EMPO mediated oxidation effects on thermomechanical pulp components

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Abstract

TEMPO-mediated oxidation was carried out on thermomechanical pulp to further investigate the oxidation effect on TMP base components. Successive extractions on non-oxidized, bleached and oxidized TMP had shown that components were easier to extract in the oxidized pulp. Pulps lignin content demonstrated that highest part of lignin was removed by sodium hydroxide extraction. Moreover, more than twice more lignin was extracted in oxidized pulp compared to non-oxidized pulp. Carboxylic groups measured shown that highest oxidized components were excerpt after the first extraction but extracted material after each extraction step present an important carboxylic group content. Thermogravimetric analysis have shown that fiber structure was clearly weakened by TEMPO oxidation. Results also demonstrated that some components of the highly oxidized pulp were more easily dissolved because of critical extraction conditions. Furthermore, recovered precipitate in the extraction solvent has presented different XPS characteristics according to the initial pulp treatment. Oxidized TMP precipitate's analysis have shown that precipitate from hot water extraction presented higher oxidation properties while precipitate from sodium hydroxide approached pure lignin characteristics.

Keywords: TEMPO-mediated oxidation, thermomechanical pulp, wood components extraction, lignin content, thermogravimetric analysis, X-ray photoelectron spectroscopy

Introduction

The TEMPO mediated oxidation effects and applications are well known on Kraft pulp and more precisely on cellulose. Saito et al. (2006) had proposed a reaction mechanism of TEMPO oxidation on cellulose. TEMPO oxidation is interesting because of its regioselectivity to the cellulose primary alcohol (Isogai et al., 2011). This regioselectivity allows cellulose modifications with a very limited amount of water-soluble fraction (Isogai and Kato, 1998), thus not decreasing the mass yield. In that matter alone, this make TEMPO oxidized cellulose very useful for several applications (Saito et al., 2007; Johnson et al., 2008).

In parallel, researches were carried out on TEMPO mediated oxidation but this time, applied to thermomechanical pulp (Okita et al., 2009) and have also show some interesting applications (Ma et al., 2009 and 2013). However, the mechanism of TEMPO oxidation effect on thermomechanical pulp is still partly unknown. A proposed mechanism is known for cellulose but unexplored for lignins and hemicelluloses. In some conditions, part of the lignins was dissolved in

the water during the oxidation (Okita et al., 2009). More recently, Sakakibara et al. (2016) has shown that the TEMPO reaction seems to oxidize pure galactomannans (hemicellluloses). In addition, during an optimization of TEMPO mediated oxidation conditions on thermomechanical pulp (Myja et al., 2018), we have observed several pulp with a carboxyl content (more than 2000 mmol/kg) much higher than the maximum value observed on cellulose (~ 1700 mmol/kg, Isogai et al., 2011). Still in this study, other conditions have presented high carboxyl content (higher than 1500 mmol/kg) with only a small yield decrease (less than 5%). For all these considerations, we decided in this work to further investigate the TEMPO oxidation effects on the hemicelluloses and lignin of a thermomechanical pulp.

Experimental

Material

The raw material used was a secondary unbleached softwood thermomechanical pulp purchased from Kruger S.E.C. (Trois-Rivières, Canada). The Canadian Standard Freeness (CSF) was adjusted to 150 mL in our pilot refiner (Valmet CD300 refining system, Valmet, Espoo, Finland). Chemicals used for the TEMPO mediated oxidation were used as received. The sodium hypochlorite was from Sigma-Aldrich (Oakville, Canada), the 4-acetamido-TEMPO was purchased from Chemos (Regenstauf, Germany), the sodium bromide from Thermo Fisher Scientific Chemicals Inc. (Ward Hill, USA) and the hydrogen peroxide was from Thermo Fisher Scientific Chemicals Inc. (Fair Lawn, USA). Dichloromethane and sulfuric acid used were purchased from Fisher Scientific Chemicals Inc. (Fair Lawn, USA).

