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Comprehensive NMR Analysis of Pore Structures in Superabsorbing Cellulose Nanofiber Aerogels

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ABSTRACT: Highly porous cellulose nanofiber (CNF) aerogels are promising, environmentally friendly, reusable, and low-cost materials for various advanced environmental, biomedical, and electronic applications. The aerogels have a complex and hierarchical 3D porous network structure with pore sizes ranging from nanometers to hundreds of micrometers. The morphology of the network has a critical role on the performance of aerogels, but it is difficult to characterize thoroughly with traditional techniques. Here, we introduce a combination of nuclear magnetic resonance (NMR) spectroscopy techniques for comprehensive characterization of pore sizes and connectivity in the CNF aerogels. Cyclohexane absorbed in the aerogels was used as a probe fluid. NMR cryoporometry enabled us to characterize the size distribution of nanometer scale pores in between the cellulose nanofibers in the solid matrix of the aerogels. Restricted diffusion of cyclohexane revealed the size distribution of the dominant micrometer scale pores as well as the tortuosity of the pore network. $T_2$ relaxation filtered microscopic magnetic resonance imaging (MRI) method allowed us to determine the size distribution of the largest, submillimeter scale pores. The NMR techniques are nondestructive, and they provide information about the whole sample volume (not only surfaces). Furthermore, they show how absorbed liquids experience the complex 3D pore structure. Thorough characterization of porous structures is important for understanding the properties of the aerogels and optimizing them for various applications. The introduced comprehensive NMR analysis set is widely usable for a broad range of different kinds of aerogels used in different applications, such as catalysis, batteries, supercapacitors, hydrogen storage, etc.
NMR spectroscopy is one of the most powerful tools in chemical analysis. It provides versatile chemical, dynamic, and spatial information. The radiofrequency radiation used in the technique is nondestructive and can penetrate inside even optically opaque materials. Therefore, NMR is an ideal method for investigating dynamics and adsorption phenomena of fluids in porous materials. Furthermore, the fluids may provide detailed information about porous structures from nanometer to millimeter scale. NMR cryoporometry is based on the fact that the melting point of a liquid in a small pore is lower than that of bulk liquid, and the melting point depression is inversely proportional to the pore size. The method relies on the same principle as thermoporosimetry, but it differs in the detection. While the thermoporosimetry utilizes differential scanning calorimeter (DSC), in the NMR cryoporometry the amount of unfrozen liquid in the sample is measured using a spin echo technique filtering out the signal of frozen liquid to determine the melting point distribution, and the distribution is converted into the pore size distribution using the Gibbs–Thomson equation. A thorough comparison between two methods has been provided by Gane et al. The methods can be used to determine pore sizes in the nanometer scale. NMR is also one of the rare methods for measuring self-diffusion of molecules without tracers. The walls of porous materials restrict the diffusion of adsorbed fluids, and therefore the diffusion experiments provide information about pore sizes in micrometer scale as well as pore connectivity. Magnetic resonance imaging (MRI) technique, which also relies on the NMR phenomenon, can in turn be used to characterize millimeter scale pores.

NMR is also a useful tool for characterization of aerogels. For example, solid-state NMR has been exploited in the investigation of chemical structures of aerogels. Pore structures of aerogels have been studied by MRI and diffusion measurements of gases, such as methane as well as hyperpolarized xenon and helium, adsorbed in aerogels. Nanopore size distributions of silica aerogels have been studied with NMR cryoporometry.

In this article, we demonstrate that the combination of three different advanced NMR techniques, namely NMR cryoporometry, diffusion NMR, and T2 relaxation weighted MRI, can be used for comprehensive determination of pore sizes of CNF aerogels from nanometer to millimeter scale, as well as the tortuosity of the pore network. The CNF aerogels were manufactured from waste cellulose fibers (recycled milk container board). The manufacturing process included a pretreatment based on a green deep eutectic solvent (DES) and mechanical grinding to form a nanofiber hydrogel, followed by freeze-drying and hydrophobic modification (silylation). The resulting CNF aerogels have ultralow density (down to 0.0029 g/cm3) and high porosity (up to 99.81%). Furthermore, they own outstanding absorption properties for several oils and organic solvents (absorption capacities of up to 142.9 g/g) and are considered as superabsorbents. They are reusable; the absorbed liquids can be recovered by mechanical squeezing, and high absorption capacity is maintained at least for 30 cycles.

## MATERIALS AND METHODS

**Materials.** Recycled milk container board (MCB) was used as raw materials for fabrication of cellulose nanofibers. MCB was pulped without any additional chemicals using a Kenwood KM020 pulper (U.K.) at a consistency of 15% using temperature of 45 °C. Pulping time was 10 min with rotor speed of 2 (i.e., ~250 rpm). After pulping MCB pulp was washed and screened using a Somerville apparatus (Lorentzen & Wettre, Sweden).

A deep eutectic solvent (DES) was prepared by heating 1620 g of choline chloride and 1223 g of urea in a 5 dm3 beaker at 100 °C until the mixture melted. Next 25 g (abs) of MCB pulp (moisture content of ~30%) was dosed to the DES for 2 h at 100 °C. Then, the pulp was washed with water using a Somerville apparatus (Lorentzen & Wettre, Sweden) until clear rinsewater was obtained.

