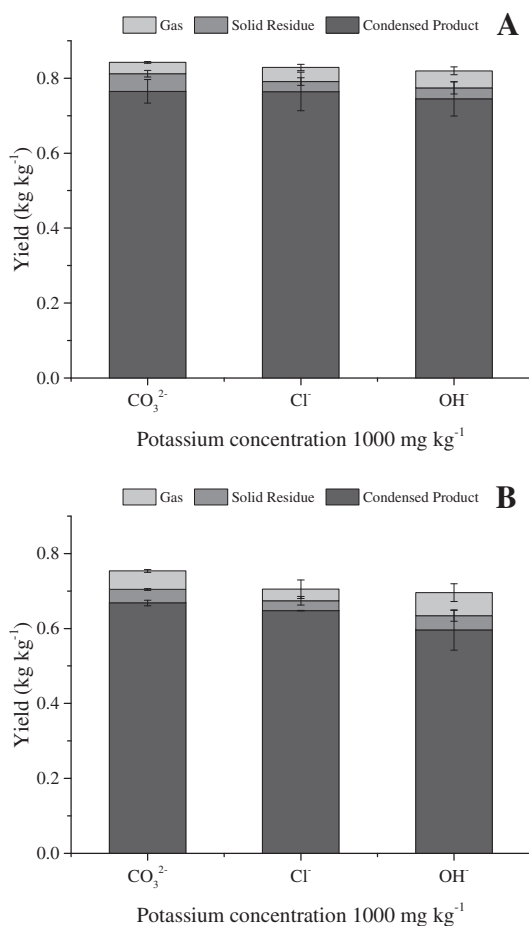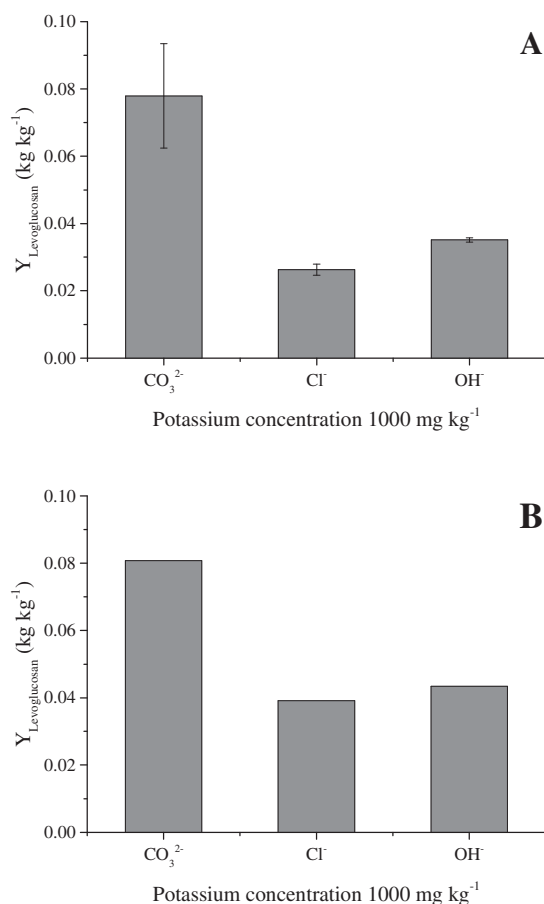
Fig. 13. Levoglucosan yield for different anions with constant potassium concentration; A) 5 mbar B) 1000 mbar. T_{FS} = 530 °C.

analysed for the levoglucosan and glucose content, see Fig. 13 (see Table S10) and Fig. 14 (see Table S10).

Fig. 13 shows the levoglucosan recovery plotted for the different type of anions at 5 mbar (A) and at 1000 mbar (B). There was almost no effect of pressure on the levoglucosan production. Our findings suggest that anions are active in reducing the levoglucosan yield in following descending order Cl$^-$ > OH$^-$ > CO$_3^{2-}$. Nicely, a similar trend was observed, as far as the levoglucosan yield is concerned, by Patwardhan [17]. A slight decrease in glucose recovery (Fig. 14) can be found at 1000 mbar compared to at 5 mbar for all three different anions. The glucose recovery includes both levoglucosan and oligomeric anhydro-sugars with higher degree of polymerization (e.g. cellobiosan, cellotriosan, etc.). The activity of AAEMs in reducing the hydrolysable anhydro-sugars, expressed as glucose recovery, (see Fig. 14) shows the following order. OH$^-$ > Cl$^-$ > CO$_3^{2-}$. The latter is the relevant order to explain the activity of different anions on the destruction of all anhydro-sugars. Density Functional Theory (DFT) calculations suggest that cations can form cation-carbohydrate complexes. In general, cations are more active in forming salt-carbohydrate complex than anions [22]. A theoretical study by Mayes et al. [23] shows that distinct anion's have different affinity towards the cation. They also reports that anions are primarily involved in binding with their counter cation and compete with cation-carbohydrate complex reactions instead of influencing cellulose pyrolysis chemistry directly [23]. Nevertheless, more detailed research (experimental and theoretical) is needed to gain deeper understanding to investigate the role of different anions.

