



## Hydrothermal carbonization of pulp mill streams



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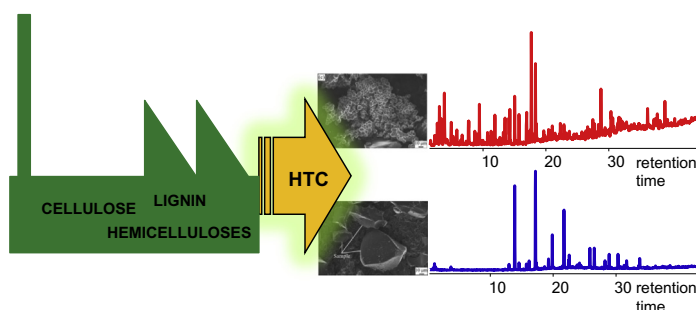
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### HIGHLIGHTS

- Different types of carbonaceous particles were produced in HTC.
- Impure carbohydrate containing pulp mill streams have potential for HTC.
- Kraft lignin was processed in HTC in alkaline conditions with high yields.
- Analytical pyrolysis was applied successfully to study biomass conversion.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The progress of the conversion, the yield, the structure and the morphology of the produced carbonaceous materials as a function of time were systematically studied with pyrolysis-GC/FID and FESEM microscope. The conversion of galactoglucomannan, bleached kraft pulp and TEMPO oxidized cellulose nanofibrils followed the reaction route of glucose being slower though with fibrous material, higher molar mass and viscosity. The conversion of kraft lignin was minor following completely different reaction route. Carbonaceous particles of different shape and size were produced with yields between 23% and 73% after 4 h with being higher for lignin than carbohydrates. According to the results, potential pulp mill streams represent lignocellulosic resources for generation of carbonaceous materials.

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## 1. Introduction

Growing population and increasing standard of living enhance the demand for novel materials. This demand combined with the environmental and energy concerns have increased the interest and awareness in using biomass feedstock to meet growing needs, not only in energy production, but also in value-added products. The different components from wood components – cellulose, hemicelluloses and lignin – have great potential to replace fossil-

based materials in various uses. Unfortunately, several industrial lignocellulosic side streams are mixed and contain substantial amounts of water, making them less attractive for utilization. Presently, most carbon material used in many applications has a fossil origin.

The possibility to process wet biomass with energy-efficient and easily up-scalable technology makes hydrothermal carbonization (HTC) an interesting alternative for the generation of carbonaceous materials at a larger scale. HTC is an efficient biomass conversion technology using mild processing temperatures (~180–250 °C) and water as the carbonization medium, under self-generated pressures. Several chemical reactions occur during

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the process including hydrolysis, dehydration, decarboxylation, polymerization, aromatization and condensation (Funke and Ziegler, 2010). As a consequence, carbonaceous solid fraction accompanied by liquid phase and minor gas phase are formed. In general, the solid carbonaceous material consists of particles with different shapes and size having functional groups on the surface (Sevilla and Fuertes, 2009a, 2009b; Titirici and Antonietti, 2010) and distinct properties such as a high energetic value, a high chemical and thermal stability, and a relatively high adsorption capacity (Hu et al., 2008; Wang et al., 2001). Owing to the properties, potential uses for these materials include, for example, carbon sequestration in soil, the sorptive materials for extraction of harmful chemicals from water, use in energy storage and for burning as fuel, in municipal waste management, in solid state catalysts or as anode materials for lithium-ion batteries.

The process has increasingly attracted interest in recent years even though this process was first patented over hundred years ago by Bergius (Funke and Ziegler, 2010). During the last decade it has been studied and applied extensively and several recent review articles have been published (Funke and Ziegler, 2010; Hu et al., 2010, 2008; Libra et al., 2011; Titirici and Antonietti, 2010; Titirici et al., 2015; Wikberg et al., 2015a).

HTC has been demonstrated to be an effective process for the production of functional carbonaceous materials from simple monosaccharides, such as glucose (Falco et al., 2011; Sevilla and Fuertes, 2009b; Titirici et al., 2008). Under acidic hydrolytic conditions, the hydrothermal process allows the effective conversion of glucose to hydroxymethyl furfural, HMF (Falco et al., 2011; Titirici et al., 2012, 2008). By time, HMF forms polymeric carbonaceous particles and simultaneously decomposes into low molecular weight acids (e.g. levulinic acid and formic acid). Hydrothermal carbonization of pure cellulose has also been studied in several articles (Falco et al., 2011; Kang et al., 2012; Sevilla and Fuertes, 2009a). Two different conversion pathways for cellulose have been reported either via hydrolysis (Sevilla and Fuertes, 2009a) or direct transformation (Falco et al., 2011). In hydrolysis cellulose is degraded to monosaccharides, which forms carbonaceous material with similar route as glucose (Sevilla and Fuertes, 2009a). In direct transformation cellulose can carbonize without complete hydrolysis to monosaccharides through intramolecular condensation, dehydration and decarboxylation reactions (Falco et al., 2011). Contrary to the polysaccharides, lignin is more complex biomass component composing of phenyl propane units linked with ether and carbon-carbon bonds. This makes lignin more stable in higher temperatures. Therefore, the structure of lignin is only slightly altered when applying the conventional HTC process conditions (Dinjus et al., 2011; Kang et al., 2012; Lu and Berge, 2014; Wikberg et al., 2015b).