Nanofibrillation of MCB was performed using a Masuko supermasscolaider grinder MKCA6–2J (Japan) to obtain cellulose nanofibers (CNF) using negative gap values of –20, –40, –50, –70, and –80 µm to obtain gel-like MCB CNF.

Methyltrimethoxysilane (MTMS) and hexadecyltrimethoxysilane (HDTMS) in ethanol were used for cross-linking and hydrophobization of the CNF. Freshly prepared MTMS and HDTMS solutions (20 wt %) were mixed using a magnetic stirrer for 10 min. Then, 25 wt % of freshly prepared silane solutions (MTMS and HDTMS, ratio of 50:50) against CNF amounts were added by micropipette to the CNF suspensions and stirred with a magnetic stirrer at room temperature for 2 h.

Silylated MCB CNF suspensions were placed directly into 10 mm NMR sample tubes (5 cm height pillar) with various consistencies (i.e., 0.3%, 0.5%, 0.75%, and 1.0%), frozen in liquid nitrogen, and freeze-dried using Scanvacc CoolSafe S5–15 Pro (Denmark) for 72 h to obtain hydrophobized and cross-linked CNF aerogels for NMR-analysis. Similarly, aerogel samples around 30 cm3 were prepared for the FESM analysis using 100 mL plastic beakers. The detailed characteristics of the aerogels are presented in our previous work.

For the magnetic resonance analysis the samples were immersed in cyclohexane (purchased from Merck). The volume of the solvent was chosen to cover whole sample. The NMR tube was then sealed with a cap and which was tightened with Parafilm to avoid solvent evaporation during experiment.

**NMR.** The experiments were performed by Bruker AVANCE III spectrometer with the static field strength of 11.7 T and 1H resonance frequency of 500 MHz, using a 10 mm broad band observe (BBO) probe.

**NMR Cryoporometry.** For the T2 relaxation and NMR cryoporometry analysis, a series of CPMG experiments was performed over the temperature range of 239.7–287.4 K, from low to high temperatures. From 239.70 to 266.2 K, the temperature step was about 2 K, from 267.2 to 283.2 K, the step was about 1 K, and from 285.2 to 287.4 K, the step was about 2 K. The experiment series was set using modified TReNDS acquisition script. After each temperature change system was let to stabilize for 7.5 min. Then the probe was automatically tuned and a CPMG experiment was acquired with 8 scans, 512 echoes, 1 ms echo time, 30 s relaxation delay and experiment time of 4 min. The overall heating rate was about 10 and 5 K/h for the steps of 2 and 1 K, respectively, which are slow enough for keeping the sample well in thermal equilibrium. We note that, although the air-filled aerogels are excellent thermal insulators (as the immobilized air is a great thermal insulator), the aerogel filled by cyclohexane is not, and thermal equilibrium is reached relatively fast.

According to the Gibbs–Thomson equation, the melting point depression is...
Here, $T_0$ and $T$ are the melting points of bulk and confined liquids, respectively, $K_P$ is a constant characteristic of the liquid, and $R_p$ is the pore radius. In the NMR cryoporometry analysis, the $K_P$ of 190.1 K nm was used for cyclohexane.46

By assuming that the intensity of NMR signal, $I$, is proportional to the volume of the pores containing molten liquid at a given temperature, the pore size distribution can be calculated by the following equation:24,47

$$p(R_p) = -\frac{K_P}{R_p^2} \frac{dI}{d\Delta T}$$

The $T_2$ relaxation time distributions were reconstructed from CPMG data using ITAMeD in MATLAB. After the reconstruction, the region corresponding to the liquid phase ($T_2 > 6$ ms) was integrated for the NMR cryoporometry analysis. The effect of the temperature dependence of the thermal polarization on the intensity was compensated out according to the Curie law,49 and the NMR cryoporometry pore distributions were calculated using eq 2.

**NMR Diffusometry.** The apparent diffusion coefficients $D$ were measured by pulsed gradient stimulated echo (PGSTE) NMR. The diffusion times $\Delta$ used in the experiments were 50, 100, 200, 400, and 800 ms and the corresponding gradient pulse lengths were 2, 2, 1.5, 1.06, and 0.75 ms. The experiments were performed at temperature 285 K with 8 scans and 12 s relaxation delay. The gradient strengths were linearly increased from 0.963 to 47.187 G/cm (total 32 values).

The apparent diffusion coefficients were calculated using ITAMeD program.48 Surface to volume ratios were determined by fitting the following equation to the initial part of the $D$ vs $\Delta$ data:21

$$\frac{D(\Delta)}{D_0} = 1 - \frac{4}{9\sqrt{\pi}} \frac{S}{V} \sqrt{\frac{D_0}{\Delta}}$$

Here, $S$ is the surface of the pores, $V$ is the volume of the pores, and $D_0$ is the diffusion coefficient of bulk liquid.