Methods

TEMPO mediated oxidation

The TEMPO mediated oxidation conditions were determined to allow a high carboxyl content in the pulp with the lowest mass yield decrease. Exact conditions were calculated according to the model obtained in a previous work on TEMPO mediated oxidation conditions optimization (Myja et al., 2018). Selected conditions were near point n°9 of high oxidation optimization of Myja et al. (2018) work. For the oxidation of 30 g of dry pulp, 2.56 g of TEMPO (0.4 mmol/g dry pulp), 2.78 g of sodium bromide (0.9 mmol/g dry pulp) and 211 mL of sodium hypochlorite at 1280 mmol/L (9.0 mmol/g dry pulp) were used. The reaction was made at 25°C for 60 minutes. The pH was maintained at 10 with a pH controller pumping buffer solutions of sodium hydroxide and hydrochloric acid at 0.1 M. TEMPO and sodium bromide were directly added to the 1% pulp suspension. A metering pulp was used to add the required sodium hypochlorite volume in 45 minutes. The reaction time was started when the first drop of sodium hypochlorite was added to the solution. After a given time, the oxidation was stopped by the addition of 100 mL of hydrogen peroxide at 3% concentration. After filtration and washing with deionized water, the pulp was finally stored at 6°C until further uses.

Pulp denomination and description

In this work, 3 types of pulp were compared to determine the TEMPO oxidation effect on the main pulp components. The first pulp was a non-oxidized pulp (NO), which was only stirred for 60 minutes in deionized water at pH 10, and used as reference. The second pulp was a bleached pulp (Bl). This thermomechanical pulp had the same treatment as the non-oxidized pulp (reference) but with the addition of 211 mL of sodium hypochlorite solution in 45 minutes timescale. This pulp was used to study if a bleaching effect could happen during the TEMPO oxidation due to an excess of sodium hypochlorite. Finally, the oxidized pulp (Ox) was a TMP after a TEMPO oxidation treatment.

Extractions process

Successive extractions were made to extract wood extractives, hemicelluloses and lignin. Each extraction was made in a Dionex ASE 350 (ThermoFisher Scientific, Waltham, Ma, USA) at 150°C and 1460 PSI. The first extraction was made with dichloromethane to excerpt wood extractives. This extraction was made in 20 minutes. The second extraction has extracted hemicelluloses with deionized water for 20 minutes. The last extraction was carried out with sodium hydroxide solution at 0.1 M. According to Korotkova et al. (2015), a multiples extractions methodology will allows to remove a higher amount of lignin. Therefore, the lignin extractions were made following 3 extraction cycles of 40 minutes each. After dichloromethane, hot water and sodium hydroxide extractions, the pulp was recovered to measure the extraction mass loss. In addition, a thermogravimetric analysis and the carboxylic groups content titration were made on the final pulp. Extraction solvents of each extraction were also recovered separately and poured in glass crystallizers. Sulfuric acid was added in order to decrease the pH under 3 and precipitate the lignin. Finally, crystallizers were placed in an oven at 60°C to evaporate the remaining solvent. The precipitate was then analyzed by X-ray photoelectron spectroscopy.

Acid-insoluble lignin in pulp determination

Lignin content in pulp was analyzed according to the TAPPI T222 standard method. This procedure measure the sulfuric acid insoluble lignin. 2 g of dry pulp were first stirred during 2 hours in 40 mL of sulfuric acid at 72%. The solution was then poured in deionized water and boiled during 4 hours maintaining the same water level. Finally, the solution was filtered to measure the acid insoluble lignin mass.

Lignin yield after extraction and lignin composition in extracted material

Overall lignin yield (OLY) after extraction was calculated to observed lignin removal during the total extraction process. This yield was calculated according to the equation (1).

$$OLY\ (\%) = \frac{lignin\ mass\ in\ pulp\ after\ extraction\ process}{lignin\ mass\ in\ initial\ pulp} = \frac{PLae \times Ye}{PLi} \qquad (1)$$

With :

- PLae : Pulp lignin content after extraction (%)

- Ye : Total extraction mass yield (%)
- PLi : Initial pulp lignin content (%)

It was also interesting to observe the lignin amount in the extracted material at each extraction step. In that way, the extracted material lignin composition (Lem) was calculated as shown in equation (2).

