



Structural changes of *Salix miyabeana* cellulose fibres during dilute-acid steam explosion: Impact of reaction temperature and retention time



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ABSTRACT

Dilute-acid steam explosion of *Salix miyabeana* has been carried out to understand the effect of processing conditions, expressed through a severity factors (SFT), on the changes in cellulose fibre structures in a perspective of using these in polymer composites. This thermo-chemico-mechanical extraction leads to the isolation of cellulose fibres as observed by SEM images. Fibre length as well as length to diameter aspect ratios decreased with the severity of the treatment. Likewise, fibre whiteness diminished with an increasing severity factor, which could be a tangible effect of physical degradation. Variations in crystallinity seemed to be dependent upon the reaction temperature, generally decreasing with regards to retention time. Above a severity threshold, a structural disorganization was observed. Overall, dilute-acid steam explosion was shown to be a valuable cellulose extraction process that can provide a variety of fibre structures.

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1. Introduction

Cellulose fibres are generally produced from lignocellulosic feedstock (wood, straw, grass, etc.) and they can be extracted and/or purified depending on the final targeted application. Beside its large and well-known use in the pulp and paper industries, cellulose is increasingly being considered as a potential feedstock for biofuel production, implying its hydrolysis to glucose and fermentation to “cellulosic” ethanol (Beauchet et al., 2013). However, the crystalline fraction of the cellulose is the most resistant to acid-hydrolysis and thus may be found as a post-treatment residue. In the current work, in an effort to minimize chemical and energy requirements, it is envisioned that fermentable sugars could be produced out of the easily hydrolysable amorphous cellulose fractions. The crystalline residues could then be used in a second step as natural fibre reinforcement for polymer composites.

Various standard pulping methods are available at an industrial level including but not limited to mechanical, thermo-mechanical, chemical and chemico-mechanical pulping. Recent studies by Liu, Ju, Li, and Jiang (2014) and Wang, Li, Cao, and Tang (2011) investigated the use of ionic liquid extraction of cellulose from various

sources and showed that up to 62% cellulose extraction could be obtained using these green solvents, which in addition can be recycled.

Among the less common techniques, steam processes as steam explosion, which were first introduced in 1926 by Mason (1926) is getting increasing attention in the field of biofuels. The technique is more challenging to scale to an industrial level than classical pulping process although it allows efficient separation of the different constitutive fraction of biomass (Lavoie, Capek-Menard, Gauvin, & Chornet, 2010). The process involves cooking water-impregnated lignocellulosic biomass under pressure at temperatures in the range of 160–260 °C. After a few minutes of reaction, the content is rapidly purged out of the pressurized vessel and undergoes a rapid decompression or “explosion”. The process is environmentally friendly due to the low acid concentration and no organic solvents.

The hydrolytic power of the steam processes is often assessed through a severity factor, which is a valuable tool used to quantify the intensity of the hydrolytic conditions of the steam treatments. When using an acid catalyst, the role of the pH in the reaction is combined to the other hydrolytic parameters (temperature and residence time) generating a combined severity factor (Chum, Johnson, Black, & Overend, 1990). The versatility of the severity factor has been demonstrated by adapting it to lignin removal for a wide array of biomass and conversion processes including steam processes (Lee & Lavoie, 2013). Compared to other pre-treatment

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technologies, steam-explosion presents several advantages particularly for the biorefineries. These advantages are summarized in the work of Garrot, Domínguez, and Parajó (1999). They noted the high hemicellulose yield with by-products showing little degradation and disruption of the solid residues from bundles to individual fibres that occur during the explosion effect. Steam-explosion is generally performed without addition of any chemicals. When a dilute-acid (i.e. with acid concentration ranging between 1 and 5%) is used as a catalyst, it increases the hydrolysis rate of hemicellulose and thus further improves the process.

Many investigations reporting on the steam processes focused on the extractability of cellulose as a source for high yield fermentable sugars (Brownell, Yu, & Saddler, 1986; Mosier et al., 2005). However, fewer researchers considered the impact of the steam-process on the fibre structure and properties when used for other purposes as in pharmaceutical, biocomposites and biomaterials. The use of steam processes on lignocellulosic materials can lead to significant changes in their structure and properties, such as reduction of the fibre length, fibre degradation and modification of the crystalline structure. This process should be better optimized to better understand the parameter for the production of high quality natural fibres.

The utilization of natural fibres as reinforcing fillers for polymer composites has previously been investigated in the open literature. As an example, Petinakis, Yu, Simon, and Dean (2003) reviewed that using natural fibres compared with other reinforcing agents such as glass fibres, talc or carbon fibres for improving the performance of biodegradable polymers include the retention of the biodegradability of the composite, but generally also exhibit lower density, superior performance, and lower cost due to the abundance of cellulose fibres.

Han and Choi (2010) explained the role of surface areas especially with regards to the different mechanical properties of reinforced biocomposites. They showed as well that the surface morphology of cellulose fibres is a significant factor to consider for the composite interfacial adhesion. Other important fibre specifications include fibre strength, length to diameter ratio and surface area.

In this work, the physical modifications induced by a dilute-acid steam explosion treatment on *Salix miyabeana* (willow tree) cellulose fibres were investigated. In particular, the objective of the work was to determine how dilute-acid steam-explosion process modifies the fibre length, whiteness, thermal stability, crystallinity and degree of polymerization of cellulose. These results were correlated with the steam process conditions via the combined severity factor. The resulting equations generated from simple linear regressions allow an estimation of the properties of the cellulose fibres at a known severity factor. In addition, the dimensions of extracted fibres were compared with those of the existing commercial microcrystalline cellulose. The potential use of dilute-acid steam-explosion as a new route for microcrystalline cellulose isolation from biomass residues is discussed.

2. Materials and methods

2.1. Material

Salix miyabeana residues obtained from Le Saule Magique Inc. (Laval, Québec, Canada) were used as feedstock. Biomass was processed using an 800 g pilot-scale steam gun, which was extensively described by Beauchet et al. (2013), Lavoie et al. (2010) and Lavoie and Beauchet (2012). Sulfuric acid 98% and sodium chlorite (technical grade nominally 80%) were bought from Anachemia Canada Inc. Acetic acid glacial (99.8%) was purchased from VWR International LLC. All reagents were used as received.