The tortuosity, $\alpha$, was determined by fitting the following equation to the whole $D$ vs $\Delta$ data:28

$$\frac{D(\Delta)}{D_0} = 1 - \left(1 - \frac{1}{\alpha}\right) \times \frac{c\sqrt{\Delta} + (1 - 1/\alpha)\Delta/\theta}{(1 - 1/\alpha) + c\sqrt{\Delta} + (1 - 1/\alpha)\Delta/\theta}$$

Here, $c$ is defined as

$$c = \left(\frac{4}{9\sqrt{\pi}}\right) \left(\frac{S}{V}\right) \sqrt{D_0}$$

and $\theta$ is a scaling constant proportional to the pore size. Further, the pore diameter was calculated using the following equation introduced by Lawrence et al.:24,28

$$D(\Delta) = \frac{c(\Delta)}{\Delta^2}$$
The fittings were done by using Origin 2018b (S/V and tortuosity) and Microsoft Excel 2018 for the diameter.

MRI. MRI experiments were performed by the Bruker Avance III 300 MHz spectrometer equipped with Micro2.5 microimaging unit with x, y, and z gradients, using a 10 mm RF insert. The multi-slice multi-echo (MSME) sequence was used in the experiments. The number of echoes was 16, and the echo time was 20 ms. Altogether eight slices were measured from each sample with 500 μm slice thickness and a field of view of 1 cm. The image was acquired on the grid of 300 × 300 points, and the size of individual pixel was 33 μm. The image was averaged 16 times with the repetition time of 48 s. The axial images were acquired for all four samples, and for the 1% consistency sample, an additional coronal image was acquired. After the acquisition, the analysis was performed in MATLAB software. For each pixel the $T_2$ value was calculated. Then all the pixels with $T_2$ within the range 350–650 ms where assigned as macro-pores and selected for further analysis. The selected pixels where grouped according to connections with other pixels to separate shapes corresponding to single pore. For each pore the ellipsis was fitted to determine the length, width and angle of main axis. The analysis was possible by using MATLAB functions “bwlabel” and “regionprops” from Image processing toolbox. The pore diameter was defined to be a mean of the longer and shorter axis of the ellipsis.

FESEM. A FEI Quanta 200 FEG ESEM was used for FESEM analysis of the aerogels. The samples were Au-coated using a Quorum Q150T ES (Quorum Technologies, Ashford, Kent, UK) sputter coater for 140 s with a current of 20 mA. A deposition rate of 20 nm/min is typically achieved, however, the porosity and resulting high surface area of the aerogel lead to a much thinner coating (<10 nm thickness on average) throughout the sample. Samples were imaged with an Everhardt Thornley detector (ETD) for secondary electrons at 10 kV in high vacuum. The pore size analysis followed the MRI method. Each FESEM picture was imported to MATLAB. The pixels were classified as part of a pore if they had the intensity lower than 40% of the most intense pixel. Then pixels were grouped and fitted with ellipsis identically to that in MRI analysis.

Optical Laser Microscopy. The CNF aerogel samples were examined under a 3D Laser Scanning Confocal Microscope, VK-X200 by Keyence Ltd. To acquire the high-resolution images, the aerogel samples were prepared in circular Petri dishes (90 × 15 mm). Random, representative, and macroscopically flat areas (1.4 × 1.06 mm) were used to obtain the images. The photoreceptor detects the reflected light at each pixel by dividing the planar field of view into 2048 × 1536 pixels to scan a layer of an image. The intensity of each pixel at every position on the Z-axis was obtained with a pitch

$$d = \frac{6(1/\theta - 1)}{S/V} \quad (6)$$

Figure 2. (A) Apparent diffusion coefficients of cyclohexane adsorbed in CNF aerogels as a function of diffusion times. The solid lines show the fits of eq 4 to the data. (B) Surface-to-volume ratios derived from the initial slope of the $D$ vs. $\Delta$ curves. (C) Pore diameters calculated from the S/V values assuming a cylindrical pore geometry. (D) Tortuosities of the pore networks resulting from the fits.
of 0.1 μm by changing the position of the objective lens. With the Z axis position of the highest intensity being the focal point, the height information and the laser intensity were detected through the aerogel to a depth where no pores could be longer detected.

Such information provides three types of images: a deep field color image, a laser intensity image, and a height map. The final maps were created in the way that the latter two images were overlaid creating a laser intensity image with height information encoded with color.

**RESULTS AND DISCUSSION**

Four hydrophobic CNF aerogel samples with the initial consistencies (mass of cellulose in solvent before freeze-drying during manufacturing) of 0.3%, 0.5%, 0.75%, and 1% were prepared for the NMR analysis. Reference data was collected by field emission scanning electron microscopy (FESEM) and laser microscopy.

