Supplementary information

The Interplay Between Chemistry and Heat / Mass Transfer during the Fast Pyrolysis of Cellulose

R.J.M. Westerhof[a], S.R.G. Oudenhoven[a], P.S. Marathe[a], M Engelen[a], M. Garcia-Perez[b], Z Wang[b], S.R.A. Kersten[a].

Table of Contents

S1. Materials

Avicel ph101 (Sigma-Aldrich, particle size ~50 µm, 60.5% crystallinity [1], ash content 0.005 wt%, AAEM content 1 mg kg^{-1}, degree of polymerization specified < 350 average 220 [2]), levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth purity >98%) and cellobiosan (1,6-Anhydro-b-D-cellobiose, Carbosynth purity >95%) were used as a feedstock for the pyrolysis experiments. The feedstocks were dried in a vacuum oven (Heraeus FVT420) at room temperature and 1 mbar for at least 24 h before usage.

The screens (2.5 cm by 5 cm) for the reactor were cut from a large metal wiremesh (Dinxperlo, Wire Weaving Co. Ltd, mesh 200 wire thickness 0.06 mm * 0.06 mm, twilled weave, AISI 316). The screens were cleaned with Milli-Q water followed by acetone (Sigma Aldrich, purity >99.5%) and dried before use (24 h at 105°C). The reactor was rinsed with methanol (Sigma Aldrich, purity 99.9%) or Milli-Q water, to recover the condensed product, depending whether the GC/MS or HPLC, respectively, was used for analysis.

Sulfuric acid (Sigma Aldrich, purity 99.99%) was used for hydrolysis and barium carbonate (Sigma Aldrich, purity >99%) was used to neutralize the hydrolyzed samples before HPLC analysis.

Levoglucosan (1,6-Anhydro-b-D-glucopyranose, Carbosynth purity >98%) cellobiosan (1,6-Anhydro-b-D-cellobiose, Carbosynth purity >95%) cellotriosan (LC Scientific purity > 98%) celloterasan (LC Scientific purity >98%) and glucose (Sigma-Aldrich purity 99.5%) were used as standards for calibration of the HPLC.

S2. Detailed description of the screen-heater

S2.1. Sample preparation

50-80 mg of feedstock (e.g. cellulose) was distributed evenly over a stainless steel screen (wiremesh). 0.5 cm of the screen was kept free of feedstock to be able to clamp the screen between the electrodes. A second screen was pressed on top of it with a hydraulic press (Rodac RQPPS30 30t, 450 kg.cm^{-2}). The exact amount of feedstock between the screens was determined by weighing the pressed screens, including the feedstock, on an analytical balance (Mettler Toledo AX205, max 220 g, readability 0.01 mg) and subtracting the weight of the initial screens. Fig. S1 shows the front view of the screens with the cellulose sample between. Fig S2 shows the side few of the screens.

S2.2. Screen-heater setup

The screen-heater reactor consisted of a glass vessel (Duran 250ml centrifuge tube, round bottom, D=5 cm #1). In this glass vessel, the pressed screens with in between the feedstock (#2) was clamped between two electrodes (#5). After installing, a vacuum was created of 5 mbar using a vane vacuum pump (10, Edwards E2M-1.5), see Fig. S3. The reactor was filled with nitrogen gas to remove the remaining air. After this procedure again a vacuum was created of 6 mbar. A liquid nitrogen bath (#4) was placed around the vessel to cool the vessel wall to approximately -100 °C. Nitrogen could be supplied to the vessel to control the pressure inside the vessel around 960 mbar in the case of the atmospheric pressure experiments. Note, during the atmospheric experiments a gas bag was connected to the reactor by a valve. After the experiment the valve was opened and the reactor was warmed to ambient temperature. The expanded gas flows inside the gas back. Therefore, the reactor vessel pressure never exceeded the maximum allowable reactor pressure of 1.1 bar. In addition, a 20 ml syringe was installed in all experiments. The 20 ml syringe was used to collect a gas sample (#8) after the experiments.

Fig. S1 Front view of the screens with cellulose in between. The left picture is a detailed picture of the right picture.

Fig. S2 Side view of the screens with cellulose in between.

The pressure was precisely monitored during the experiment using an accurate and fast enough pressure gauge (Heise DXD3765) #8). A pyrometer (#12) was used to monitor the temperature. To prevent disturbance in measuring the thermal radiation emitted by the screens by the liquid nitrogen during the experiment, a glass tube (#13) with a silicone sealing (#14) was placed in the liquid nitrogen bath. During the experiment an electrical current was passed through the wires, which served as an electrical resistance heater. This method supplies the heat required for heating the sample and maintaining it at the set temperature, in this work termed final screen temperatuur (T_{FS}), for a specified time called the holding time. The required power was supplied by two sets of two batteries connected in series. For the heating period these were two Varta Silver Dynamic batteries (12 V/100 Ah, 830 A) and for the supply of heat during the reaction two Varta Pro Motive batteries (12 V/225 Ah/1150 A) were used. The temperatures and pressures were recorded using a DAQ card (NI PCI-6281). The data was processed in a Labview program (running on a pc at 2000 Hz) which regulated the screen temperature via a PID controller. In an separate experiment a thermo-couple (unsheathed K-type, wire diameter 0.025 mm connected to a Weidmuller MAS K thermocouple signal conditioner) was installed on the screens or in the gas phase to check the temperature of the screens (comparison with the pyrometer) and to measure the temperature of the produced vapour/gas leaving the screens on their way towards the cooled vessel wall.

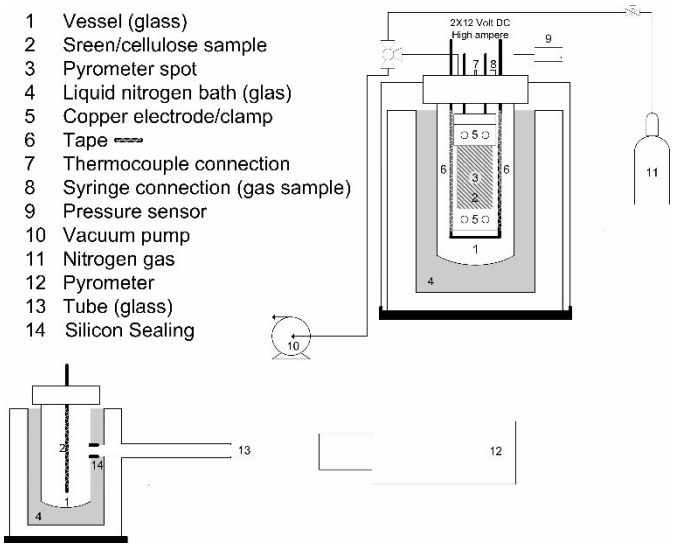

Fig. S3 Schematic drawing of the screen-heater setup. Top: front view. Bottom: side view.

S2.3. Run procedure

Before each experiment the screens & feedstocks (#2), copper clamps (#5), vessel (#1) and tape (#6) were weighed. Teflon tape was wrapped around the electrodes to be able to quantify the condensed products on this part. Hereafter, the different parts of the setup were put together. Air was removed from the vessel by creating a vacuum (6 mbar). The reactor is than flushed with nitrogen. After 2 times flushing a vacuum was created of approximately 6 mbar. The bath (#4) surrounding the reactor vessel was filled with liquid nitrogen. As a result the pressure reduces to 5 mbar In case of an experiment at atmospheric pressure (960 mbar) nitrogen was added to the vacuum vessel immersed in the liquid nitrogen bath. After everything was in position, the pyrolysis run was started following a pre-programmed procedure using the Labview program (with the set temperature, holding time and PID value). After the run, the setup was removed from the liquid nitrogen bath and consequently warmed till ambient temperature.

S2.4. Sample recovery and mass balance

Once the setup was at room temperature, in the case of the vacuum experiments, the pressure inside the vessel (#1) was increased to approximately 900 mbar by adding nitrogen gas (#11). Once this pressure was reached a gas sample was taken using the 20 ml syringe. In the case of experiments at atmospheric pressure the volume of the gas was determined as being the volume of the gas bag and the reactor vessel at ambient temperature and known pressure. The volume of the gas bag was determined by applying a water displacement method. Also in the atmospheric pressure experiments a gas sample was withdrawn from the reactor using a 20 ml syringe. The gas samples were analyzed using a Micro GC. (Varian MicroGC CP4900, 2 analytical columns, 10 m Molsieve 5A, 10 m PPQ. Carrier gas = He, calibrated for H_2, N_2, O_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8).The gas yield was calculated by:

$$Y_{gas} = \sum_{i=CO,CO_2} \frac{\frac{P_{gassample} \cdot Vol\%_i \cdot (V_{vessel} + V_{bag})}{R \cdot T_{room}} \cdot MW_i}{M_{screens+biomass} - M_{screens} - M_{UEC}} \quad (1)$$

Note, the V_{bag} is zero in the case of vacuum experiments. The unreacted-ejected cellulose (UEC) in this formula is explained below. MW is the molecular weight of the gas component. Vol% is the volume concentration of a specific gas compound analyzed by Gas Chromatography. R is the gas constant (8.314 J K^{-1} Mol^{-1}).

After the gas analysis, the reactor was dismantled and the screen (#2), vessel (#1), tape (#6) and clamps (#5) were weighted. The mass of condensed products (excluding residue between the screens and gas) was determined by subtracting the initial weight of the vessel, tape and clamps. The reactor was rinsed with approximately 6 mL (in batches of 2 ml) of solvent. Note, >90 wt% of these products were collected on the vessel wall and thus only < 10 wt% of these products was collected on the clamps and tape. The solvent was milli-Q water for HPLC analysis or methanol for GC/MS analysis. It turned out that a very small amount of product on the vessel was insoluble, but still collected, in the rinsing solvent. The amount of these solvent insoluble compounds was determined as follow. A centrifuge tube was weighted empty and filled with the rinsing solvent (including insoluble compounds) and weighted again. After centrifugation the solvent insoluble compounds were precipitated and collected at the bottom. The solvent was then removed by decantation leaving the solids behind in the tube. After vacuum drying of the tube at 20 °C and 10 mbar the tube was weighted and the initial weight was subtracted. The weight difference represent these solids of which the mass did not exceeded (except for one experiment) the 6 % by weight of the cellulose feedstock. The solids were analyzed by FTIR (see S6.5 Fig. S24) and compare with the cellulose feedstock. It turned out that these solids have the same structure as the cellulose feedstock. In addition, the solids were completely white representing the original color of the cellulose feedstock. Therefore, this fraction is hereafter referred to as unreacted-ejected cellulose (UEC), see Formula 2. With known amount of products (excluding residue and gas) and known amount of unreacted-ejected cellulose the weight difference is hereafter called condensed product, see Formula 3. Note that the mass of unreacted-ejected cellulose is excluded from the amount of cellulose feedstock.

$$M_{UEC} = M_{tube+condensed\ product+EC} - M_{tube+condensed\ product} \quad (2)$$

$$Y_{condensed\ product} = \frac{M_{vessel+tape+clamp+product} - M_{vessel+tape+clamp}}{M_{screens+cellulose} - M_{screens} - M_{UEC}} \quad (3)$$

The vessel and screens were stored in the freezer at -24 °C before analysis. The residue was defined as the material remaining between the screens after an experiment. The solid residue yield was calculated by:

$$Y_{residue} = \frac{M_{screens+residue} - M_{screens}}{M_{screens+cellulose} - M_{screens} - M_{UEC}} \quad (4)$$

S2.5. Temperature registration using a pyrometer

The temperature of the screen was measured with a Kleiber KGA 730 pyrometer. This pyrometer measures the radiation between a wavelength of 1.58 µm and the 2.20 µm. The output of the pyrometer is a 4 mA - 20 mA signal which was converted into a voltage signal by a resistor. The voltage was continuously recorded, using a DAQ card (NI PCI-6281), in a Labview program.

