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Drying and pyrolysis of cellulose nanofibers from wood, bacteria and algae for char application in oil absorption and dyes adsorption

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Abstract

Native cellulose nanofibers (CNF) constitute an abundant resource for pyrolysis leading to char materials offering a wide range of properties and application possibilities. With the aim to produce chars having large surface area and pore volume for dyes adsorption and oil absorption, respectively, we herein explore the slow pyrolysis process of cellulose nanofibers from wood, *Cladophora* algae and bacteria that were subjected to various drying routes. Whereas algae CNF with their large crystallites lead to high surface area (S_{BET}) substrates using conventional drying from aqueous suspension, CNF from wood having smaller crystallites require drying from solvents to reach high S_{BET} substrates, which results in chars with a good adsorption capacity for both anionic and cationic dyes. Moreover, the porosity of the CNF substrate can be tuned via an ice-templating freeze-drying procedure reaching values as high as 99.7% and corresponding chars capable of absorbing 64-120 g.g⁻¹ of various oils and organic solvents. Besides the absorption/adsorption properties of the chars, we report effects of CNF source and structure on the thermal properties assessed by thermogravimetric and thermomechanical analyses, differential scanning calorimetry and mass spectrometry, and we identified over 20 decomposition products and 3 expansion events occurring during CNF pyrolysis.

KEYWORDS: Cellulose nanomaterials, Thermal decomposition, Activation energy, TG-MS, Thermomechanical analysis, Environmental remediation.

1 Introduction

Industrialization and human activities have led to an increasing number of pollutants entering our environment, thus urging for sustainable remediation solutions.^{1, 2} Such solution requires the combination of sustainable materials and processing technologies offering enhanced performance compared to current remediation methods. Thus, the role of cellulose nanofibers (CNF) in these depollution technologies is expected to grow due to their abundance, environmentally benign character and large surface area where functional entities could be included for specific interaction with contaminants.³ Functional cellulose nanofibers have been used in aqueous systems for the adsorption of heavy metal ions,^{4, 5} dyes,^{6, 7} radioactive species,⁸ organic matter,⁹ bacteria and viruses,⁷ nitrate and fluoride,^{10, 11} and in the atmosphere for carbon dioxide capture.^{12, 13} To absorb/adsorb non-polar species, hydrophobization of CNF, which can be e.g. achieved through attachment of hydrocarbon chains,¹⁴⁻¹⁶ application of an inorganic coating,¹⁷⁻¹⁹ or pyrolysis is necessary. The development of an economical hydrophobic CNF-based sorbent would contribute to environmental depollution for the removal of organic compounds from air and water. For instance, it can be used for cleanup of oil spills from aquatic medium and for the treatment of oily and dye-contaminated industrial wastewater.

^{17, 20-22}

While activated carbon is being largely used for water and air purification, its preparation requires large quantities of activating agents like ZnCl_2 , H_3PO_4 , KOH (chemical activation), or a high temperature combined with steam, carbon dioxide or air atmospheres (physical activation).²³ CNF is therefore an interesting substrate for pyrolysis since the material structure from various CNF sources and from various drying pathways of CNF suspensions offer a wide array of substrates whose pyrolysis should lead, without an activation step, to numerous material structures of potential interests as high surface area adsorbents,^{22, 24} catalysts,²⁶ energy storage devices^{23, 25} and sensors.^{26, 27, 28} Furthermore, a better understanding of the cellulose pyrolysis mechanisms necessitates the exploration of various material structures, and could ultimately lead to a more efficient biofuel production.

CNF are obtained either through a top-down approach from woody, plant, or algal biomass wherein the major part of non-cellulosic components is first removed, which is followed by a mechanical disintegration of the obtained pulp in the presence of water,²⁹⁻³¹ or through a bottom-up approach by cultivating *Acetobacter xylinum* in the presence of sugar (also known as bacterial cellulose).³² While displaying the cellulose I crystalline structure of native cellulose, these CNF have different crystal size, degree of polymerization and proportions of I_α and I_β allomorphs.³³ In addition, various drying routes of the aqueous CNF suspension result in different material structures, which in turn affect the final material's properties.³⁴⁻⁴⁰ Hence, it becomes apparent that the pyrolysis process of native cellulose and the resulting char material can be adequately represented only when the structure of the CNF substrate is comprehended, taking into account its hierarchical structure, and this is the purpose of the present work.

Here, we adopt a bottom-up approach to investigate the pyrolysis process of cellulose and the adsorption/absorption properties of the chars. We first examine physical properties of raw CNF from various sources (wood, bacteria and *Cladophora* algae), we then analyze the structure and thermal properties of CNF obtained via different drying routes of CNF gels, and we finally evaluate the structure and adsorption/absorption properties of CNF chars. Various analytical tools including thermogravimetric and thermomechanical analyses, differential scanning calorimetry, mass spectrometry and elemental analysis were employed in order to generate complementing data whose interpretation allowed for a thermal degradation pathway of CNF discerning phenomena occurring in the crystalline and amorphous portions of cellulose to be proposed.

2 Experimental Methods

CNF extraction. Cellulose nanofibers from bleached softwood pulp fibers (ECF, Stendal Berlin, Germany) denoted WCNF were prepared by mechanical disintegration of the pulp at 2 wt% combining a high shear grinding process at a nominal velocity of 1500 rpm of the rotating grinding stones (Supermass Colloider MKZA10-20J CE, Masuko Sangyo Co., Japan), and a homogenization whereby the suspension underwent two passes through 400 μm and 200 μm chambers, then another

two passes through 200 μm and 75 μm chambers under a pressure of up to 1200 bars (Microfluidizer® High-Shear Processor, Microfluidics Corporation, USA).⁴¹ Bacterial cellulose nanofibers (BCNF) were prepared as described elsewhere.⁴² BCNF hydrogels with ~1 vol% cellulose fraction were produced by the bacterial strain *Acetobacter xylinum* FF-88 using a culture of 5 vol% of coconut milk and 8 vol% of sucrose. The hydrogel was boiled in 10 vol% of a concentrated NaOH solution for 3 h, then thoroughly washed with distilled water and Milli-Q water. BCNF hydrogel thus obtained was homogenized by an Ultraturax T25 homogenizer for 5 min to produce BCNF suspension. *Cladophora* algae were collected from the Chriesbach creek in the region of Zurich, and used for the preparation of algae cellulose nanofibers (ACNF) following the procedure described by Mihranyan et al.⁴³ *Cladophora glomerata* algae at 2 wt% in water were treated 3 times with a 1 wt % NaOH solution at 80 °C for 2 h under mechanical stirring. The fibers were thereafter filtered and washed with distilled water and subsequently bleached at 80 °C for 4 h under mechanical stirring. The bleaching solution comprises of equal parts acetate buffer, aqueous chlorite (1.7 wt % in water), and distilled water. The fibers were then filtered, washed with distilled water and treated with 2.5 N HCl for 70 min under reflux and mechanical stirring. The suspension was finally washed until neutrality, dialyzed against distilled water, and homogenized by an Ultraturax T25 homogenizer for 5 min to produce ACNF suspension.