**Nanometer Scale Pores.** These inside the solid matrix of the CNF aerogel were investigated by NMR cryoporometry. Before the analysis, the samples were submerged in cyclohexane in an NMR tube at room temperature. No visible changes in the size and shape of the samples after addition of solvent were observed. 1H CPMG temperature series of the adsorbed cyclohexane was performed over the temperature range of 239.7–328.4 K. Figure 1A shows the T2 distributions resulting from the Laplace inversion of the CPMG data of the aerogel sample with a consistency of 0.3%. Above the melting point of bulk cyclohexane (280 K), there is only a single component visible with T2 over 100 ms. Below the melting point, cyclohexane forms cubic plastic crystal with a long T2 (slightly below 5 and 1 ms at the higher and lower temperatures, respectively) as compared to typical solids. Below 265 K, the distributions include another, minor component with T2 around 10 ms and intensity smaller than 10% of the main component. That minor component was observed from all the aerogel samples and a neat cyclohexane sample as well, and it was tentatively assigned to arise from crystal defects of cyclohexane.

Figure 1B plots the integral of the liquid component (T2 > 6 ms) with temperature for all the aerogel samples as well as for bulk cyclohexane. The aerogel samples show significantly
higher liquid intensities below 280 K than the bulk cyclohexane sample due to the lowered melting point of cyclohexane in the nanopores of the aerogels. The changes of the integrals revealed the melting point distributions, which were converted into pore size distributions by using the Gibbs–Thomson equation as explained in Materials and Methods. The distributions (see Figure 1C) include a dominant peak around 0−200 nm, which was interpreted to arise from interfibrous nanopores between the cross-linked cellulose nanofibers, as the size range matches with the widths of the CNF observed by transmission electron microscopy (TEM, 2−80 nm).43 Previously, a notably smaller pore size of 8 nm with very narrow size distribution obtained from Barrett–Joyner–Halenda analysis of BET measurements was reported for the cellulose nanocrystal (CNC) based aerogels.52 However, these CNCs had significantly smaller diameter of <10 nm compared to the CNF used in the present work. The nanopore size distributions of CNF aerogels were similar for all four samples, and the median and mean pore sizes (Figure 1D) varied between 70 and 110 nm. It is likely that interfibrous voids are more affected by cross-linking chemistry and colloidal forces between the CNFs, and a small variation in CNF consistency has only a minor effect on nanoporosity.

**Micrometer Scale Pores.** These are the dominant pores in the CNF aerogels and were studied via diffusion of adsorbed cyclohexane. The self-diffusion coefficients ($D$) were determined by the pulsed-field-gradient stimulated-echo (PGSTE) sequence53 including two magnetic field gradient pulses separated by a diffusion delay $\Delta$, and the results are shown in Figure 2A. The observed apparent $D$ become shorter with increasing diffusion time because the molecules experience more the restrictions caused by pore walls, and the initial slope of $D$ vs $\Delta$ is proportional to the surface-to-volume ratio ($S/V$) of the material (see Materials and Methods).21 The $S/V$ values derived from the initial slopes increases with increasing sample consistency from $1.2 \times 10^4$ to $2.6 \times 10^4$ $m^{-1}$ (see Figure 2B). The values were converted into pore diameters by assuming a cylindrical pore geometry (see Figure 2C). Naturally, the pore

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**Figure 4.** (A) Axial spin-density MR image of cyclohexane in the CNF aerogel of 1% consistency. (B) Corresponding $T_2$ map. (C) Image of the submillimeter pores derived from the $T_2$ map using the $T_2 = 500 \pm 150 \mu s$ selection criterion. (D) Coronal plane $T_2$ map of the same sample. (E) Distributions of the submillimeter pore diameters in all the aerogel samples. (F) Mean and median values of the pore diameters.
geometry of the CNF aerogels is very complex and irregular, but based on FESEM pictures, the cylindrical model was the most appropriate approximation. Opposite to nanopores, here a clear correlation between pore size and consistency of aerogels was noted as the average pore size decreased with increasing consistency from 4.9 to 2.5 μm.

The tortuosity factor α is defined as a ratio between the diffusion coefficients corresponding to 0 and infinite diffusion delay (D₀ and D∞), and it was determined by fitting eq 4 to the D vs Δ data (see Materials and Methods). The tortuosity of the CNF aerogels was high (Figure 2D) due to open and interconnected structure of the porous networks. The tortuosity decreased from 0.95 to 0.92 when the consistency of the samples increased from 0.3% to 1%, respectively. Red and blue colors correspond to high and low levels, and the large continuous blue regions represent the submillimeter pores. For comparison, the micrometer scale pores were also investigated using a 3D laser scanning confocal microscope. In the laser microscopy images shown in parts A–D of Figure 5, a clear transition from low to high consistency of aerogels is seen, the reddish and blueish colors indicating higher and lower depths, respectively. The bluish regions highlight the largest pores, and the mean and median sizes of these submillimeter pores were determined from the images (Figure 5E). The values vary between 140 and 200 μm, and they are in good agreement with the values given by the MRI analysis (Figure 4F), which supports its reliability. In the MRI analysis, the pore size distribution was actually derived from eight slices measured from different heights of the sample, resulting in the overall surface area of the analysis of 50 mm², while in the laser microscopy the analyzed area was only 1.5 mm² to ensure sufficient resolution. Therefore, in this regard, the MRI analysis was statistically more comprehensive, and the small deviations between the MRI and laser microscopy values are addressed to the low coverage of the laser microscopy analysis.