$$Lem\ (\%) = \frac{lignin\ mass\ in\ extracted\ material}{total\ mass\ of\ extracted\ material} = \frac{PLbe \times Ybe - PLae \times Yae}{Ybe - Yae} \qquad (2)$$

With :

- PLbe/ae : Pulp lignin content before/after extraction step (%)
- Ybe/ae : Mass yield before/after extraction step (%)

Carboxylic groups content determination

Carboxylic groups introduced by the TEMPO oxidation at fibers surfaces were measured by conductimetric titration with sodium hydroxide according to Beatson's (1992) method. After the pulp protonation with hydrochloric acid at 0.1 M, the pulp was dispersed in salted water at 10^{-3} M. Before the titration starts, 10 mL of hydrochloric acid was added to get the specific titration curve, which allows the carboxylic groups determination. The carboxylic groups content determination on pulps also allowed to calculate the theoretical carboxylic groups content of extracted material. Equation (3) was used to determine the extracted material carboxylic groups content (CGem) at each extraction.

$$CGem\ \left(\frac{mmol}{kg}\right) = \frac{number\ of\ carboxylic\ groups\ in\ extracted\ material}{total\ mass\ of\ extracted\ material}$$

$$= \frac{CGbe \times Ybe - CGae \times Yae}{Ybe - Yae} \qquad (3)$$

With :

- CGbe/ae : Pulp carboxylic groups content before/after extraction step (mmol/kg)
- Ybe/ae : Mass yield before/after extraction step (%)

Thermogravimetric analysis

Each sample was analyzed according to the same thermogravimetric analysis process. The pulp was heated under nitrogen in platinum pans from 50°C to 105°C at a rate of 20°C/min. The temperature was held at 105°C for 15 minutes in order to remove all the sample moisture. Still under nitrogen, the sample was then heated from 105°C to 600°C at 10°C/min. The temperature was then held for 15 min before a last increase from 600°C to 700°C by 10°C/min but this time, under an air atmosphere. In addition to the thermogravimetric analysis (TGA) curve, the derivative thermogravimetric (DTG) curve was calculated.

X-ray photoelectron spectroscopy

XPS analysis was made on precipitates from the extraction solvent. The measurements were done with a Kratos AXIS Ultra (Kratos Analytical, Manchester, England) with a monochromatic Al X-ray source of 225 W. First, a survey scan was made with 1 eV step and 160 eV analyzer pass energy to determine all the different atoms in the surface lignin and their percentage of presence. Secondly, high resolution spectrums were made for oxygen and carbon with 0.1 eV step and 40 eV analyzer pass energy to determine and quantify surface carbon and oxygen bonds.

Results and discussion

Pulp analysis and mass yield

According to Table 1, thermomechanical pulp treatments had different impact on the mass yield. For the non-oxidized (NO) and the oxidized pulp (Ox), the treatment had nearly no effect on the yield as expected from our previous work (Myja et al., 2018). However, the lignin was affected by the treatment. Without a significant treatment mass yield decrease, the acid-insoluble lignin content decrease significantly with the oxidation. That observation shows a lignin modification leading to a higher amount of acid-soluble lignin. Ma et al. (2012) shown the same TEMPO oxidation effect on TMP lignin. On the contrary, the treatment of the bleached pulp has decreased the mass yield significantly. For this treatment, the sodium hypochlorite acted as a chemical pulp-bleaching agent, which has conducted to the dissolution of some wood components. The treatment mass yield comparison between bleached and oxidized TMP show that the sodium hypochlorite was mostly consumed as co-oxidant rather than as bleaching agent in the oxidation treatment. Therefore, it was more interesting to compare extractions effects on non-oxidized and oxidized TMP.

