Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

For

Cellulose acetate as convenient intermediate for the preparation of 5-acetoxymethylfurfural from biomass

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Material and Methods

All the chemicals were purchased from Sigma-Aldrich and used as received.

IR analysis

Infrared spectra were recorded on a ThermoScientific Nicolet iS5 FT-IR spectrometer at a resolution of 4 cm^{-1} and 64 scans.

NMR analysis

^1H spectra were measured on a Bruker Spectrospin 400 MHz Ultrashield Spectrometer in $CDCl_3$, with chemical shifts referenced to the residual solvent signal and using standard instrument conditions (512 scans). The degree of substitution was calculated according to the ^1H-NMR signal ratio between the cellulose backbone signals (5.2-3.4 ppm) and the acetyl signals (2.3-1.8 ppm).

GPC analysis

The number and weight average molecular weight (Mn, Mw) were calculated from molecular weight distributions determined by size exclusion chromatography (SEC) in tetrahydrofuran as solvent on the basis of polystyrene standards (PSS; Mainz)[1]. The GPC was run at 25 °C in THF using a column system by PSS (SDV 100/1000/100,000, 8 x 300 mm, 5 mm particle size) with UV- (260 nm) and refractive index detection systems. The number of glucose units per cellulose acetate chain was calculated dividing the average molecular weight by the molecular weight of each glucose acetate unit:

Nº glucose units = average molecular weight/ Mr (g/mol)

The molecular weight of each glucose acetate unit (Mr) was calculated according to its degree of substitution (DS). The cellulose repeating unit, anyhdroglucose, has a weight of 162 g/mol; each of the 3 free hydroxyl groups can however be acetylated (acetyl group: 43 g/mol). Thus, Mr is calculated as follows:

Mr (g/mol) = 159 + 43 x DS + (3 - DS) x 1

Glucose acetate synthesis

To a cold mixture of glucose (10 g, 55.5 mmol) and pyridine (30 mL, 373 mmol) acetic anhydride (30 mL, 317 mmol) was added. The mixture was stirred overnight and then transferred to a separation funnel with ethyl acetate (100 mL). The solution was washed with 2 M hydrochloric acid, saturated sodium bicarbonate and brine, dried over sodium sulfate and concentrated.

Organocat pulp preparation

Organocat pulp was prepared according to the method described by Grande et. al[2]. Briefly, in an autoclave, beech wood (25 g) was suspended in water (500 mL). Oxalic acid (2,25 g) was added followed by 2-Methyl tetrahydrofuran (500 mL) and the reaction was stirred at 130 °C for 3 h. The obtained solid was thoroughly washed with water and dried at 80 °C overnight.

Cellulose acetate synthesis from cellulose

In a round bottom flask, cellulose (2 g, 12 mmol) was suspended in acetic acid (35 mL) and stirred for 1 hour at 55 °C. Thus, a mixture of acetic anhydride (10 mL, 105 mmol) and sulfuric acid (0.4 mL, 7.5 mmol) was slowly added, while the mixture was kept at 55 °C for 2 hours[3]. The mixture was thus poured into cold water, the precipitate was filtered, washed and dried at 40 °C in a vacuum oven.

Cellulose acetate synthesis from pulp or wood

In a round bottom flask, 2 g of wood or pulp were suspended in acetic acid (35 mL) and stirred for 1 hour at 55 °C. Thus, a mixture of acetic anhydride (10 mL, 105 mmol) and sulfuric acid (0.4 mL, 7.5 mmol) was slowly added, while the mixture was kept at 55 °C for 2 hours[3]. The mixture was poured into cold water, the precipitate was filtered, washed and dried at 40 °C in a vacuum oven. In order to purify the cellulose acetate, the precipitate was stirred in dichloromethane (30 mL) at 30 °C for 1 hour; afterwards 2/3 of the solvent was evaporated with a rotary evaporator and poured into 20 mL of ethanol, the precipitate was washed with ethanol and dried at 40 °C in a vacuum oven.

General procedure for the acetolysis of cellulose acetate

Solutions of cellulose acetate in acetic acid were prepared under the approximation that all cellulose acetate is composed of triacetylated anhydroglucose units (molar mass: 288 g/mol). The following molarities (mM) and the number of equivalents are therefore calculated with respect to triacetylated anhydroglucose units. Briefly, the corresponding amount of cellulose acetate to reach a final concentration of 5 g/L (17.4 mM) of cellulose acetate were dissolved in acetic acid and 35 mM of acetic anhydride (2 eq) and 35 mM of acid (2 eq) was added each run, unless otherwise stated. (The same procedure was adapted for non-acetylated cellulose [molar mass: 162 g/mol] as control experiment).

Batch acetolysis

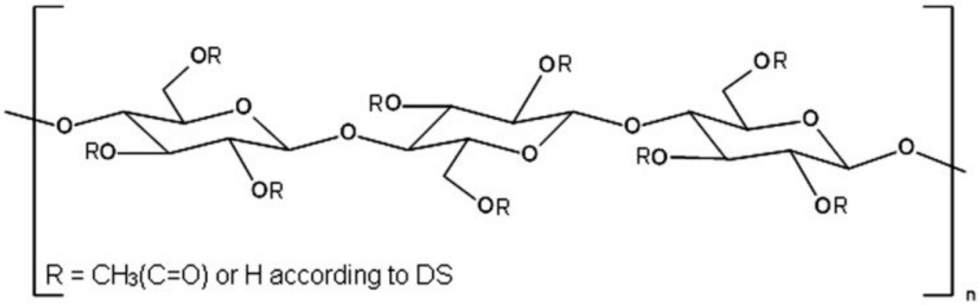
The above mentioned solution (15 mL), was charged in a Teflon lined, stainless steel autoclave (45 ml volume, purchased from Parr Instruments). The autoclave was placed into an oven at the desired reaction temperature and kept for the desired reaction time.