CNF drying. *Heat drying (HD):* A paper-making approach was used for the preparation of the heat-dried substrate.^{35, 43} 400 mg (dry weight) of CNF in water at a total volume of 300 ml was vacuum filtered on a glass filter funnel (8 cm in diameter) using a 0.65 μm DVPP filter membrane from Millipore, and the resulting cake was hot pressed at 120 °C for 20 minutes under a pressure of 2.2 bars (Carver Inc., USA) giving a film denoted as the HD substrate. *Supercritical CO₂ drying (SCD):* The resulting cake from CNF suspension filtration (400 mg dry weight) was solvent exchanged to ethanol, then to liquid CO₂ in a critical point dryer chamber (E3000, Quorum technologies). The chamber was then brought above the CO₂ critical point conditions to ca. 100 bar and 36 °C, and depressurized leading to an aerogel denoted as the SCD substrate.³⁸ *Freeze-drying (FD):* An aqueous CNF suspension at 0.5 wt% was placed in a copper mold (15*15 cm²) and frozen in liquid nitrogen, then

sublimated under vacuum with a Lyovac freeze-dryer (SRK system technik GMBH) yielding a foam having a density of $\sim 5 \text{ kg m}^{-3}$ denoted as the FD substrate. FD substrates having other densities were prepared similarly by freeze-drying CNF suspensions having a concentration of 0.3%, 1.5%, 3.5% or 5.4%, as reported elsewhere.^{35, 40} *Tert-butanol freeze-drying (BuFD)*: The aqueous CNF suspension was solvent-exchanged to t-butanol via successive t-butanol addition, centrifugation and removal of supernatant. The CNF in t-butanol was thereafter frozen in liquid nitrogen, then sublimated under vacuum with a Lyovac freeze-dryer (SRK system technik GMBH) yielding BuFD substrate.^{37, 39}

CNF substrates characterization. *CNF substrate density* (ρ_{CNF}) was calculated by dividing the weight of the dry CNF substrate by its volume determined using a micrometer with a precision of 1 μm . The porosity of CNF substrate (P) was given by: $P = 1 - \rho_{\text{CNF}} / \rho_{\text{cellulose}}$ by taking 1500 kg m^{-3} as the density of cellulose ($\rho_{\text{cellulose}}$).⁴⁴ *The specific surface area* of the CNF substrates (S_{BET}) was determined according to the multipoint Brunauer–Emmett–Teller (BET) method by N_2 physisorption at relative vapor pressure of 0.05–0.2 on a surface area and pore size analyser (Coulter SA3100, Beckman coulter Inc). *Scanning Electron Microscopy* was carried out using a FEI Nova NanoSEM 230 instrument (FEI, Hillsboro, Oregon, USA) at an accelerating voltage of 5 kV and a working distance of 5 mm. Prior to SEM observation, the samples were sputter-coated with a platinum layer of about 7.5 nm (BAL-TEC MED 020 Modular High Vacuum Coating Systems, BAL-TEC AG, Liechtenstein) in Ar as a carrier gas at 5×10^{-2} mbar. *Dynamic vapour sorption* experiments were performed in a VTI-SA+ Vapor Sorption Analyzer (TA-Instruments, New Castle, USA). A sample weighing ca. 10 mg was placed in the sample cup and dried at 105°C for 2 hours. Thereafter, the weight of the sample compared to a reference empty cup was registered with a resolution of 0.1 μg while the relative humidity surrounding the cups was controlled in the range 10%-95%. Samples were tested at a temperature of 23°C . *X-ray diffraction analyses* of CNF substrates were registered in a PANalytical X'Pert PRO θ – 2θ MPD system (Cu– $K\alpha$ radiation $\lambda = 1.54060 \text{ \AA}$). The diffraction patterns were obtained from 5° to 40° in 2θ with angular step interval of 0.017° . The Segal crystallinity indexes (CI) were calculated according to XRD peak height method (Segal method), i.e., $\text{CI}(\%) = 100 \times (1 - I_1/I_2)$, where I_1 is the minimum intensity of the amorphous phase ($\sim 19^\circ$) and I_2 is the maximum intensity of

the crystalline phase ($\sim 22.5^\circ$).⁴⁵ The d-spacing was determined from Bragg equation, and the crystallite size perpendicular to the plan (L) was calculated using the Scherrer equation: $L = 0.9\lambda / (H \cdot \cos\theta)$ where H is the full-width at half-maximum and θ is the Bragg angle.⁴⁶ *Elemental analyses* of carbon, oxygen and hydrogen in the CNF were performed by the microelemental laboratory of ETH Zurich on a LECO CHN-900 instrument (Leco Corporation, St. Joseph, MI, USA).

CNF pyrolysis and thermal properties. CNF samples were pyrolysed in a furnace under a nitrogen flow of $\sim 110 \text{ ml min}^{-1}$ at 500°C for 1 hour using a heating rate of 10 K min^{-1} (Carbolite, Liwag Industrieofenbau und Wärmetechnik AG furnace). Thermogravimetric analysis was performed on Setsys Evolution device (Setaram) interconnected with a mass spectrometer QMG 700 (Pfeiffer) coupled by Supersonic system (Setaram) for analysis of evolved gases. All measurements were performed using $\alpha\text{-Al}_2\text{O}_3$ crucibles in argon atmosphere (20 ml min^{-1}). The temperature programme consisted of drying at 100°C for 1 hour to remove adsorbed moisture, followed by a linear heating to 500°C with the rate of 10 K min^{-1} . The mass spectrometer worked in multi-ion detection mode and ions with signal of m/z between 2 and 126 were analysed during heating to identify thermal degradation products of cellulose pyrolysis at 10 K min^{-1} . From TGA graph, the temperature at the onset of weight loss (T_{onset}) is taken as the temperature at 1% weight loss. The kinetic evaluation of thermogravimetric data was based on one-step approximation (mathematical description of pyrolysis process as one reaction) and the use of isoconversional principle.^{89,90} The Ozawa⁶⁰ and Starink⁶¹ equations were used for calculation of dependence of apparent activation energy E_a on conversion. TMA analysis was performed on Setsys Evolution device (Setaram) with thermomechanical modulus. The measurements were carried out in argon atmosphere (20 ml min^{-1}) with a load of 5 g using quartz hemispherical flat probe. The temperature programme consisted of a linear heating to 500°C with the heating rate of 1 K min^{-1} .