Table 1. Treatment mass yield and initial pulp lignin content for each studied pulp

	Non-oxidized TMP (NO)	Bleached TMP (Bl)	Oxidized TMP (Ox)
Treatment mass yield (%)	99.8	87.6	98.0
Lignin content (%)	27.9	22.8	17.8

Table 2 show the differences between these two pulps after each extraction. This second table gives information about pulp and extracted material composition. For example, after the dichloromethane extraction (n°1) of non-oxidize TMP, 97.6 % of the initial mass was recovered and the pulp contained 28.5 % of lignin. With those information, according to equations (1) and (2), 99.7 % of the initial lignin was still in the pulp while the extracted material was composed of 3.5 % of lignin, the rest being wood extractives or hollocellulose. For the non-oxidized pulp, the 2.4 % mass loss after dichloromethane extraction can be principally attributed to the wood extractives dissolution as expected. However, the mass loss with dichloromethane for the oxidized pulp was much higher than the normal extractives content of this type of the pulp. It seems that the oxidation is reducing the fibers structure strength, allowing extraction of other wood components than only wood extractives. Nevertheless, the lignin yield decreases after the first extraction as the extracted

material contain only 6.8 % of lignin. Therefore, at this step, the extracted material was mainly composed with holocellulose. Exactly the same observations could be made for the extraction with hot water. As expected, the higher amount of lignin was removed after the third extraction, with sodium hydroxide. The lignin yield was still important after all extraction for non-oxidized TMP but more than 50 % of the initial acid-insoluble lignin in the oxidized TMP was removed by the extraction process. Fibers structure and moreover, lignin structure, were surely affected by the TEMPO oxidation. Which as conducted to an easier wood components extraction.

Table 2. Extractions effects on mass and lignin yield and pulp and extracted material lignin content after dichloromethane (1), hot water (2) and sodium hydroxide (3) extraction

Extraction		1	2	3
TMP NO	Mass Yield (%)	97.6	86.7	78.0
	Pulp lignin content (%)	28.5	31.7	28.9
	Lignin Yield* (OLY, %)	99.7	98.5	80.8
	Extracted material lignin content* (Lem, %)	3.5	3.0	56.8
TMP Ox	Mass Yield (%)	87.3	68.6	50.0
	Pulp lignin content (%)	19.4	21.9	17.3
	Lignin Yield* (OLY, %)	95.1	84.4	48.6
	Extracted material lignin content* (Lem, %)	6.8	10.2	34.3
* calculated				

To further investigate this phenomenon, Table 3 presents the carboxylic group's content at fibers surface of the oxidized TMP.

Table 3. Carboxylic groups content (mmol/kg) measured for oxidized TMP and calculated for the extracted material after initial treatment and each extraction

	Oxidized TMP (mmol/kg)	Extracted material* (CGem, mmol/kg)
After treatment	1820	/
After dichloromethane extraction	1190	6151
After hot water extraction	860	2401
After sodium hydroxide extraction	540	1720
* calculated		

Huge variations of the surface carboxylic groups content has appeared for the oxidized pulp. After the dichloromethane extraction, the carboxylic groups content decreased by 34.6 %. Thus, the 12.7 % mass loss observed previously (Table 2) was then highly oxidized material. Isogai et al. (2011) had shown that highly oxidized material was easier to disperse as the cellulose structure was more charged but that could also be damaged in the process. The highly oxidized part of TMP was easier to extract resulting in a higher mass loss for the oxidized pulp and the subsequent drop in the carboxylic group’s content. With the observation made previously, it is possible to affirm that TEMPO treatment of TMP highly oxidize the pulp holocellulose. The hot water and the sodium

hydroxide extractions also present a higher mass loss than non-oxidized TMP with a significant carboxylic group's content drop. It is although possible to suppose that part of pulps lignin was then oxidized. The extracted material of oxidized TMP sodium hydroxide extraction contained 34.3 % of lignin. In addition, the carboxylic groups content of this extracted material was calculated at 1720 mmol/kg. This high carboxylic groups content value presumed that all extracted material components were oxidized, including lignin.

The thermogravimetric analysis derivative curves of non-oxidized and oxidized pulps at each extraction step shown on Fig. 1 also support the previous observations.