Flow acetolysis

For the continuous flow acetolysis a commercial reactor (X-Cube Flash, Thales Nano) equipped with a 4 mL hastelloy reaction loop was used. After equilibrating the system at the desired temperature over a period of 2 min, 5 mL of a filtered feed solution were passed through the coil using an HPLC pump. Then, a minimum of 1 mL of sample was collected for analysis. The residence time was controlled by adjusting the flow rate. HPLC analysis of the reaction mixture was performed as described below.

HPLC analysis

After filtration of the reaction mixture, 100 µL of sample were diluted with 900 µl of a 1:1 mixture of acetonitrile-water. Thus, 20 µL of the resulting solution were injected for analysis. The HPLC analysis was performed using an Agilent 1200 instrument connected to a Hypersil GOLD C8 column, DAD was used as detector and the signal at 260 nm was used for quantification. ACN-water (1:1) was used as the mobile phase with a flow of 0.4 mL/min. The HPLC column was kept at 40 °C, and data acquisition was performed over 20 minutes intervals. Prepared glucose acetate and commercial AMF or HMF were used as standards for the preparation of calibration curves.



AMF yield was calculated correcting the molecular weight of the acetylated anhydroglucose unit with the acetyl content per unit (DS calculated by 1H-NMR):

Cellulose acetate unit Mr (g/mol) = 159 + 43 x DS + (3 - DS) x 1

AMF yield (%) = 100 x [AMF] HPLC measured (g/L) / [AMF] max (g/L)

[AMF] max (g/L) = cellulose acetate (g) x 168 (g/mol) / (cellulose acetate Mr (g/mol) x V (L))

Crude AMF from the 2h time on stream experiment and recovery

Commercial cellulose acetate (500 mg, 1.74 mmol) were dissolved in acetic acid (100 mL) and sulfuric acid (3.45 mmol, 184 µL) and acetic anhydride (3.5 mmol, 333 µL) were added. The solution was flowed through the reactor at 175 °C with a flow rate of 0,8 m/L and the eluate was collected over 2 hours. The collected solution (96 mL) was poured into ethyl acetate (200 mL) and the solution was washed with saturated sodium bicarbonate (150 mL) and brine (150 mL), dried over anhydrous sodium sulfate, concentrated and dried at 40 °C in a vacuum oven. 191 mg of crude AMF (see Fig S5) were recovered.