Organic solvent and oil absorption. The solvents selected for the test were acetone, ethanol, toluene, chloroform and dodecane. These have a purity of at least 99 %. Shell rimula R6 LME 5w-30 was used as motor oil. Mineral oil (Hydrosal G250H) and silicone oil were supplied by Falcone chemical

Specialties Ltd (Siebnen, Switzerland). In the absorption experiment, a piece of the char weighing ca. 10 mg was dipped in 20 ml of the oil/solvent for 5 seconds, and weighed to determine its absorption capacity i.e., the weight of the absorbed liquid divided by the dry weight of the char material. 3 replicates per sample were performed and the results were averaged.

Dye adsorption. Methylene blue (MB), crystal violet (CV) or congo red (CR) were dissolved in water at various concentrations and put in contact with the char at $\sim 1 \text{ g L}^{-1}$ and shaken at 150 min^{-1} (IKA HS 260). Aliquots of the solution were then taken at given time intervals to measure their dye concentration via UV spectrophotometry at the maximum absorption wavelength of the dyes (664 nm for methylene blue, 497 nm for congo red and 590 nm for crystal violet).

A list of abbreviations used in the present work is given in table 1.

Table 1. Abbreviation list

CNF	Cellulose nanofibers
WCNF	Cellulose nanofibers from wood
BCNF	Cellulose nanofibers from bacteria
ACNF	Cellulose nanofibers from <i>Cladophora</i> algae
HD	Heat-drying
FD	Freeze-drying
SCD	Supercritical CO_2 drying
BuFD	Tert-butanol freeze-drying
S_{BET}	Specific surface area according to BET method
BJH	Barrett-Joyner-Halenda (sorption analysis)
ρ_{CNF}	Density of the CNF substrate
$\rho_{\text{cellulose}}$	Density of cellulose
P	Porosity
XRD	X-ray diffraction
CI	Crystallinity index
L	Crystallite size
TGA	Thermogravimetric analysis
TMA	Thermomechanical analysis
MS	Mass spectrometry
T_{onset}	Temperature at the onset (1%) of thermal degradation
DSC	Differential scanning calorimetry
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
MB	Methylene blue
CV	Crystal violet
CR	Congo red

3 Results and Discussion

CNF originating from wood, bacteria or algae cellulose were prepared as an aqueous gel, and are denoted WCNF, BCNF, and ACNF, respectively. These CNF have the very similar elemental composition characteristic for cellulose (44% carbon, 49% oxygen and 6% hydrogen; Supporting information S1) and x-ray diffraction peaks of native cellulose at 2θ angles of 14.8° , 16.6° , 22.3° and 34.4° , corresponding to 1-10, 110, 200 and 004 lattices (Figure 1).^{33, 47} Their SEM micrographs show typical high aspect-ratio fibrils forming a network structure (Figure 1), while their TEM micrographs allow a more precise estimation of their diameter, which was 10-110 nm for WCNF and BCNF, and 5-20 nm for ACNF (Figure 1). TEM micrographs also reveal differences between CNF, namely ACNF are completely straight and uniform single fibrils, while BCNF and to a larger extent WCNF have a greater tendency to bend and bundle. We estimate that 2-4 fibrils associate to form BCNF, while at least 5 fibrils form WCNF. These latter have a great mobility and can easily bend forming a loop, and this is due to their low crystallinity. The crystallinity index (CI) and the crystallite size of various CNF were estimated from their XRD spectra (Table 2). WCNF have the lowest CI of 72% which is consistent with the small wood microfibril diameter (~ 3 nm) presenting a large surface consisting of less ordered cellulose chains.⁴⁸ BCNF have a CI of 90% and larger crystallites of ~ 6 nm, while ACNF present both the highest CI of 96% and crystal size (~ 12 nm) reflecting the large microfibrils of *Cladophora*.⁴⁹ The increase in the CI is expectedly accompanied by an increase in the crystallite size since the crystallite surface area corresponding to amorphous cellulose is diminished.

Figure 1. SEM / TEM micrographs and XRD spectra of WCNF, BCNF and ACNF.

Table 2. CNF characteristics.

sample	WCNF				BCNF			ACNF		
CI (%)	72				90			96		
Lattice	(1-10)	(110)	(200)		(1-10)	(110)	(200)	(1-10)	(110)	(200)
d-spacing (nm)	0.604	0.536	0.398		0.619	0.531	0.396	0.619	0.535	0.395
L (nm)	3.1	2.7	3.7		5.8	6.7	6.0	10.7	13.5	12.2
drying	SCD	BuFD	HD	FD	HD	FD		HD	FD	
ρ_{CNF} (kg m ⁻³)	246	47	1070	5	1080	5		780	5	
Porosity (%)	84	97	29	99.7	28	99.7		48	99.7	
BJH pore volume (cm ³ g ⁻¹)	0.26	0.26	<0.1	<0.1	<0.1	0.17		0.22	0.21	
S _{BET} (m ² g ⁻¹)	157	100	0.1	13	13	66		64	88	
Char S _{BET} (m ² g ⁻¹)	257	95	7	27	196	68		361	92	
Char BJH pore volume (cm ³ g ⁻¹)	0.19	<0.1	<0.1	<0.1	0.11	<0.1		0.64	0.12	
T _{onset} (°C)	248	236	268	215	288	236		286	274	
TGA char yield (%)	17.9	15.9	27.4	19.6	26.4	10.1		12.6	11.8	

Effect of WCNF drying on pyrolysis.

Aqueous gels of WCNF were subjected to heat-drying (HD), freeze-drying (FD), tert-butanol freeze-drying (BuFD) or supercritical CO₂ drying (SCD). These drying routes are either from water-based (HD and FD) or solvent-based (BuFD and SCD) suspensions. The conventional HD of WCNF results in a massive aggregation of the fibrils forming a dense film ($\rho=1070 \text{ kg m}^{-3}$), (Figure 2). The aggregation of the fibrils occurs via their external surface formed by “amorphous” cellulose and is due to capillary forces acting on the fibrils during evaporation of water.^{34, 36, 50} Subsequently, the low specific surface area (S_{BET}) of the HD sample ($0.1 \text{ m}^2 \text{ g}^{-1}$) determined by nitrogen adsorption indicates that the fibrils act collectively as a single mass, whose internal surface is not accessible to nitrogen molecules. FD results in a highly porous foam with a low density (5 kg m^{-3}) and large pores reflecting the ice-crystals formed during the freezing step (Figure 2).^{35, 40} The pores are surrounded by sheets constituted of aggregated fibrils (zoom in Figure 2), conferring the foam a moderate S_{BET} of $13 \text{ m}^2 \text{ g}^{-1}$. Drying WCNF from low polarity solvents is a mean to prevent their aggregation since surface tension effects are largely reduced.^{37, 39, 50, 51} Consequently, BuFD results in highly porous foam with a finer structure compared to FD and a higher S_{BET} of $100 \text{ m}^2 \text{ g}^{-1}$ (Figure 2). Supercritical drying results in the

substrate presenting the largest S_{BET} ($157 \text{ m}^2 \text{ g}^{-1}$) reflecting a preserved structure during drying attributed to the low polarity of CO_2 and its gradual transition from the liquid to the gas phase via the supercritical fluid phase (Figure 2).³⁸ Unlike the HD substrate, the fibrils in the SCD sample act as interconnected individual entities.

