Electronic Supplementary Information

Studies on staged precipitation of cellulose from ionic liquid by compressed carbon dioxide

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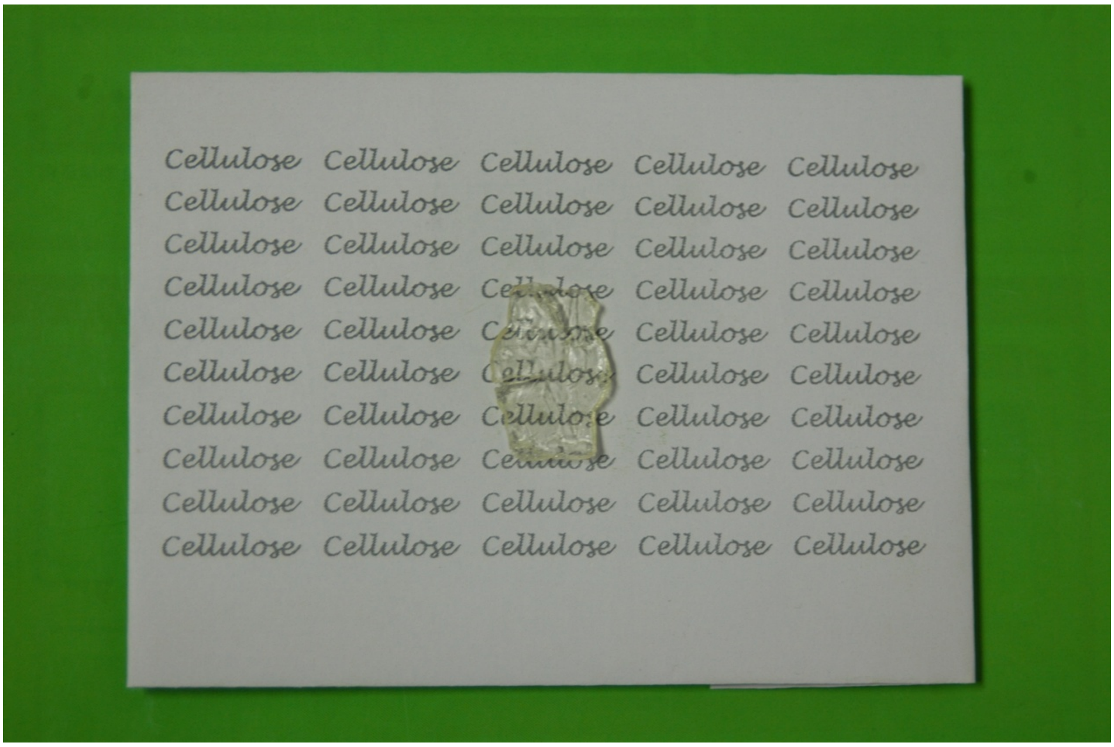

Fig. S1 Picture illustrating the transparent regenerated cellulose obtained from 10 wt% MCC/[Bmim]OAc solution by adding compressed CO_2 (25°C, 6.60 MPa) for 1 h.

Table S1. The yield and DP value of the regenerated cellulose from [Bmim]OAc/MCC (10 wt%) and [Bmim]OAc/co-solvent (1:1(w/w))/MCC (10 wt%) by using compressed CO_2 (6.6 MPa, 25 °C).

Entry.	Co-solvent	Reaction time	Yield / %	DP value
1	--	1	17.1	217
2	--	2	34.5	208
3	--	3	58.2	202
4	--	4	58.7	203
5	DMSO	1	37.0	206
6	DMSO	2	63.3	175
7	DMSO	3	63.7	173
8	DMSO	4	64.1	170
9	DMI	1	35.1	206
10	DMI	2	62.7	178
11	DMI	3	62.9	177
12	DMI	4	63.3	174
13	DMF	1	33.7	210
14	DMF	2	61.0	188
15	DMF	3	61.3	185
16	DMF	4	61.7	180

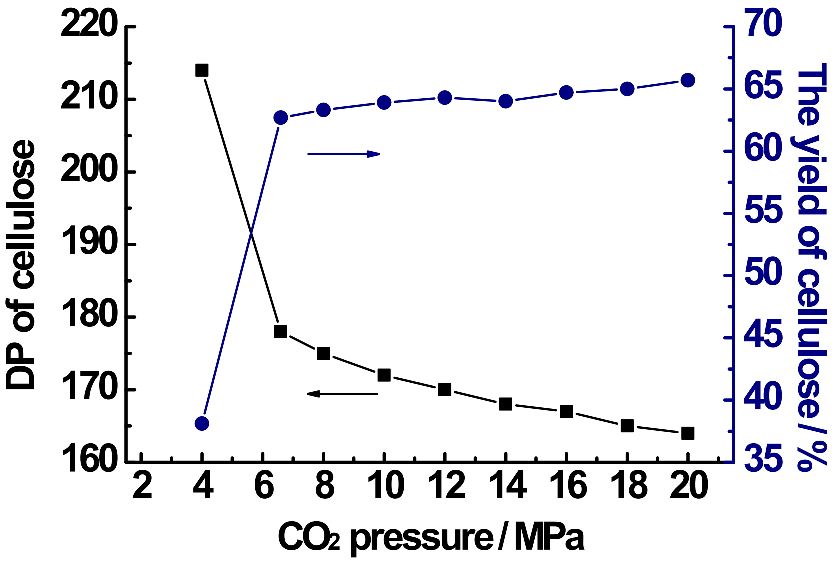

Fig. S2 The DP value and yield of the regenerated cellulose obtained from the system of [Bmim]OAc/DMI (1:1(w/w))/MCC (10 wt%) by using compressed CO_2 during a 2 h anti-solvent reaction under different pressure at 25°C.