Fig S1. ^{1}H-NMR of acetylated cellulose

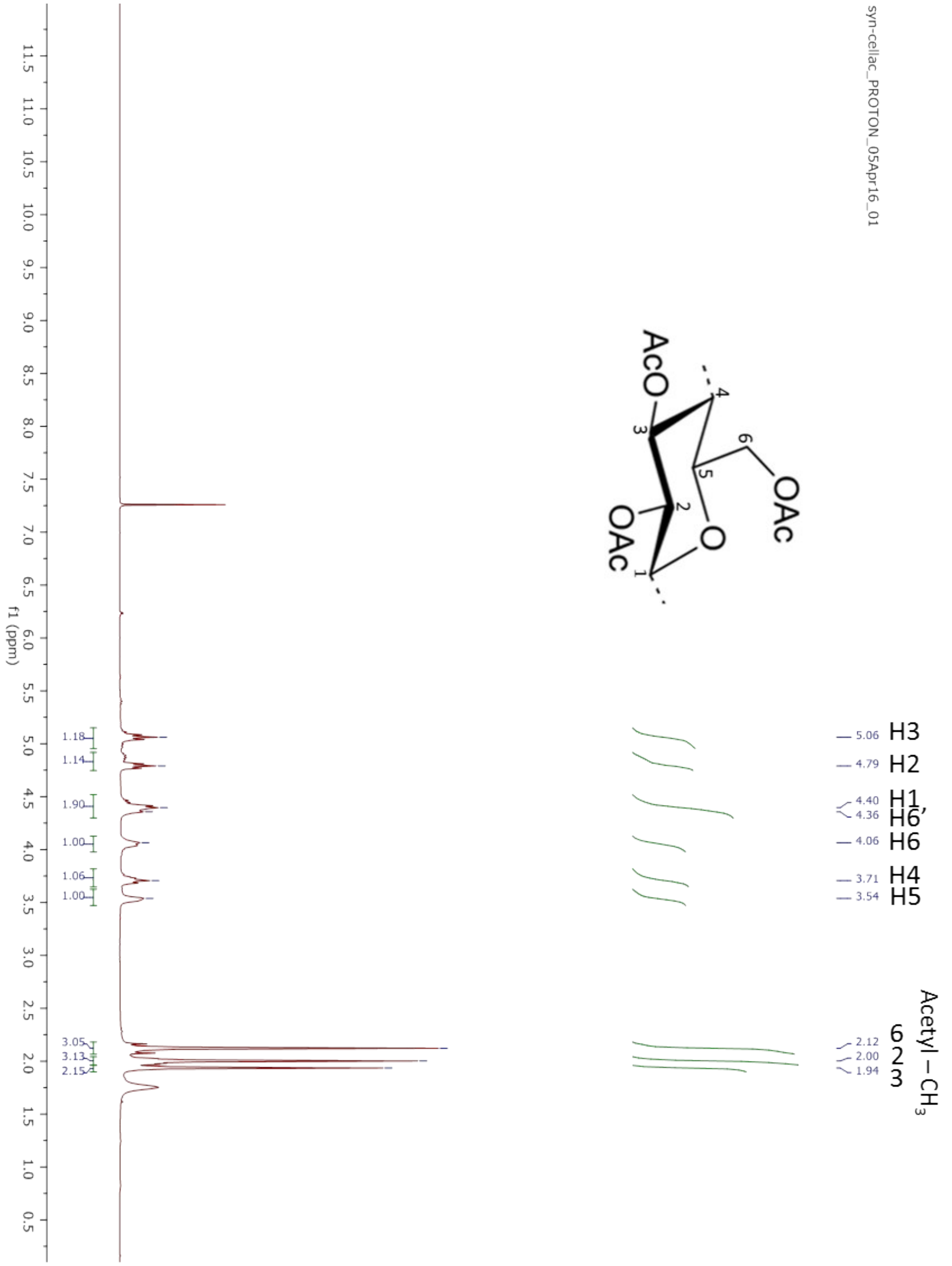


Fig S2. ^{1}H-NMR of acetylated beech wood

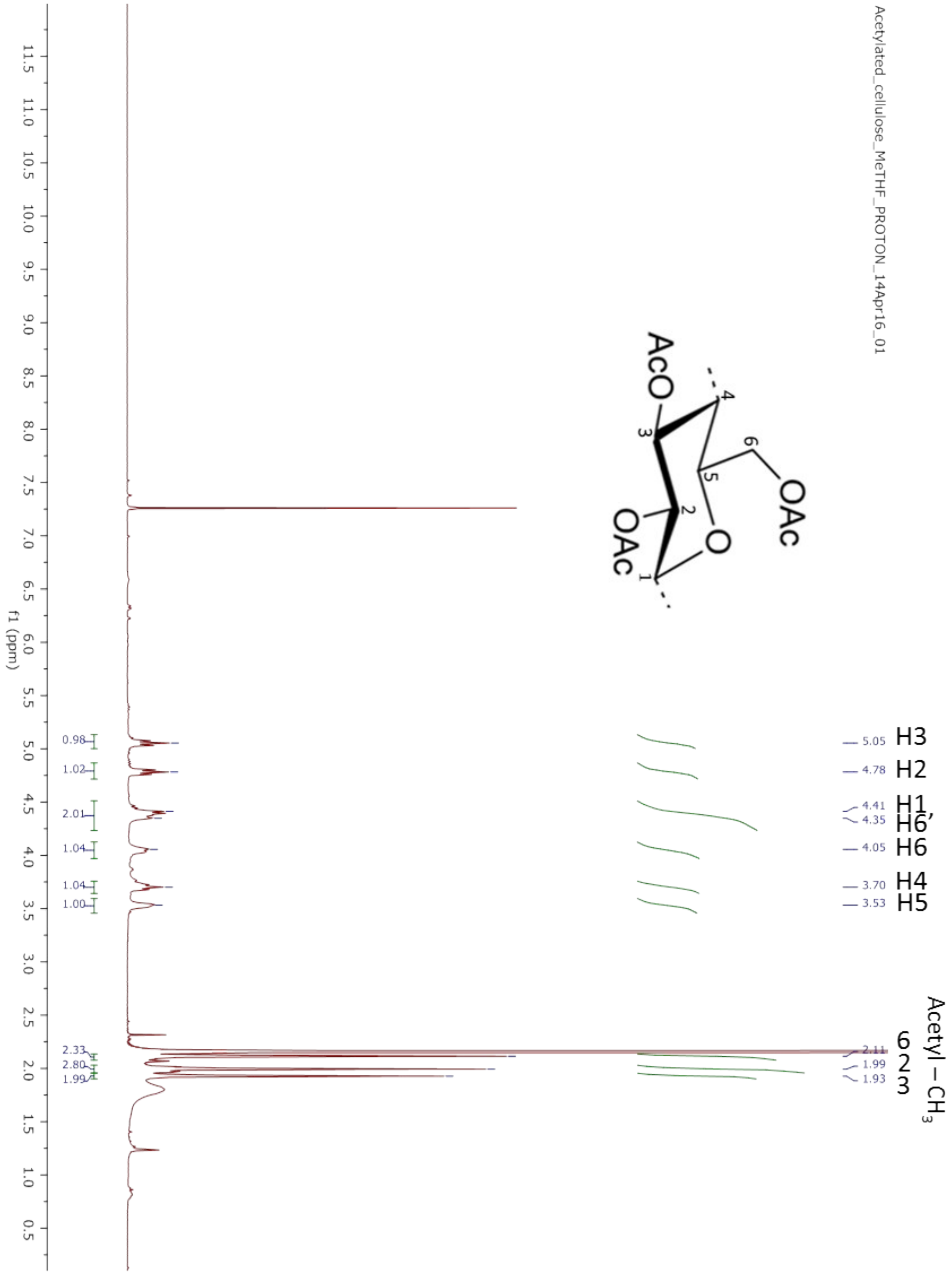