Figure 2. SEM micrographs of WCNF substrates and their corresponding chars. WCNF substrates are prepared via heat-drying (HD), Freeze-drying (FD), Supercritical CO_2 drying (SCD), and Tert-butanol freeze-drying (BuFD).

After pyrolysis of various WCNF substrates, most non-carbon elements are removed in a gaseous form via pyrolytic decomposition leading to char materials with a carbon content of $\sim 85\%$ compared to the initial 44% carbon content of cellulose (Supporting information S2). SEM micrographs of these chars show a similar structure to their original form (Figure 2), in agreement with previous works.^{52, 53} Pyrolysed HD sample displayed a dense structure without noticeable micro/nanostructure and a low S_{BET} , thus resembling the structure of the HD sample. Pyrolysed FD and BuFD samples maintained a high porosity after pyrolysis, with a higher surface area of the latter attributed to its finer structure prior to pyrolysis (Table 2). The pyrolysed SCD sample resulted in the highest S_{BET} ($257 \text{ m}^2 \text{ g}^{-1}$)

reflecting the presence of the highest fraction of exposed nanofibers (also visible in Figure 2). The increase in the S_{BET} of the pyrolysed SCD sample accompanying the pyrolysis process as compared to the quasi-constant S_{BET} of the pyrolysed BuFD sample suggests a beneficial role of the sample's high density for the stabilisation of the carbonaceous sample nanostructure, and this is possibly due to higher density and mechanical properties of SCD sample preventing fibrils aggregation during pyrolysis.^{37, 38}

Thermogravimetric analysis of various WCNF substrates is shown in Figure 3.a. Three distinct regions can be identified, i.e. evaporation of adsorbed moisture without thermal degradation at $T < 220\text{ }^{\circ}\text{C}$, major mass-loss stage at $220\text{ }^{\circ}\text{C} < T < 370\text{ }^{\circ}\text{C}$, and minor mass-loss stage at $T > 370\text{ }^{\circ}\text{C}$. The thermal behaviour of CNF is clearly affected by the drying, i.e., the structure of the sample. The temperature at the onset of weight loss (T_{onset}) correlates with the substrate's density (Figure 3.e), with a difference of $\sim 50\text{ }^{\circ}\text{C}$ registered between T_{onset} of HD and FD substrates (Table 2). Difference in T_{onset} was also observed elsewhere in TGA thermograms of CNF prepared via various drying routes,⁵⁴ which is in disagreement with results by Uetani et al.⁵⁵ Since water is likely the first thermal decomposition product of cellulose pyrolysis,⁵⁶ the difference in T_{onset} could be due to higher water vapour pressure encountered inside samples with higher density and this inhibits further dehydration.

Thereafter, there is a rapid weight loss during which over 20 products were identified by TG-MS during the thermal decomposition of WCNF including water, carbon monoxide and dioxide (Figure 3.c, Table 3, full MS spectra in Supporting information S3). At the end of the weight loss, WCNF substrates display different char yields (Table 2), and higher values are achieved for substrates dried from water (HD and FD) compared to substrates dried from solvent (SCD and BuFD). This shows that the extent of fibrils aggregation influences the char yield. This latter is about twice as high for the HD sample presenting the least S_{BET} compared to high surface area SCD and BuFD substrates. Hence, volatiles and tarry substances released during pyrolysis of low surface area substrates are trapped within the aggregated fibrils, leading to secondary reactions whereby char is formed. The higher weight loss rate of high surface area BuFD and SCD samples as compared to that of HD and FD

samples (Figure 3.b) supports a short residence time of volatiles in the high S_{BET} BuFD and SCD samples. These observations are in agreement with those by Peng et al.⁵⁴

Pyrolysis of WCNF samples is accompanied by dimensional changes evaluated by thermomechanical analysis (Figure 3.d). Except the HD sample that expanded during heating, other substrates registered a noticeable shrinkage. The volume change correlates well with the char yield, i.e. samples presenting the lowest yield shrink the most (Figure 3.f). The large shrinkage observed for the BuFD sample indicates that this substrate is subjected to high stresses during pyrolysis, what can be explained by a combination of its high S_{BET} , low density and weak mechanical properties.³⁷ The expansion of the HD sample is explained by its dense structure having low gas permeability,^{57, 58} as indicated by its negligible S_{BET} . Hence, thermal degradation vapors released during heating of the HD substrate can hardly escape the sample and push its inner surfaces causing its expansion. The three expansion events occurring during heating of the WCNF at temperatures of ~ 220 °C, 240 °C and 270 °C indicate that there are mainly 3 thermal decomposition steps leading to vapor release during the slow pyrolysis process of WCNF.

Figure 3. a. TGA, b. DTG, c. TG-MS and d. TMA analyses of WCNF. e. Relationship between T_{onset} and CNF density. f. Relationship between the TMA displacement and TGA char yield at 500 °C.

Table 3. m/z signals obtained by TG-MS and the possible corresponding compound/fragmented compound.

m/z	Possible compounds or fragmented compounds	Formula
2	Hydrogen	H ₂

12	Hydrocarbons	CH _x
13		
14		
15		
16	Methane, derivates of hydrocarbons	CH ₄ , CH _x R
17	Water	H ₂ O
18		
28	Carbon monoxide, formaldehyde	CO, CH ₂ O
29	Acetaldehyde, hydroxyaldehyde, formaldehyde, formic acid	C ₂ H ₄ O, C ₂ H ₄ O ₂ , CH ₂ O, HCOOH
30	Formaldehyde	CH ₂ O
31	Hydroxyaldehyde	C ₂ H ₄ O ₂
32	Hydroxyaldehyde, oxygen	C ₂ H ₄ O ₂ , O ₂
39	Phenol, furan, furfural	C ₆ H ₆ O, C ₄ H ₄ O, C ₅ H ₄ O ₂
41	Hydroxymethylfurfural	C ₆ H ₆ O ₃
43	Acetone, acetaldehyde, acetic acid	C ₃ H ₆ O, C ₂ H ₄ O, C ₂ H ₄ O ₂
44	Carbon dioxide, acetaldehyde	CO ₂ , C ₂ H ₄ O
45	Acetic acid, formic acid	C ₂ H ₄ O ₂ , HCOOH
46	Formic acid	HCOOH
53	Methylfuran	C ₅ H ₆ O ₂
57	Levoglucothane	C ₆ H ₁₀ O ₅
58	Acetone	C ₃ H ₆ O
60	Levoglucothane	C ₆ H ₁₀ O ₅
68	Furan	C ₄ H ₄ O

Effect of cellulose source on the pyrolysis.