The measured temperature (radiation) by the pyrometer needs to be corrected for the emissivity (ε), the ratio between amount of radiation emitted by a real body and a blackbody, of the screen with cellulose and the transmittance (Tr) of the glass transitions. The following equation was used for this [3]:

$$\frac{1}{T_{screen\ \&\ cellulose}} = \frac{1}{T_{measured}} + \frac{\lambda}{C_2} \cdot ln(\varepsilon') \quad (5)$$

$$\varepsilon' = Tr_{vessel} \cdot Tr_{tube} \cdot \varepsilon_{screen\ \&\ cellulose} \quad (6)$$

$$C_2 = \frac{ch}{k} \quad (7)$$

In this equation, c is the speed of light ($3*10^8$ m s^{-1}), h Planck's constant ($6.63*10^{-34}$ J s), λ the wavelength (m), k the Boltzmann constant ($1.38*10^{-23}$ J K^{-1}) and T the temperature (K). An effective emissivity (ε') was used to lump the emissivity of the screen with cellulose and the transmittance of both glass parts. Since the majority of the radiation is detected at 2.2 µm this value is used as "effective wavelength" in equation 5.

The blackbody temperature calibration of the pyrometer was obtained by measuring a black copper cylinder (painted with Rust-oleum Heat Resistant 7778 BBQ Black) inside a tube oven at different temperatures (300 °C – 700 °C). The transmittance of both glass parts (vessel (#1) and tube (#13)) was determined by placing these glass parts separately between the black copper cylinder (3 different temperatures) and pyrometer. Using equation 5 the transmittance of the reactor vessel (#1) and the tube (#13) was determined to be 0.84 ± 0.01 and 0.77 ± 0.03, respectively. To verify these separate measured values, both glass objects were placed in series between the pyrometer and the black sample. The determined transmittance for the glass parts together was consistent with the separated determined transmittence. To determine the emissivity of the screens with cellulose the temperature of the screen with cellulose should be known. Therefore a K-type thermocouple (bare wire, diameter 0.025 mm connected to a Weidmuller MAS K thermocouple signal conditioner, reading every 16 ms) was attached to the screens to measure the temperature, see Fig. S4. Due to the slower response of the thermocouple compared to the high heating rate of the screen-heater it was only possible to measure the temperature accurate with the thermocouple during the stable holding time (see Fig. S6). Moreover, the very fast pyrolysis reactions at temperatures above 450°C (~200 ms) made it impossible to accurately measure the temperature of the screen with pyrolyzing cellulose using the thermocouple. Therefore, the temperature of the screen with pyrolyzing cellulose was only measured with the thermocouple on the screen for experiments below 420 °C. Additional measurement were performed to obtain an estimate of the boundaries between which the emissivity of the screen with cellulose will be at higher temperatures. In these measurements a single screen was used as lower boundary (cellulose emits no radiation), whereas a double screen with black foil in between was used as upper boundary (cellulose emits radiation as a black body). The emissivity of the single screen, double screen with cellulose and double screen with black foil as function of temperature are shown in Fig S5. It can be observed that the emissivity at temperatures above 400 °C is quite constant around 0.65 ± 0.15 (for error calculation). Knowing this emissivity and transmittance (determined for the glass tube and vessel) the measured temperature by the pyrometer can be converted to the actual screen (plus cellulose) using Formula 5. From the uncertainties in the emissivity and transmittance the error on the temperature was calculated to be ± 20 °C at 330 °C increasing to ± 45 °C at 750 °C. A typical temperature profile measure by the pyrometer can be seen in Fig. S6. The heating rate was around 5000 °C/s.

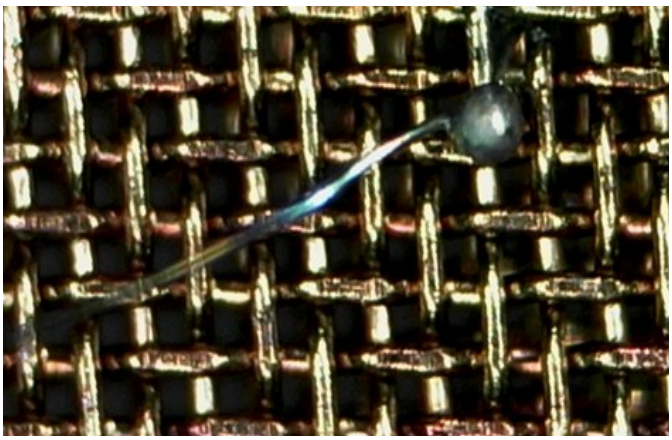

Fig. S4 Microscopic picture of the thermocouple located on the screen.

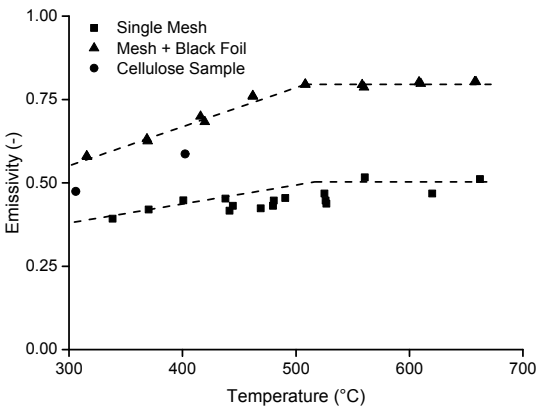

Fig. S5 Emissivity of a single screen, double screen with cellulose and double screen with black foil as function of temperature.

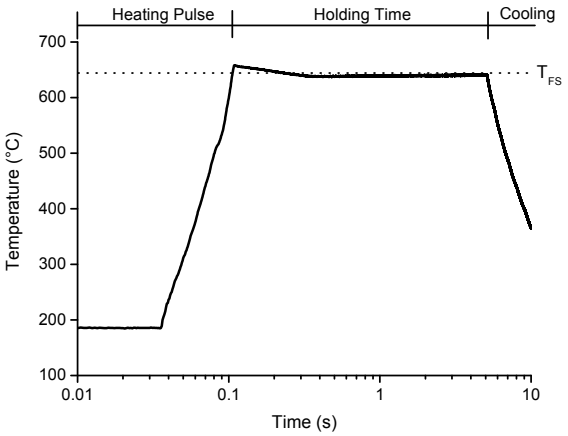

Fig. S6 Typical temperature profile of the screen (5 mbar). The heating pulse is started at 0 s. The pyrometer doesn't detect temperatures lower than 190 °C therefore no temperature is shown between 0 and 36 ms.

S2.6. Visualization of pyrolysis using a high speed camera

Movies of the pyrolysis experiments were recorded using a high speed camera (Casio EX FH25, 240fps, 448 * 336 pxl). A blue LED was connected to the electrodes outside of the reactor and lighted up when current was passed through the screens. The screen with cellulose between was lighted from the back with two white LED lights. The recorded videos were partitioned into separate frames using the freeware program IRfan view. Fig. S7 shows some selected frames 0 ms and 346 ms. reaction time. In this experiment cellulose was pyrolyzed at 530 °C and at 1 bar. As can be seen, at 104 ms smoke is visible close to the screen which means very fast cooling. The smoke stays visible for a long time.

The evaporation time of levoglucosan and cellulose at 1 bar could not be determined on basis of the frames from the high speed recordings, because the aerosols in the vessel blocked the view of the screen. To obtain an indication of the evaporation time of levoglucosan an experiment was performed without vessel, to improve the view on the screen. Fig. S8 shows the frames of the test with levoglucosan without vessel. In this figure it can be seen that the produced vapors ignited after 350 ms. Since the produced vapors are directly cooled they can only ignite when they, together with oxygen, come into contact with the hot screen. Oxygen can only reach the hot screen if the levoglucosan has been evaporated, due to the mass flux going from the screen during evaporation. Therefore, at the time of ignition (350 ms) the majority of the levoglucosan should have been evaporated.

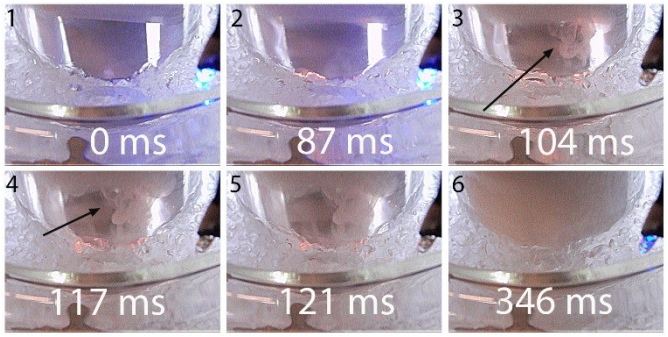

Fig. S7 Frames from the recording of a screen-heater experiment with cellulose performed at 530 °C and 1 bar. It is advised to view the figure in colour.

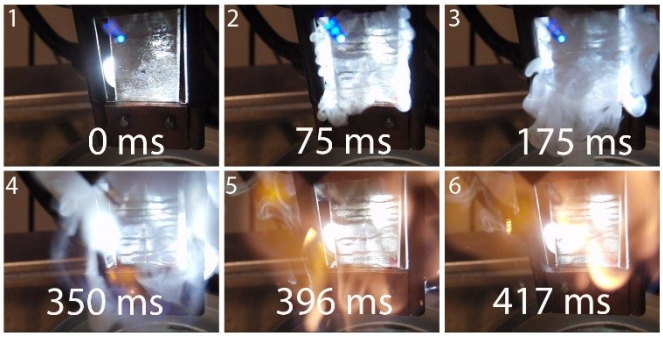

Fig. S8 Frames from the recording of a screen-heater experiment with levoglucosan performed at 450 °C without vessel. It is advised to view the figure in colour.