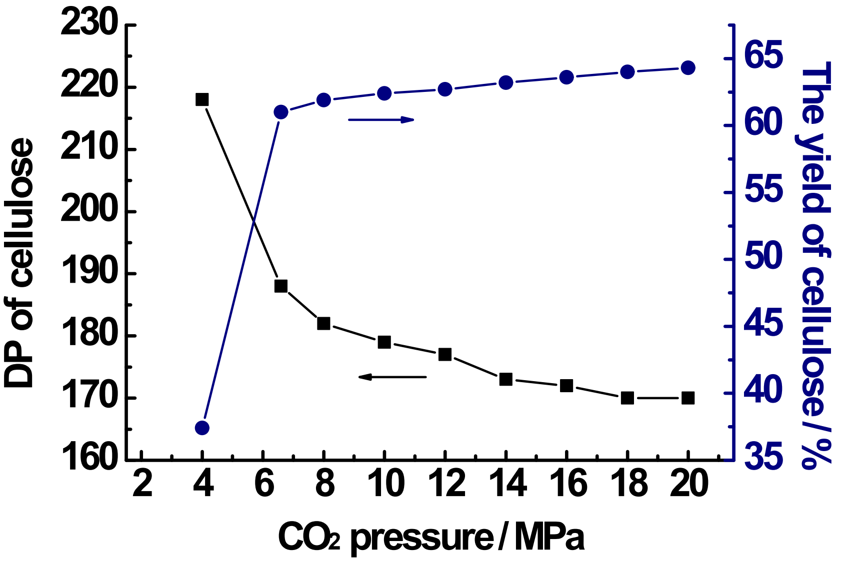

Fig. S3 The DP value and yield of the regenerated cellulose obtained from the system of [Bmim]OAc/DMF (1:1(w/w))/MCC (10 wt%) by using compressed CO_2 during a 2 h anti-solvent reaction under different pressure at 25°C.

Energy consumption comparison of methods with different anti-solvents

For the cost-efficient production, the desired bio-refinery process may demand minimal energy consumption and compatible with continuous mode. In this work, by compressing and depressurizing CO_2, the cellulose can be regenerated and the CO_2 can be utilized circularly as well. Then, we give an approximate estimation on the energy consumption for comparing the methods by using compressed CO_2 and ethanol as anti-solvent. Let's take the system of 1 g [Bmim]OAc with 0.1 g MCC (10 wt%) as an example. We point it again that this is only an approximation.

For compressed CO_2, we estimated the compression energy under the condition of 6.63 MPa at 25 °C. After finishing CO_2 loading, the system had a weight gain of 1.0352 g. In order to achieve the cellulose separation, we needed to compress 1.0352 g CO_2 (0.0235 mol) from 0.1 MPa to 6.63 MPa at 25 °C. The energy can be approximately calculated using the eqn:

$$W = -\int_{V_1}^{V_2} p_e dV = nRT\int_{V_2}^{V_1} \frac{1}{V} dV = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{p_2}{p_1}$$

which needs 244.6 J. Considering the extraction yield of 58.2 % after 3 h under this condition, 0.0582 g regenerated cellulose can be obtained. We can conclude that if we want to acquire 1 g regenerated cellulose by precipitation using 6.63 MPa compressed CO_2at 25 °C, the energy of 4202.7 J might be consumed.

On the other hand, ethanol need be added 4 times as that of the volume of the IL, if cellulose was regenerated from the above system by anti-solvent ethanol completely. According to our measurement, the density of [Bmim]OAc and ethanol are 1.0488 g/mL and 0.7890 g/mL at 25 °C, respectively. It suggests that adding 3.009 g ethanol (0.0653 mol) was necessary. The enthalpy of vaporization of ethanol is 4.25×10^4 J/mol at 25 °C. So if we remove ethanol from IL after extracting, the energy of 2775.3 J is consumed under this condition. In the meantime, through the extraction yield of 90.3 %, we can figure out the energy of 30734.2 J might be consumed when we obtain 1 g regenerated cellulose using ethanol as anti-solvent at 25 °C. It is over 7 times than that of using CO_2, so we can conclude that using compressed CO_2 is more energy-efficient than using conventional high boiling-point solvents.

Although the method to estimate the energy consumption of the two processes is very approximate, the over 7 times energy consumption can still demonstrate that the compressed CO_2 anti-solvent process is more energy saving compared with the ethanol anti-solvent process. Since there are much less energy consumption, they can bring more benefits after covering the fixed costs required in compressed CO_2 anti-solvent process. So we can deem this process as energy-efficient.