

FTIR and Autofluorescence spectroscopy to understand and predict properties of dilute acid pretreated poplar

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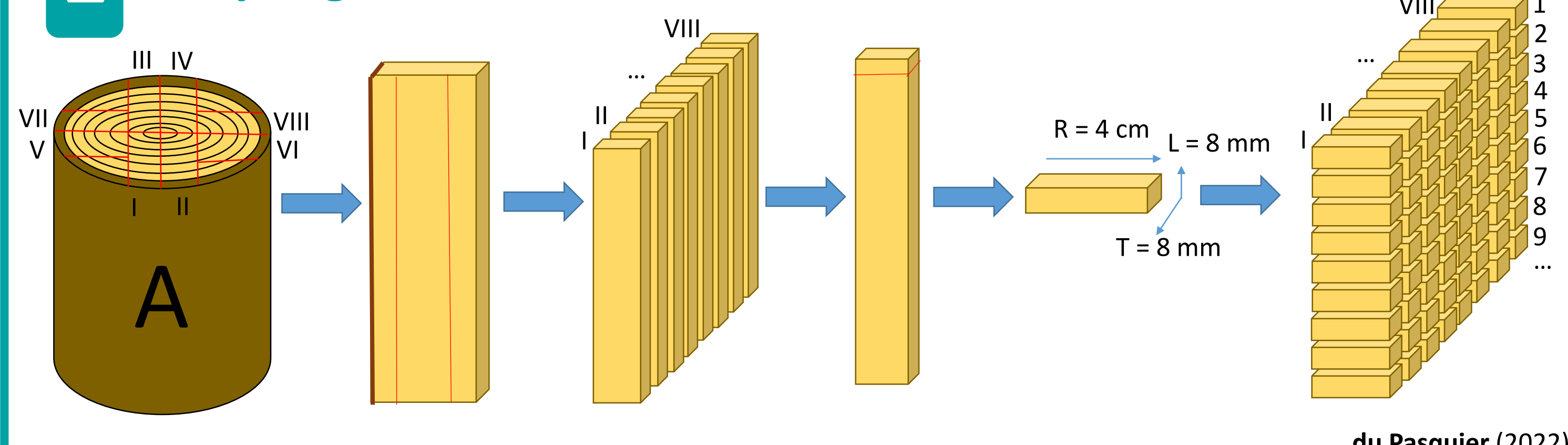
INTRODUCTION

The transformation of lignocellulosic biomass (LB) into chemicals, materials and biofuels is in full development [1]. The difficulty in valuing this LB lies in its chemical and physical complexity, with cellulose, hemicelluloses and lignin forming a complex 3D network [2]. In order to facilitate the accessibility, progression and action of the catalysts (notably enzymes) in the LB matrix, a physico-chemical pretreatment step of the LB is necessary [3]. Given the high cost of pretreatment, it is critical to understand and predict its multiscale effects.

Here, a set of dilute acid pretreatment experiments on poplar wood was designed, aiming to cover a wide range of conditions related to time, temperature and acid concentration and generating no less than 32 different samples. Each sample was characterized for its chemical composition and spectral properties by FTIR and autofluorescence spectroscopy. The measurement of autofluorescence intensity indicates how the lignin environment, which is known as a barrier to enzymes accessibility and thus activity, is altered. The FTIR spectral analysis shows the evolution of specific absorption bands, in particular those linked to hemicelluloses which are mostly degraded during the pretreatment.