S3. Fast pyrolysis of cellulose in a bench-scale fluidized bed reactor

Cellulose was also pyrolyzed in a fluidized bed reactor at a temperature of 530 °C. This setup is explained in more detail in our previous paper [4]. Short recap: silica sand was used as bed material and preheated nitrogen was used to fluidize the sand. Per experiment around 100 g of cellulose was fed manually to the reactor in batches of 2 g – 5 g together with 4 g - 8 g sand, via a gas lock system consisting of two valves. The total experiment time was 25 min. The vapor residence time in the hot zone of the set-up (reactor + tubing) was ~1.6 s. In this calculation the flowrates of the nitrogen, produced vapors and gasses were considered. The char was separated from the gas/vapor stream using two wiremesh filters (pore size 9 µm and 5 µm). The pyrolysis vapors were condensed using an electrostatic precipitator (ESP) operated at 20 °C (outgoing gas temperature). A double walled glass condenser was placed in series to recover the remaining vapors and was operated at -5°C (outgoing gas). The liquid bio-oil production, in the screenheater experiments termed condensed product, was measured by weighing both condensers before and after the experiment. The char yield, in the screenheater experiments termed solid residue, was determined by collecting the char/sand mixtures from the reactor and char-filters and subtracting the initial weight of sand present at the start of the experiment and the amount of sand fed during the experiment. The amount of produced gasses was calculated by difference.

The heating rate of a cellulose particle in the fluidized bed reactor was calculated using:

$$\frac{dT_c}{dt} = \frac{6\alpha}{\rho C_p d_p}\left(T_C - T^{\infty}\right) = \frac{6 * 200}{1500 * 1500 * 50 * 10^{-6}} * 500 = \sim 5000 \frac{°C}{S} \quad (8)$$

In this equation is, α the heat transfer coefficient (200 W m^{-2} K^{-1} from Prins [5], ρ the density of cellulose (1500 kg m^{-3}) [6], C_p the heat capacity of the cellulose (1500 J kg^{-1} K^{-1}) [7], d_P the particle diameter, T_C the temperature of the cellulose particle and T^{∞} the temperature of the fluidized bed. Note that this equation gives the initial heating rate, which decreases in the trajectory.

S4. Analysis techniques

ICP-OES: The ash content of Avicel ph101 was determined by quantifying the residue remaining after 24 hours of dry oxidation at 575°C. The ash was dissolved in 2 wt% nitric acid and analyzed for its Na, K, Mg and Ca content using ICP. (Sequential ICP-OES with a radial plasma (Varian Liberty II)).

Gas Chromatography: The gas samples were analyzed for H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 using gas chromatography (Varian CP 4900, 2 analytical columns, 10 m

Molsieve 5 A, 10 m PPQ. Carrier gas = He, calibrated for H_2, N_2, O_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8)

GC/MS: The identification and quantification of light oxygenates (glycolaldehyde, 5-hydroxymethyl furfural and acetol) was done by GC/MS analysis (GC 7890A MS 5975C Agilent Technologies) equipped with a capillary column (Agilent HP-5MS, HP19091S-433). Samples were dissolved in methanol (10 mg - 20 mg condensed product/gr methanol) and filtered before analysis (Whatman 0.2 µm filter).

FTIR: The residue, remaining between the screens, and unreacted-ejected cellulose was analyzed by FTIR (Bruker Tensor 27). The samples were scanned from wavenumber 650 cm^{-1} - 4000 cm^{-1}, every sample was scanned 16 times with a resolution of 1 cm^{-1}. Baseline correction of the obtained IR spectra was applied.

HPLC and LC/MS analysis of the Anhydrosugars and Glucose: The anhydrosugars in the condensed product were analyzed by HPLC (Agilent 1200 series, column Hi-Plex-pb operated at 70°C, eluent milli-Q water (0.6 ml min^{-1})). The different peaks were identified by the available standards (DP_1 (levoglucosan) up to DP_4 (cellotetrasan)). DP_4 and DP_5 (for DP_5 the calibration of DP_4 was used) were quantified separately but due to a large overlap of those peaks they were lumped as DP_{4+5}. Large anhydrosugars with more than 5 units were quantified and summarized as $DP_{>5}$. As will be discussed later in more detail, these large compounds ($DP_{>5}$) and also the compounds between DP_1 and DP_2 ($DP_{1\text{-}2}$,) were identified using LC/MS analysis (see S6.4). A typical HPLC chromatogram of a condensed product (T = 725 °C) can be seen in Fig. S10. The position of the DP_1 - DP_4 standards are determined and a 4 point (different concentrations) calibration is performed, see figure S9. The peak wide, at the baseline, is a function of the peak height as can be observed from the calibration peaks. With known peak position, height and coupled peak wide (from the calibrations) and the height of the condensed product curve at these specific DP positions, the DP_1 -DP_{4+5} and $DP_{>5}$ integration borders are known for the condensed product spectra. With known surface area of the identified peak the concentration in the HPLC sample can be calculated from the calibration using the standards. Thanks to the large temperature range studied and resulting large changes in DP distributions this method is found to be sufficient accurate to be used in this study. For the LC/MS analysis, 0.2 ml min^{-1} of the 0.6 ml min^{-1} flow was split and lead to a Thermo Scientific LCQ ion trap mass spectrometer equipped with an ESI source. Note, the Hi-Plex -PB column could not be placed in the oven of the LC/MS, therefore the column was operated at room temperature. As a result the retention times of the peaks has slightly shifted compared to the measurements the HPLC analysis. The LCQ was operated using the LCQ Tune Plus interface and Xcalibur 2.0 software. The internal nominal pressure of the LCQ was maintained at about $0.798*10^{-5}$ mbar, as read by an ion gauge. ESI experiments were carried out both in positive and in negative ion mode, for which a concentrated ammonium acetate solution was added post-column to a final concentration of 1.0 mM. ESI conditions were: 4.1 kV spray voltage, sheath and auxiliary gas (N_2) flow of 35 and 5 (arbitrary units), and a heated ion transfer capillary/mass spectrometer inlet temperature of 300 ºC.

Condensed product hydrolysis: The hydrolysable anhydrosugars in the condensed product were hydrolyzed to glucose using NREL LAP method "Determination of sugars, byproducts, and degradation products in liquid fraction process samples". The glucose was quantified using the HPLC. Basically, 30 mg - 50 mg of condensed product was dissolved in 10 ml of Milli-q water. H_2SO_4 was added to the water solution to a final concentration of 3.5 vol%. The temperature of the mixture was kept at 120 °C for 60 min. After the experiment the mixture was neutralized by adding $BaCO_3$ and filtered (Whatman 0.2 µm filter) before HPLC analysis (Agilent 1200 series, column Hi-Plex-pb operated at 70 °C, eluent milli-q water (0.6 ml min^{-1})). The expression for the sugar recovery (equation 33) can be found in S6.3

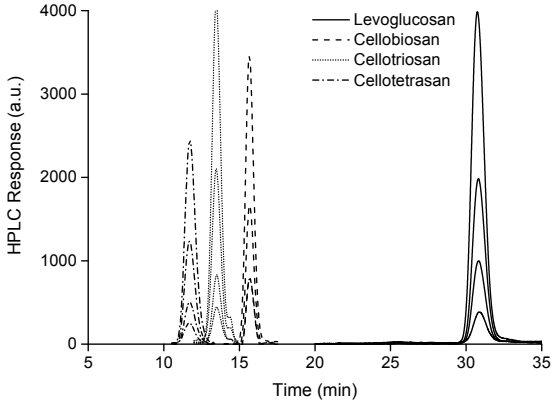

Fig. S9 HPLC chromatogram of DP_1 to DP_4 used for calibration.

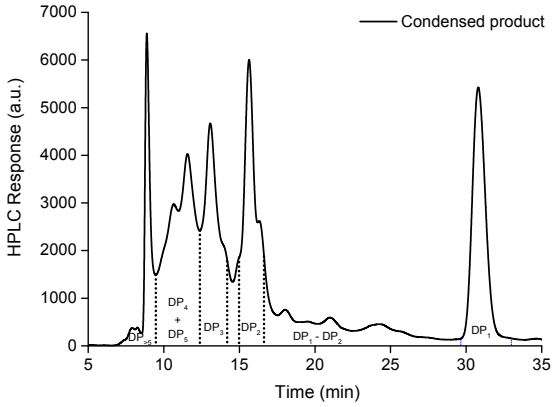

Fig. S10 HPLC chromatogram (Hi Plex PB column) for a typical condensed product. The integration (peak) areas (vertical dotted lines) for varies anhydrosugars are included in the figure.

S5. Interpretation models

S5.1. Evaporation model

The purpose of this model is to estimate the evaporation time of DP_3 (cellotriosan) from the screens, particularly the difference in evaporation time between an experiment at 5 mbar and 1 bar. A model was built that describes the evaporating of pure DP_3 from the screens. Evaporation is described by the film-model. The vapor pressure relation was determined from an estimated normal boiling point of 792 °C [8] taking the A value [9] of levoglucosan (DP_1) in the Antoine equation:

$$\mathrm{Ln}\left(P^*\right) = 31.19 - \frac{20956}{T}\ [Pa] \tag{9}$$

The mass flux (Θ_m) from the screen was described by the film model assuming that the DP_3 concentration in the bulk is zero (0):

$$\Theta_m = -k_g C M_w \frac{P^*}{P}\ [\frac{kg}{m^2 s}] \tag{10}$$

C is the molar concentration (mol m^{-3}) as calculated with the ideal gas law at P (bulk) and the sample temperature. M_w is the molecular weight (0.486 kg mol^{-1} for cellotriosan). For k_g at ambient conditions ($k_{g,0}$ at T_0 , P_0) a conservative estimate of 0.01 m s^{-1} was taken and it was scaled to the prevailing conditions by the dependency of the diffusion coefficient to T (sample) and P (vessel).

$$k_g = k_{g,0}\left(\frac{T}{T_0}\right)^{1.5}\left(\frac{P_0}{P}\right)^1\ [\frac{m}{s}] \tag{11}$$

The evaporation was modelled by the following equations:

$$\frac{dL}{dt} = \frac{A_m \Theta_m}{\rho} \tag{12}$$

$$\frac{dT_c}{dt} = \frac{A_h \alpha\left(T_s - T_c\right) + \Theta_m \Delta H_v}{\rho C_p L} \tag{13}$$

$$\frac{dT_s}{dt} = 5000\ if\ T_s \leq T_{FS}, else\ \frac{dT_s}{dt} = 0 \tag{14}$$

With initial conditions:

$L = L_0$, $T_c = 298$ K and $T_s = 298$ K at $t = 0$.

In these equations, L is (half) the thickness of the cellulose sample, A_m the fraction of the flat surface of the screens available for mass transfer, Θ_m the flux, ρ the density of cellotriosan, T_c the temperature of the cellotriosan, A_h the fraction of the flat surface available for heat transfer, α the heat transfer coefficient, T_s the temperature of the screens, C_p the heat capacity of the cellulose and ΔH_v the enthalpy of evaporation. In Table 1 the numerical values used are listed.

The model was solved using MATLAB (ode15s solver). This model predicts that time needed to evaporate the DP_3 sample is 0.4 and 75 seconds at 5mbar 1 bar respectively.

Table 2: Constants used for evaporation model.

parameter	Value	Comment
ρ	1500 kg m^{-3}	Particle density cellulose [6]
C_p	1500 J kg^{-1} K^{-1}	Specific heat capacity cellulose [7]
L_0	25*10^{-6} m	Half the thickness of the sample between the screens
A_m	0.5	Estimated based on the estimate of the porosity of the screens and the filling of the cellulose between the wires.
A_h	3	Estimated based on the porosity of the screens (~0.25), the diameter of the wires (6*10^{-5} m) and the filling of the cellulose between the wires.
α	1*10^4 W m^{-2} K^{-1}	Direct contact of wire to cellulose
ΔH_v	0.7*10^6 J kg^{-1}	Data of Suuberg [9] for cellulose realizing that on mass basis ΔH_v is reasonably constant in a homologous series.