We further selected HD and FD samples for the pyrolysis process of cellulose nanofibers originating from bacteria and algae (BCNF and ACNF, respectively) having a higher crystallinity index and larger crystal size than WCNF (Table 2). As expected, micrographs of the FD substrates show a highly porous structure compared to HD substrates (Figure 4). Interestingly, the sheets forming the FD substrate reveals the presence of individual fibrils for ACNF and BCNF samples that were barely visible for freeze-dried WCNF sample. The increase in crystal size of CNF thus prevents to some extent their aggregation as they become stiffer and less flexible (see TEM micrographs of various CNF in Figure 1), and this leads to interspace between fibrils when they are stacking. The greater mobility of WCNF on the other hand facilitates their dense packing. Subsequently, the S_{BET} of the FD substrates increases with the increase in the crystal size of CNF (Table 2 and Supporting information S4). The same trend is observed for HD samples, i.e., S_{BET} increases with the crystal size from a value of $0.1 \text{ m}^2 \text{ g}^{-1}$ for WCNF to $64 \text{ m}^2 \text{ g}^{-1}$ for ACNF giving more discernible fibrils in SEM micrographs (Figure 4, Table 2 and Supporting information S4). The BJH pore volume which takes into account pores up to $\sim 200 \text{ nm}$ is supporting this observation, and increases with the increase in the crystal size of CNF (Table 2).

SEM micrographs of the pyrolysed ACNF and BCNF samples reflect the structure prior to pyrolysis (Figure 4). We note that chars from HD samples display a larger S_{BET} than chars from FD samples (Table 2). This can be attributed to the weaker mechanical properties of the FD substrates favouring nanofibers aggregation during pyrolysis, or to difference in fibrils arrangement in both substrates. Interestingly, for the same heat-drying, the corresponding char of ACNF has a much higher S_{BET} than that of WCNF ($361 \text{ m}^2 \text{ g}^{-1}$ vs $7 \text{ m}^2 \text{ g}^{-1}$) and a BJH pore volume as high as $0.64 \text{ cm}^3 \text{ g}^{-1}$ (Table 2), thus reflecting positive effect of large crystallites for structure preservation upon drying and pyrolysis.

Figure 4. SEM micrographs of BCNF and ACNF substrates and their corresponding chars.

The effect of the CNF crystal size on their thermal degradation behaviour has been investigated by thermogravimetric analysis coupled with a mass-spectrometer. CNF with larger crystals show enhanced thermal stability leading to a difference of 60°C between the T_{onset} of the freeze-dried WCNF and ACNF substrates (Figure 5.a, Table 2). Similarly, a difference of 40°C was observed between the T_{onset} of Funacel cellulose ($\text{CI}=54\%$; $T_{\text{onset}}=285^\circ\text{C}$) and Halocynthia cellulose ($\text{CI}=74\%$; $T_{\text{onset}}=325^\circ\text{C}$) as the crystal size shifted from 4.5 nm to 10.6 nm , respectively.⁴⁶ The reduction in cellulose crystallinity from 65% to 6.5% via ball-milling led also to a reduction in thermal degradation

temperature in TGA graphs.⁵⁹ Poletto et al. reported that thermal decomposition of wood shifted to higher temperatures with increasing wood cellulose crystallinity and crystallite size.⁹¹ All these results indicate that large cellulose crystals require a higher temperature to break their crystal structure, i.e., hydrogen bonds before weight loss takes place in the inner part of the crystal.^{46, 59, 91} The melting of ACNF crystals was clearly observed as an endothermic peak in DSC thermogram with a maximum at 380 °C for a heating rate of 10 K min⁻¹, while melting of WCNF and BCNF crystals was less obvious in DSC thermograms, and may be maximum at 277 °C and 361 °C, respectively (Supporting information S5). With the increase in the crystal size, volatiles emission during pyrolysis is also shifted to higher temperature (Figure 5.c; full spectra in Supporting information S3). The higher weight loss rate accompanying the increase in the crystal size of CNF (Figure 5.b) is attributed to the higher surface area minimizing volatiles retention.

For BCNF samples, a higher char yield is observed for the HD sample as compared to the FD sample due to nearly 5 times lower S_{BET} (13 m² g⁻¹ for HD vs 66 m² g⁻¹ for FD). In contrast, ACNF gives a similar char yield for both substrates due to a close S_{BET} (64 m² g⁻¹ for HD vs 86 m² g⁻¹ for FD) and less fibrils aggregation in both substrates. Furthermore, unlike heat-dried WCNF which expanded during heating, heat-dried ACNF and BCNF shrank upon heating (Figure 5.d) as they have a larger S_{BET} than WCNF permitting vapours evacuation.

Figure 5. a. TGA, b. DTG, c. TG-MS signals vs their peak temperature, d. TMA, e. ΔT vs weight and f. Activation energy (E_a) vs conversion for various CNF.

We now analyse the difference between the thermal degradation of FD and HD substrates. The FD samples present a density more than 2 orders of magnitude lower than HD samples' density (Table 2), and this should give inside the substrate a different vapour pressure of the volatiles released during heating. As for WCNF, FD samples from BCNF and ACNF have a lower T_{onset} than HD counterparts (Table 2), attributed to a lower water vapour pressure in the former favouring dehydration. We denote the temperature difference between the HD and FD substrates for the same weight loss as ΔT . In the TGA graph (Figure 5.a) and in the graph showing ΔT as a function of the weight (Figure 5.e), it is interesting to note that, unlike WCNF, ΔT for BCNF and ACNF nullify at temperatures of 336 °C and 342 °C corresponding to a weight loss of 21% and 8%, respectively. We expect these values to correspond to the consumption of the amorphous part of BCNF and ACNF. Subsequent to $\Delta T=0$, HD and FD substrates being crystalline, show a similar degradation pattern with a slightly negative ΔT .