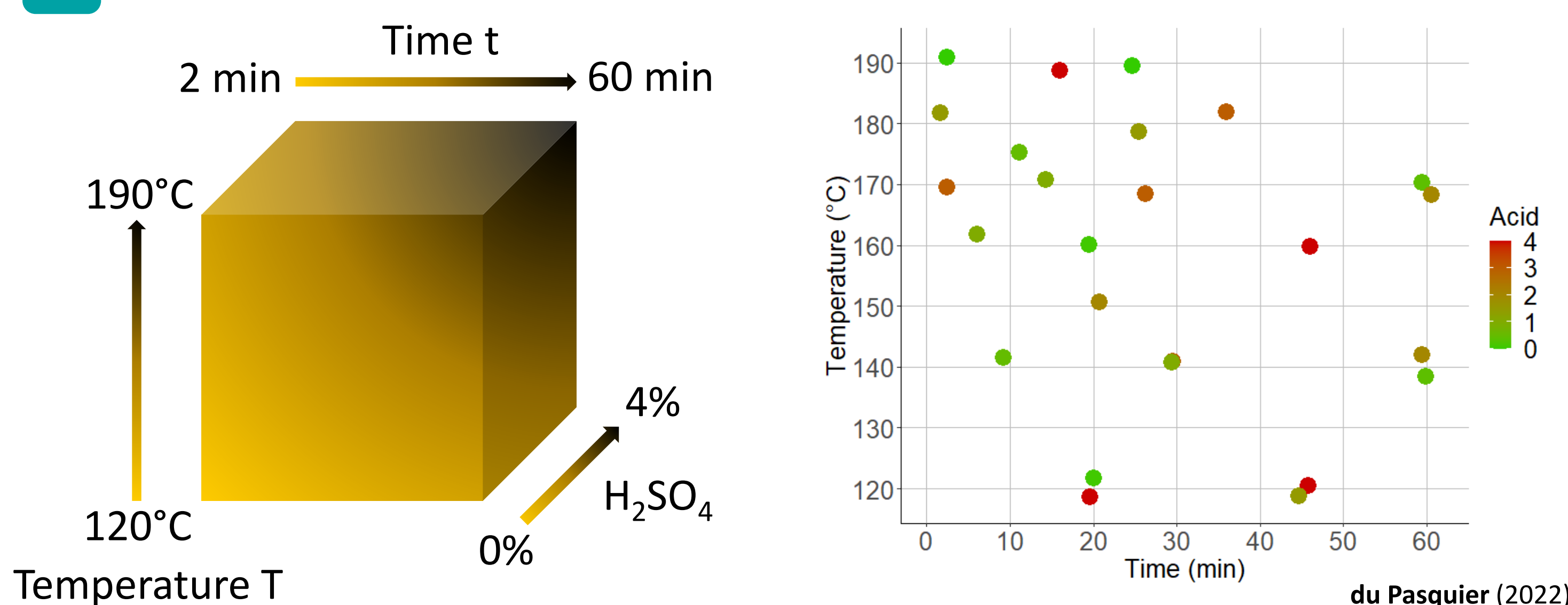
MATERIAL AND METHODS

1 Sampling



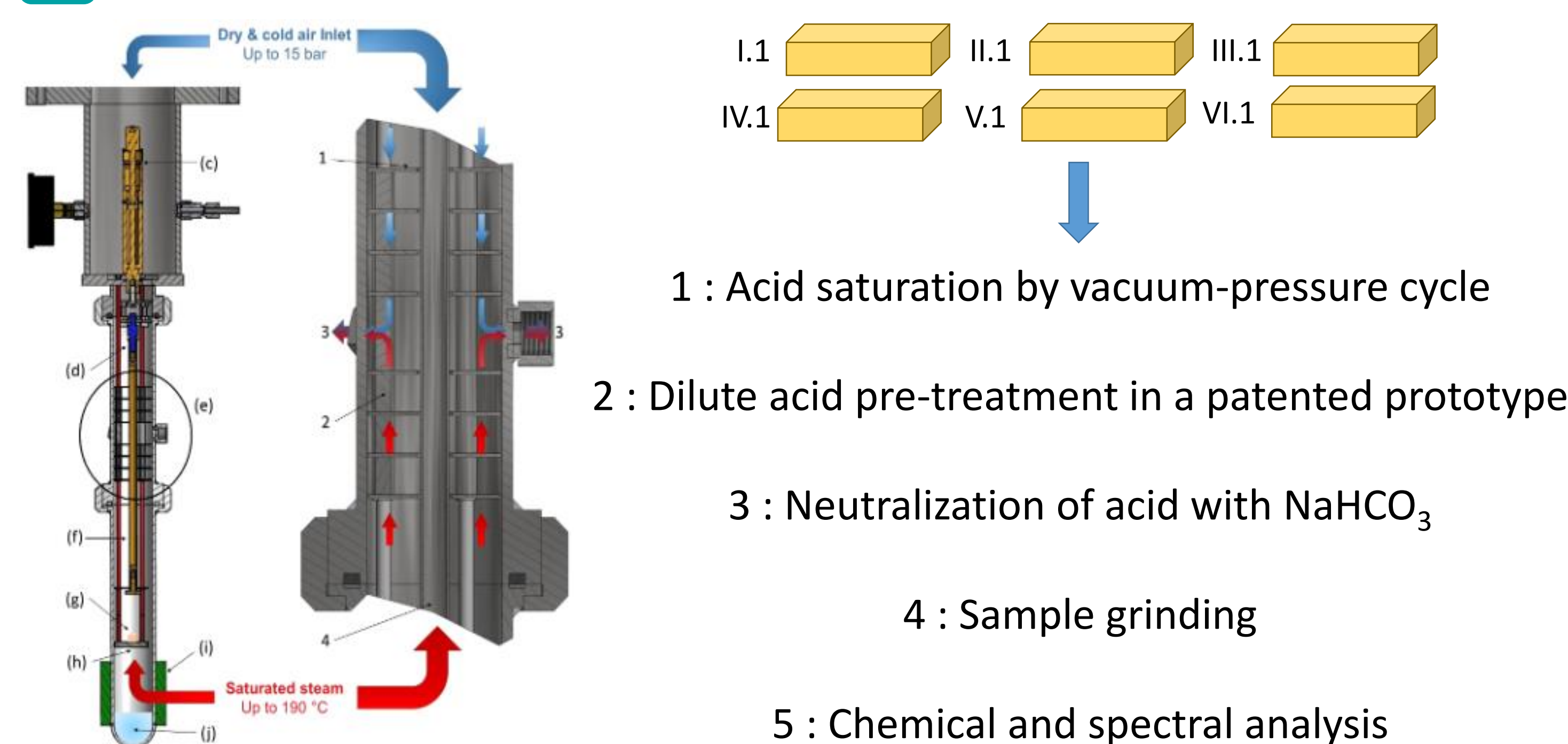
- Raw material (RM) : poplar block approximately 30 cm high (A)
- Traceability of each bar: Block.Plank.Bar (Ex : A.I.1, C.IV.3)
- Low material variability in the longitudinal dimension

