Evaluation of Kraft cooking behaviour for six different softwoods species

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SUMMARY

The main goal of this paper is to observe de differences of behaviour between six softwoods species during the kraft cooking sequence, knowing that morphological, physicochemical and hygroscopic characters are different. Six wood species (Scots pine, maritime pine, Aleppo pine, black pine, Douglas fir and Spruce) were analysed separately.

Different parameters were evaluated (Lignin content, Polysaccharides content (cellulose and hemicelluloses), Yield, Hexenuronic acids) and for each wood species three temperatures (150ºC, 160ºC and 170ºC) and different cooking times, allowing to study the behaviour of the wood species. Common cooking conditions were applied and temperature program included cold impregnation, a plateau at 110°C during 2.5 hours to perform initial delignification separately followed by a second plateau at cooking temperature. Non-uniform cooking behaviour was observed; chestnut and oak trees consumed much more caustic soda and had a lower yield in the initial phase of the cook. It was possible conclude that in a genera way, the behaviour of the six softwoods is highly homogeneous, for the three temperatures studied.

Data analysis was made with Principal component analysis (PCA) and ANOVA. The results of PCA show that all parameters: Yield (Y), Klason lignin (L), cellulose content (C), and effective residual alkali (EA) are well correlated. The cellulose content was negatively correlated with the other factors. The hexenuronic acids (HA) and hemicelluloses content was well correlated witch other. The coking time in the 2nd plateau influence all factors. Moreover, the three different temperatures are very similar they present statically differences with Tukey's test ($P<0.05$). For the highest cooking time all parameter present lower values. The time on the 2nd plateau do not influence the yield and the delignification.

Keywords: Kraft cooking, softwoods, lignin content, polysaccharides content, Hexenuronic acids.

INTRODUCTION

Being wood on of the most important material used in the pulp and paper industry, moreover there are two parameters: wood quality and wood cost; that should always be taking in account.

Kraft pulping kinetics has been extensively studied and described since the late 50's. Several studies concerning different wood species may be found in literature [1-11]. From this time, experimental methods and interpretation methods have changed and one of the main difficulties is to compare the different behaviours observed for the number of wood species that were studied.

Quite a few wood species are used for the production of Kraft pulp, due to their chemical and morphological properties. Although the chemical kinetics and its variability among species is probably the most important factor that affects cooking characteristics, in a general way it would be economically benefit if the pulp at the end of the cooking sequence presents a lower quantity of lignin content and higher percentage of hemicelluloses.

EXPERIMENTAL

Samples wood chips were cut as thin half-disks (~1.8 mm thickness). The wood species used in this study are represented in Table 1.

Table 1. Softwood species submitted to kraft cooking, scientific name and symbol adopt in the work.

Wood	Scientific name	Abbreviation
Scots pine	*Pins sylvestris*	Ps
Maritime pine	*Pinus pinaster*	Pp
Aleppo pine	*Pinus halepensis*	Ph
Black pine	*Pinus nigra*	Pn
Douglas fir	*Pseudotsuga menziesii*	Pm
Spruce	*Picea abies*	Pa

Cooking conditions

11 g of chips (o.d. basis) and 65 mL of white liquor were introduced in mini-digesters (85 mL). Heating-up program allowed to perform initial delignification first (30 min to 110°C, 2.5 h), then bulk delignification: rapid heat-up to cooking temperature at 150°C (18 min), 160°C (21 min), 170°C (25 min), and plateau time. Cooking conditions were EA=25% NaOH/wood, S= 37%, L/W=6.

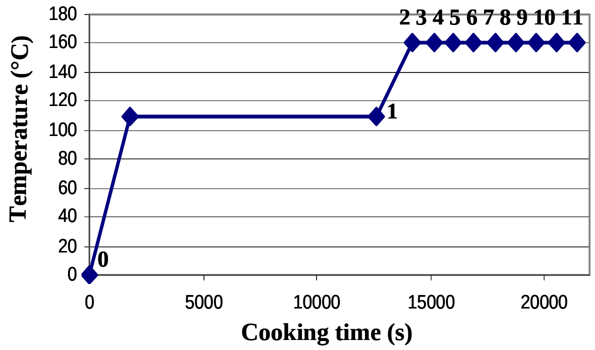


Figure 1. Example of a non-uniform cooking sequence (160ºC).