The apparent activation energy (E_a) of the thermal decomposition of various heat-dried CNF was first analysed by the Ozawa method from the peak position in the DTG curves at heating rates of 1, 2, 5 and 10 °C min⁻¹ (Supporting information S5).⁶⁰ In the Arrhenius plots showing the logarithms of heating rate versus reciprocal absolute temperature of DTG peak of three CNF samples (Supporting information S6), a good fit (R^2 values > 0.99) was obtained for WCNF and BCNF with corresponding E_a values of 200 and 205 kJ mol⁻¹, respectively, versus $E_a=158$ kJ mol⁻¹ for ACNF. We thereafter

determined the dependence of activation energy on the conversion using the isoconversional method by Starink (Figure 5.f).⁶¹ At a conversion of $\alpha=0.1$, the E_a is similar for all sample (160.7-166.6 KJ mol⁻¹), and might be associated with the thermal decomposition of the amorphous cellulose. With the increase in the conversion, E_a for ACNF sample decreases reaching 149 KJ mol⁻¹ at $\alpha=0.75$. In contrast, E_a for WCNF increases with the conversion to a maximum value of 198 KJ mol⁻¹ at $\alpha=0.75$, while E_a for BCNF increases to 184 KJ mol⁻¹ at $\alpha=0.5$ then stabilizes somewhat at this value. In the work by Kim et al., similar activation energy of ~ 160 KJ mol⁻¹ (from Ozawa method) was reported for native cellulose nanofibers of the same crystal type from Funacel, cotton, and Halocynthia sources, although no information on the structure of the samples was reported.⁴⁶ It was concluded that the crystallite size does not affect the activation energy of the thermal degradation. Ornaghi Jr. et al. found that the activation energies for six different vegetal fibers are similar and do not correlate with the crystalline content.⁹² In the present work, we attribute higher E_a for WCNF and BCNF samples as compared to E_a of ACNF to the additional formation of a secondary char in these samples whereby fibrils aggregation is considerable. After comparing the E_a of heat-dried and freeze-dried WCNF, we found a lower E_a for the FD sample that we associate to easy evacuation of thermal degradation products during pyrolysis of the FD sample (Supporting information S6). We concluded that the structure of the sample (density and surface area) influences its thermal decomposition activation energy. This is in line with observations by Milosavljevic and Suuberg who reported that lower activation energy values are generally found for short residence time of volatiles during pyrolysis corresponding to the fast pyrolysis process.⁶²

Possible thermal degradation pathway of cellulose nanofibers under slow pyrolysis.

Initially, cellulose is composed by amorphous and crystalline fractions with a higher reactivity and faster kinetic of thermal decomposition of the former. The thermal degradation starts once the glass transition temperature of cellulose (~ 210 °C)⁶³ has been surpassed permitting chains rearrangement and dehydration of cellulose mostly occurring in the amorphous part of cellulose.⁶⁴ An intramolecular dehydration mechanism of cellulose starting from 220 °C has been suggested by Scheirs et al. after their FTIR study revealed new C=C and C=O stretching vibrations at this temperature.^{56, 65, 66} The first

expansion of WCNF at 220 °C is thus attributed to cellulose dehydration via the chemical elimination of water molecules. The released water combined with the elevated temperature then depolymerizes/hydrolyses the amorphous cellulose chains (the crystals being impermeable to water) leading first to oligo-sugars and to single sugar molecules, which were identified by Lin et al. using HPLC to correspond to DP=2-7 sugars and to levoglucosan (DP=1).⁶⁷ The TMA expansion is subsequently followed by an abrupt contraction of the substrate that may possibly come from crosslinking of the structure via intermolecular dehydration of cellulose/oligomers, further leading to a primary char which retains the structure of the starting CNF material.^{59, 64, 68-72} In the TMA graph, the second expansion at 240 °C indicates a subsequent release of other vapors possibly emanating from the dehydration of oligomers and levoglucosan forming intermediate sugars.⁶⁷ These fragmentizes after C-O and C-C bonds break giving volatiles and light gases that were identified by TG-MS (Table 3), and that may contribute to the third expansion of WCNF at 270 °C.⁷³ Based on density functional theory calculations, Zhang et al. found that acetaldehyde ($m/z=44$) and carbon monoxide ($m/z=28$) can be formed from the C-O bond breaking reactions of levoglucosan, while 1,2-Dihydroxyethene ($m/z=60$) can be formed from the C-C bond breaking reactions.⁷⁴ Other products such as hydrogen ($m/z=2$), methane ($m/z=16$), carbon monoxide and dioxide ($m/z=28, 44$), formaldehyde ($m/z=30$), acetaldehyde ($m/z=44$), glycolaldehyde ($m/z=60$), methanol ($m/z=32$), ethanol ($m/z=46$) and acetone ($m/z=58$) may form according to the degradation routes of cellulose/levoglucosan proposed by Shen et al.⁷⁵ These volatiles, when trapped between the fibrils, e.g., for low S_{BET} substrates, will condense into an additional “secondary char”, although the two char types may have similar reactivity^{76, 77} and composition (Supporting information S2). Provided the cellulose crystals have not broken apart during thermal decomposition of amorphous cellulose, the consumption of the amorphous part of cellulose will then lead to a low DP crystalline cellulose so-called active cellulose.^{65, 78-80}

The thermal degradation of crystalline cellulose cannot start unless the hydrogen bonds in the crystal have been broken, which releases free “amorphous” cellulose chains. This is in agreement with computational work in which the importance of the interchain hydrogen bonds in the thermal degradation process of cellulose has been highlighted, showing that the glucosyl moiety inside the

cellulose crystal is considerably more stable and that the thermal degradation occurs selectively on the surface of the cellulose crystal.⁸¹ We expect two scenarios to occur depending on the crystal size of cellulose. Melting of small crystals will occur at relatively low temperature whereby the free cellulose chains undergo the same degradation pathway of the initial amorphous phase, i.e., dehydration followed by hydrolysis and fragmentation. This leads to a positive ΔT for both the amorphous and crystalline phases (WCNF in Figure 5.e). On the other hand, melting of large crystals occurs at a high temperature whereby fragmentation via bonds scission should be dominant. This would then nullify ΔT for ACNF and BCNF samples once the amorphous part has been consumed, subsequently leading to a slightly negative ΔT that might come from exothermic effect of bond scission.^{77, 82-84} Breakage of the glucosidic C—O bond would lead to levoglucosan, whose fragmentation via other C—O and C—C breakage would lead to volatiles and light gases,⁷⁴ that can eventually form a secondary char when trapped within the substrate. The proposed thermal degradation pathway of CNF under slow pyrolysis is illustrated in Figure 6. Note that this pathway shares similarities with cellulose hydrolysis in hot compressed water, in which oligomers are first formed in the amorphous portion of cellulose, then in the crystalline portion once the hydrogen bonds in crystalline cellulose have been broken to make the glycosidic bonds accessible to the hot compressed water.⁸⁵

Figure 6. Proposed thermal decomposition pathway of CNF under slow pyrolysis.