Fig S3. ^{1}H-NMR of acetylated organocat pulp

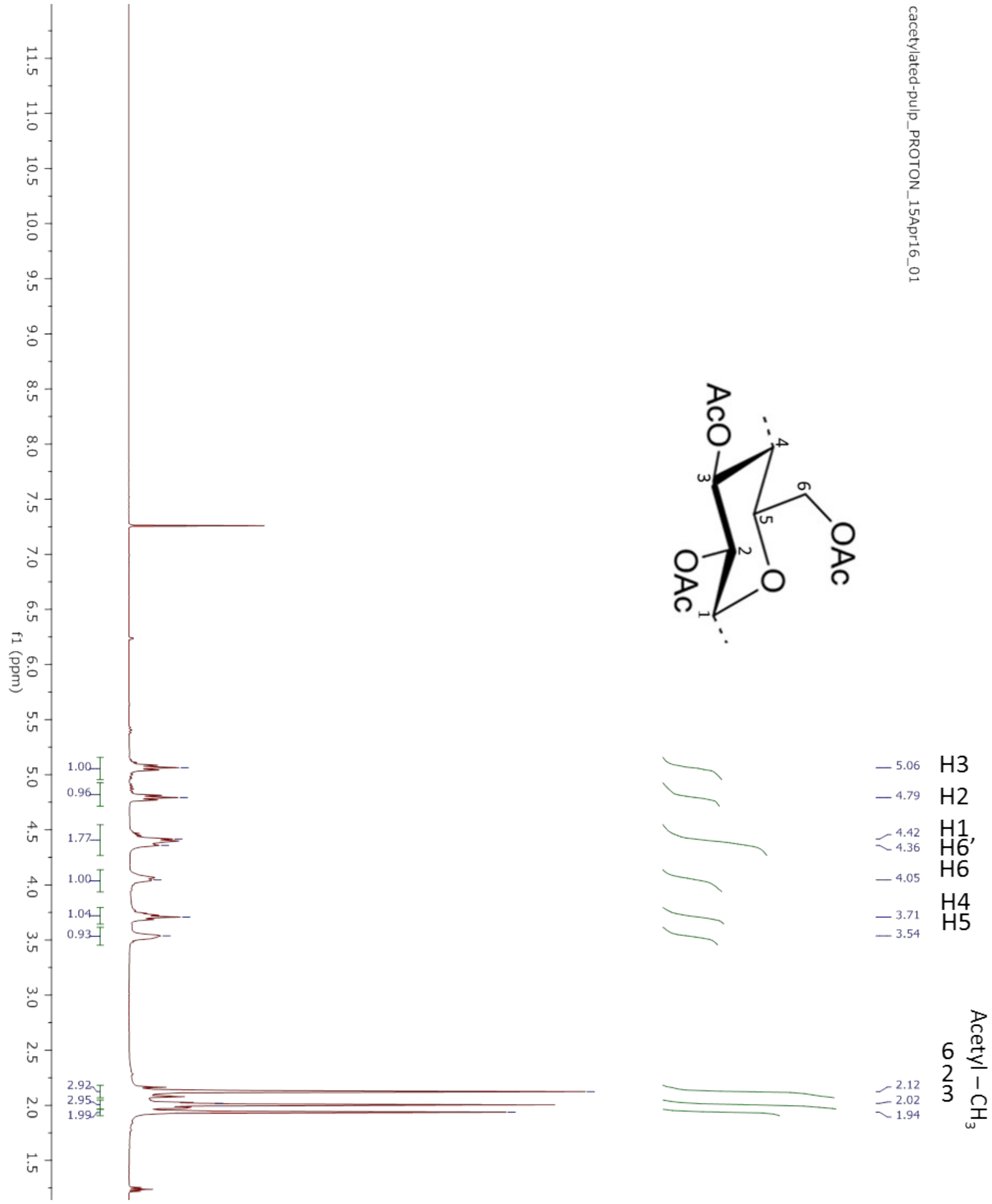


Fig S4. ^{1}H-NMR of commercial cellulose acetate

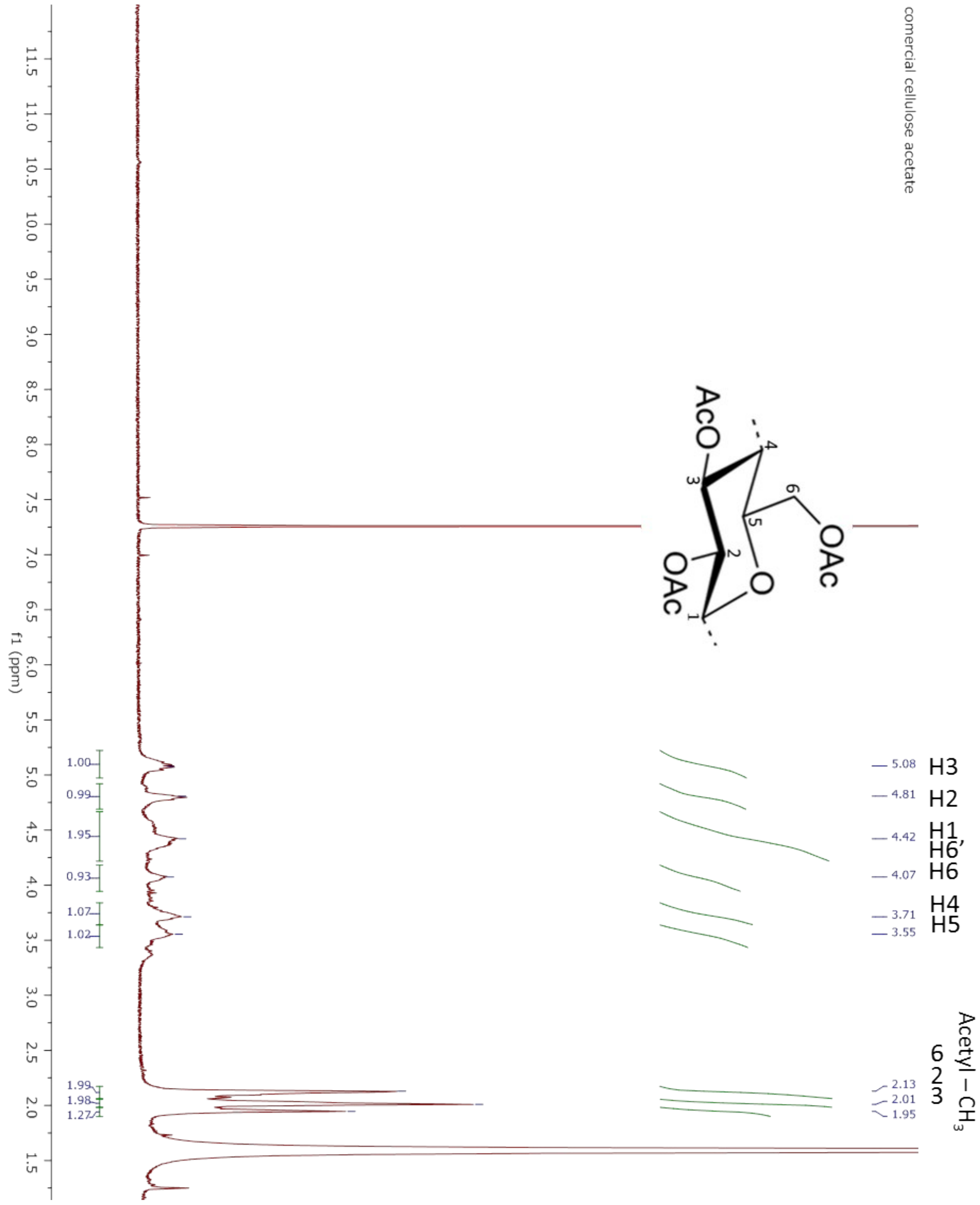