2 Experimental Design



- Severity factor (SF) is determined from time, temperature and acid level conditions
- Definition of 25 pretreatment conditions with their associated SF from 0 to 4
- Avoid conditions when time and temperature are simultaneously very high or low
- Add 7 conditions with different acid levels (0.86% to 6.84%)

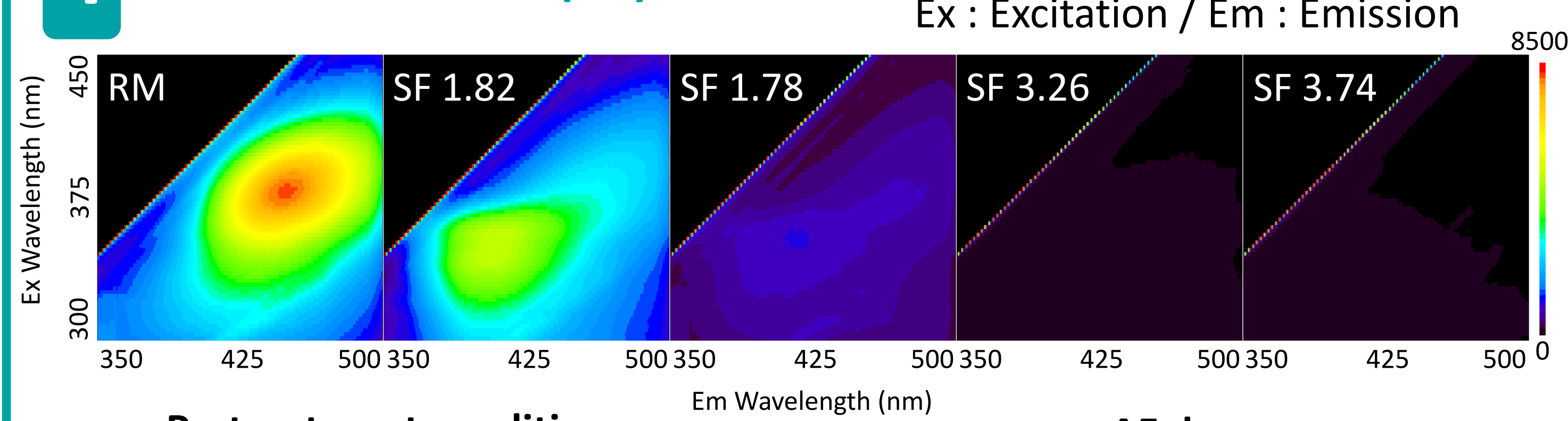
3 Dilute acid pretreatment



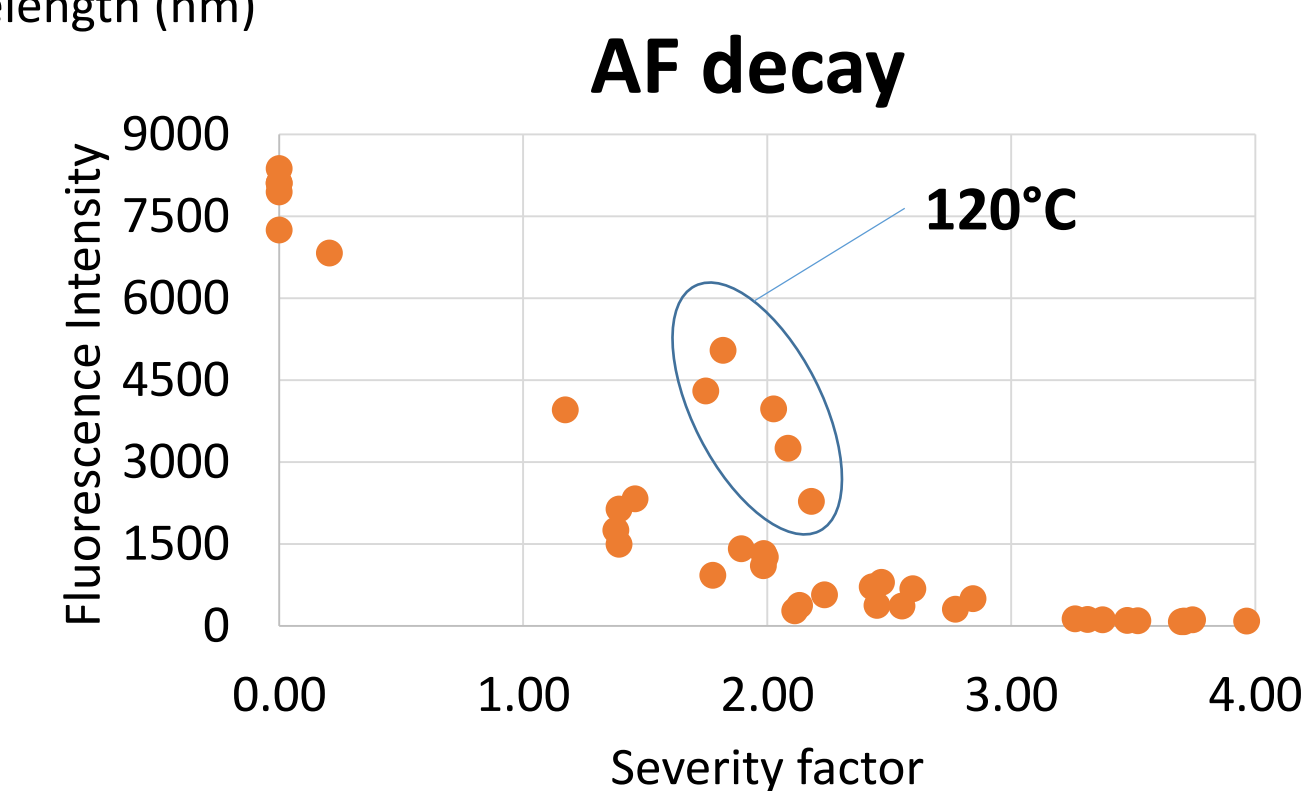
Parlatore Lancha et al., Bioresour Technol (2021) 341:11