For comparison, the micrometer scale pores were also investigated using a 3D laser scanning confocal microscope. The tortuosity factor α is defined as a ratio between the diffusion coefficients corresponding to 0 and infinite diffusion delay (D₀ and D∞), and it was determined by fitting eq 4 to the D vs Δ data (see Materials and Methods). The tortuosity of the CNF aerogels was high (Figure 2D) due to open and interconnected structure of the porous networks. The tortuosity decreased from 0.95 to 0.92 when the consistency of the samples increased from 0.3% to 1%. For comparison, the micrometer scale pore structures were investigated by FESEM as well. The FESEM images of the CNF aerogel samples are shown in parts A–D of Figure 3. The mean and median pore sizes resulting from the automatized analysis of the FESEM images (see Materials and Methods) are plotted in Figure 3E. Similar to diffusion NMR analysis, the FESEM analysis shows the decreasing trend of the pore size with increasing consistency. However, the pore size values given by FESEM (about 1-3 μm) are slightly smaller than the values measured by NMR (about 2-5 μm) presumably because the diffusion NMR experiments explore the real 3D pore space, while the FESEM analysis is based on 2D projections.

The micrometer scale pores of the aerogels are attributed to hierarchical ordering of nanofibers to larger aggregates due to cross-linking and hydrogen bonding. These pores exist between and within the aggregated, sheet-like areas as illustrated by FESEM images (Figure 3A–D). In addition, the ice crystal formation during aerogel fabrication creates assembled structures of the CNFs within the aerogel. Decreasing trend of micropore size against aerogel consistency is logical due to density increase of the aerogels (presented in our previous work) which decreases the available open space. Overall, the NMR and FESEM analysis are in good qualitative agreement and even quantitatively close to each other, confirming the reliability of the NMR analysis.

Submillimeter Pores. The CNF aerogel samples included also some larger pores with the pore size close to 1 mm, which existed as few inhomogeneous patches between the large sheet-like aggregated areas (Figure 3). These pores were investigated by high-resolution microscopic MRI. Figure 4A shows the spin-density image (slice thickness 500 μm, resolution 33 μm) of cyclohexane adsorbed in the CNF aerogel with the consistency of 1%. There are significant differences in the amounts of adsorbed cyclohexane in different parts of the sample due to the millimeter range heterogeneities of the sample. Corresponding T₂ map is shown in Figure 4B. The T₂ maps were utilized to identify the largest, submillimeter pores. T₂ relaxation time of bulk cyclohexane at room temperature was determined to be 420 ms. The values in the T₂ maps in the range of 350−650 ms were interpreted to arise from bulk like cyclohexane in the large pores. Based on this criterion, the T₂ maps were converted into submillimeter pore maps (see Figure 4C), and the size distributions as well as mean and median pore sizes were calculated (Figure 4, parts E and F). The mean and median pore sizes were about 200 and 160 μm and quite similar for all the aerogel samples.

For the comparison, the submillimeter pores were also investigated using a 3D laser scanning confocal microscope. In the laser microscopy images shown in parts A–D of Figure 5, a clear transition from low to high consistency of aerogels is seen, the reddish and blueish colors indicating higher and lower depths, respectively. The bluish regions highlight the largest pores, and the mean and median sizes of these submillimeter pores were determined from the images (Figure 5E). The values vary between 140 and 200 μm, and they are in good agreement with the values given by the MRI analysis (Figure 4F), which supports its reliability. In the MRI analysis, the pore size distribution was actually derived from eight slices measured from different heights of the sample, resulting in the overall surface area of the analysis of 50 mm², while in the laser microscopy the analyzed area was only 1.5 mm² to ensure sufficient resolution. Therefore, in this regard, the MRI analysis was statistically more comprehensive, and the small deviations between the MRI and laser microscopy values are addressed to the low coverage of the laser microscopy analysis.

Overall Porous Structure. The results of the mean pore sizes measured by different methods are summarized in Figures 6 and 7. The complex and hierarchical 3D structure of aerogels is reflected as trimodal pore size distribution and can be provided by the combination of three different independent NMR techniques, namely NMR cryoporometry, diffusion NMR, and T₂ relaxation weighted MRI. The interfibrous small voids between the cross-linked nanofibers are illustrated as nanometer size pores, the size of which is relative independent of aerogel density. The larger micrometer and submillimeter pores are attributed to patches between the aggregated nanofibers, and the size of micrometer pores clearly
decrease as a function of aerogel density, while the few submillimeter voids have a relatively constant size. The comparison of results from microscopic visualization with NMR based techniques show good similarity and indicates good reliability of the obtained results.

The interaction between the aerogel material and cyclohexane solvent during the adsorption process may change the structure of the material, and therefore, the NMR analysis may not represent precisely the structure of intact, dry aerogel. However, the changes are expected to be minor, because we did not observe visually any changes in the dimensions of the aerogel piece during the adsorption process. On the other hand, NMR provides the information about the material structure in the conditions for which it was designed, which can be considered to be a strength of the method. As discussed earlier, the CNF aerogel is an organic specific superabsorbent, and therefore, it is highly important to know its structure during the interaction between the solvent and material.

Figure 6. Summary of mean pore diameters determined by different methods.

