Electronic Supplementary Material (ESI) for RSC Sustainability.

Influence of DP and MMD of the pulps used in the Ioncell® process on processability and fibre properties

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1. Kinetics of DP adjustment

In the rate equation describing the DP degradation kinetics of cellulose under acidic aqueous conditions. a distinction is made between the number of amorphous segments with regularly (M) and weakly (W) linked glycosidic bonds. The assumption of first-order reactions leads to the following description of the time evolution of M (regular linkages) and W (weak linkages) and the number of chain cleavages $DP_0/DP-1$:

$$\frac{dM}{dt} = -k_1 M \qquad \frac{dH_1}{dt} = k_1 M$$

$$\frac{dW}{dt} = -k_2 W \qquad \frac{dH_2}{dt} = k_2 W \tag{S1}$$

H_1 and H_2 stand for the number of scissions in the regularly and weakly linked subcategories.
k_1 is rate constant for the hydrolysis reaction in regularly linked part
k_2 represents rate constant for the fast reaction for weakly linked elements

Solving the simple differential equations leads to expressions of H_1 and H_2 which comprise the total number of scissions on that chain. Since n scissions on average reduce the length of the chain by a factor of (n+1) the chain length development can be expressed in equation (S2) as:

$$DP = \frac{DP_0}{H_1 + H_2 + 1} \tag{S2}$$

The initial variables of M and W are M0 and W0. Thus. the simple differential equations can be solved. and by calculating the DP value from the intrinsic viscosities. the number of chain scissions per cellulose molecule CSv can be calculated with DP0/DP-1 using equation (S3) [1]:

$$CS_V = \left(\frac{DP_0}{DP} - 1\right) = M_0\left(1 - e^{-k_1 t}\right) + W_0\left(1 - e^{-k_2 t}\right) \tag{S3}$$

The kinetics of chain cleavage CSv by an enzyme treatment can be described by the Michaelis-Menten equation according to equation (S4) [2]:

$$CS_V = CS_{v.max}\frac{[EG]}{([EG] + K_M)} \tag{S4}$$

With CSv. max is the maximum chain scission, [EG] is the endoglucanase charge and K_M is the Michaelis constant.

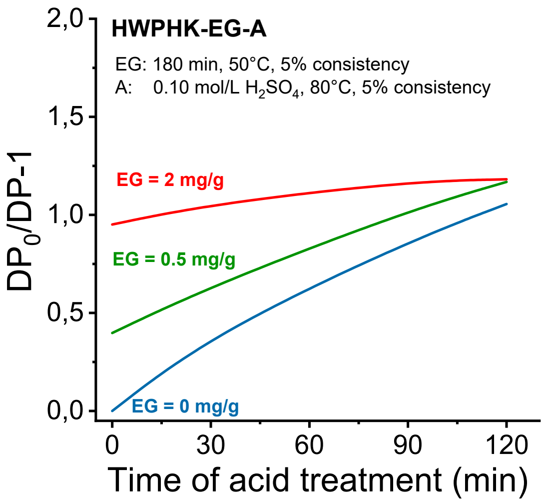

Figure S1: The chain scission rate of cellulose during successive endoglucanase and acid treatments as a function of the duration of acid treatment.

2. **Relationship of the intrinsic viscosity and pretreatment on the high MW faction of the pulps**

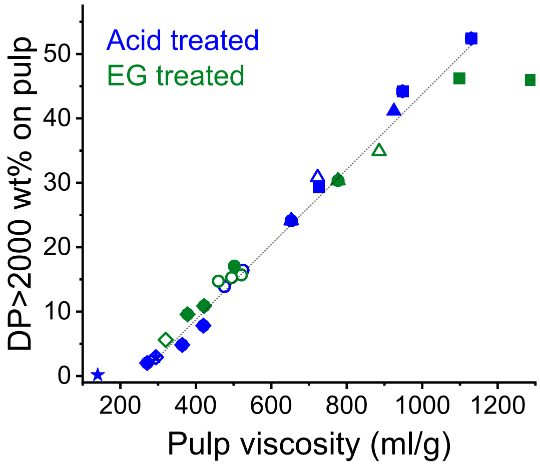

Figure S2: Relationship between the weight fraction of cellulose chains with a DP greater than 2000 and the intrinsic viscosity

3. Comprehensive data on the pulp properties and the corresponding rheological properties. spinning conditions and the resulting fibre properties.