2.2. Method

2.2.1. Steam explosion treatment

Prior to steam processes, the feedstock was grinded and screened to an average size of two (2) cm. The severity factor of the steam treatment was determined using an empirical equation developed by Overend and Chornet (1987), which correlates temperature and residence time:

$$\log(R_0) = \log[t \times e^{(T-T_{\text{ref}})/14.75}] \quad (1)$$

where $\log(R_0)$ is the severity factor, t is the residence time (min), T is the reaction temperature ($^{\circ}\text{C}$), T_{ref} is the reference temperature arbitrarily settled at 100°C assuming that the hydrolytic effect of water on cellulosic material is negligible below this temperature.

By including the effect of the pH on the reaction, Eq. (1) was further adapted to the experimental conditions for the determination of the combined severity factor (SFT), under an acidic catalysts (Chum et al., 1990):

$$\text{SFT} = \log(R_0) - \text{pH} \quad (2)$$

with $\log(R_0)$ obtained from Eq. (1).

Screened woodchips (200 g, dry basis) were initially impregnated in a solution of 3% (wt.%) sulphuric acid (ratio solid to liquid 1:10, m/v) for 10 min after which they were dewatered with a filter press. The acid concentration was fixed to 3% (wt.%) following preliminary investigation on the feedstock (not published). The acidic-wet biomass was then cooked in the steam gun at three different temperatures (190, 205 and 220°C), which were maintained for a residence time arbitrarily fixed at 3, 5 and 10 min respectively. Following steam treatment, the resulting lignocellulosic material was washed using hot water and press filtered until neutral pH was attained. A laboratory filter press was used for dewatering the wet biomass after treatment. By applying a controlled pressure of 0.7 MPa, the water content was reduced to the minimum in order to facilitate the drying process. Fibres were then dried at room temperature in a convection oven for 72 h. The experimental uncertainty on the process temperature was around 2°C . For the concentration measurement and residence time, the relative uncertainty is below 0.5%. Based on the above, the overall uncertainty on the calculated SFT was less than 1%.

2.2.2. Fibre delignification and bleaching

Following the steam explosion treatment, *Salix miyabeana* cellulose fibres were bleached using a slight modification of the chlorine dioxide method employed by Kumar, Mago, Balan, and Wyman (2009). Bleaching was performed during six hours at 75°C , using distilled water (ratio solid to liquid 1:20 wt/v) sodium chlorite (0.6 g/g of dry matter) and acetic acid (0.2 ml/g of dry matter). The reaction was done in three stages of two hours in which an equal amount of sodium chlorite and acetic acid were added to the medium. Fibres were then repeatedly washed with hot and distilled water and dried at room temperature in an air-circulating oven for 72 h and then kept in a sealed plastic bag until analysis.

2.2.3. Fibres characterization

2.2.3.1. Fibre quality analysis. Length of the cellulose fibres as well as diameter and length to diameter aspect ratios were determined using a Fibre Quality Analyzer (FQA) (Optest Hires model, Hawkesbury, Canada).

2.2.3.2. X-ray diffraction analysis (XRD). The X-ray diffraction patterns were obtained using a Philips X'Pert diffractometer using copper radiation K_{α} ($\lambda = 1.5418 \text{ \AA}$), a voltage of 40 kV and an operation current of 50 mA. All scans were performed from $2\theta = 5^{\circ}$ to $2\theta = 40^{\circ}$. MDI Jade 10 software packages were used for pattern processing as well as for calculation of the degree of crystallinity

(DC). The degree of crystallinity was calculated using the height ratios between the intensity of the crystalline peak ($I_{002} - I_{Am}$) and total intensity (I_{002}) after subtraction of the background signal measured without cellulose as also previously reported by Park, Baker, Himmel, Parilla, and Johnson (2010).

The I_{002} intensity of the crystalline peak was taken at $2\theta = 27^\circ$ and I_{Am} is the intensity of the amorphous phase at $2\theta = 18^\circ$.

2.2.3.3. Scanning electron microscopy (SEM). The microstructure of the fibres was observed using a Hitachi scanning electron microscope model S-3000N (Hitachi High-Technologies Corporation, Japan) equipped with a tungsten hairpin filament, under different magnifications. Prior to analysis, the surface of the cellulose fibres was sputter-coated with gold/platinum using a vacuum plasma spray and argon as inert gas. The images were taken at an accelerating voltage of 10 kV.

2.2.3.4. Thermogravimetric analysis (TGA). Thermal properties of the different samples were measured using a SETSYS TG-DTA/DSC 24 Thermal Analyser with a mass spectrometer (Setaram Instrumentation, Canada). A known weight of each sample that was previously dried at 60°C for 24 h was taken into silica crucible for analysis. The mass loss analyses were performed using argon as a purge gas, with a furnace flow of 20 ml/min and a temperature profile of $10^\circ\text{C}/\text{min}$. The normalized mass loss was plotted as differential thermogravimetric curves from 30 to 600°C .

2.2.3.5. Optical properties. The steam-treated bleached fibres were submitted to Technibrite Micro TB-1C reflectometer for optical analysis. Difference in CIE L^* , a^* , b^* color coordinates and whiteness index, expressed in percentage were measured according to the TAPPI T 452 om-98 method.

2.2.3.6. Degree of polymerization. Degree of polymerization was obtained following a method reported by Ibrahim, Agblevor, and El-Zawawy (2010). Bleached steam-exploded fibres (0.06 g) were wetted in 7.5 mL distilled water and stirred during 2 min after what 22.5 mL of 1 M cupri-ethylenediamine (CED) (copper concentration 0.98–1.02 M, Anachemia Canada Co.) solution was added (H_2O : CED ratio of 1:3 (v:v)). The solution, protected from light and oxygen, was agitated during 2 h until complete dissolution of the cellulose was reached. A Cannon-Fenske viscometer N# 75 was used to measure the flow time of the CED-cellulose solution that was used to calculate the intrinsic viscosity $[\eta]$ according to the equation of Solomon-Gatesman:

$$[\eta] = \frac{(2 \times (\eta_{sp} - \ln(\eta_{rel})))^{0.5}}{C} \quad (3)$$

with η_{sp} , specific viscosity; η_{rel} , relative viscosity and C, solution concentration.