The traveling time of a hot escaped molecule from screens to the cooled wall was estimated based on the random walk approximation:

$$t = \frac{{L_V}^2}{2D} = \frac{0.02^2}{2 * 10^{-2}} = 20\ ms \tag{15}$$

In these equations, L_V is the distance from the screen to the vessel wall and D the diffusion coefficient scaled to 100 Pa (1 mbar). The order of magnitude of the calculated traveling time is in good agreement with the traveling time estimated based on analysis of the frames ~ 15 ms (Fig. 4, main article).

S5.2. Pyrolysis models

S5.2.1. Pyrolysis model 1

To describe the weight loss and temperature of the cellulose sample we have used a modified version of the model as described by Lede and co-workers [10]. We used the reaction rate parameters as given by Shafizadeh [11]. In our model, contrary to Lede's, the sample has a spatially uniform temperature and the state of the intermediate/active cellulose is not defined (can liquid and/or solid). The purpose of this model is to predict the conversion (mass loss) as a function of the temperature (of the screens) and holding time for comparison with the measured data. Also the reaction temperature (T_r) defined as the mean temperature of the sample between 10 and 90% conversion as a function of the

final temperature of the screens can be calculated. The following lumped reaction pathway scheme is used:

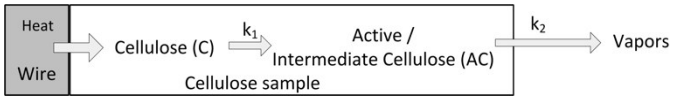

Fig. S11 Schematic representation of interpretation model 1.

In Fig S11 it is also indicated which reactions proceed on the particle. The vapors are recovered in the condensed product (on the cold wall of the vessel of the screen-heater, see S1). The reaction rate constant k_2 describes both chemical reactions and the escape rate of products from the reacting sample [11]. Both reaction 1 and 2 are described by first order rate equations and the Arrhenius temperature dependency. Mass balance equations are solved for C and AC. Symmetry is assumed as a result of which only one side of the sample is modelled.

$$\frac{dM_C}{dt} = -k_1(T_C)M_C \quad (16)$$

$$\frac{dM_{AC}}{dt} = k_1(T_C)M_C - k_2(T_C)M_{AC} \quad (17)$$

$$M_S = M_C + M_{AC} \quad (18)$$

$$X = 1 - \frac{M_S}{M_{S,0}} \quad (19)$$

In these equations, M_C and M_{AC} and M_s are the masses of cellulose, active cellulose and sample respectively, T_C the temperature of the sample (cellulose + active cellulose) and X the conversion on mass basis. The following energy balance is solved assuming that the heat of reaction 1 is negligible:

$$\frac{dT_C}{dt} = \frac{A\alpha(T_S - T_C) - k_2(T_C)M_{AC}\Delta H_2}{M_s C_p} \quad (20)$$

In this equation, C_p the heat capacity of the sample, Ar the area available for heat transfer, ΔH_2 the enthalpy of the reaction / evaporation and T_S the temperature of the screen. The temperature of the screens is modelled by:

$$\frac{dT_S}{dt} = B \; if \; T_S < T_{set} \; \& \; t \leq t_h \quad (21)$$

$$\frac{dT_S}{dt} = 0 \; if \; T_S = T_{set} \; \& \; 0 \leq t \leq t_h + \frac{T_{set}}{B} \quad (22)$$

$$\frac{dT_S}{dt} = -B' \; if \; t > t_h + \frac{T_{set}}{B} \quad (23)$$

Here t_h is the holding time and T_{set} the set-point of the screen temperature. For the calculation of the solid residue yield (Fig. S14) the cooling period was taken into accound. For the calculation of the average reaction temperature, the cooling period is not taken into account; after heating the screen remains at the set-point temperature. The average reaction temperature is defined as:

$$T_r = \frac{\int_{x=0.1}^{x=0.9} T_s(x)dx}{\int_{x=0.1}^{x=0.9} dx} \quad (24)$$

The initial conditions are:

$M_{S,0}$ ($M_{C,0}$) = 2.5*10^{-5} kg, M_{AC} = 0,

$T_{C,0}$ = 298 K, $T_{S,0}$ = 298 K

In Table 2 the range of numerical values of the parameters used are listed. The model is solved using MATLAB (ode15s solver).

Table 3: Constants used for pyrolysis model 1.

parameter	Value	Comment
B	5000 °C s^{-1} (10000 °C s^{-1})	Heating rate of the screens. 5000 °C s^{-1} was the experimentally determined value. In the sensitivity analysis also 10000 °C s^{-1} was used.
B'	60 °C s^{-1}	Cooling rate (measured) of the screens after the holding time.
$k_{1,0}$	2.8*10^{19} s^{-1}	Pre-exponential constant of reaction1 [11]
$K_{2,0}$	3.2*10^{14} s^{-1}	Pre-exponential constant of reaction 2 [11]
E_1	2.42*10^5 J mol^{-1}	Activation energy of reaction1 [11]
E_2	1.98*10^5 J mol^{-1}	Activation energy of reaction 2 [11]
C_p	1500 J kg^{-1} K^{-1}	Specific heat capacity cellulose [7]
A	0.003 m^2	Estimated based on the porosity of the screens (~0.25), the diameter of the wires (6*10^{-5} m) and the filling of the cellulose between the wires.
α	1000 to ∞ W m^{-2} K^{-1}	A low estimate of the heat transfer coefficient and infinite.
ΔH_2	-0.25*10^6 to 0.7*10^6 J kg^{-1}	Slightly exothermic reaction till heat of evaporation of levoglucosan.

S5.2.2. Pyrolysis model 2

To predict the trend of the product distribution as function of the temperature model 1 has been extended by: i) an intermediate / active cellulose phase that consists of heavies ($DP_{\geq 2}$) and DP_1, ii) a reaction of heavies to compounds of lower DP that takes place on the sample and iii) a lower escape rates of heavies compared to lights. This is shown schematically in Fig. S12. In this figure it is also indicated which reactions proceed on the particle. The vapors are recovered in the condensed product (on the cold wall of the vessel of the screen-heater, see S1) In this model the rate constants k_2 and k_4 only describe the escape rate of the products from the sample which is assumed to be a first order process. k_4 is chosen to be smaller than k_2 in order to describe that the larger sugars have a lower escape rate as compared to DP_1. k_3

is chosen/set arbitrary to 10% of the value of k_2. k_1 and k_2 are the constants derived by Shafizadeh [11].
Note that the purpose of the model is to investigate if a model including chemical reactions and mass transfer can predict the measured trends in DP-distribution of the condensed product as function of the temperature of the screens not for any quantitative prediction.

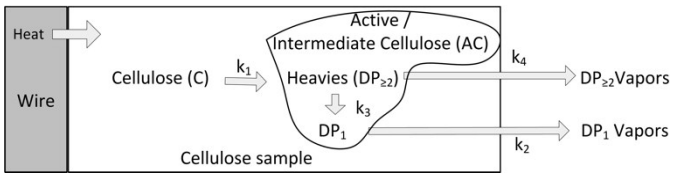

Fig. S12 Schematic representation of interpretation model 2.

The latter would need a model that includes independently measured or disentangled values for the rate constants of the chemical reactions on the particle and escape rates (velocity) of products from the sample.
The mass balances are:

$$\frac{dM_C}{dt} = -k_1(T_C)M_C \quad (25)$$

$$\frac{dM_{DP\geq 2}}{dt} = k_1(T_C)M_C - (k_3(T_C) + k_4(T_C))M_{DP\geq 2} \quad (26)$$

$$\frac{dM_{DP_1}}{dt} = k_3(T_C)M_{DP\geq 2} - k_2(T_C)M_{DP_1} \quad (27)$$

$$M_S = M_C + M_{DP\geq 2} + M_{DP_1} \quad (28)$$

$$X = 1 - \frac{M_S}{M_{S,0}} \quad (29)$$

In these equations, M_C, $M_{DP\geq 2}$, M_{DP1} and M_s are the masses of cellulose, $DP_{\geq 2}$, DP_1 and sample respectively, T_C the temperature of the sample (cellulose + $DP_{\geq 2}$ + DP_1) and X the conversion on mass basis. The following energy balance is solved assuming that the heat of reaction 1 is negligible and that the heat effect involved with the escape of (evaporation of) DP_1 and $DP_{\geq 2}$ from the particle is equal on mass basis:

$$\frac{dT_S}{dt} = \frac{A\alpha(T_S - T_C) - (k_2(T_C)M_{DP_1} + k_4(T_C)M_{DP\geq 2})\Delta H}{M_s C_p} \quad (30)$$

In this equation, C_p the heat capacity of the sample, A the area available for heat transfer, ΔH the enthalpy of the evaporation and T_S the temperature of the screen. The temperature of the screens is modelled as described under model 1.
The yields (Y) of DP_1 and $DP_{\geq 2}$ in the condensed product are calculated by:

$$Y_{DP_1} = \frac{\int_{t=0}^{t=\infty} k_2(T_C)M_{DP_1}dt}{M_{S,0}} \quad (31)$$

$$Y_{DP\gg 2} = \frac{\int_{t=0}^{t=\infty} k_4(T_C)M_{DP\geq 2}dt}{M_{S,0}} \quad (32)$$

The initial conditions are:

$M_{S,0}$ ($M_{C,0}$) = 2.5*10^{-5} kg, M_{DP1} & $M_{DP\geq 2}$ = 0,

$T_{C,0}$ = 298 K, $T_{S,0}$ = 298 K

In Table 3 the numerical values of the parameters used are listed. The model is solved using MATLAB (ode15s solver).

Table 4: Constants used for pyrolysis model 2.

parameter	Value	Comment
$k_{1,0}$	2.8*10^{19} s^{-1}	Pre-exponential constant of reaction1 [11]
$K_{2,0}$	3.2*10^{14} s^{-1}	Pre-exponential constant of reaction 2 [11]
E_1	2.42*10^5 J mol^{-1}	Activation energy of reaction1 [11]
E_2	1.98*10^5 J mol^{-1}	Activation energy of reaction 2 [11]
$K_{3,0}$	3.2*10^{13} s^{-1}	10% of $k_{2,0}$ (arbitrary choice)
E_3	1.98*10^5 J mol^{-1}	Equal to E_2 (arbitrary choice)
$K_{4,0}$	10*10^{20} s^{-1}	Overall k lower than k_2 (arbitrary choice)
E_4	3.0*10^5 J mol^{-1}	Overall k lower than k_2 (arbitrary choice)
C_p	1500 J kg^{-1} K^{-1}	Specific heat capacity cellulose [7]
A	0.003 m^2	Estimated based on the porosity of the screens (~0.25), the diameter of the wires (6*10^{-5} m) and the filling of the cellulose between the wires.
α	1*10^4 W m^{-2} K^{-1}	Good contact between sample and wires
ΔH	0.7*10^6 J kg^{-1}	Heat of evaporation of levoglucosan [7].