Significant amounts of pulping side streams are underutilized at the moment. Efficient utilization of side streams is important basis for a successful biorefinery. However, these streams are wet and the streams containing polysaccharides are seldom free from lignin making them less attractive for many purposes. HTC as a simple, fast and easily scalable process could offer an option for pulp mills to convert wet side streams into value-added carbon materials, integrating at the same time the majority of the carbon within the solid material reducing greenhouse gas emissions compared to current treatment processes. The assessment of the suitability of HTC technology in real environment requires understanding of industrially relevant raw materials' behavior in the process. This study focuses on investigating the feasibility of HTC for converting selected lignocellulosic precursors (galactoglucomannan, kraft pulp, kraft lignin) into carbonaceous materials and structures using industrially relevant conditions. Our work provides understanding of the relationship between the precursor characteristics, HTC pro-

cessing parameters and the structure of the produced carbonaceous material.

## 2. Methods

### 2.1. Materials

Following precursors were selected to this study representing pulp mill streams:

Glucose (purity  $\geq 99.5\%$ ) was purchased from Sigma-Aldrich.

Galactoglucomannan (GGM) was obtained by hot water extraction according to conditions reported in the literature (Rissanen et al., 2014). The obtained sample was precipitated in tenfold amount of ethanol (ETAX B, Altia, Finland) and the precipitate recovered by filtration. The precipitate was redispersed in ethanol, again recovered by filtration and dried in the oven at 80 °C overnight. The sample contained 3.6 wt.% total lignin, 72 wt.% GGM and 7.3 wt.% other polysaccharides (xylan and pectic compounds).

Bleached softwood Kraft pulp (kraft pulp) sample contained 7 wt.% xylan and 8 wt.% GGM, the rest being cellulose. It was obtained from a Finnish pulp mill.

TEMPO oxidized cellulose nanofibrils (TEMPO CNF) was produced using the oxidation method described by Saito et al. (2006) and followed by mechanical disintegration with a Microfluidizer. The oxidized fibers were made of never-dried bleached softwood kraft pulp. The target carboxylate content was 1 mmol/g. The fiber slurry with a solid content of 2% passed once through the Microfluidizer, which was equipped with the 400  $\mu\text{m}$  and 100  $\mu\text{m}$  chambers. Disintegration was performed at 1850 bar. The slurry became a translucent and viscous gel after the mechanical treatment.

Kraft lignin used in the studies was softwood kraft lignin extracted from industrial black liquor by acidification with  $\text{CO}_2$ , purified by acidic washing, and dried before the thermal treatment.

### 2.2. Hydrothermal carbonization (HTC)

The precursors were either dissolved (glucose, GGM) or suspended to water (kraft lignin, kraft pulp, TEMPO CNF). The dry matter content of all the experiments was 7 wt.% except for TEMPO CNF 2.3 wt.%. Sulfuric acid was added as a catalyst. The concentrated sulfuric acid was added 0.18 g for the glucose and GGM batches and 0.534 g for kraft pulp and TEMPO CNF batches. For the acidic and alkaline HTC experiments of kraft lignin 1.74 g of 1 M sulfuric acid and 0.37 g of NaOH was added, respectively. Initial pHs for different experiments are presented in Table 1. The solutions/suspensions were placed to autoclaves. The autoclaves were equipped with gas vents and spring-loaded pressure relief valves (set pressure of 50 bars). The autoclaves were placed to an electrically heated hot air oven with a rotating carousel at a rotation angle of 30° (horizontally) for multiple autoclaves. The reactor was controlled via PC software. Stirring at 5 rpm was started after fitting the autoclaves to the oven. The desired reaction temperature of 220 °C was reached in 55 min. This temperature was maintained for desired time 10 min, 30 min, 1 h and 4 h. The reactor was cooled down to room temperature using water cooling during approximately 10 min. Reactor was vented from gases at ambient temperature. Carbonaceous solids were collected and separated from process water in suction. Solids were disintegrated for two minutes using a Waring blender in 600 ml of deionized water and collected in suction. Disintegration and washing treatments were repeated and the solid product was finally dried in oven at 70 °C and the yield determined (Table 1). Solids were powdered with a mortar and pestle to make the homogeneous before the

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