Fig S5. ^{1}H-NMR of crude AMF from the 2h time on stream experiment

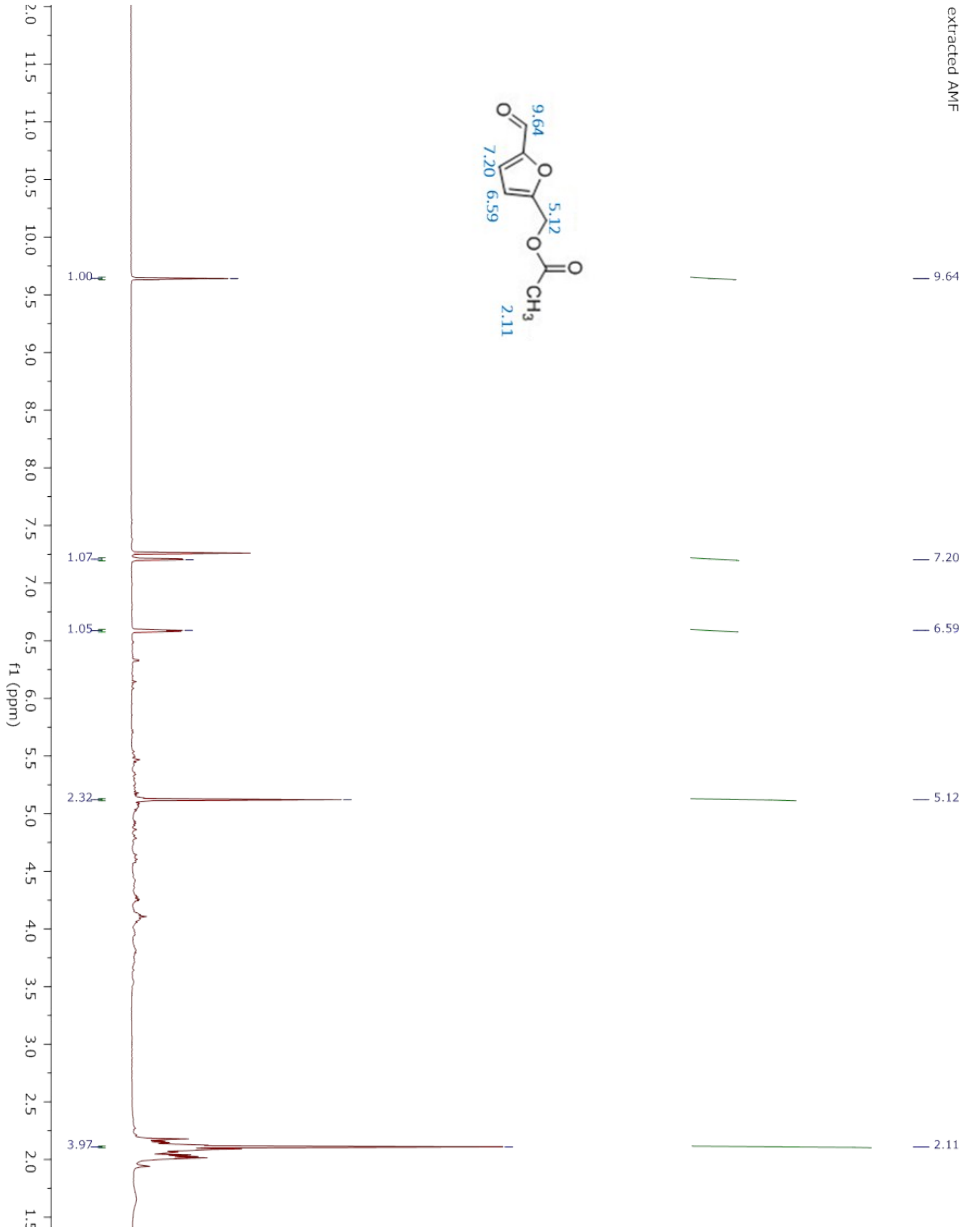


Fig S6. FTIR spectra of the acetylated materials and the commercial cellulose acetate