S6. Supporting experimental data

S6.1. Product yields including gas

The product yields as function of the final screen temperature (T_{FS}) can be seen in Fig. S13, Fig. S14 and Fig. S15. The yields are expressed on cellulose basis. Fig. S13 shows the condensed product yield as function of T_{FS}. Fig. S14 shows the solid residue product left between the screens. Including in this figure are the modelling predictions. Details on the model can be found in S5.2.1. The gas yield as function of the temperature can be seen in Fig. S15. The gas yield does not seem to be much higher than 0.01 kg kg^{-1} cellulose. Although, two points were somewhat higher; they seem to be out layers. Note, experiments were performed at 1 s or 5 s holding time. Four different experimenters (Exp) we used in these sets of experiments.

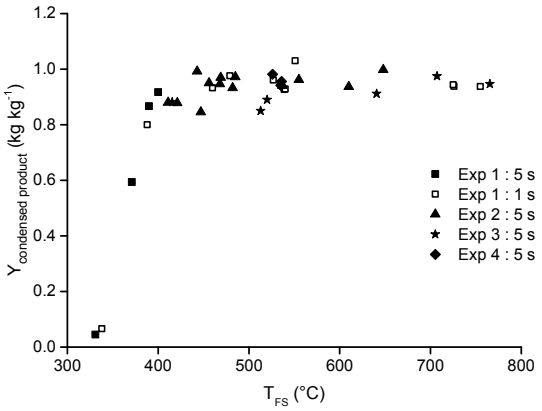

Fig. S13 Yield of condensed product at 5 mbar as function of temperature, experimenter and holding time.

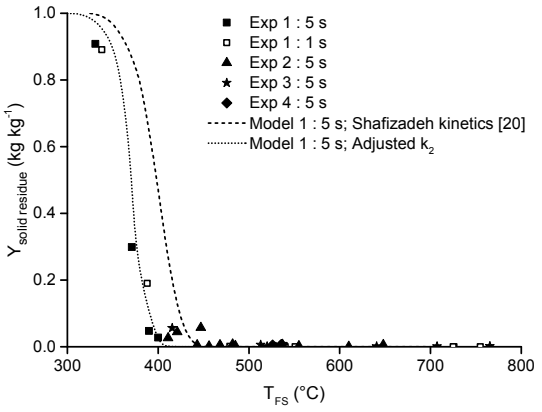

Fig. S14 Yield of solid residue at 5mbar as function of temperature, experimenter and holding time.

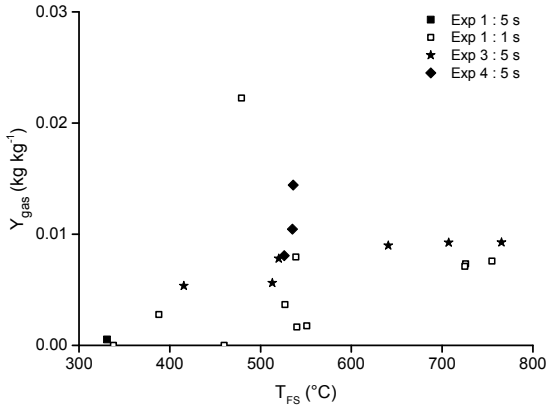

Fig. S15 The yield of gas at 5 mbar as function of temperature, experimenter and holding time

S6.2. Sugars distribution

The DP_1, DP_2, DP_3, DP_{4+5} and $DP_{>5}$ selectivity as function of the temperature are plotted in Fig. S16 and Fig. S17. The difference between Fig. S16 and Fig. S17 are the type of trend lines. In Fig. S16 the linear fit trend line is shown and in Fig S17 the best-fit trend line. Note, that only in the case of DP_2 the linear fit is the best describing our data and is therefore not depictured in Fig. S17. For illustration the linear fit for all DP's are shown. The R^2 for the linear trend lines and the best fit trend lines are shown in Table 4. Again, for DP_1, DP_3, DP_{4+5} and $DP_{>5}$ the highest R^2 is for the best model fit option. These trend lines together with the linear fit trend line for DP_2 are used in the paper. The sugar distribution of the test with gold sputtered screens lays within the range of the sugar distribution from test at comparable T_{FS} (see table S9). This shows that the mesh has no significant effect on the sugar distribution

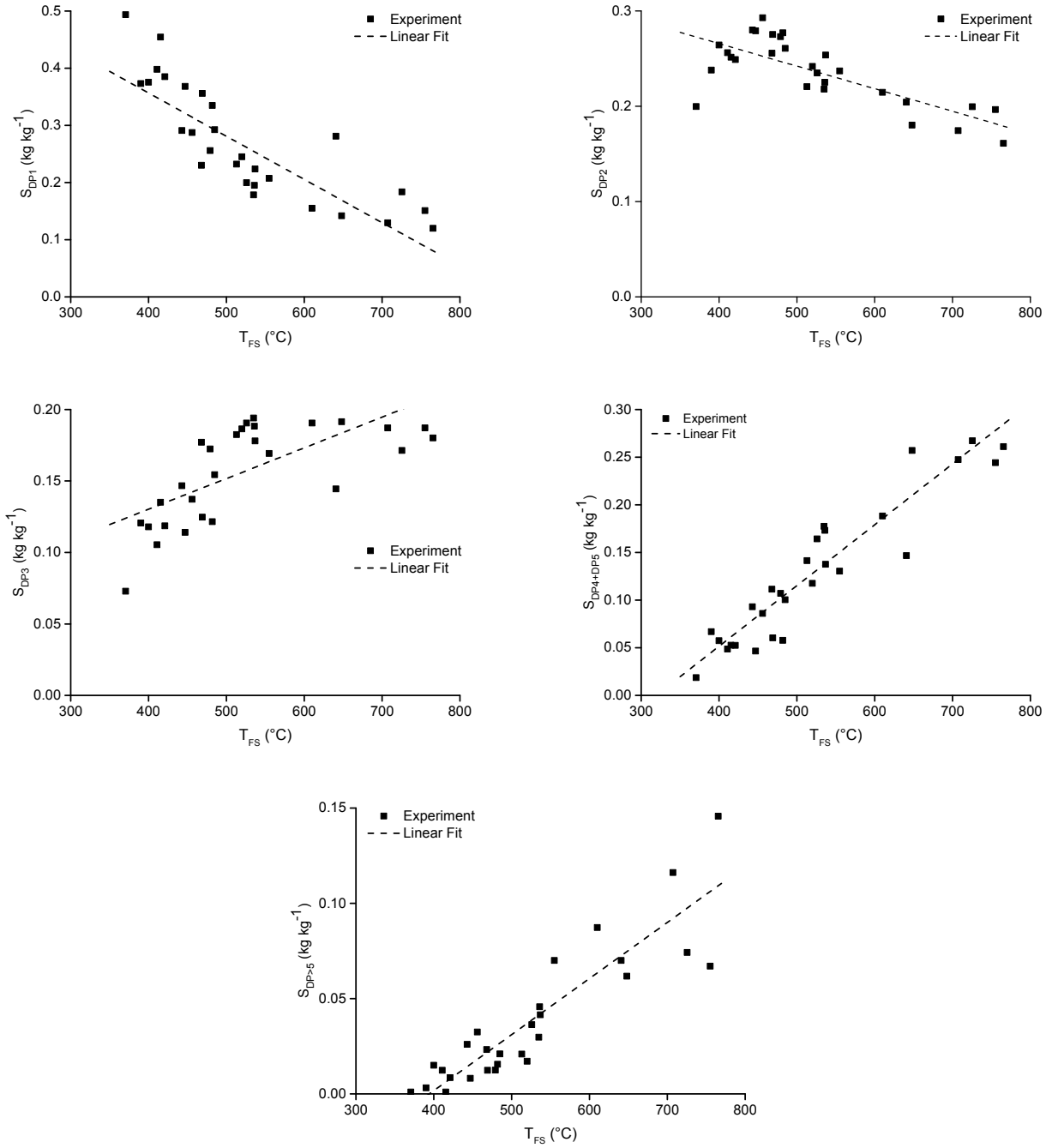

Fig. S16 DP_1, DP_2, DP_3, DP_{4+5} and $DP_{>5}$ selectivity as function of T_{FS}. Dotted line shows trendline for the linear fit. The pressure was 5 mbar.

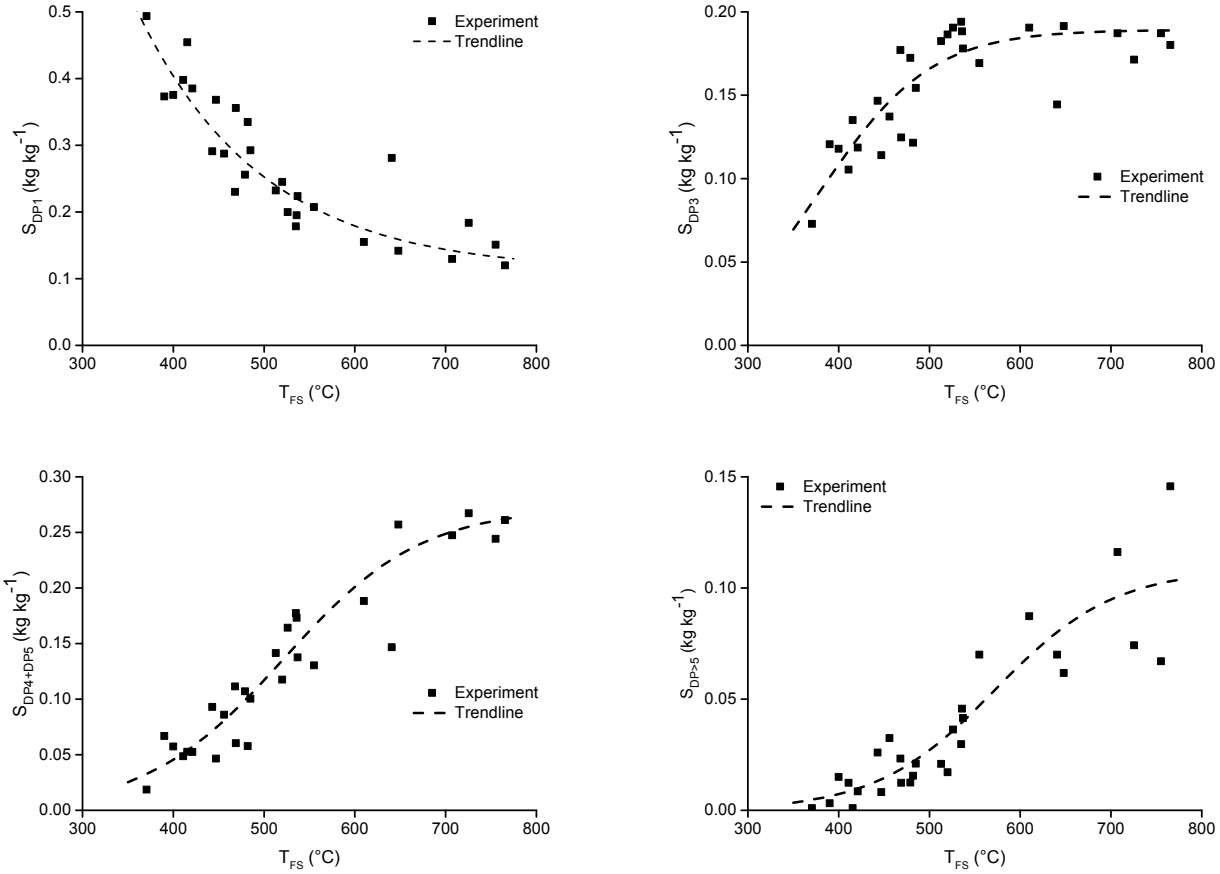

Fig. S17 DP_1, DP_3, DP_{4+5} and $DP_{>5}$ selectivity as function of T_{FS}. Dotted line shows trendline for the best fit (DP_1 (a*exp(-b*T)+c) DP_3, DP_{4+5} and $DP_{>5}$ (a/(1+exp(-b*(x-c)))).The pressure was 5 mbar.