The degree of polymerization DP was calculated using the following equation proposed by Evans and Wallis (1989):

$$\text{DP}^{0.9} = [\eta] \times 1.65 \quad (4)$$

Finally, the average number of chain scissions (CS) per cellulose chain unit during the time course of degradation was calculated using the equation:

$$\text{CS} = \left(\frac{\text{DP}_0}{\text{DP}} \right)^{-1} \quad (5)$$

where DP_0 is the degree of polymerization before scission. In the present work, the DP obtained at lower severity factor (SFT = 2.88) was taken as the reference DP_0 for CS calculation.

3. Results and discussion

3.1. Crystallinity and optical properties

Table 1 presents a summary of the steam explosion process conditions and severity factor as well as key structural features of the treated cellulose: optical properties, and degree of crystallinity. The reaction temperature was varied between 190 and 220°C while the residence time was varied from 3 to 10 min. The sulfuric acid content was kept constant at 3 wt.%. These conditions allowed calculating severity factor ranging from 2.88 to 4.29 for the different samples. The fibres, recovered after the steam explosion treatment, were highly crystalline with degrees of crystallinity superior to 85% (determined by X-ray analysis). It is noteworthy that no detectable amount of lignin or hemicellulose was present in the samples. The crystallinity was relatively constant although a slight decrease was observed for higher severity factors. X-ray diffraction patterns (not shown) showed that type I crystalline cellulose was present in all treated samples showing characteristics peaks at 2θ of 14.9° , 16.3° , 22.5° and 34.6° which were assigned to the 101, $1\bar{0}1$, 002 and 040 crystallographic planes respectively.

Similar observations were made by Wang, Jiang, Xu, and Sun (2009), when working with *Lepedeza crybototrya* species steam exploded for a fixed retention time of 4 min. Nonetheless, other reports aiming at the crystallinity of cellulose after steam process operated on longer periods mentioned that the crystallinity at one point seemed to be increasing proportionally to the severity factor (Ibrahim et al., 2010; Wang & Chen, 2013). Both observations can be logically correlated to the chemical hydrolysis occurring during steam processes. The severity of the latter being amplified by the dilute acid catalyst led to a more crystalline material with the attack and the dissolution of part of the amorphous regions.

Kang, Bansal, and Realff (2013) on the other hand, when using SO_2 as catalyst observed the same reduction of the fibre crystallinity when more severe treatment was employed. From this, they managed to determine a severity threshold above which a decrease of the crystallinity was perceived during steam treatments. This threshold although not localized in our work could possibly explain the crystallinity reduction after a certain severity value was reached. In that case, according to the reduction of the crystallinity noticed, it seem that the fibres degradation at higher treatment severity was not limited to the cellulose wall, but also could in a lesser extent affect the internal fibre crystalline organization.

On the other hand, when considering the percent crystallinity discussed in our work, higher crystalline values were noticed compared to those of microcrystalline cellulose investigated by other authors. As an example, Leppänen et al. (2009) when comparing micro cellulose from different sources, revealed a crystallinity of 59% for commercial Avicel and 65% for microcrystalline cellulose obtained from cotton linter.

The optical properties were characterized using the CIE-LAB color coordinates data where L^* (lightness), represents the reflectance in the mid-range of visible spectrum, a^* measures the redness (negative value) versus greenness (positive values) of the material and b^* corresponds to the measure of the color space going from yellowness (positive value) to blueness (negative value). The variations of those optical parameters for each of the willow cellulose samples are as well provided in Table 1. The latter shows that increasing the severity of the steam treatment leads to a decrease of fibre lightness while the yellowness increased accompanied by a color change from red to green. Fig. 1 represents the changes of the bleached cellulose fibres as a function of the temperature and residence time.

Temperature, in the investigated range, had a stronger effect of fibre discoloration than residence time. As an example of the

Table 1Steam explosion conditions, severity factor, degree of crystallinity, and optical properties of bleached steam exploded *Salix miyabeana* cellulose fibres.

#	Temperature (°C)	Retention time (min)	H ₂ SO ₄ (wt.%) ^a	Severity factor ^b	Degree of crystallinity (%)	Optical properties		
						L*	a*	b*
A	190	3	3	2.88	88.6 ± 0.7	92.7	−0.51	7.82
B	190	5	3	3.1	90.6 ± 0.8	93.25	−1.11	7.75
C	190	10	3	3.4	85.2 ± 0.7	90.05	−1.02	10.56
D	205	3	3	3.32	87.1 ± 0.6	91.94	−0.93	8.85
E	205	5	3	3.55	87.4 ± 0.7	86.75	−0.02	13.31
F	205	10	3	3.85	85.7 ± 0.6	69.86	2.18	22.82
G	220	3	3	3.77	88.2 ± 0.6	80.11	1.17	18.99
H	220	5	3	3.99	85.5 ± 0.7	73.23	1.8	17.95
I	220	10	3	4.29	85.3 ± 0.6	42.62	5.78	20.61

^a H₂SO₄ concentration corresponding to a pH of 0.24.^b Combined severity factor calculated according to Eq. (1).

correlation between appearance of the pulp and severity factor, samples C and D, which were treated at similar severity factor of respectively 3.4 and 3.32 shows similar discoloration. When the severity factor reached 3.55 and above, irreversible visible discoloration took place, light at the beginning, but increasing proportionally with the severity factor.

A simple estimation of the optical properties of the material post-bleaching can as well be provided by the percent whiteness since it is measured across the entire visible spectrum. Fig. 2 presents the correlation between the whiteness of bleached fibres and the severity factor (Fig. 2a) and the combined influence of the couple reaction temperature/residence time on cellulose whiteness (Fig. 2b). The whiteness (*W*) decreased linearly with the increase of the severity factor, a relation that can be described using the following equation:

$$W = a \cdot \text{SFT} + b \quad (6)$$

with *W*, percent whiteness; $a = -40.487 \pm 1.323$ and $b = 197.3 \pm 5.2$.