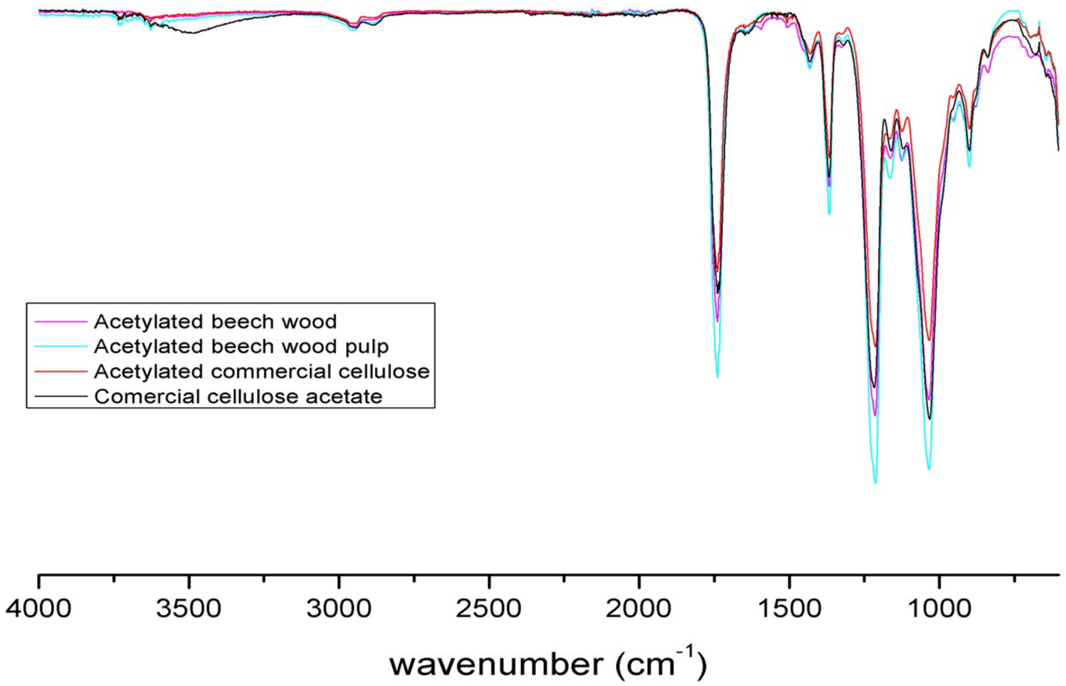


Fig S7. GPC of commercial cellulose acetate

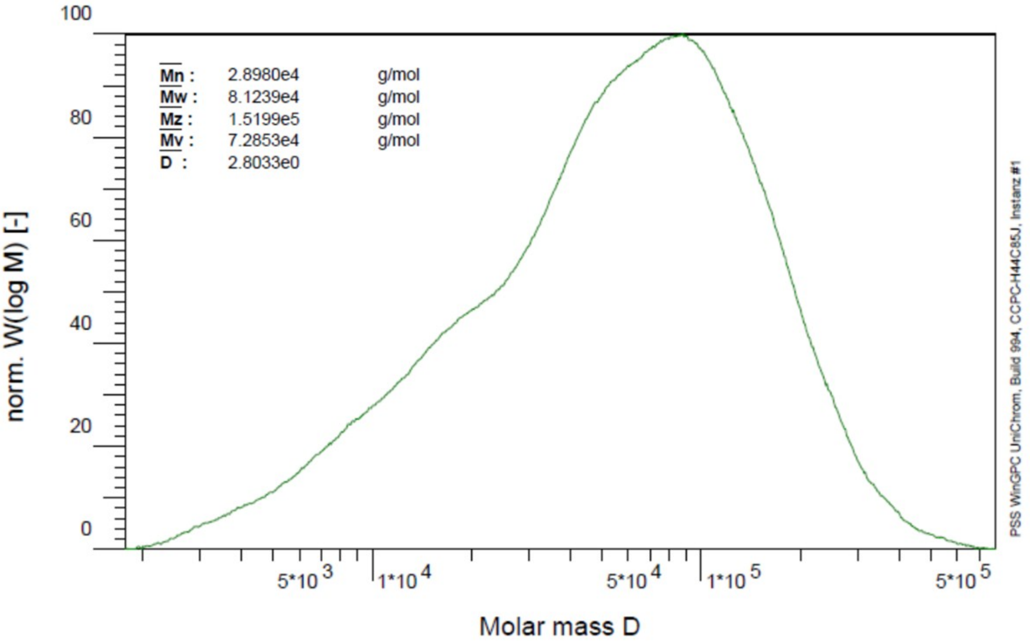


Fig S8. GPC of acetylated cellulose

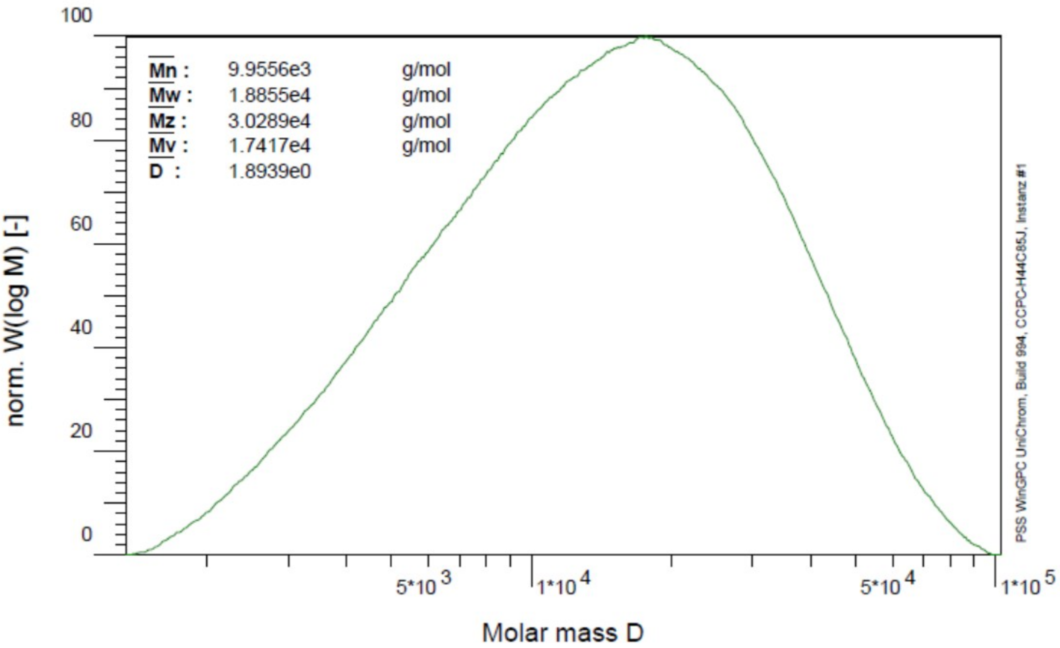


Fig S9. GPC of acetylated Organocat pulp

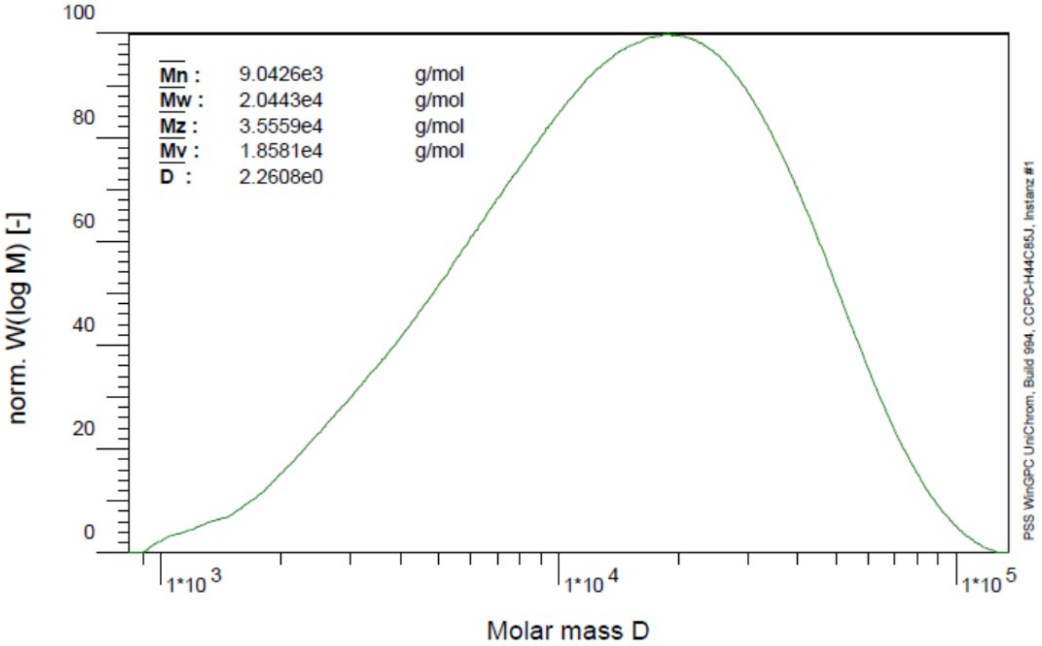


Fig S10. GPC of acetylated beech wood

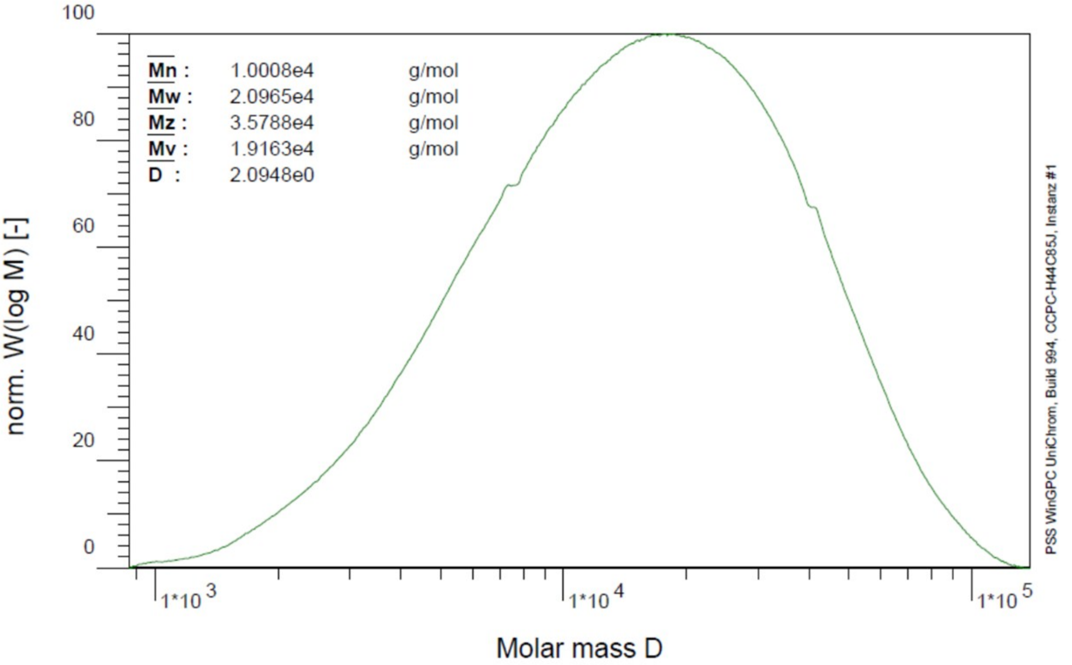
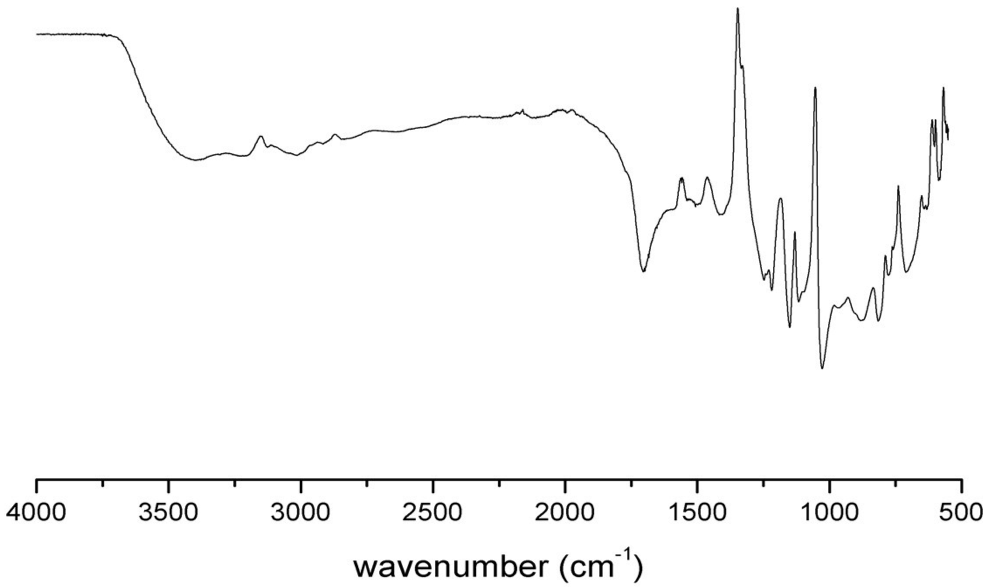
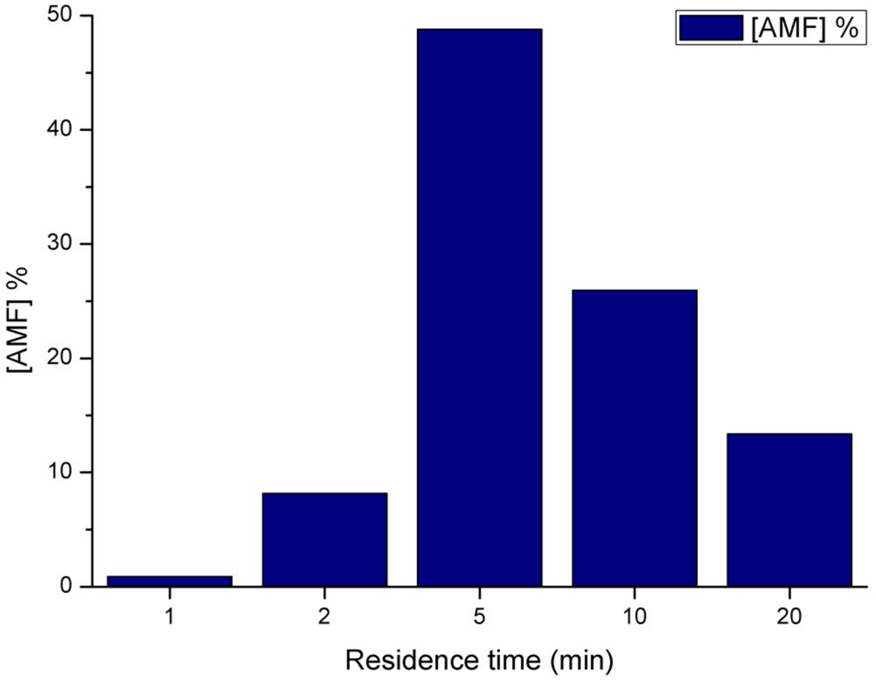


Fig S11. FTIR spectra of recovered humic material (after reacting 3 g/L of AMF in 15 mL of acetic acid for 6 hours at 220 °C)