The pulp yields, residual effective alkali, Klason lignin (wood and pulp), polysaccharides content (wood and pulp) and hexenuronic acids content were determined according to the standard methods.

RESULTS AND DISCUSSION

Figure 2 shows an example of the behaviour for two wood species studied, in this case, we only present maritime pine and black pine. In this Figure it is possible to observe pulp yield, Klason lignin content, carbohydrates content, hemicelluloses content and Hexenuronic acids content, in function of removal time from the second plateau.

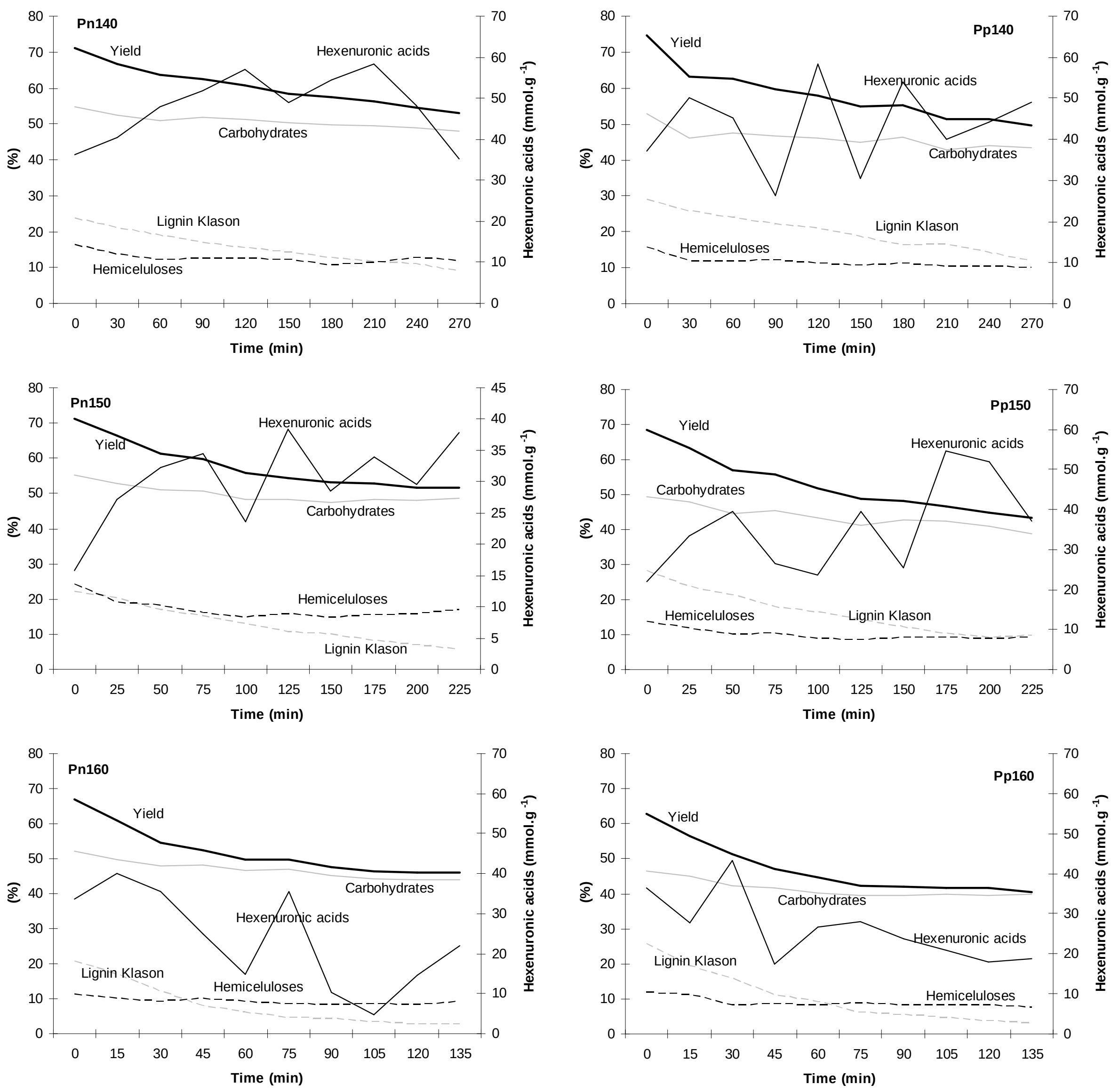


Figure 2. Variation of different parameters measured during the kraft cooking (Yield, Klason lignin, Carbohydrates, Hemicelluloses and Hexenuronic acids) in function of time, for the three temperatures (150ºC, 160ºC and 170ºC) studied.

With Figure 2, is possible to see the behaviour between two wood species for the several components studied in wood and different times and temperatures, during the kraft cooking sequence. In the left graphics of this Figure, the behaviours for the different temperatures of maritime pine are represented, in the right part of the Figure the specie that is analysed is the Black pine.

Normally, the consumption of ERA (Effective residual alkali) during the impregnation phase is rather low, around 12% of the initial concentration, that can be explain by the lower amount of extractives, acetyl groups and secondary products of wood, also that the very low dissolution of polysaccharides and lignin in the impregnation phase leads to a loss of yield of only 6 to 8%.