Hemicellulose present in the initial biomass could be responsible of the discoloration observed in the fibres. However, it should be mostly hydrolyzed during the dilute-acid steam explosion (Tucker, Kim, Newman, & Nguyen, 2003). It is thus improbable that hemicelluloses are to be taken accountable for the observed color changes. As well, the bleaching process used in this work (chlorine dioxide) was proven to have no evident effect on cellulose fibres structure, attacking only the aromatic rings of the remaining lignin on the lignocellulose (Lemeune, Jamee, Chang, & Kadla, 2004). Therefore, the observed browning of the fibres could be related to a partial degradation of cellulose via successive degradation of carbohydrate structures to furans (or aromatic rings) that would ultimately lead to the production of char at high severity. Coloration of the fibres was also observed by Ibrahim et al. (2010) who related this event to the cell wall components, extractives and sugar degradation after steam pre-treatment at higher severity factor.

In this work, all steam-exploded (SE) lignocellulosic materials were bleached under the same conditions. Chlorine dioxide

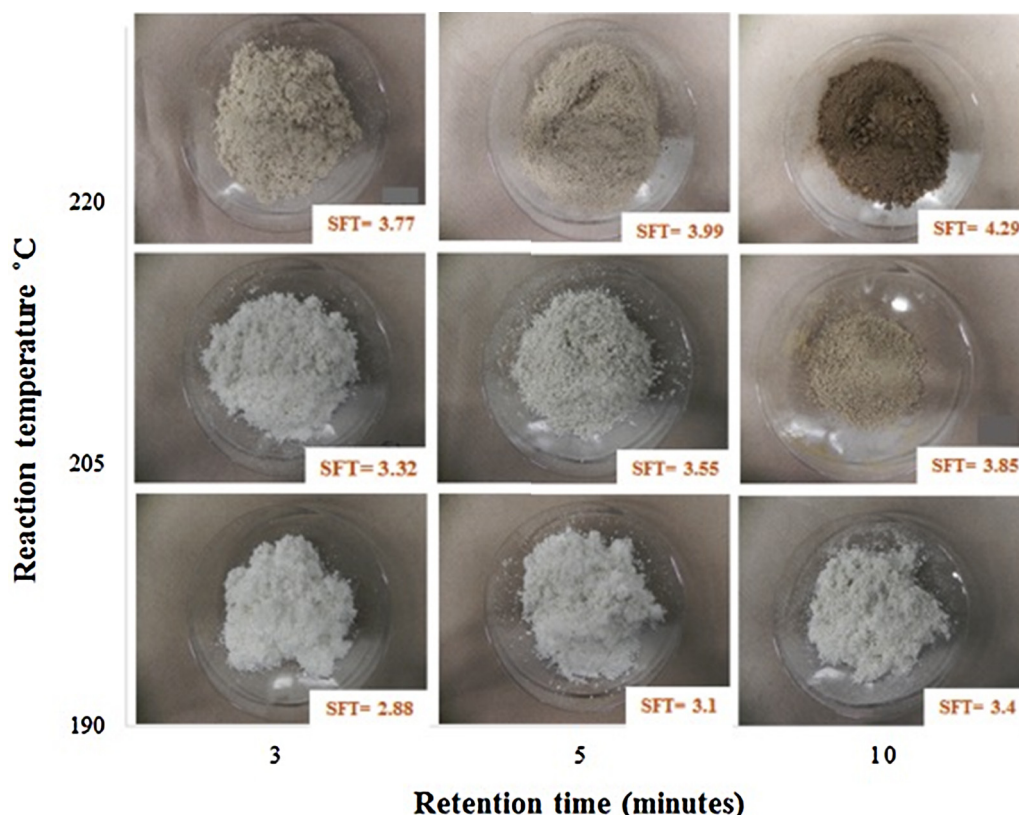


Fig. 1. Aspects of bleached dilute acid steam-exploded cellulose fibres as a function of the reaction temperature and retention time (conditions described in Table 1).

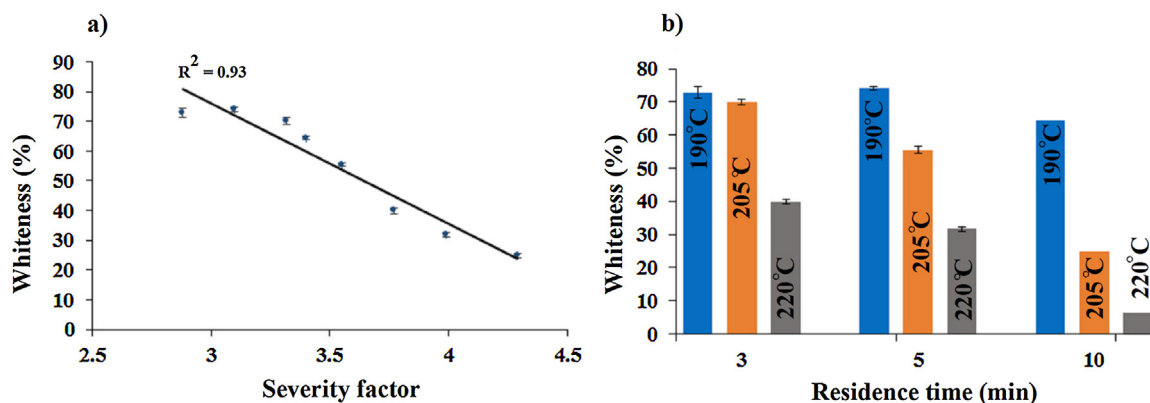


Fig. 2. (a) Cellulose fibre whiteness (%) as a function of the severity factor and (b) evolution of the whiteness with the retention time.

