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.

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-ᴅ-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-ᴅ-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.