Table S1. Summary table of dope rheological properties. spinning conditions and fibre mechanical properties. The spinning was carried out with 200 holes spinneret; 100 µm diameter; L/D = 0.2; extrusion velocity = 3.5 m/min; temperature of coagulation bath = 10°C.

Raw material	Pretreatment	Viscosity ml/g	Dope conc.	Zero shear viscosity Pa.s	COP	Moduli Pa	Spinning temp.	Max. DR	Titer dtex	draw ratio	Dry tenacity cN/tex	Dry tenacity STDV ±	Dry tenacity MPa	Dry elong. %	Dry elong. STDV ±	Wet tenacity cN/tex	Wet tenacity STDV ±	wet elong. %	Wet elong. STDV ±
Rayonier HV+	Ioncell-P + acid	1130	5 %	53627	0.06	759.5	Not spinnable	-											
Rayonier HV+	Ioncell-P + acid	1130	6 %	25630	0.13	781.0	Not spinnable	-											
Rayonier HV+	Ioncell-P + acid	1130	9 %	103220	0.06	1682.3	85	10	1.29	8	56.86	3.32	852.9	10.54	1.20	52.04	3.78	12.13	1.28
Rayonier HV+	Ioncell-P + acid	1130	10 %	81278	0.08	1651.0	80	9	1.15	9	59.16	2.78	887.4	10.98	0.84	52.26	4.47	12.32	1
Rayonier HV+	Ioncell-P + acid	948	11 %	117870	0.0762	2176.4	80	11	1.13	10	53.48	4.61	802.2	11.68	1.41	49.45	3.91	13.97	1.75
Rayonier HV+	Ioncell-P + acid	948	8 %	42484	0.12	1090.3	Not spinnable	-											
Rayonier HV+	Ioncell-P + acid	948	10 %	87564	0.13	2239.7	80	11	1.21	9	59.29	3.42	889.35	11.82	1.25	55.03	3.26	14.61	1.33
Rayonier HV+	Ioncell-P + acid	726	12 %	96062	0.13	2549.5	75	13	1.16	11	56.05	3.16	840.75	12.93	1.12	51.33	4.39	14.32	1.63
Rayonier HV+	Ioncell-P + acid	726	9 %	31670	0.25	1651.6	60	13	1.28	9	54.05	4.56	810.75	8.75	1.08	48.78	5.14	11.21	1.06
Rayonier HV+	Ioncell-P + acid	726	10 %	51334	0.00	2729.7	70	16	1.26	9	55.28	6.02	829.2	11.18	1.47	47.6	4.53	11.92	1.54
Rayonier HV+	Ioncell-P + EG	1288	9 %	82272	0.0696	1426.7	90	10	1.16	9	56.32	5.82	844.8	10.46	1.58	52.16	4.45	11.68	1.8
Rayonier HV+	Ioncell-P + EG	1288	10 %	184230	0.0364	2040.1	85	10	1.22	10	57.23	4.84	858.45	11.06	1.65	52.26	5.05	11.02	1.47
Rayonier HV+	Ioncell-P + EG	1098	9 %	78720	0.0853	1663.8	85	12	1.14	9	54.34	4.73	815.1	9.83	1.07	47.63	5.93	11.5	1.94
Rayonier HV+	Ioncell-P + EG	1098	10 %	90454	0.093	1887.7	85	14	1.12	10	55.75	5.8	836.25	11.03	1.76	51.04	4.9	12	1.92
Rayonier HV+	Ioncell-P + EG	886	11 %	54309	0.1615	1646.2	85	14	1.16	10	50.51	3.87	757.65	10.79	1.94	46.11	3.08	13.32	1.62
Rayonier HV+	Ioncell-P + EG	886	12 %	126890	0.0665	1803.4	85	12	1.17	11	51.43	3.70	771.45	11.94	1.47	47.73	5.87	13.2	1.42
Rayonier 92 mv	Ioncell-P + EG	777	12 %	115470	0.0792	1976.1	85	14	1.20	11	51.22	2.63	768.3	13.6	1.98	48.33	6.43	14.56	2.72
Rayonier 92 mv	Ioncell-P + EG	777	13 %	70674	0.1975	2409.7	90	15	1.21	12	52.26	2.82	783.9	13.56	1.54	51.71	6.02	13.37	2.55
Bracell	-	653	11 %	28363	0.60	2822.0	80	19	1.04	11	55.22	3.29	828.3	10.35	1.04	48.42	5	13.12	1.87
Bracell	-	653	13 %	65859	0.32	3692.7	80	17	1.11	12	55.64	4.69	834.6	11.84	1.84	50.24	3.99	12.63	1.89
Bracell	-	653	12 %	29817	0.68	3288.1	85	17	1.07	12	54.29	6.58	814.35	11.35	2.1	49.22	3.28	12.86	1.74
Bracell	acid	525	13 %	30864	0.85	4029.2	80	16	1.19	12	50.55	5.23	758.25	10.22	1.21	45.17	6.65	11.5	1.97
Bracell	acid	525	14 %	68560	0.40	4244.6	75	18	1.19	13	54.19	2.97	812.85	11.61	1.2	48.5	5.08	14.12	1.68
Bracell	acid	476	13 %	37553	0.68	4028.0	70	16	1.31	11	55.1	2.9	826.5	12.14	1.17	48.52	3.34	13.38	0.98
Bracell	acid	476	14 %	22833	1.25	4365.8	80	17	1.16	13	56.37	2.92	845.55	11.93	1.46	50.07	4.09	14.55	1.19