bleaching is usually done in three stages using the same amount of reagent for each stage under identical time and temperature conditions. Chlorination of cellulose fibres was proven to produce white cellulose, free or with a relatively low lignin content (Patrick & Martin, 1997) depending on the specie and the initial lignin content of the material. The fact that white samples were obtained under the lower severity factors implies that the browning cannot be related to a remaining lignin content. It seems that utilization of sulphuric acid as catalyst, in addition to its fibres destructuration potential at high temperature also induces a variety of secondary reactions. These reactions could involve formation of new chemicals (such as furans) by the transformation carbohydrate (as cellulose or cellulose side-chain). The darkening of steam-exploded fibres has been previously attributed to the production of acetic, formic and other pyrolytic acids as well as the reactions of these organic acids with lignocellulosic material (Morgan & Stewart, 1941). In addition, a possible polymerization of furans and of other sugar degradation products is also an option (Wang et al., 2009). A simple experiment with carbohydrate in an acid catalyzed mixture provides a pitch-black mixture after reacting at 200 °C for a few minutes. Another possibility, although these combined reactions are hard to monitor, could be the generation of “pseudo-lignin”, defined as aromatic compounds yielding a positive klason lignin value not derived from native lignin during dilute-acid steam-explosion pre-treatment (Hu, Jung, & Ragauskas, 2012). These compounds could be formed following combination of carbohydrate macromolecules and by-products (such as furans) formed during the acid pre-treatment of biomass at high temperature (Sannigrahi, Kim, Jung, & Ragauskas, 2011). Pseudo-lignin could be resistant to bleaching procedures and its formation may become more likely at high severity.

3.2. Fibre dimensions

Acid-catalyzed steam processes leads to defibrillation of the lignocellulosic biomass matrix while the amorphous and peripheral fractions of cellulose are most likely hydrolyzed.

Fig. 3a shows the evolution of average single fibres length (L), diameter (D) and length to diameter (L/D) aspect ratio as a function of the severity factor (SFT). The fibre lengths were drastically reduced following the steam treatments in a linear fashion with regards to the increasing severity of the treatments. This tendency has been reported by various authors including Datar et al. (2007) when working on non-catalyzed as well as dilute acid steam exploded corn stover performed in the temperature range of 190–200 °C for a retention time of 3–5 min. Under high temperature and for long residence time (severe treatments), the chemical hydrolysis, condensation, mechanical defibreization and

structural disorganization are amplified, thus leading to the production of shorter cellulose fibres. At lower SFT value of 2.88, an average length of 0.23 mm was recorded, while shorter fibres with an average length of 0.14 mm were produced at higher severity. The linear relationship between fibre length and SFT can be described by the following equation:

$$L = c \cdot \text{SFT} + d \quad (7)$$

with L , fibre length; $c = -0.057 \pm 0.013$ and $d = 0.387 \pm 0.045$.

Fig. 3b presents the evolution of the fine (defined here as fibres with length ranging from 0.07 to 0.2 mm) as a function of the severity factor.

The fines (F%) accounted for 52% at a severity of SFT=2.8 and their fraction increased linearly with the increasing SFT to reach value of 82% at the higher severity (SFT=4.3). The correlation between the two parameters followed the equation:

$$F\% = e \cdot \text{SFT} + g \quad (8)$$

with F%, percentage of fine; $e = 21.39 \pm 2.31$ and $g = 8.51 \pm 2.59$.

By contrast, the average fibre diameters value (D) was more stable with only a slight increase as function of the SFT leading to a decreasing L/D ratio with regards to severity. This trend could be explained by agglomeration due to fibre degradation at higher temperature/retention time as mentioned earlier. The curvature after the separation of fibre bundles as a result of the steam processes could also explain the augmentation of the average fibre diameter detected using FQA.

The products obtained after the dilute acid steam explosion could be related to microcrystalline cellulose. In fact, Leppänen et al. (2009) reported that hydrolysis of cellulose with dilute-acid cannot isolate nanosize particles of cellulose even after mechanical disintegration. Strong acid must be used for this purpose. When dilute acid hydrolysis is considered, the strong inter-crystalline contacts remain intact and the micron-size crystallites aggregates leading to the formation of microcrystalline cellulose. The average fibre length for commercial Avicel was found to be in the range of 0.02–0.25 mm, while it ranged from 0.02 to 0.125 mm for microcrystalline cellulose obtained from cotton linter (Leppänen et al., 2009). This must be compared to average particle length ranging from 150 to 200 nm and the average particle width ranging from 10 to 20 nm for nanocellulose (Ioelovich, 2012). On the other hand, Owwoavworhwa and Adelakun (2010) found an average fibre diameter of 95 µm for microcrystalline cellulose produced by hydrochloric acid hydrolysis of α-cellulose extracted from *Sorghum caudatum*. In term of fibre length, the average length of the steam exploded cellulose fibres obtained in this work ranged from 0.15 to 0.23 mm, while their diameter varied between 15.8 and 32.8 µm. To some extent, these facts could corroborate the