It is also observed that, the difference for individual wood specie between the 3 temperatures it is not very observed, but the difference between wood species it increase slightly with the temperature.

It appears to present a variation most important of the hemicelluloses, always in the initial phase (around 50%) that persists along the cooking sequence. The quantity of xylans is not very high at the beginning then regular and not very degraded until the end of cooking. At the contrary, the quantity of glucommanans is very abundant, but they are strongly eliminated at the initial phase of cooking, but they persist until the end of the cooking.

Concerning the Hexenuronic acids, it appears to be observed that the values obtained are very irregular and is not possible to define a tendency.

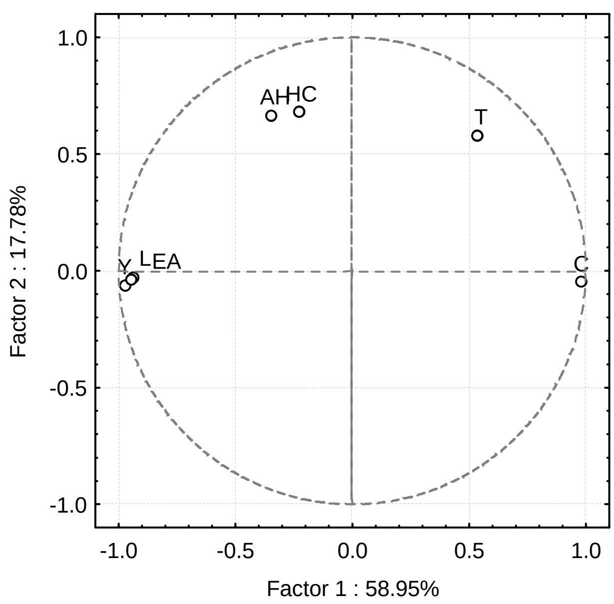
Statistical analysis

Principal components analysis was used to investigate the correlations between yield ad the other parameters studies and the different times and temperatures level.

For the correlation between evaluated parameters two factors were chosen because explains 77% of total variation. Figure 3 represents the projection of variables on the factor-plane. The first component, which represents the Yield variation, explains 59 % and the second, who represent the hemicelulose content, explains 18 % of total variation.