Bracell	acid	420	14 %	17496	1.68	4535.1	70	16	1.25	12	53.57	2.73	803.55	10.11	1.19	46.01	3.14	11	1.3
Bracell	acid	420	15 %	24703	1.38	5285.8	75	17	1.17	14	51.84	4.44	777.6	10.99	1.82	47.88	3.44	12.86	1.33
Bracell	acid	364	14 %	30899	0.80	4952.0	60	15	1.2	13	50.84	3.56	762.6	9.51	1.06	45.92	2.97	11.08	0.94
Bracell	acid	364	15 %	26000	1.24	5414.7	65	14	1.26	13	52.92	2.83	793.8	11.6	1.11	46.18	4.56	12.47	1.61
Bracell	acid	294	16 %	26812	1.69	4563.7	75	11	2.24	11	34.58	5.09	518.7	8.75	0.86	27.48	3.39	10.05	1.5
Bracell	acid	294	17 %	56246	0.80	4621.9	70	11	1.64	11	45.11	4.53	676.65	10.33	1.61	38.04	3.58	11.7	1.78
Bracell	acid	271	15 %	14833	2.01	5815.1	60	13	1.33	13	44.8	4.84	672	8.4	1.61	39.52	3.76	9.82	0.94
Bracell	acid	271	14 %	7428.7	4.61	5545.9	60	15	1.08	14	45.2	3.93	678	9.13	1.36	38.76	4.11	9.56	1.08
Bracell	acid	140	13 %	-	-	-	Not spinnable	-											
Bracell	acid	140	17 %	-	24.343	20140	45	4											
Bracell	acid	140	20 %	-	-	-	60	4											
Bracell	EG	521	13 %	33181	0.7574	2779.8	80	17	1.27	11	49.74	3.7	746.1	12.1	1.55	42.11	3.73	13.2	2.22
Bracell	EG	521	14 %	33048	0.774	3311.2	80	15	1.24	13	49.93	4.06	748.95	11.72	1.55	46.46	2.32	14.69	1.37
Bracell	EG	460	14 %	34393	0.64	3047.5	75	15	1.22	12	47.05	3.94	705.75	10.79	1.44	41.56	4.26	13.08	2.01
Bracell	EG	460	13 %	19294	1.34	3541.0	80	14	1.26	12	45.15	5.34	677.25	11.92	2.49	42.01	4.17	13.7	2.52
Bracell	EG+acid	495	13 %	21351	1.1552	3533.8	75	18	1.19	12	53.69	2.78	805.35	13.2	1.51	47.61	4.42	14.2	1.46
Bracell	EG+acid	495	14 %	38416	0.643	3402.4	80	20	1.17	13	51.71	4.75	775.65	10.57	1.57	47.12	5.35	12.51	1.76
Bracell	EG+acid	422	14 %	25288	1.014	3939.6	70	18	1.15	13	53.77	3.6	806.55	10.03	1.22	47.05	4.49	11.95	1.46
Bracell	EG+acid	422	15 %	37100	0.789	4604.1	75	20	1.36	12	51.69	4.66	775.35	11.46	2.04	46.11	4.6	13.29	1.77
Bracell	EG+acid	378	14 %	18608	1.3897	2938.3	75	16	1.26	12	49.27	3.39	739.05	11.88	1.59	42.16	4.92	13.76	2.22
Bracell	EG+acid	378	15 %	29678	1.0586	3415.8	80	16	1.22	13	47.05	4.36	705.75	11.67	1.49	40.3	3.74	12.54	1.17
Bracell	EG+acid	320	15 %	25638	1.33	4787.1	70	17	1.16	14	49.92	3.09	748.8	10.43	0.98	42.92	3.71	13.21	7.6
Bracell	EG+acid	320	16 %	45405	0.827	4215.1	75	19	1.24	14	48.51	4.85	727.65	10.72	1.81	41.84	3.5	11.93	1.93