Figure 7. Pore size distributions combined from all NMR methods. The intensity of each method is normalized separately. The micrometer scale pores were visualized by assuming a Gaussian pore size distribution with the mean and standard deviation corresponding to the mean pore diameter and statistical error measured by diffusion NMR, respectively.
CONCLUSIONS
We have proved that combination of a set of advanced NMR techniques can be used for comprehensive analysis of porous networks of novel, environmentally friendly, recyclable, superabsorbing CNF aerogels. NMR cryoporometry provided information about the size distribution of nanometer scale pores in between the cross-linked cellulose nanofibers. The observed pore sizes (0–200 nm) were similar to the widths of the nanofibers and did not vary much with the consistency of the samples. Diffusion NMR experiments revealed the mean pore diameters of the dominant, micrometer pores as well as the tortuosity of the pore network. The mean pore diameter decreased from 4.9 to 2.5 μm when the consistency of the sample increased from 0.3% to 1%. The observed tortuosity was very high due to the open structure of the pore network, and it decreased from 0.95 to 0.92 with increasing consistency. Relaxation filtered MRI showed that the sample included also some larger submillimeter pores with the pore size of about 200 μm. FESEM and laser microscopy confirmed the reliability of the NMR analysis. The NMR toolbox introduced in this article can be broadly applied in the analysis of the pore networks in various aerogels and other porous media including very heterogeneous pore structures.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b08339.

Figure S1, distributions of pore diameters for 1% sample measured in axial and coronal plane, distribution of orientation of main axis of pore to the x-plane, and distribution of ratio of major to minor axis of pore; and Table S1, summary of pore sizes from all methods used (PDF)

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Author Contributions
Y.K. performed all the NMR experiments, analyzed diffusometry and optical laser microscopy data and wrote the first draft of the paper. M.U. supervised all the NMR experiments and data analysis and analyzed cryoporometry, MRI and FESEM data. O.L., H.L. and K.K. prepared the aerogel samples and measured the FESEM data. S.P. measured the optical laser microscopy data. S.K. performed preliminary cryoporometry experiments. V.-V.T. planned the experiments, supervised all the data analysis, and wrote the final version of manuscript.

Notes
The authors declare no competing financial interest.

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ABBREVIATIONS
NMR nuclear magnetic resonance; MRI magnetic resonance imaging; CNF cellulose nanofibers; FESEM field-emission scanning electron microscopy

REFERENCES

(1) Hüsing, N.; Schubert, U. Aerogels—Airy Materials: Chemistry, Structure, and Properties. Angew. Chem., Int. Ed. 1998, 37 (1–2), 22–45.
(2) Feng, J.; Nguyen, S. T.; Fan, Z.; Duong, H. M. Advanced Fabrication and Oil Absorption Properties of Super-Hydrophobic Recycled Cellulose Aerogels. Chem. Eng. J. 2015, 270, 168–175.
(3) Payne, K. C.; Jackson, C. D.; Aizpurua, C. E.; Rojas, O. J.; Hubbe, M. A. Oil Spills Abatement: Factors Affecting Oil Uptake by Cellulosic Fibers. Environ. Sci. Technol. 2012, 46, 7725.
(4) Wei, X.; Huang, T.; Yang, J.; Zhang, N.; Wang, Y.; Zhou, Z. Green Synthesis of Hybrid Graphene Oxide/Microcrystalline Cellulose Aerogels and Their Use as Superabsorbents. J. Hazard. Mater. 2017, 335, 28–38.
(5) Ilera, D.; Mesa, J.; Gomez, H.; Maury, H. Cellulose Aerogels for Thermal Insulation in Buildings: Trends and Challenges. Coatings 2018, 8 (10), 345.
(6) Duong, H. M.; Nguyen, S. T. Nanocellulose Aerogels as Thermal Insulation Materials. Nano and Biotech Based Materials for Energy Building Efficiency 2016, 411–427.
(7) Stergar, J.; Mauer, V. Review of Aerogel-Based Materials in Biomedical Applications. J. Sol-Gel Sci. Technol. 2016, 77, 738–752.
(8) Zhang, Y.; Nypelö, T.; Salas, C.; Arboleda, J.; Hoeger, I. C.; Rojas, O. J. Cellulose Nanofibrils: From Strong Materials to Bioactive Surfaces. J. Renew. Mater. 2013, 1 (3), 195–211.
(9) Korhonen, J. T.; Kettunen, M.; Ras, R. H. A.; Ikkala, O. Hydrophobic Nanocellulose Aerogels as Floating, Sustainable, Reusable, and Recyclable Oil Absorbents. ACS Appl. Mater. Interfaces 2011, 3 (6), 1813–1816.
(10) Zhou, S.; Liu, P.; Wang, M.; Zhao, H.; Yang, J.; Xu, F. Sustainable, Reusable, and Superhydrophobic Aerogels from Microfibrillated Cellulose for Highly Effective Oil/Water Separation. ACS Sustainable Chem. Eng. 2016, 4 (12), 6409–6416.
(11) Olalekan, A. P.; Dada, A. O.; Adesina, O. A. Review: Silica Aerogel as a Viable Absorbent for Oil Spill Remediation. J. Encapsulation Adsorp. Sci. 2014, 04 (04), 122–131.
(12) Martucci, A. Characterization Methods. Sol-Gel Nanocomposites 2014, 83–108.
(13) De France, K. J.; Hoare, T.; Cranston, E. D. Review of Hydrogels and Aerogels Containing Nanocellulose. Chem. Mater. 2017, 29 (11), 4609–4631.
(14) Sasanian, S.; Newson, T. A. Use of Mercury Intrusion Porosimetry for Microstructural Investigation of Reconstituted Clays at High Water Contents. Eng. Geol. 2013, 158, 15–22.
(15) Lewis, W. K., Whitman, W. Absorption Symposium: Principles of Gas Absorption. In Meeting of the American Chemical Society; UTC: 1924; Vol. 08, p 23.
(16) Keeler, J. Understanding NMR Spectroscopy, 2nd ed.; John Wiley & Sons: 2010.
(17) Telkki, V. V. Hyperpolarized Laplace NMR. Magn. Reson. Chem. 2018, 56 (7), 619–632.
(18) Kärger, J.; Valiullin, R. Mass Transfer in Mesoporous Materials: The Benefit of Microscopic Diffusion Measurement. Chem. Soc. Rev. 2013, 42 (9), 4172–4197.
(19) Kekkonen, P. M.; Ylisassi, A.; Telkki, V. V. Absorption of Water in Thermally Modified Pine Wood as Studied by Nuclear Magnetic Resonance. J. Phys. Chem. C 2014, 118 (4), 2146–2153.
(20) Javed, M. A.; Kekkonen, P. M.; Ahola, S.; Telkki, V.-V. Magnetic Resonance Imaging Study of Water Absorption in
Thermally Modified Pine Wood. *Holzforschung* **2015**, *69* (7), 899–907.