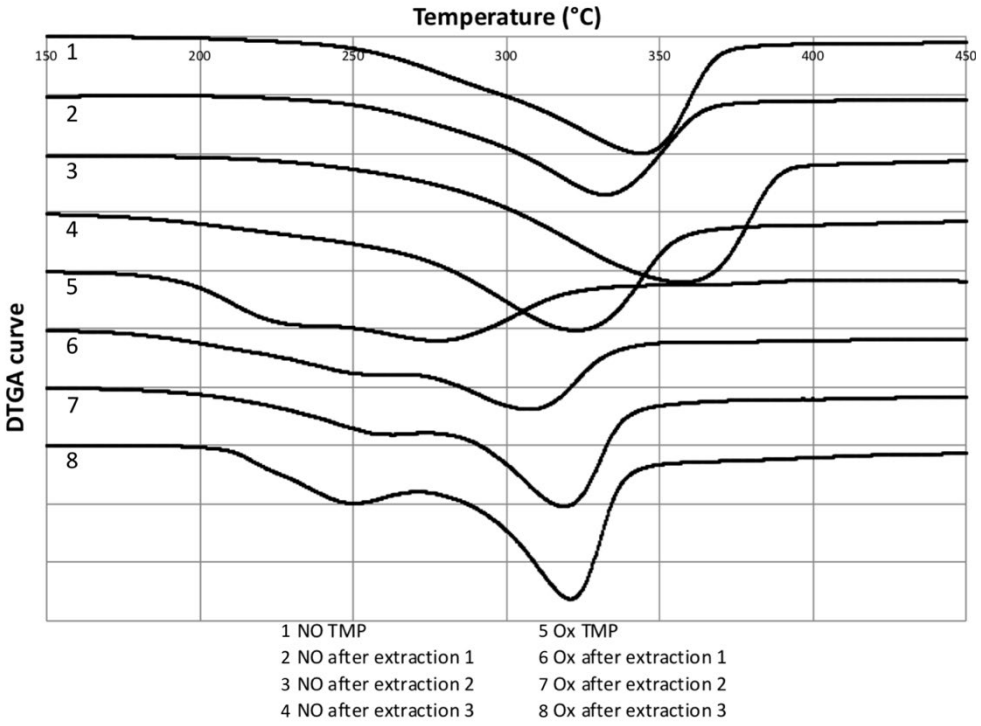

Fig. 1. Thermogravimetric analysis of non-oxidized and oxidized TMP before extraction and after each step of the successive extraction

The main peak displacement between curves 1 and 2 came from the fiber structure weakening due to high temperature and pressure during the first extraction. Between curves 2 and 3, the pulp thermal resistance as increase because of the hemicelluloses extraction, which have lower thermal resistance. Thermal degradation peak for the non-oxidized pulp after the last extraction (curve 4) presents a closer temperature value to cellulose pulp (313°C) observed by Fukuzumi et al. (2010). Therefore, a significant lignin amount was dissolved during the sodium hydroxide extraction, which also confirm previous results.

Thermogravimetric derivative curves of oxidized pulps present at least 2 peaks. According to Britto and Assis (2009), the first peak is related to the sodium content into the pulp. This sodium came from the COONa groups formed during the TEMPO oxidation. Between curves 1 and 5, we can see that the main thermal degradation peak was significantly decreased. This drop was due to the pulp oxidation, as also observed by Fukuzumi et al. (2010). Moreover, pulp thermal resistance increase after each extraction of the oxidized pulp until a thermal degradation temperature close to

pure cellulose pulp is reached. The higher difference was observed between curves 5 and 6, which coincides with the highest oxidized pulp material dissolution.

Recovered precipitate analysis

A sufficient amount of non-oxidized, bleached and oxidized TMP were extracted with hot water and sodium hydroxide to get enough sulfuric acid precipitate for XPS analysis. Table 4 shows results from survey analysis.