RESULTS

4 Autofluorescence (AF)

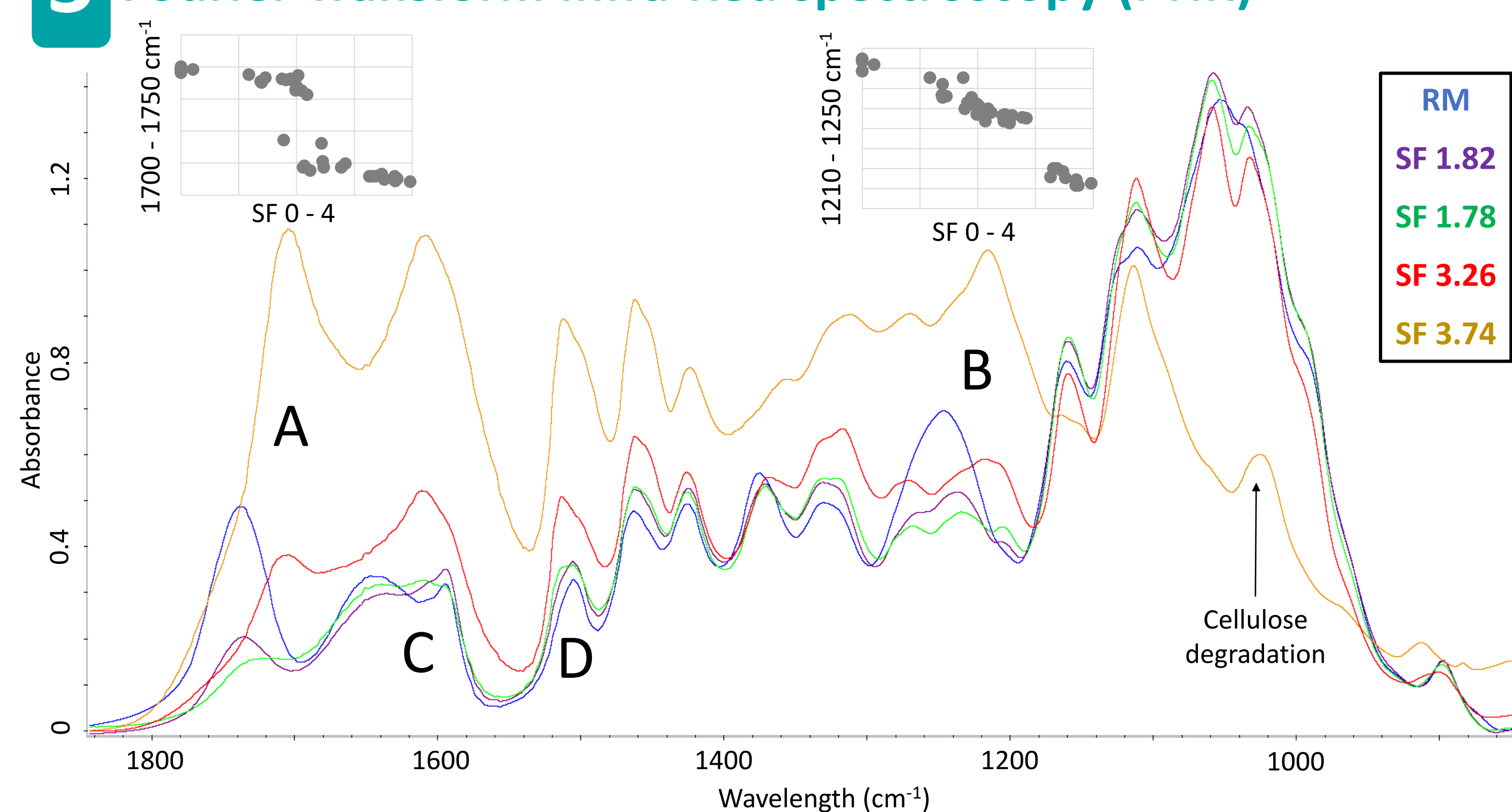


Pretreatment conditions			
SF	t (min)	T (°C)	H ₂ SO ₄ (%wt)
RM	/	/	/
1.82	20	120	4.0
1.78	5	160	2.0
3.26	25.2	180	1.5
3.74	15	190	4.0



- Immediate peak shift from 378 nm Ex / 450 nm Em (SF 0.21) to 353 nm Ex / 417 nm Em (SF 1.17), then peak intensity decreases but peak position remains very stable at higher SF.
- Difference in lignin modifications between 120°C and higher temperatures, which implies that close SF conditions can give different results.

5 Fourier Transform Infra-Red spectroscopy (FTIR)



- 1730 cm⁻¹ (A) : absorbance decrease on 1740-1730 cm⁻¹ (SF 0 – 2), wavelength shift from 1730 to 1710 cm⁻¹ (SF 2), absorbance increase until 1705 cm⁻¹ (SF 3 – 4).
- 1230 cm⁻¹ (B) : similar observation with a shift from 1230 to 1220 cm⁻¹ (SF 3).
- The SF of 1730 shift coincides with a complete degradation of hemicelluloses, and SF of 1230 shift coincides with a rapid degradation of cellulose.
- Other shifts followed by an increase in absorbance at 1600 cm⁻¹ (C) and 1510 cm⁻¹ (D), which may represent the increase and S/G modification of lignin content.

REFERENCES

- [1] Beig et al., Fuel (2021) 287:18
- [2] Pu et al., Biotechnol Biofuels (2013) 6:13
- [3] Mankar et al., Bioresour Technol (2021) 334:12

CONCLUSION

- AF shows a very rapid decrease in lignin intensity with increasing SF, while FTIR shows an increase in absorbance of the corresponding peaks. It is therefore not a loss of lignin which is observed, but one or more modifications of its conformation which annihilates its autofluorescence and increases its IR absorbance (S/G ratio, recondensation...).
- FTIR seems to be able to describe the degradation of polysaccharides and the modification in lignin content, with changes in absorbance and wavelength at the same level of severity as the chemical changes. Other analysis will have to be carried out to establish correlations between these different indicators.
- Variable results are obtained on samples treated at close SF: this indicator is therefore not very precise in describing the state of the biomass.