(21) Erdem, Ö. F.; Michel, D. 1H MAS NMR Investigations of Ethylene Glycol Adsorbed in NaX. *J. Phys. Chem. B* **2005**, *109* (24), 12054–12061.

(22) Song, Y. Q. Magnetic Resonance of Porous Media (MRPM): A Perspective. *J. Magn. Reson.* **2013**, *229*, 12–24.

(23) Mitchell, J.; Webber, J.; Strange. J. Nuclear Magnetic Resonance Cryoporometry. *Phys. Rep.* **2009**, *481* (1), 1–36.

(24) Petrov, O. V.; Furo, I. NMR Cryoporometry: Principles, Applications and Potential. *Prog. Nucl. Magn. Reson. Spectrosc.* **2009**, *54* (2), 97–122.

(25) Pircher, N.; Carbajal, L.; Schimper, C.; Bacher, M.; Rennhofer, H.; Nedelec, J.-M.; Lichtenegger, H. C.; Rosenau, T.; Liebner, F. Impact of Selected Solvent Systems on the Pore and Solid Structure of Cellulose Aerogels. *Cellulose* **2016**, *23* (3), 1949–1966.

(26) Gane, P. A. C.; Ridgway, C. J.; Lehtinen, E.; Valiullin, R.; Furo, I.; Schoelkopf, J.; Paulapuro, H.; Daicic. J. Comparison of NMR Cryoporometry, Mercury Intrusion Porosimetry, and DSC Thermo-porosimetry in Characterizing Pore Size Distributions of Compressed Finely Ground Calcium Carbonate Structures. *Ind. Eng. Chem. Res.* **2004**, *43*, 7920.

(27) Callaghan, P. T. *Translational Dynamics and Magnetic Resonance: Principles of Pulsed Gradient Spin Echo NMR*; Oxford University Press: 2011.

(28) Latour, L. L.; Mitra, P. P.; Kleinberg, R. L.; Sotak, C. H. Time-Dependent Diffusion Coefficient of Fluids in Porous Media as a Probe of Surface-to-Volume Ratio. *J. Magn. Reson., Ser. A* **1993**, *101* (3), 342–346.

(29) Latour, L. L.; Svoboda, K.; Mitra, P. P.; Sotak, C. H. Time-Dependent Diffusion of Water in a Biological Model System. *Proc. Natl. Acad. Sci. U. S. A.* **1994**, *91* (4), 1229–1233.

(30) Hurlimann, M. D.; Helmer, K. G.; Latour, L. L.; Sotak, C. H. Restricted Diffusion in Sedimentary Rocks. Determination of Surface-Area-to-Volume Ratio and Surface Relaxivity. *J. Magn. Reson., Ser. A* **1994**, *111* (2), 169–178.

(31) Stallmach, F.; Kärger. J. Potentials of Pulsed Field Gradient NMR for Investigation of Porous Media. *Adsortion* **1999**, *5* (2), 117–133.

(32) Blumich, B. NMR *Imaging of Materials*; Oxford University Press: 2003.

(33) Devreux, F.; Boilot, J. P.; Chaput, F.; Sapoval, B. NMR Determination of the Fractal Dimension in Silica Aerogels. *Phys. Rev. Lett.* **1990**, *65* (5), 614–617.