4. **Selection of the pulp viscosity and dope concentration for optimum dope spinnability**

The optimum spinnability was found for pulps with viscosity of 550 (460 - 770) at 13 wt% pulp concentration and 430 mL/g (300 - 520) at 14 wt% pulp concentration as shown in Figure S3.

The associated rheological characteristics here are ω ranging from 0.7 rad/s (0.2 - 1.3) to 1.1 rad/s (0.4 - 2.5), the G'=G'' ranging from 3300 Pa (2400 - 4200) to 4000 Pa (2800 - 5500) and the complex viscosity η_0^* ranging from 36000 Pa.s (19000 - 70000) to 29000 Pa.s (12000 - 65000).

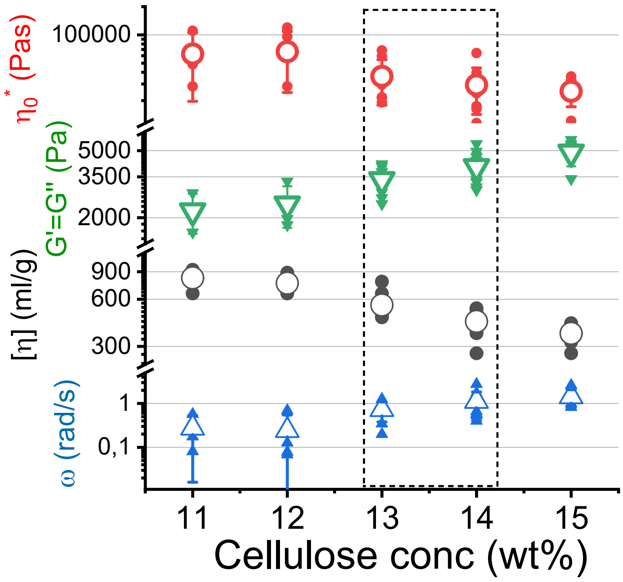

Figure S3: The pulp viscosity and the pulp concentration in the dope are related to the corresponding rheological properties of the spinning dopes. The optimum range of pulp concentration in the dope is between 13 and 14 wt%. which lead to the best spinning performances.