Table 4. XPS survey analysis for recovered precipitate of non-oxidized, bleached and oxidized TMP after hot water and sodium hydroxide extraction

Lignin from …	Oxygen	Carbon	Sodium	Chlorine	Sulfur
NO TMP after hot water extraction (NO2)	35.68 ± 0.08	61.61 ± 0.34	< 1	1.63 ± 0.11	U.D.
NO TMP after sodium hydroxide extraction (NO3)	37.40 ± 2.05	59.59 ± 0.04	1.57 ± 0.01	< 1	1.42 ± 0.06
Bl TMP after hot water extraction (Bl2)	36.59 ± 0.16	57.08 ± 0.11	2.45 ± 0.03	1.04 ± 0.04	2.86 ± 0.04
Bl TMP after sodium hydroxide extraction (Bl3)	34.21 ± 1.31	52.80 ± 0.22	3.05 ± 0.18	4.34 ± 0.90	3.83 ± 0.04
Ox TMP after hot water extraction (Ox2)	30.84 ± 1.05	51.06 ± 0.25	6.33 ± 0.26	10.38 ± 0.49	< 1
Ox TMP after sodium hydroxide extraction (Ox3)	29.35 ± 0.40	60.85 ± 2.10	3.71 ± 1.73	4.41 ± 0.03	< 1
U.D. : Undetected					

In ours samples, 5 atoms were mostly found on precipitates surface. In addition to oxygen and carbon, sodium, chlorine and sulfur were indeed detected. Sodium could come from the sodium bromide or the sodium hypochlorite used during TEMPO oxidation or even, from the sodium hydroxide extraction. Moreover, observed sodium amounts were higher for precipitate from oxidized pulp. During the oxidation, COONa groups could have been formed on the precipitates. Chlorine bonded on precipitates surface may come from sodium hypochlorite or dichloromethane extraction. We could observe the residual chlorine of dichloromethane extraction by comparing NO2 and NO3 precipitate. Obviously, the sulfur came from the sulfuric acid used for precipitation. The more interesting thing to observe with our XPS analysis is the oxygen / carbon atomic ratio. Yet, before calculating this ratio, it is useful to further analyze the oxygen with a narrow scan. The deconstructed peaks will enable us to confirm that the oxygen measured was bonded with carbon from the precipitate structure.

On oxygen narrow scans, we could observed a main peak around 533 eV, which matches to the oxygen to carbon bonds. Yet, for some analyzed precipitate, two additional peaks were also found at around 531.7 and 536 eV. The peak at 531.7 eV corresponds to oxygen bonded with sulfur (SO_2/SO_3). Therefore, oxygen measured at this energy should not be considered to calculate the oxygen / carbon ratio of precipitate. The peak at 536 eV is related to sodium Auger transition and is

a known interference for oxygen measurement and must also be subtracted. After all these considerations, Table 5 present the amounts of those 3 peaks for all analyzed sample.

Table 5. Peaks proportion observed in the oxygen peak deconstruction

Precipitate from …	Oxygen bonded to carbon	Oxygen bonded to sulfur	Sodium Auger peak
NO TMP after hot water extraction (NO2)	100	U.D.	U.D.
NO TMP after sodium hydroxide extraction (NO3)	88.36 ± 2.70	8.30 ± 1.73	1.76 ± 1.28
Bl TMP after hot water extraction (Bl2)	88.62 ± 3.02	11.38 ± 2.74	U.D.
Bl TMP after sodium hydroxide extraction (Bl3)	83.35 ± 1.22	14.38 ± 2.64	2.28 ± 1.41
Ox TMP after hot water extraction (Ox2)	73.38 ± 5.16	15.25 ± 0.77	11.38 ± 4.39
Ox TMP after sodium hydroxide extraction (Ox3)	79.25 ± 4.15	15.38 ± 2.14	5.38 ± 2.01
U.D. : Undetected			

The precipitates surface of non-oxidized TMP presented a higher content of oxygen bonded directly to carbon compared to bleached TMP precipitate and even more, when compared to oxidized TMP precipitate. In addition, a low amount of sodium Auger peak was observed after sodium hydroxide extraction of non-oxidized and bleached TMP. Still, sodium Auger peak was more important after sodium hydroxide extraction of oxidized TMP. The additional sodium observed should be from the TEMPO oxidation. This phenomenon was easier to observe after hot water extraction of non-oxidized and bleached TMP. Indeed, after hot water extraction, no sodium Auger peaks were found but a high amount was observed for oxidized TMP. During the hot water extraction, oxidized precipitate was obtained from the oxidized TMP probably due to structure weakening induced by the TEMPO oxidation.