Fig. 12. Condensed product, solid residue and gas yields for different anions with constant potassium concentration. A) 5 mbar B) 1000 mbar, T_{FS} = 530 °C.

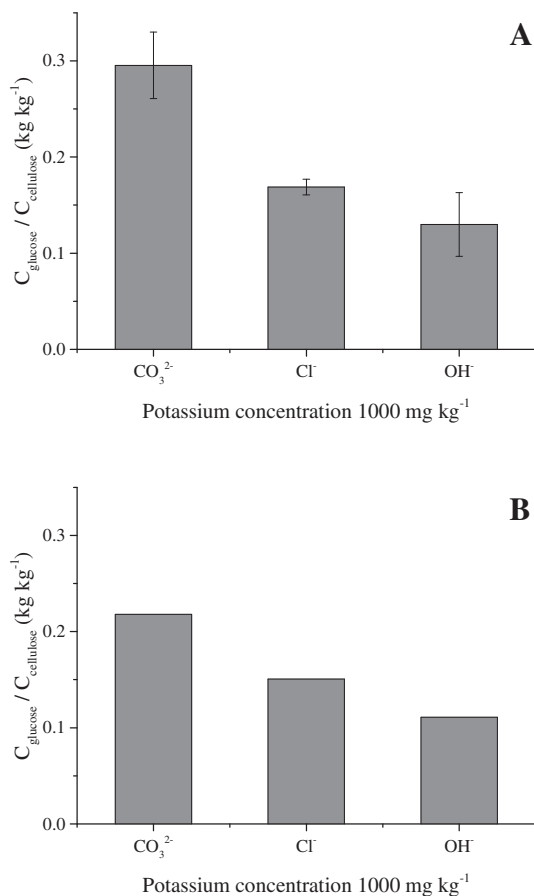**Fig. 14.** Glucose recovery after hydrolysis of condensed product for different anions with constant potassium concentration. A) 5 mbar B) 1000 mbar, T_{FS} = 530 °C.

4. Conclusions

This work provides a deeper understanding of the effect of potassium salts on the primary reactions of cellulose pyrolysis. The primary pyrolysis products of cellulose with low potassium content are anhydrosugars. A major drawback hampering the sugar production at high yield are the AAEMs naturally present in biomass. To study if the catalytic effects of potassium on cellulose pyrolysis can be minimized by very fast removal of the pyrolysis products from the hot reacting particle a dedicated screen-heater reactor is used. This reactor can be operated at vacuum (5 mbar) to enhance the escape rate of pyrolysis products from the hot reacting cellulose particle (including potassium). Consequently, the vapour phase residence time at 5 mbar is only ∼20 ms. The reactor can also be operated at atmospheric pressure (1000 mbar) while still suppressing vapour phase reactions by very fast cooling. Next, a fluidized bed reactor is used with a hot vapour residence time of 1.6 s at 530 °C. The catalytic effects of potassium on cellulose pyrolysis is evidently noticeable in the range of milliseconds. Hence, the oil yield, obtained from the screen-heater operated at 5 mbar, decreases from 0.96 kg kg^{-1} to 0.52 kg kg^{-1}. Furthermore, the glucose recovery, after hydrolysis of the condensed product, decreases from 0.68 $C_{glucose}/C_{cellulose}$ to almost zero $C_{glucose}/C_{cellulose}$. It was found that in the case of levoglucosan the anions were active in the following order $Cl^- > OH^- > CO_3^{2-}$. The activity in reducing the hydrolysable sugars (levoglucosan and oligomers), expressed as glucose recovery, shows the following order. $OH^- > Cl^- > CO_3^{2-}$. Vacuum helps to improve the oil and sugar yield by increasing the escape rate of products (minimizing mass trans-fer limitations) from the hot reacting sample. However, this only holds for cellulose with low potassium content. When the potassium content is low, most of the non-condensable gas is produced by thermal reactions in the vapour phase. When the potassium content increases, CO and CO_2 are produced at the reacting sample. It can be concluded that removing or passivation of the AAEMs prior to pyrolysis is mandatory for AAEMs rich feedstocks to ensure high oil and sugar yields.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2017.05.134.

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