Table 5: Curve fitting summary, linear fit vs exponential fit **.**

	DP1	DP2	DP3	DP4+5	DP>5
			Linear model		
SSE	0.063	0.015	0.016	0.015	0.008
R2	0.744	0.561	0.495	0.900	0.794
			Exponential model		
SSE	0.028	-	0.008	0.011	0.008
R2	0.887	-	0.751	0.927	0.798

Table 6: Recovery of glucose, levoglucosan and cellobiosan after hydrolysis at 120 °C, 3.5 vol% H_2SO_4 and 1 h.

Glucose		Levoglucosan		Cellobiosan	
Concentration (mg sample/ml solution)	Glucose recovery (wt% sample)	Concentration (mg sample/ml solution)	R_{DP1}: Glucose recovery (wt% sample)	Concentration (mg sample/ml solution)	R_{DP2}: Glucose recovery (wt% sample)
5	95.8	5	92.2	5	83.3
10	95.3	10	91.7	10	85.1
15	92.4	15	95.2	15	84.5
average	**94.5**	**average**	**93.1**	**average**	**84.3**

S6.3. Hydrolysis results

The condensed product contains a wide range of DP's. A rough estimation of the total amount of anhydrosugars in the oil can be obtained by hydrolysis of the condensed product to produce glucose. These sugars are often referred to as hydrolysable sugars. The hydrolysis efficiency, in other words the glucose recovery, of the condensed product was estimated by hydrolyzing glucose, levoglucosan and cellobiosan. The result are presented in Table 5. As can be observed, the glucose recovery decreases significantly for cellobiosan compared to levoglucosan. Therefore, it is decided that the glucose recovery of the condensed product should be corrected for the obtained efficiencies, see Formula 33. The R is the glucose recovery from DP_1 or DP_2, S_{DP1} is the selectivity of DP_1. The selectivity is defined as the specific sugar concentration divided by the total sugar concentration detected. The glucose recovery is expressed as the amount of carbon recovered in glucose divided by the amount of carbon originally in the cellulose.

$$\frac{C_{Glucose}}{C_{Cellulose}} = \frac{\frac{M_{Glucose}}{M_{Cellulose}} * \frac{162}{180}}{(1 - Cellulose_{ejected}) * (S_{DP1} * R_{DP1} + (1 - S_{DP1}) * R_{DP2})} \quad (33)$$

S.6.4. LC/MS results

Fig. S18 shows the spectra of a typical oil produced at 725 °C. The peak at 8.83 min represents the compounds, in our work, lumped as $DP_{>5}$. The mass spectra measured at 8.83 min is presented in Fig. S19. As can be seen this fraction contains indeed many large compounds up to DP_{11}. The smaller compounds like DP_2 etc. are fragmentation products produced during ionization of the large sugars, a well-known feature of the MS. Note, the peak intensities around 191 and 391 are background noise.

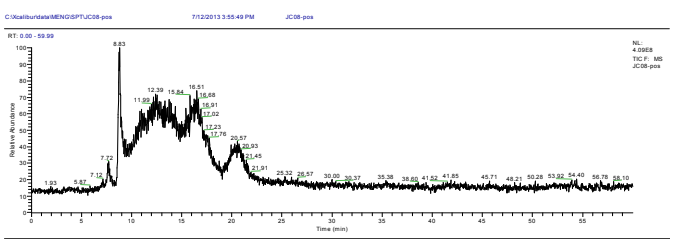

Fig. S18 Full LC/MS chromatogram of the condensed product. 725 °C and 5 mbar.

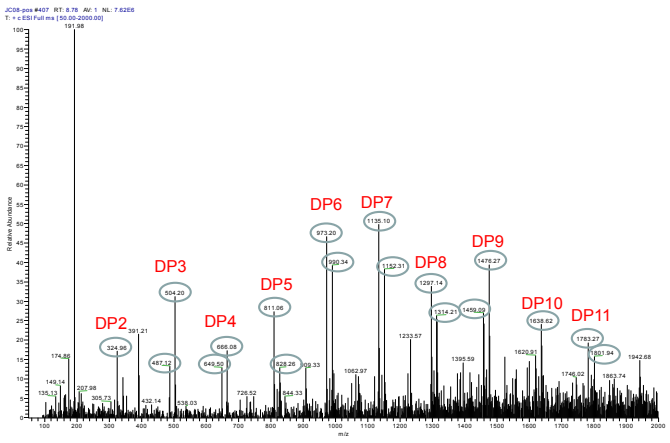

Fig. S19 Peak intensities (mass spectra) at a retention time of ~8.8 min.

In all HPLC and LC/MS spectra's typically 3 peaks can be observed between DP1 and DP2. No standards were found that could be used to identify these peaks. Therefore, LC/MS analysis was used to get a rough idea about the composition of these compounds. In Fig. S20 a spectra of the oil produced at 524 oC is shown. The levoglucosan (DP1) and cellobiosan (DP2) peaks are highlighted as well as the peaks between, numbered 1, 2 and 3. The mass spectra of these compounds can be seen in Fig. S21. The numbers in the mass spectra correspond to the numbers in Fig. S20. As can be seen a clear peak appears around 342 in all spectra's representing the same mass as cellobiosan. Therefore, it is likely that these peaks between DP1 and DP2 represent isomers of cellobiosan. Note, the peaks 191 and 390 are background noise.

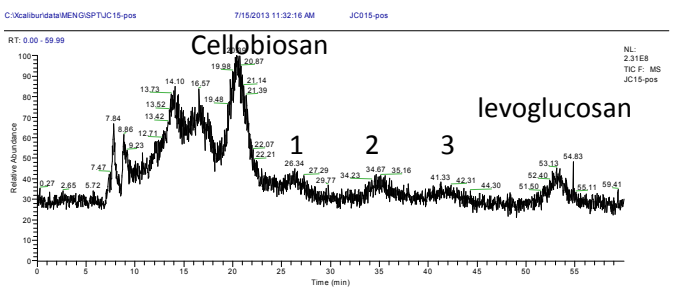

Fig. S20 LC/MS spectra of a condensed product produced at 524 °C. The reactor pressure was 5 mbar. Highlighted are Levoglucosan, cellobiosan and the peaks termed; between DP_1 - DP_2 (3 peaks).

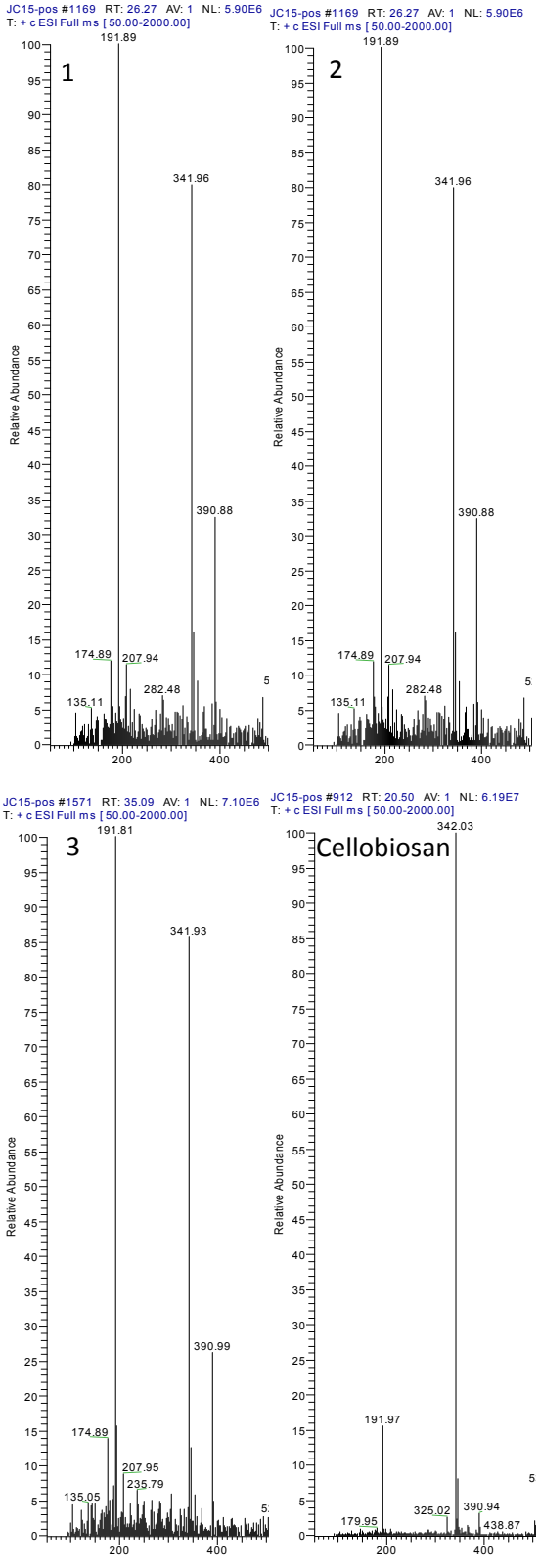

Fig. S21 Mass spectra of Peak 1, 2, 3 and cellobiosan.

S6.5. FTIR

FTIR analysis have been performed on levoglucosan, cellobiosan, cellotriosan, cellotetrasan and cellulose. The FTIR spectra of the anhydrosugars are compared with the FTIR spectra of cellulose to identify the mean peak differences. The results can be seen in Fig. S22. The biggest difference between cellulose and the anhydrosugars (DP_1 - DP_4) is highlighted with an arrow (solid line). Some additional peaks appear for the DP_1 - DP_4 sugars which were absent in the spectra of cellulose and vice versa. This information will be used to find out whether the unreacted-ejected cellulose spectra compares to cellulose or the anhydrosugars.