A representation of the total C-C bonded carbon amount by the oxygen / carbon atomic ratio as allowed us to better evaluate the precipitates characteristics (Fig.2). Precipitates were compared to pure lignin and pure cellulose theoretical data according to Johansson et al. (1999).

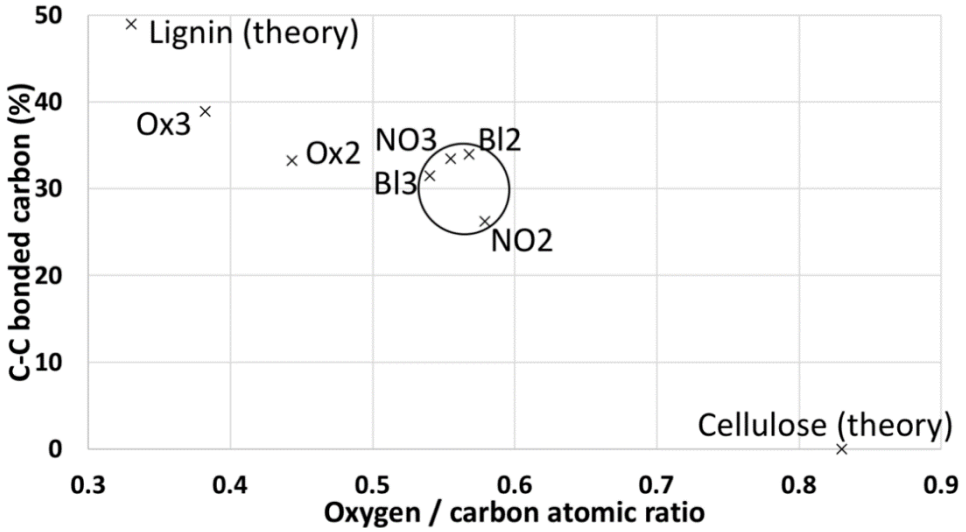

Fig. 2. C-C bonded carbon amount by oxygen / carbon atomic ratio for all extracted precipitate

Precipitates from non-oxidized and bleached TMP after hot water or sodium hydroxide extraction (NO2, NO3, Bl2 and Bl3) were grouped closely to a mid-value, between theoretical lignin and cellulose. Precipitate extracted from oxidized TMP (Ox2) presented closer proportions to theoretical lignin. As explained previously, according to sodium Auger peak observation, precipitate from oxidized TMP after hot water extraction was oxidized. That means that the precipitate containing more lignin, compared to non-oxidized or bleached precipitate, was oxidized by TEMPO. Therefore, we can presume that the lignin extracted at this step was oxidized. Precipitate from oxidized TMP after sodium hydroxide extraction (Ox3) was really close to theoretical lignin. This lignin was less oxidized but TEMPO oxidation effect on fiber structure as allowed lignin to be more easily extracted with lower chemical modifications.

Conclusions

1. Pulp carboxyl group content, pulp lignin content and XPS analysis shown that lignin was modified during the oxidation. We can conclude that TEMPO-mediated oxidation is not only selective to cellulose C6 carbon but can also react on lignin during TMP oxidation.
2. This study has not allowed us to prove formerly that TMP hemicelluloses were oxidized by the TEMPO-mediated system. However, an easier components extraction or dissolution indicate a fiber structure modification. Moreover, extracted material mainly composed with holocellulose presented very high carboxylic groups content. Thus indirectly proving that hemicelluloses could potentially be affected by TMP TEMPO oxidation.
3. TEMPO-mediated oxidation affects fibers structure according to TGA analysis and as allowed an easier wood components extraction. In addition, the oxidation increase the lignin acid-soluble fraction.
4. Mass yield difference between bleached and oxidized TMP confirmed the used of sodium hypochlorite as a co-oxidant in TEMPO oxidation instead of a bleaching agent.

Acknowledgments

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