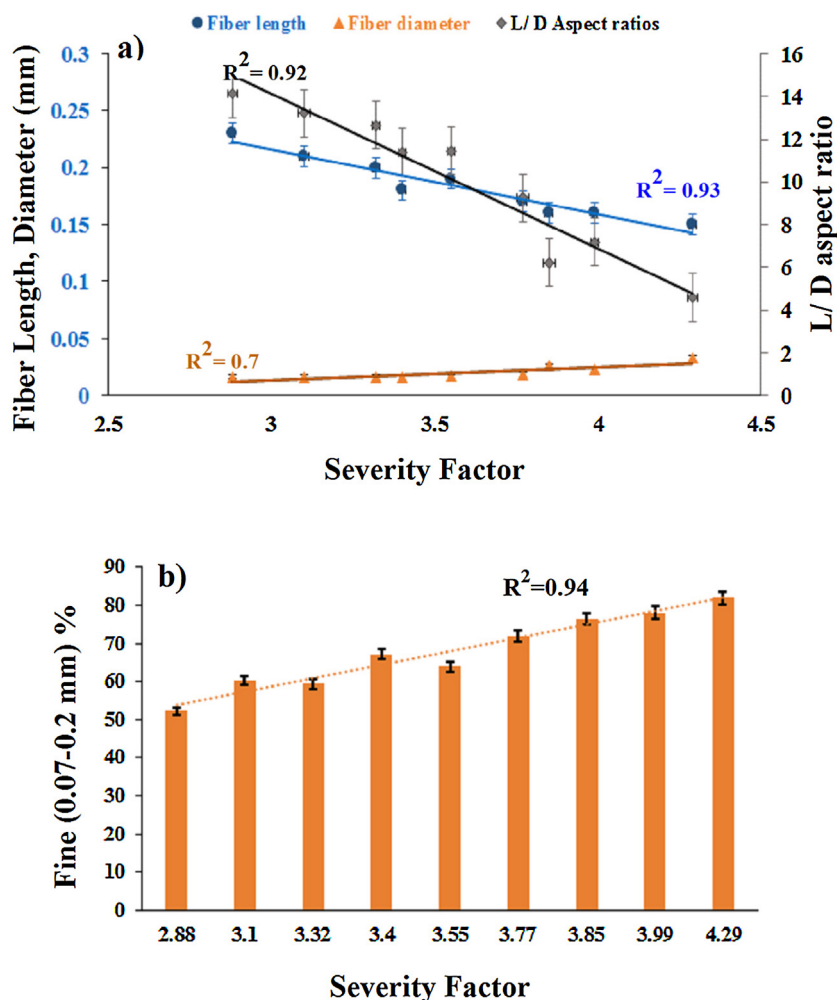


Fig. 3. (a) Fibre length, diameter, and length/diameter ratio as a function of the severity factor and (b) fine fraction (fibres with length between 0.07 and 0.2 mm) as a function of the severity factor.

possibility to extract microcrystalline cellulose directly by using dilute-acid steam explosion, which could be a new process route to explore.

3.3. Microstructural characterization

Fig. 4 presents pictures of bleached steam-exploded cellulose fibres obtained with a SEM system. The micrographs reveals separated elementary cellulose fibres with some irregular filament bundles persisting in some cases (Fig. 4A–D).

This observation is of interest for an application as polymer reinforcement since isolated fibres are usually targeted for such an application (Altman et al., 2003). In comparison to the lower severity factor (SFT = 2.88), fibres obtained with higher severity (up to SFT = 3.77) seemed to “unfold”. This observation, in addition to the fibre agglomeration observed at higher SFT values (Fig. 4E and G–I), could explain the difference in fibre diameter generated from steam processes as reported in Fig. 3. The severity of the applied treatment impacted clearly on the final cellulose microstructure with fibre length reduction and loss of fibrous structure occurring progressively with increasing SFT.

These structural changes, happening at higher severity factor, could be elucidated by the extension of the hydrolytic chemical phases, subsequent to the lengthening of the residence time. The pressure rise inside the reactor generated by the increasing reaction temperature as well led to more intense depressurization and

thus defibrillation. This phenomenon generates a disordering of the biomass cell wall, as previously observed for wheat straw by Anupama and Singh (2011).

On the other hand, two spherical globules with diameters in the 10 μm range in the upper left part of Fig. 4I may be pseudo-lignin particles as observed by Hu et al. (2012) and Sannigrahi et al. (2011) when severe treatments were applied.

3.4. Derivative thermo gravimetric analysis

Thermo gravimetric analyses were performed in order to determine the thermal stability of bleached cellulose fibres treated at different severities. Fig. 5 presents the relative weight loss and weight loss derivative (WLD) of the treated fibres. The weight loss occurred in two stages for all the tested specimens. The main degradation phase occurred around 300 °C while a second minor phase occurs at temperatures above 400 °C. The onset degradation temperature (T_{onset}) as well as the maximum temperature of degradation (T_{max}) did not significantly change with treatment severity.

The weight loss derivative curves (WLD) for all bleached cellulose fibres revealed that the maximum degradation rate occurred between 298 °C and 308 °C. This main peak, with maximum WLD appearing between 298 °C and 308 °C depending on the applied conditions, was accompanied with two secondary peaks between 70 °C and 100 °C and between 380 °C and 550 °C attributed respectively to H_2O evaporation and remaining impurities (Morán,