The bands at 1506, 1218, 1026, 956 and 774 cm^{-1} can be attributed to the presence of the furan ring (AMF condensation), while bands at 760 and 710 cm^{-1} can be allotted to the aromatic nature of humins[4].

Fig S12. AMF recovery experiments as a function of the residence time in the flow reactor at 175 °C. Conditions: cellulose acetate (5 g/L), acetic acid as solvent, Ac_2O (2 eq), H_2SO_4 (2 eq)



Economic balance for 1000 grams scale

An initial qualitative estimation of costs was performed for the processing of cellulose acetate (1 kg) on the basis of laboratory prices (Sigma-Aldrich).

<u>Costs</u>

1000 g of cellulose acetate (0.11€/g) → 110 €

200 L of acetic acid (9 €/L) → 1800 €

372 mL of sulfuric acid (26 €/L) → 9.7 €

714 grams of acetic anhydride (14.5 €/kg) →10.3 €

<u>Total costs: 1930 €</u>

With a 49 % yield of AMF, 350 g of AMF can be obtained. So the production costs for AMF would be 1930/350 = 5.51 €/g.

References

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2 P. M. Grande, J. Viell, N. Theyssen, W. Marquardt, P. Domínguez de María and W. Leitner, *Green Chem.*, 2015, 3533–3539.

3 S. S. Z. Hindi and R. A. Abohassan, *Bioresources*, 2015, **10**, 5030–5048.

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