Fig. S23 shows the spectra of a water soluble condensed product, cellotetrasan, cellulose and unreacted-ejected cellulose. The two spectras at the bottom are cellulose and ejected cellulose. The two spectras at the top are cellotetrasan and condensed product. As can be seen the spectra of unreacted-ejected cellulose looks similar to the initial cellulose whereas the spectra of the water soluble condensable product is comparable with the spectra of cellotetrasan.

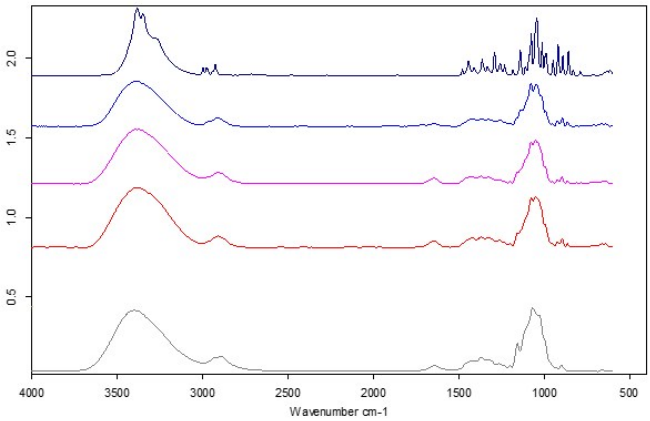

Fig. S22 FTIR spectra of Levoglucosan (top), cellobiosan, cellotriosan, cellotetrasan and cellulose (bottom).

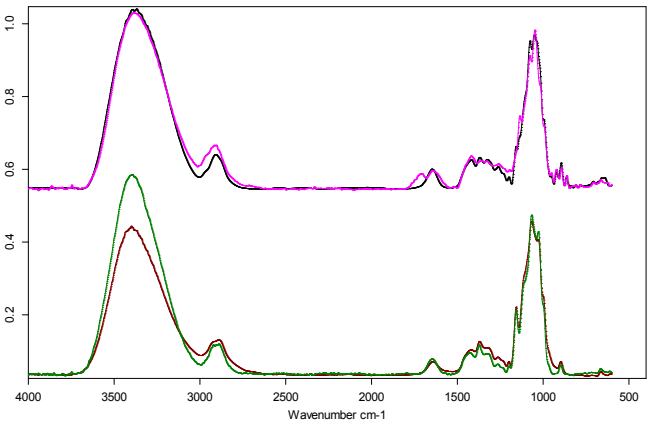

Fig. S23 FTIR spectra of water soluble condensed product, cellotetrasan, cellulose and unreacted-ejected cellulose. The arrows highlight the differences between the spectra's. The two spectras at the bottom are cellulose and unreacted-ejected cellulose. The two spectras at the top are cellotetrasan and condensed product.

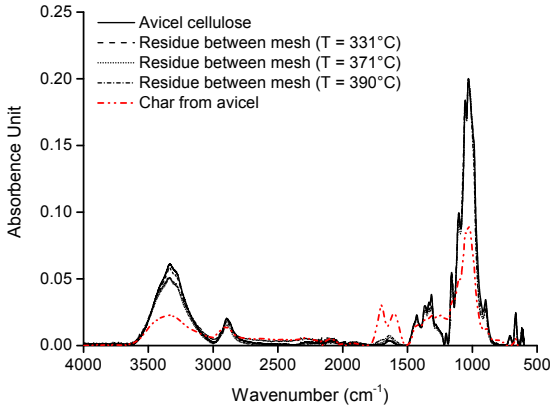

Fig. S24 FTIR spectra of avicel cellulose and char obtained from avicel cellulose. The residues between the screens were obtained after pyrolysis at 331 °C, 371 °C, and 390 °C under 5 mbar.

The FTIR spectra of avicel cellulose, char obtained from avicel cellulose and the residues between the screens after the screen-heater experiments can be seen in Fig. S24. The screen-heater experiments were performed at 331 °C, 371 °C and 390 °C. The char was obtained from a pyrolysis experiment performed with avicel cellulose at 530 °C in an oven in a nitrogen environment. As can be seen the residue between the screens show a similar spectra as the cellulose. Moreover, the spectra of the char is clearly different as the rest. This indicates that the residue remaining between the screen after low temperature pyrolysis is unreacted cellulose.

S6.6. Pyrolysis experiments with levoglucosan (DP_1) and cellobiosan (DP_2)

Levoglucosan was pyrolyzed at various temperatures and pressures, see Table 7. The results of these levoglucosan experiments are almost the same for all temperatures and pressures (1mbar – 889 mbar): there is no residue or gas fraction found after the experiment, the entire sample is converted to condensed product. HPLC analysis shows that for both temperatures the condensed product consists of only levoglucosan. This is supported by the observation that the condensed product present on the vessel wall still has the original white color of levoglucosan.

Cellobiosan was pyrolyzed at various temperatures and pressures, see Table 7. The results for the cellobiosan experiments shows that cellobiosan just evaporated at 603 °C and 5 mbar. At higher pressures or lower temperature also some cracking to levoglucosan besides evaporation has occurred see Fig. S25. No polymerization products were observed. Due to the high hygroscope of cellobiosan the standard method of applying an equal thin layer with a sieve was not possible. Therefore a concentrated mixture of cellobiosan with water was smeared as a thin layer on a screen. This method is less precise and therefore a small amount of sample was located between the electrodes, this was also the location were the residue was found after pyrolysis at 603 °C and 5 mbar. FTIR analysis of the residue at low temperature and low pressure shows that the residue is unreacted cellobiosan (not shown).

Table 7: Product yields (kg.kg^{-1} levoglucosan) for levoglucosan feedstock at varied temperatures and pressures

Temp (°C)	Pressure (mbar)	Holding Time (s)	Condensed product (kg kg^{-1})	Gas (kg kg^{-1})	Residue (kg kg^{-1})	DP1 (kg kg^{-1})	DP2 (kg kg^{-1})
270	5	1	0.96	<0.01	<0.01	0.96	N.D.
585	5	1	0.97	<0.01	<0.01	0.97	N.D.
484	479	1	0.90	<0.01	<0.01	0.90	N.D.
488	889	1	0.88	<0.01	<0.01	0.88	N.D.

N.D. not detected

Table 8: Product yields (kg.kg^{-1} cellobiosan) for cellobiosan experiments at different temperatures and pressures.

Temp (°C)	Pressure (mbar)	Holding Time (s)	Condensed product (kg kg^{-1})	Gas (kg kg^{-1})	Residue (kg kg^{-1})	DP_1 (kg kg^{-1})	DP_2 (kg kg^{-1})
333	1	5	0.43	<0.01	0.53	0.02	0.40
345	1	5	0.75	<0.01	0.15	0.04	0.71
603	1	1	0.94	<0.01	0.06*	0.00	0.94
500	93	5	0.97	0.01	0.03*	0.05	0.80
500	946	5	0.68	0.03	0.18*	0.28	0.37

* Residue was located between the clamps which remain colder during the experiments. The residue was still white which indicates unreacted cellobiosan.

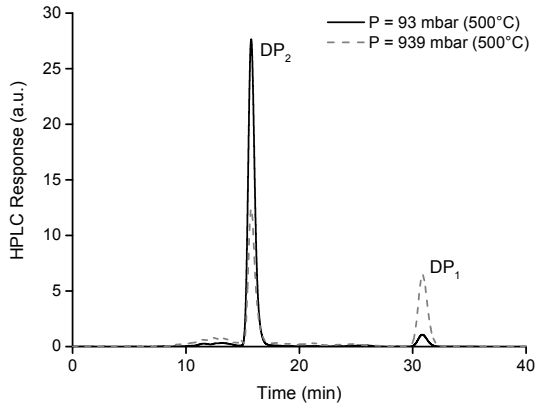

Fig. S25 Levoglucosan and cellobiosan spectra. The temperature was 500 °C and pressure 5 mbar.

S6.7. Summary of all screen-heater experimental data

Table 9: Overview of yields (g/g cellobiosan) for cellobiosan experiments at different temperatures and pressures