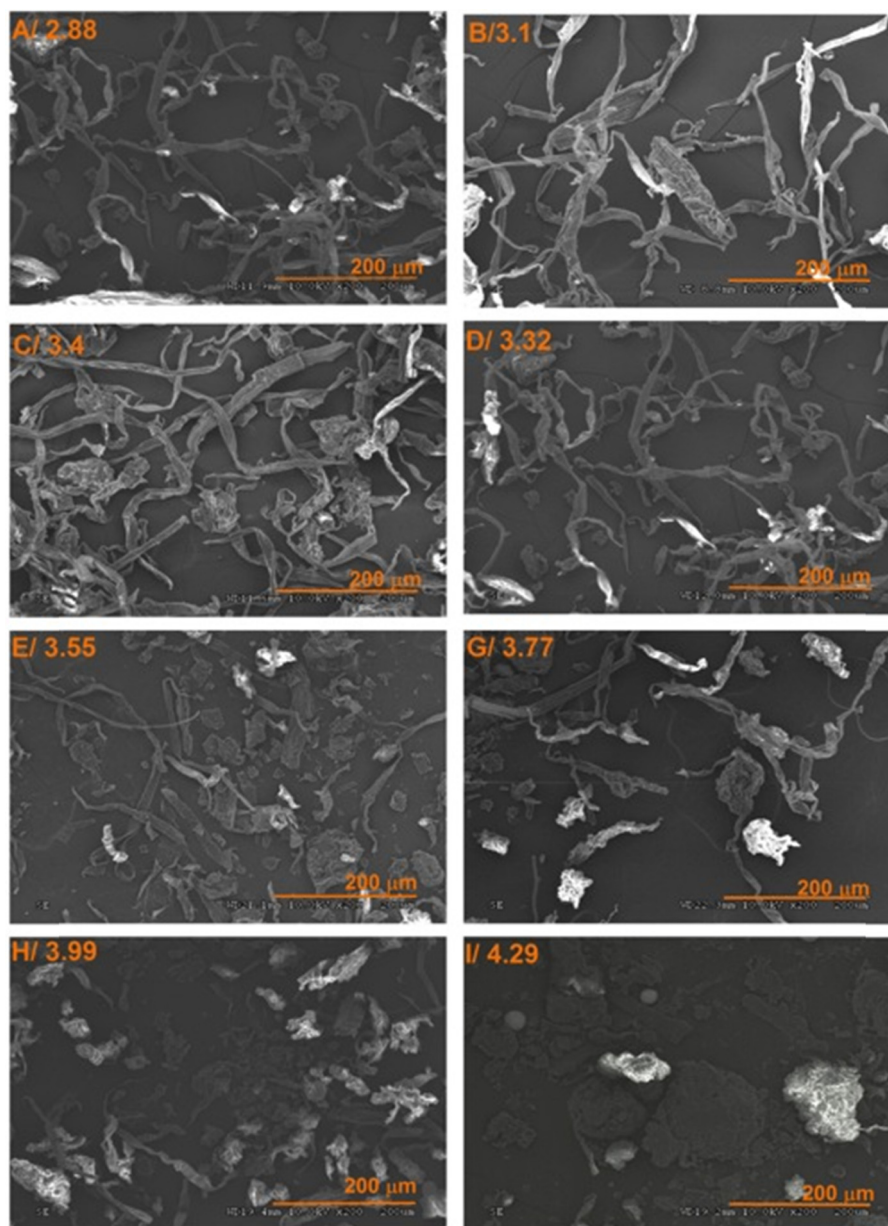


Fig. 4. SEM micrographs of bleached *Salix miyabeana* fibres steam exploded at different severity factors as described in Table 1.

Alvarez, Cyras, & Vázquez, 2008). The last cited peak evidenced that these impurities degraded around temperature range of 400–550 °C that may approximately correspond to the degradation temperature of isolated lignin discussed by Ibrahim et al. (2010) for cotton stalk and banana plant.

However, due to the strong bleaching process applied and the absence of lignin, this peak could be assigned to the pseudo-lignin molecules that present a similar structure with lignin.

The total carbonaceous residues (char) found at the end of the heating process were low, between 2 and 4.2% with the highest value found for the highest severity factor. The same trend was observed by Jacquet et al. (2011), for steam exploded cellulose fibres.

3.5. Degree of polymerization

The average chain length of the cellulose macromolecules in the bleached cellulose fibres can be expressed as a degree of polymerization (DP) of the cellulose chains. The variation of the degree of

polymerization as a function of the severity factor (SFT) is presented in Fig. 6a. Fig. 6b presents variation of DP as a function of the average fibre length and Fig. 6c shows the evolution of DP as a function of the actual treatment conditions (temperature, residence time).

As for the fibre length presented earlier, the degree of polymerization decreased as a function of the severity factor. The linear relation between these two parameters can be described by the equation:

$$DP = h \cdot SFT + i \quad (9)$$

with DP, degree of polymerization; $h = -1326.3 \pm 31.8$ and $i = 5645 \pm 129$.

It is noteworthy that macromolecular chain length expressed as degree of polymerization and the macroscopic fibre length are closely related through a linear relationship.

High value of DP of 1830 was observed for fibres treated at the lowest SFT (2.88). A significant reduction of the degree of polymerization down to values around 100 was obtained at higher SFT (4.29). This corresponds to an average chain scission value of 15.7.

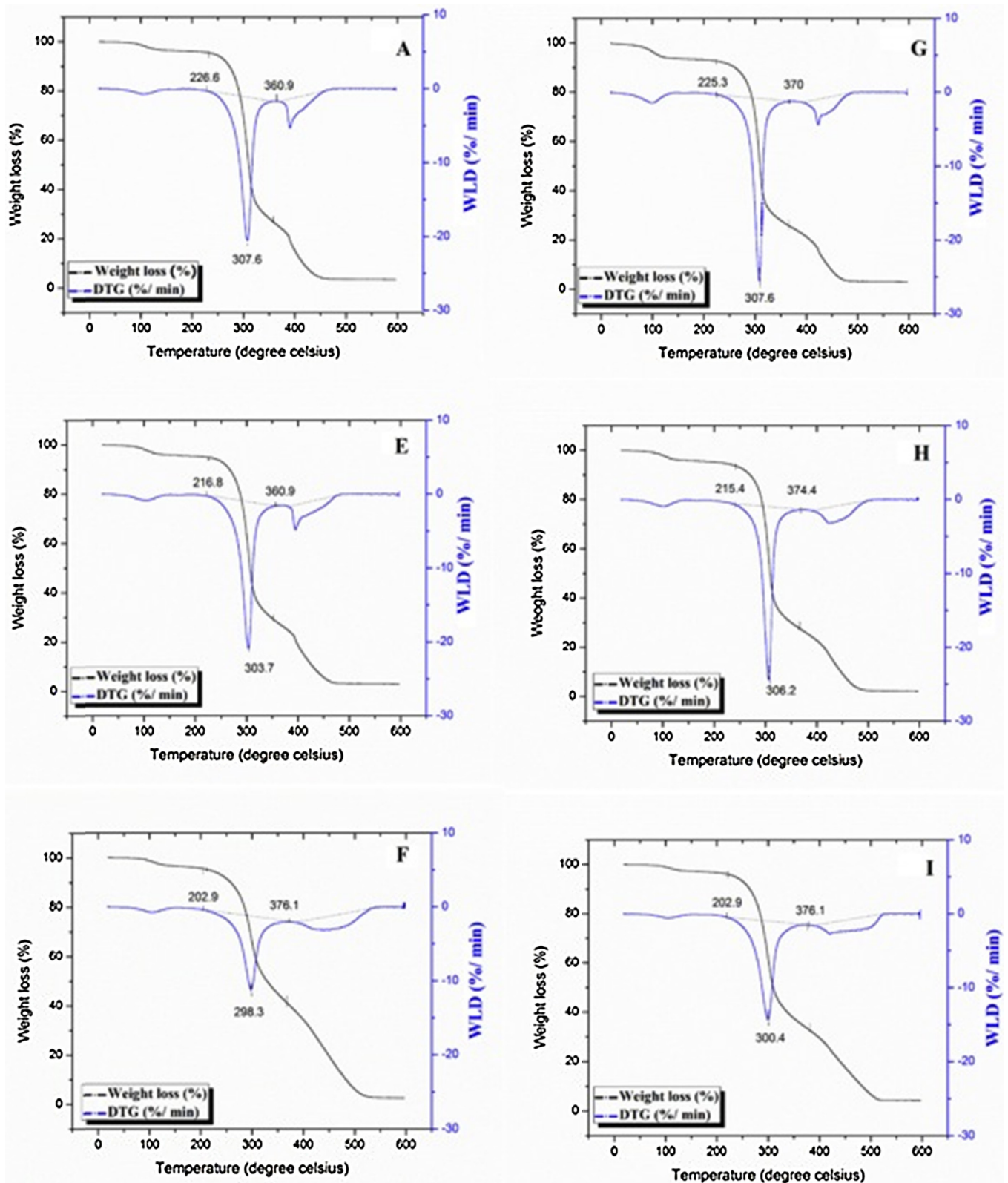


Fig. 5. Weight loss and weight loss derivative (WLD) of bleached *Salix miyabeana* fibres at different steam explosion conditions as described in Table 1.