Oil absorption by the chars

The pyrolysis process of CNF is accompanied by a loss of samples' crystallinity (Supporting information S7), an increase in their carbon content (Supporting information S2), and a reduction in their moisture uptake (Supporting information S8), which results in CNF chars with enhanced hydrophobicity. The ability of CNF char to absorb non-polar liquids was first tested by immersing it

in a water bath containing dodecane. This latter was rapidly sucked by the char leading to a clean water surface (Figure 7.a). We thereafter investigated density effect of the CNF substrate (related to its porosity) on the absorption capacity of its char. WCNF substrates were prepared by heat-drying or by freeze-drying aqueous WCNF suspensions of various concentrations leading to CNF substrates having various densities, as reported in our previous work.³⁵ The corresponding chars were used for the uptake of various oils and organic solvents. Figure 7.b shows that the absorption capacity of the pyrolysed HD substrate is quite low ($6\text{--}22\text{ g g}^{-1}$) which is attributed to its low porosity (see SEM micrograph in Figure 2). The pyrolysed FD substrates of low density have on the other hand a higher absorption capacity up to 100 g g^{-1} due to their higher porosity permitting liquid uptake (Figure 2). Interestingly, there is an optimum density of the WCNF, around 5 kg m^{-3} , giving a char with the best absorption performance. Even lower density of the WCNF did not necessarily lead to a higher absorption capacity of the corresponding char possibly due to weak mechanical properties leading to contraction of the char upon liquid uptake. Such phenomenon has already been observed by Cervin et al. who found that low density silylated CNF aerogels are more prone to collapse upon hexadecane uptake compared to their higher density counterparts.¹⁸ Amongst various liquids, the highest absorption capacity was reached for chloroform due to its higher density as compared to density of other liquids ($\rho_{\text{CHCl}_3}=1.49\text{ g cm}^{-3}$ vs $\rho_{\text{other liquids}} = 0.75\text{--}0.95\text{ g cm}^{-3}$). The high density of chloroform would have probably led to higher capillary forces on the chars during the absorption process leading to an optimum density of 15 kg m^{-3} (see arrow in Figure 7.b).

We thereafter compare the chars' performance corresponding to freeze-dried WCNF, BCNF and ACNF with a density of 5 kg m^{-3} (Figure 7.b). In most cases, chars from BCNF performed the best with an adsorption capacity of $64\text{--}120\text{ g g}^{-1}$ for various liquids versus $55\text{--}95\text{ g g}^{-1}$ for chars from WCNF, while ACNF gives the lowest uptake of 26 g g^{-1} for motor oil. After normalizing the weight uptake with respect to the density of various liquids, it becomes apparent that pore volume used for the liquid uptake is far lower for ACNF ($31.5\text{ cm}^3\text{ g}^{-1}$) as compared to WCNF ($63\text{--}83\text{ cm}^3\text{ g}^{-1}$) and BCNF ($68\text{--}118\text{ cm}^3\text{ g}^{-1}$) (Figure 7.c). Since the absorption capacity depends on a number of parameters such

as the polarity of the liquid, the oleophilicity, pore size and volume, and mechanical strength of the char, these parameters are optimized in BCNF char giving the highest absorption capacity.

Compared to other oil/solvent sorbents reported in the literature, the char prepared herein from freeze-dried BCNF at a pyrolysis temperature of 500 °C has a similar capacity compared to BCNF pyrolysed at 1450 °C or to cotton pyrolysed at 800 °C,^{22, 86} and higher capacity than char prepared from recycled newspaper at a pyrolysis temperature of 900 °C (12-22 g g⁻¹) (Figure 7.d).⁸⁷ This indicates that higher pyrolysis temperature above 500 °C does not necessarily lead to higher solvent/oil uptake. Compared to CNF/inorganic hybrids, the present BCNF char has similar adsorption capacity as MTMS/CNF,¹⁹ higher capacity than TiO₂ coated CNF aerogel (20-40 g g⁻¹),¹⁷ and lower capacity than silane-modified CNF aerogel (190-350 g g⁻¹).⁸⁸

Figure 7. a. Photograph showing dodecane removal by freeze-dried WCNF's char. b. Oil/solvent uptake by weight versus density of CNF substrate. The square and the circles correspond to chars from HD and FD samples, respectively. Black, green and red indicate WCNF, BCNF and ACNF, respectively. c. Oil/solvent uptake by volume versus density of CNF substrate. d. Comparison of oil/solvent uptake of the present BCNF char (dots in left) with other sorbents cited in the literature (data extracted from graphs).

Dye adsorption

The high surface area of the chars can be exploited for the adsorption of non-polar species. This is illustrated herein by the adsorption of 3 organic dyes, namely, methylene blue, congo red and crystal violet. Chars obtained from pyrolysis of WCNF substrates were first selected for the adsorption of a cationic methylene blue (MB) dye. As compared to chars prepared from WCNF dried from water, chars prepared from WCNF dried from solvent display a higher MB removal capacity and faster kinetic of adsorption attributed to their high S_{BET} values (Figure 8.a,d,e). The char corresponding to

freeze-dried WCNF permits a 98% removal of MB solution having a concentration of 4 mg L^{-1} , but its efficiency decreases to 43% for a ten-fold more concentrated MB solution (Figure 8.b,e). The increase in the S_{BET} of the WCNF char enhances the number of sites available for the adsorption of MB permitting the treatment of such concentrated MB solution, i.e., the SCD char can remove 99.8% of MB at a concentration of 40 mg L^{-1} (Figure 8.b,e). The maximum amount of MB adsorbed increases with the S_{BET} of the WCNF char going from 0.6 mg g^{-1} for HD to 43.7 mg g^{-1} for SCD chars (Figure 8.c). Moreover, the chars prepared from solvent-dried WCNF have a good removal capacity for crystal violet (CV; cationic dye) and congo red (CR; anionic dye), with a maximum capacity of 48 mg g^{-1} and 158 mg g^{-1} , respectively (Figure 8.c). WCNF chars have seemingly a better affinity for anionic dyes, probably due to specific interactions between the two components.