General Information				Product yields				Product yields corrected for unreacted-ejected cellulose			Oil composition (measured by HPLC)								Product yield (cellulose basis, corrected for the ejected cellulose)									
Experimenter	T_{FS}	Pressure	Holding Time	Condensed product yield	Gas Yield	Residue Yield	Unreacted-ejected cellulose Yield	CP Yield	Gas Yield	Residue Yield	DP_1	DP_2	DP_1 - DP_2	DP_3	DP_4	DP_5	$DP_{>5}$	Total	DP_1	DP_2	DP_1 - DP_2	DP_3	DP_4	DP_5	$DP_{>5}$	DP_4 + DP_5	Total by HPLC	CP minus sugar by HPLC
(-)	(°C)	(mbar)	(s)	(kg kg^{-1} Cellulose)				(kg kg^{-1} Cellulose)			(kg kg^{-1} condensed product)								(kg kg^{-1} cellulose)									
Cellulose (screen-heater; vacuum)																												
1	331	≤ 5	5	0.04	≤ 0.01	0.91	≤ 0.01	0.04	≤ 0.01	0.91	0.41	0.04	0.17	0.08	0.03	0.02	0.05	0.80	0.02	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.04	-0.01
1	371	≤ 5	5	0.61	≤ 0.01	0.29	0.04	0.59	≤ 0.01	0.30	0.46	0.19	0.20	0.07	0.01	0.00	0.00	0.93	0.27	0.11	0.12	0.04	0.01	0.00	0.00	0.01	0.55	-0.04
1	390	≤ 5	5	0.87	≤ 0.01	0.04	0.06	0.87	≤ 0.01	0.05	0.37	0.24	0.20	0.12	0.06	0.01	0.00	1.00	0.32	0.21	0.17	0.10	0.05	0.00	0.00	0.06	0.87	0.00
1	400	≤ 5	5	0.92	≤ 0.01	0.03	0.01	0.92	≤ 0.01	0.03	0.33	0.23	0.15	0.10	0.04	0.01	0.01	0.88	0.30	0.21	0.14	0.09	0.03	0.01	0.01	0.05	0.80	-0.11
2	411	≤ 5	5	0.88	*NM*	0.03	0.01	0.88	*NM*	0.03	0.38	0.24	0.17	0.10	0.03	0.01	0.01	0.95	0.33	0.21	0.15	0.09	0.03	0.01	0.01	0.04	0.83	-0.05
3	415	≤ 5	5	0.88	0.01	0.06	0.01	0.88	0.01	0.06	0.30	0.16	0.07	0.09	0.03	0.00	0.00	0.66	0.26	0.15	0.06	0.08	0.03	0.00	0.00	0.03	0.58	-0.30
2	421	≤ 5	5	0.88	*NM*	0.04	0.01	0.88	*NM*	0.04	0.31	0.20	0.15	0.09	0.03	0.01	0.01	0.79	0.27	0.17	0.13	0.08	0.03	0.01	0.01	0.04	0.70	-0.18
2	443	≤ 5	5	0.99	*NM*	≤ 0.01	0.09	0.99	*NM*	0.01	0.30	0.29	0.17	0.15	0.07	0.03	0.03	1.04	0.30	0.29	0.17	0.15	0.07	0.03	0.03	0.10	1.04	0.04
2	447	≤ 5	5	0.85	*NM*	0.06	0.01	0.85	*NM*	0.06	0.37	0.28	0.18	0.11	0.04	0.01	0.01	1.00	0.31	0.24	0.16	0.10	0.03	0.01	0.01	0.04	0.84	0.00
2	456	≤ 5	5	0.95	*NM*	≤ 0.01	0.02	0.95	*NM*	≤ 0.01	0.28	0.29	0.16	0.14	0.06	0.03	0.03	0.99	0.27	0.27	0.15	0.13	0.05	0.03	0.03	0.08	0.94	-0.01
2	468	≤ 5	5	0.95	*NM*	0.01	0.02	0.95	*NM*	0.01	0.21	0.24	0.19	0.16	0.08	0.03	0.02	0.92	0.20	0.22	0.18	0.15	0.07	0.02	0.02	0.10	0.87	-0.07
2	469	≤ 5	5	0.97	*NM*	≤ 0.01	0.01	0.97	*NM*	≤ 0.01	0.33	0.26	0.16	0.12	0.04	0.01	0.01	0.93	0.32	0.25	0.16	0.11	0.04	0.01	0.01	0.05	0.91	-0.06
1	479	≤ 5	1	0.98	0.02	≤ 0.01	0.01	0.98	0.02	≤ 0.01	0.24	0.25	0.16	0.16	0.07	0.02	0.01	0.92	0.23	0.24	0.16	0.15	0.07	0.02	0.01	0.10	0.90	-0.08
2	482	≤ 5	5	0.93	*NM*	0.01	≤ 0.01	0.93	*NM*	0.01	0.30	0.25	0.18	0.11	0.04	0.01	0.01	0.91	0.28	0.23	0.16	0.10	0.04	0.01	0.01	0.05	0.85	-0.09
2	485	≤ 5	5	0.97	*NM*	≤ 0.01	0.01	0.97	*NM*	≤ 0.01	0.28	0.25	0.17	0.15	0.07	0.03	0.02	0.97	0.28	0.25	0.16	0.15	0.07	0.03	0.02	0.09	0.95	-0.02
3	513	≤ 5	5	0.85	0.01	0.01	≤ 0.01	0.85	0.01	0.01	0.26	0.24	0.22	0.20	0.12	0.04	0.02	1.10	0.22	0.21	0.19	0.17	0.10	0.03	0.02	0.13	0.93	0.08
3	520	≤ 5	5	0.89	0.01	≤ 0.01	≤ 0.01	0.89	0.01	≤ 0.01	0.25	0.25	0.20	0.19	0.09	0.03	0.02	1.02	0.22	0.22	0.18	0.17	0.08	0.02	0.02	0.11	0.91	0.02
4	526	≤ 5	5	0.98	0.01	0.01	0.01	0.98	0.01	0.01	0.20	0.24	0.18	0.19	0.11	0.06	0.04	1.01	0.20	0.23	0.17	0.19	0.11	0.06	0.04	0.16	0.99	0.01
4	535	≤ 5	5	0.94	0.01	0.01	0.04	0.94	0.01	0.01	0.20	0.24	0.23	0.22	0.13	0.07	0.03	1.12	0.19	0.23	0.21	0.20	0.12	0.07	0.03	0.19	1.06	0.11
4	536	≤ 5	5	0.96	0.01	0.01	0.03	0.96	0.01	0.01	0.20	0.23	0.18	0.19	0.12	0.06	0.05	1.02	0.19	0.22	0.17	0.18	0.11	0.05	0.04	0.17	0.97	0.02
2	537	≤ 5	5	0.94	*NM*	0.01	0.01	0.94	*NM*	0.01	0.21	0.24	0.16	0.17	0.09	0.04	0.04	0.94	0.20	0.22	0.15	0.16	0.08	0.04	0.04	0.12	0.88	-0.06
2	555	≤ 5	5	0.96	*NM*	≤ 0.01	0.02	0.96	*NM*	≤ 0.01	0.18	0.21	0.16	0.15	0.08	0.04	0.06	0.88	0.18	0.20	0.16	0.14	0.07	0.04	0.06	0.11	0.85	-0.11
2	610	≤ 5	5	0.94	*NM*	≤ 0.01	0.01	0.94	*NM*	≤ 0.01	0.15	0.21	0.16	0.19	0.12	0.07	0.09	0.99	0.14	0.20	0.15	0.18	0.11	0.06	0.08	0.17	0.93	-0.01
3	641	≤ 5	5	0.91	0.01	≤ 0.01	0.03	0.91	0.01	≤ 0.01	0.26	0.19	0.14	0.13	0.08	0.06	0.06	0.92	0.23	0.17	0.13	0.12	0.07	0.05	0.06	0.12	0.83	-0.07
2	648	≤ 5	5	1.00	*NM*	0.01	0.06	1.00	*NM*	0.01	0.12	0.16	0.15	0.17	0.13	0.09	0.05	0.87	0.12	0.16	0.15	0.17	0.13	0.09	0.05	0.22	0.87	-0.13
3	707	≤ 5	5	0.97	0.01	≤ 0.01	0.03	0.97	0.01	≤ 0.01	0.11	0.15	0.13	0.16	0.12	0.10	0.10	0.86	0.11	0.15	0.12	0.16	0.11	0.09	0.10	0.21	0.84	-0.14
1	725	≤ 5	1	0.95	0.01	≤ 0.01	≤ 0.01	0.95	0.01	≤ 0.01	0.15	0.15	0.15	0.17	ND	ND	ND	ND	0.14	0.14	0.14	0.16	ND	ND	ND	ND	0.59	-0.36
1	726	≤ 5	1	0.94	0.01	≤ 0.01	≤ 0.01	0.94	0.01	≤ 0.01	0.17	0.18	0.09	0.16	0.15	0.09	0.07	0.91	0.16	0.13	0.09	0.13	0.14	0.09	0.05	0.19	0.79	-0.15
1	755	≤ 5	1	0.94	0.01	≤ 0.01	0.04	0.94	0.01	≤ 0.01	0.14	0.18	0.14	0.17	0.13	0.10	0.06	0.93	0.13	0.17	0.13	0.16	0.12	0.09	0.06	0.21	0.87	-0.06
3	765	≤ 5	5	0.95	0.01	≤ 0.01	0.04	0.94	0.01	≤ 0.01	0.11	0.15	0.12	0.16	0.13	0.11	0.13	0.91	0.10	0.14	0.11	0.15	0.12	0.11	0.12	0.22	0.86	-0.09
Cellulose (screen-heater; vacuum; without HPLC analysis)																												
2	338	≤ 5	1	0.07	≤ 0.01	0.89	≤ 0.01	0.07	≤ 0.01	0.89	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*
2	388	≤ 5	1	0.80	≤ 0.01	0.19	≤ 0.01	0.80	≤ 0.01	0.19	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*
2	460	≤ 5	1	0.93	≤ 0.01	-0.03	≤ 0.01	0.93	≤ 0.01	-0.03	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*
2	527	≤ 5	1	0.96	≤ 0.01	≤ 0.01	0.01	0.96	≤ 0.01	≤ 0.01	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*
2	539	≤ 5	1	0.93	≤ 0.01	≤ 0.01	0.01	0.93	≤ 0.01	≤ 0.01	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*
2	540	≤ 5	1	0.93	≤ 0.01	≤ 0.01	0.06	0.93	≤ 0.01	≤ 0.01	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*

2	551	≤ 5	1	1.03	≤ 0.01	≤ 0.01	≤ 0.01	1.03	≤ 0.01	≤ 0.01	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*	*NM*
Cellulose (screen-heater & fluidized bed reactor; atmospheric)																									
3	530	1000	5	0.83	0.01	0.01	0.02	0.83	0.01	0.01	0.38	0.13	0.20	0.04	0.01	0.01	0.01	0.78	0.32	0.10	0.17	0.04	0.01	0.01	0.01	0.02	0.65	-0.18
5	530	1000	-	0.84	0.01	0.01	≤ 0.01	0.84	0.01	0.01	0.47	0.06	0.22	0.04	0.01	0.00	0.01	0.80	0.39	0.05	0.19	0.03	0.01	0.00	0.01	0.01	0.68	-0.17
3	545	1000	5	0.83	0.02	0.01	≤ 0.01	0.83	0.02	0.01	0.41	0.08	0.18	0.06	0.02	0.01	0.01	0.77	0.34	0.07	0.15	0.05	0.01	0.01	0.01	0.02	0.64	-0.19
Experiment with Gold sputtered mesh (screen-heater; vacuum)																									
2	526	≤ 5	1	0.98	≤ 0.01	≤ 0.01	≤ 0.01	0.98	≤ 0.01	≤ 0.01	0.22	0.20	0.12	0.13	0.04	0.05	0.00	0.76	0.21	0.20	0.11	0.13	0.04	0.05	0.00	0.09	0.75	-0.23

ND: Not detected

NM: Not measured

1. References

1. Z. Wang, A. G. McDonald, R. J. M. Westerhof, S. R. A. Kersten, C. M. Cuba-Torres, S. Ha, B. Pecha and M. Garcia-Perez, *J. Anal. Appl. Pyrolysis*, 2013, **100**, 56-66.
2. J. Rojas, A. Lopez, S. Guisao and C. Ortiz, *Journal of Advanced Pharmaceutical Technology & Research*, 2011, **2**, 144-150.
3. R. P. Benedict, *Fundamentals of Temperature, Pressure, and Flow Measurements*, Wiley, 3rd edn., 1984.
4. S. R. G. Oudenhoven, R. J. M. Westerhof, N. Aldenkamp, D. W. F. Brilman and S. R. A. Kersten, *J. Anal. Appl. Pyrolysis*, 2013, **103**, 112-118.
5. W. Prins, W. Draijer and W. P. M. van Swaaij, in *Heat and mass transfer in fixed and fluidized beds (Proceedings of the International Centre for Heat and Mass Transfer)*, eds. W. P. M. van Swaaij and N. H. Afgan, Hemisphere publishing corporation, 1986, ch. 19, pp. 317-332.
6. The engineering toolbox, Densities of Solids http://www.engineeringtoolbox.com/density-solids-d_1265.html, (accessed 24 feb 2016).
7. The engineering toolbox, Specific Heat of common Substances, http://www.engineeringtoolbox.com/specific-heat-capacity-d_391.html, (accessed 24 feb 2016).
8. J. Lédé, J. P. Diebold, C. V. C. Peacocke and J. Piskorz, in *Fast Pyrolysis of Biomass: A Handbook*, eds. A. V. Bridgwater and C. V. C. Peacocke, CPL press, Newbury, 1999, vol. 1, pp. 51-65.
9. V. Oja and E. M. Suuberg, *J. Chem. Eng. Data*, 1998, **44**, 26-29.
10. O. Boutin, M. Ferrer and J. Lédé, *Chem. Eng. Sci.*, 2002, **57**, 15-25.
11. A. G. W. Bradbury, Y. Sakai and F. Shafizadeh, *J. Appl. Polym. Sci.*, 1979, **23**, 3271-3280.