In Fig. 6b, on the other hand, we can observe that the DP was reduced with increasing temperature and residence time taken individually. Similar variations were also revealed by Foston and Ragauskas (2010) for populus and switchgrass during dilute acid pre-treatment, with the increase of the residence time.

Terinte, Ibbett, and Schuste (2011) observed that the leveling off degree of polymerization (LODP) of microcrystalline cellulose ranges from 200 to 300. Actually, in this work, we noticed that the degree of polymerization of cellulose fibres dropped to around 205 when a severity of 3.99 was applied, and reached value as low

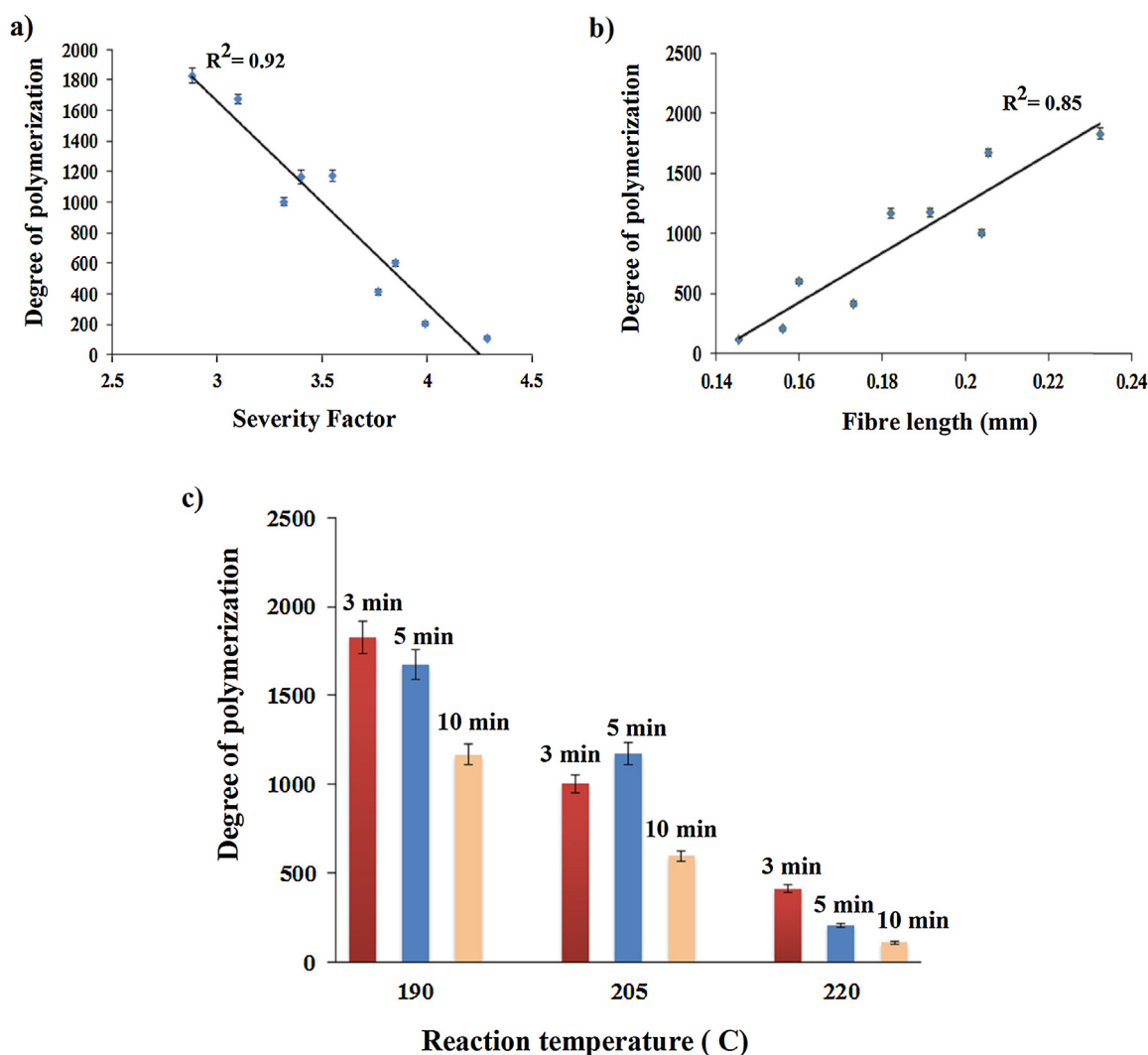


Fig. 6. (a) Degree of polymerization as a function of the severity factor (■), (b) degree of polymerization as a function of the cellulose fibre length (●) and (c) degree of polymerization of cellulose fibres as a function of the reaction temperature and residence time.

as 109 at higher severity factor of 4.29. For instance, the average degree of polymerization calculated by Leppänen et al. (2009) for commercial Avicel was found to be around 150 and was around 165 for microcrystalline cellulose obtained from cotton linter. This statement could be in agreement with the above discussed possibility that microcrystalline cellulose can be extracted directly by dilute-acid steam explosion.

4. Conclusions

The increased severity applied to *Salix miyabeana* during the Steam explosion process affects the length, whiteness, length to diameter aspect ratio as well as the degree of polymerization of the bleached cellulose fibres. The thermal stability of the fibres on the other hand was not a strong function of the reaction parameters. Finally, the obtained fibre structures in term of fibre length, diameter and degree of polymerization suggest that the dilute acid steam explosion process could be used as a new route for direct extraction of microcrystalline cellulose from biomass residues.

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