MB adsorption by chars originating from various heat-dried CNF was investigated. These chars present a dense structure (Figure 4) and S_{BET} values of 7, 196 and $361 \text{ m}^2 \text{ g}^{-1}$ for WCNF, BCNF and ACNF, respectively. Despite their dense structure and due to their high S_{BET} , BCNF and ACNF chars present a higher MB removal capacity compared to WCNF char. The adsorption process is however slow and is probably hindered by the dense structure of the chars where accessibility to the dye molecule is reduced. For a MB concentration of 40 mg L^{-1} , the % removal after 1 month of contact between the dye and the char is 19% and 78% for the BCNF and ACNF chars respectively, while it is negligible for the WCNF char. The corresponding adsorption capacities at this concentration are 6.3 and 28.4 mg g^{-1} , for BCNF and ACNF chars, respectively. This further confirms positive effects of large CNF crystallites giving chars with large S_{BET} and good dye adsorption capacity.

Figure 8. a. % Methylene blue (MB) removal by WCNF chars at different time intervals. MB concentration is 40 mg L⁻¹. b. % MB removal by WCNF chars for various MB concentrations. c. Maximum dye adsorption capacity of WCNF chars. The capacity was determined for a MB, CV and CR concentrations of 80, 50 and 100 mg L⁻¹. d&e. Photographs of MB solution after dye adsorption by WCNF chars. Ref corresponds to the MB solution alone. MB concentration is given in top left of each picture. f. Photograph of crystal violet (CV) and congo red (CR) solutions after dye adsorption by WCNF char. g. % MB removal by chars from various CNF vs time of contact. MB concentration is 40 mg L⁻¹.

Conclusions

Native cellulose nanofibers with various crystal sizes originating from wood, bacteria and algae were prepared as aqueous gels, and subsequently dried via different routes giving various CNF substrates. In the first part, thermal properties of wood CNF were found to depend on their structure, which is in turn affected by the CNF drying. The following conclusions were drawn:

- The temperature at the onset of thermal degradation of the CNF substrate depends on its density and is higher for denser samples. This might be associated with higher vapour pressure of the decomposition products inside these samples which inhibits further degradation.
- CNF substrates dried from water present a lower specific surface area compared to those dried from solvents as a result of fibrils aggregation. Consequently, they present a higher char yield and a lower weight loss rate as the thermal decomposition products are trapped within the aggregated fibrils leading to a secondary char.
- The pyrolysis is accompanied by dimensional changes of the substrate. Substrates presenting some surface area shrink upon pyrolysis and the shrinkage correlates with the char yield. In

contrast, CNF film prepared via heat-drying does not display an internal surface area and expanded during pyrolysis due to stresses from emitted volatiles. Three expansions were identified for this sample at ~220 °C, 240 °C and 270 °C reflecting three main stages of thermal decomposition of wood CNF leading to vapour release.

- After pyrolysis, the structure of the obtained char is similar to the original CNF substrate. When the CNF substrate has a low density and a high specific surface area, nanofibers aggregation during pyrolysis is expected due to the weak mechanical properties of the substrate which cannot counteract thermal stresses.

In the second part, the effects of cellulose source on CNF structure and thermal properties were investigated. The following observations were made:

- CNF with larger crystallites form substrates with higher specific surface area upon drying from aqueous suspension as they are straight and rigid permitting fibrils interspace while stacking. The corresponding chars also display a large S_{BET} .
- The increase in the crystal size of the CNF is accompanied by an increased thermal stability. Larger crystals require a higher temperature to break their hydrogen bonds before thermal degradation takes place in the inner part of the crystal.
- For CNF displaying large crystals, there are two distinct thermal degradation zones. The initial thermal degradation is associated with the amorphous phase and occurs at higher temperature for denser samples. The subsequent thermal degradation associated with the crystalline phase does not show a substantial dependence on the sample's density. This indicates a different thermal degradation pathway for the amorphous and crystalline portions of these CNF. The thermal degradation of the amorphous cellulose would be facilitated by the dehydration of the chains leading first to their depolymerization and then to further fragmentation of the sugars. The crystalline phase decomposes after the crystal melts. Large crystals display a high melting temperature at which chains fragmentation via bonds scission would be dominant mechanism of thermal decomposition.
- The activation energy (E_a) of the thermal decomposition of CNF determined according to the isoconversion method is clearly affected by the structure of the sample and varies with the

conversion. Low density CNF have a low E_a that might be associated with low vapour pressure in these samples during pyrolysis. Low surface area samples displaying fibrils aggregation have a high E_a at high conversions which might be associated with the formation of a secondary char in these samples.

In the third part, the adsorption/absorption properties of various chars were investigated. It was concluded that:

- For oil/solvent absorption, chars displaying a high pore volume are desired. These could be achieved by freeze-drying CNF suspension of low concentration prior to pyrolysis. The optimum density of the CNF substrate giving chars with the highest absorption capacity was 5 kg m^{-3} . Chars corresponding to the lowest density of the CNF (3 kg m^{-3}) most probably shrank upon liquid uptake leading to a lower absorption capacity. When comparing the absorption capacity of chars from various CNF sources, it is found that the one from bacterial CNF offers the highest absorption capacity ($64\text{--}120 \text{ g g}^{-1}$) corresponding to a pore volume for the oil/solvent uptake as high as $68\text{--}118 \text{ cm}^3 \text{ g}^{-1}$. Bacterial CNF produces thus chars with optimum properties in terms of oleophilicity, pore size and volume, and mechanical strength.
- For dye adsorption, chars displaying a large specific surface area which is accessible to the dye molecule are desired. Conventional heat-drying of wood CNF aqueous suspension results in a substrate with negligible surface area whose pyrolysis led to a char with poor adsorption capacity towards methylene blue (MB) of 0.6 mg g^{-1} and a removal capacity of only 13% for a 4 mg L^{-1} MB solution. On the other hand, drying wood CNF from solvents substantially enhances their surface area and that of the corresponding char. The char obtained via pyrolysis of supercritically dried wood CNF can remove 99.8% of a MB solution having a concentration of 40 mg L^{-1} and have maximum adsorption capacities of $44\text{--}158 \text{ mg g}^{-1}$ towards methylene blue, crystal violet and congo red. When comparing the dye adsorption capacity of chars from various heat-dried CNF suspensions, those from algae CNF displayed superior performance as a result of their larger S_{BET} .

ASSOCIATED CONTENT

Supporting Information

Elemental analysis, TG-MS spectra, TGA, DTG and DSC graphs at various heating rates, XRD spectra and dynamic vapor sorption analysis. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Drying and pyrolysis of cellulose nanofibers from
wood, bacteria and algae for char application in oil
absorption and dyes adsorption

*Jana Štefelova, Václav Slovák, Gilberto Siqueira, Richard T. Olsson, Philippe Tingaut, Tanja
Zimmermann and Houssine Sehaqui*

Synopsis: Combining cellulose nanomaterials and pyrolysis process is a promising route for char production for sustainable environmental remediation.

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