(34) El Rassy, H.; Pierre, A. C. NMR and IR Spectroscopy of Silica Aerogels with Different Hydrophobic Characteristics. *J. Non-Cryst. Solids* **2005**, *351* (19–20), 1603–1610.

(35) Gregory, D. M.; Botto, R. E. Pore Structure and Sorption Properties of Silica Aerogels Studied by Magnetic Resonance Imaging and Pulsed-Field Gradient Spectroscopy. *Appl. Spectrosc.* **2003**, *57* (3), 245–250.

(36) Harel, E.; Granwehr, J.; Seeley, J. A.; Pines, A. Multiphase Imaging of Gas Flow in a Nanoporous Material Using Remote-Detection NMR. *Nat. Mater.* **2006**, *5* (4), 321–327.

(37) Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A.; Wang, L. Q.; Exarhos, G. J.; Baumann, T. F.; Satcher, J. H. Nuclear Magnetic Resonance Studies of Resorcinol-Formaldehyde Aerogels. *J. Phys. Chem. B* **2005**, *109* (22), 11215–11222.

(38) Pavlovskaya, G.; Blue, A. K.; Gibbs, S. J.; Haake, M.; Cross, F.; Malier, L.; Meersmann, T. Xenon-131 Surface Sensitive Imaging of Aerogels in Liquid Xenon near the Critical Point. *J. Magn. Reson.* **1999**, *137*, 258–264.

(39) Pawsley, S.; Kalebaila, K. K.; Moudrakovski, I.; Ripmeester, J. A.; Brock, S. L. Pore Structure and Interconnectivity of CdS Aerogels and Xerogels by Hyperpolarized Xenon NMR. *J. Phys. Chem. C* **2010**, *114* (31), 13187–13195.

(40) Guillot, G.; Nacher, P. J.; Tastevin, G. NMR Diffusion of Hyperpolarised 3He in Aerogel: A Systematic Pressure Study. *Magn. Reson. Imaging* **2001**, *19*, 391–394.

(41) Veres, P.; Kéri, M.; Bányai, I.; Lázár, I.; Fábián, I.; Domingo, C.; Kalmár. J. Mechanism of Drug Release from Silica-Gelatin Aerogel—Relationship between Matrix Structure and Release Kinetics. *Colloids Surf., B* **2017**, *152*, 229–237.

(42) Kalmár, J.; Kéri, M.; Erdei, Z.; Bányai, I.; Lázár, I.; Lente, G.; Fábián, I. The Pore Network and the Adsorption Characteristics of Mesoporous Silica Aerogel: Adsorption Kinetics on a Timescale of Seconds. *RSC Adv.* **2015**, *5* (130), 107237–107246.

(43) Laitinen, O.; Suopajärvi, T.; Osterberg, M.; Liimatainen, H. Hydrophobic, Superabsorbing Aerogels from Choline Chloride-Based Deep Eutectic Solvent Pretreated and Silylated Cellulose Nanofibrils for Selective Oil Removal. *ACS Appl. Mater. Interfaces* **2017**, *9* (29), 25029–25037.

(44) Urbáni, M.; Shchukina, A.; Golowicz, D.; Kazimierzuk, K. TReNDS - Software for Reaction Monitoring with Time-Resolved Non-Uniform Sampling. *Magn. Reson. Chem.* **2019**, *57* (1), 4–12.

(45) Jackson, C. L.; McKenna, G. B. The Melting Behavior of Organic Materials Confined in Porous Solids. *J. Chem. Phys.* **1990**, *93* (12), 9002–9011.

(46) Mitchell, J.; Webber, J. B. W.; Strange, J. H. Nuclear Magnetic Resonance Cryoporometry. *Phys. Rep.* **2008**, *461*, 1–36.

(47) Strange, J. H.; Rahman, M.; Smith, E. G. Characterization of Porous Solids by NMR. *Phys. Rev. Lett.* **1993**, *71* (21), 3589–3591.

(48) Urban, M.; Bernin, D.; Koźmiński, W.; Kazimierzuk, K. Iterative Thresholding Algorithm for Multicomponent Decay Applied to PGSE NMR Data. *Anal. Chem.* **2013**, *85* (3), 1828–1833.

(49) Cowan, B. P. Nuclear Magnetic Resonance and Relaxation; Cambridge University Press: 1998.

(50) Telkki, V. K.; Lounila, J.; Jokisarji, J. Determination of Pore Sizes and Volumes of Porous Materials by 129Xe NMR of Xenon Gas Dissolved in a Medium. *J. Phys. Chem. B* **2005**, *109* (51), 24343–24351.

(51) Hood, G. M.; Sherwood, J. N. Self Diffusion in Cyclohexane Single Crystals. *Mol. Cryst. 1966*, *1* (1), 97–112.

(52) Yang, X.; Cranston, E. D. Chemically Cross-Linked Cellulose Nanocrystal Aerogels with Shape Recovery and Superabsorbent Properties. *Chem. Mater.* **2013**, *24* (20), 6016–6025.

(53) Tanner, J. E. Use of the Stimulated Echo in NMR Diffusion Studies. *J. Chem. Phys.* **1970**, *52* (5), 2523.