5. Fibre properties

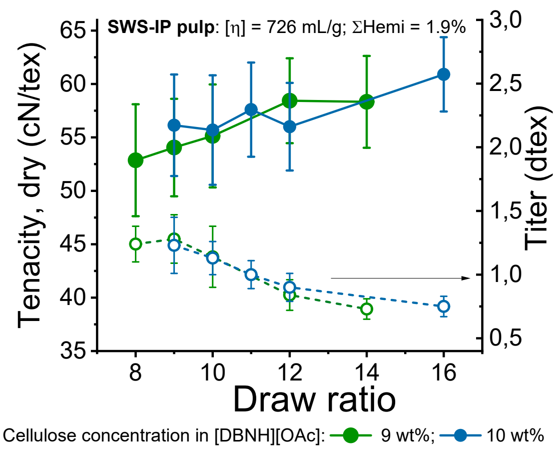

Figure S4. Conditioned fiber properties, tenacity, elongation and titer as a function of the draw ratio of a SWS-IP pulp with a viscosity of 726 mL/g. Spinning conditions: 10 wt% dope concentration, spinning temperature = 70°C; rheology at spinning temperature: $\eta_0^* = 51\ 334$ Pa.s; ω = 0.26 rad/s; G' = G'' = 2678 Pa; spinneret: 200 holes, 100 µm diameter, L/D = 0.2; extrusion velocity = 3.5 m/min, temperature of coagulation bath = 10°C.

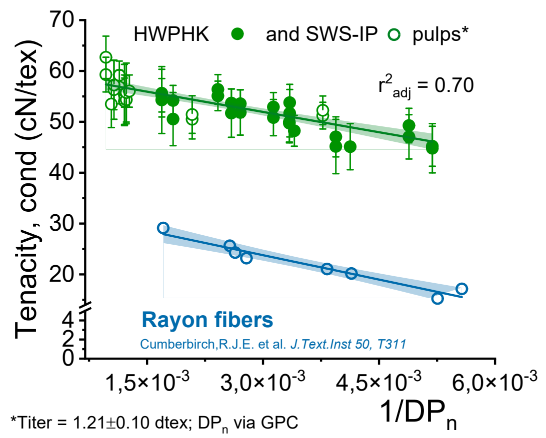

Figure S5: Conditioned tenacity of Ioncell fibers with titers of 1.21±0.10 dtex made from SWS-IP and HWPHK pulps and Rayon fibers published by Cumberbirch et al. as a function of the reciprocal DP_n [3].

6. Crystallite properties of the spun fibres

Table S2. Crystallite properties of the selected spun fibres

Sample	Viscosity ml/g	Titer dtex	HERMANS orientation function	Crystallinity	L1-10	L110	L020
Rayonier	1130	1.15	0.576	51.0	37.0	35.6	38.0
Rayonier	1098	1.12	0.738	54.9	42.2	35.7	35.7
Rayonier	886	1.16	0.763	56.1	40.7	36.1	35.1
Rayonier	777	1.21	0.73	57.4	42.1	35.1	38.1
Rayonier	726	1.16	0.646	51.0	40.0	34.8	31.1
Bracell	525	1.19	0.623	52.0	37.3	34.2	36.8
Bracell	521	1.24	0.801	54.8	39.4	35.0	36.1
Bracell	476	1.31	0.522	49.0	39.7	37.2	37.9
Bracell	460	1.22	0.779	55.9	39.5	35.4	37.8
Bracell	422	1.36	0.800	56.6	40.4	36.3	37.6
Bracell	420	1.17	0.631	52.7	32.9	34.0	29.4
Bracell	320	1.16	0.785	56.5	41.5	36.4	39.0
Bracell	271	1.08	0.763	53.6	39.0	34.8	36.4

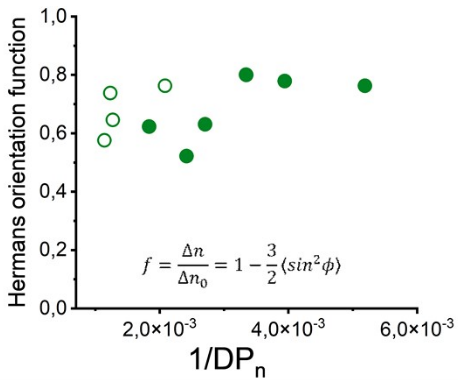

Figure S6. Hermans orientation function of the Ioncell fibers made from SWS-IP (open circles) and HWPHK pulps (full circles) as a function of the DPn.

7. References

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3 R. J. E. Cumberbirch and W. G. Harland, *J Text Inst Trans*, 1959, **50**, T311–T334.