Factor 1, which defines the first component of cooking performance, includes a series of properties, which are significantly correlated amongst themselves: Yield (Y), Klason lignin (L), cellulose content (C), and effective residual alkali (EA). The cellulose content was negatively correlated with the other factors. The hexenuronic acids (HA) and hemicelluloses content was well correlated witch other. The cooking time for the second plateau was a parameter that was well correlated with all parameters explained by the first and second factor, moreover present a higher influence in the factor 2 explained by the hexenuronic acids and hemicelluloses content. The continuous loss of hexenuronic acids is certainly linked to the continuous loss of the xylans in the pulp, which is one of the main compounds of xylans. At the end of the cooking sequence, it often appears a reprecipitation of xylan fibres that will be observed in the black liquor. This explanation is not consistent with the decline of hexenuronic acids.

In our case, if precipitation occurs, it would means that the xylans does not contain hexenuronic acids, which seems consistent with the fact that hemicelluloses carrying carboxylic groups should have a better solubility in alkaline than neutral hemicelluloses.



Legend and factor coordinates of the variables, based on correlation

Variables		Factor 1	Factor 2
Coking time (s)	**T**	0.5348	**0.5782**
Yield (%)	**Y**	**-0.9714**	-0.0618
Klason Lignin (%)	**LK**	**-0.9394**	-0.0263
Cellulose (C)	**C**	**0.9763**	-0.0491
Hemicelluloses (%)	**HC**	-0.2281	**0.6782**
Hexenuronic acids ($mmol.g^{-1}$)	**AH**	-0.3443	**0.6650**
Effective residual alkali ($g.L^{-1}$)	**EA**	**-0.9436**	-0.0397

Figure 3. Relative distribution of kraft cooking properties of different softwood species according to the factors resulting from Principal components analysis.

It was also projected cases into the same system of vectors to know the correlation between different wood species and different temperature cooking condition. For the species studied there aren't significant differences. In fact all species are the same anatomical structure and the some provenance, so don't present a higher variability. Margarido *et al.* [12] found for hardwood species differences related with the anatomical structure, but in that case the variability is higher compared with the softwood species.

The difference between the temperatures is very small, however, it is possible to observe at each temperature the species studied seen to present a slightly difference among them. In Figure 4 was represented the projection of the cases in the factor plane for PCA for *Pinus pinaster*.

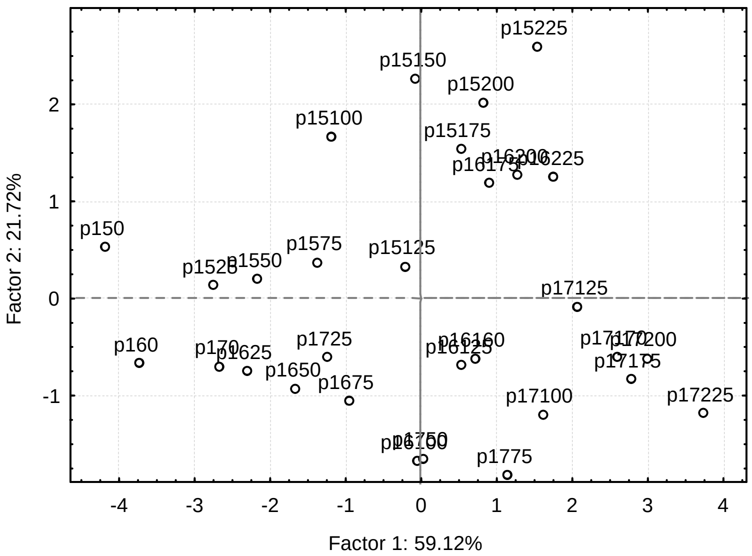


Figure 4. Projection of the wood samples from different temperatures and removing samples times, on the plane of the two main factors resulting from Principal Components Analysis. The first letter represents the wood species, in this case the *Pinus pinaster*. The second two numbers represents the cooking temperature (15 - 150 ºC, 16 - 160 ºC AND 17 - 170 ºC) and the third number represents the time on the second plateau were was removed the sample to analyse.

With ANOVA test it is possible confirm that the species present behaviour very similar and it is not found statistical differences with the Tukey's HSD test (P<0.05).

It was find also difference in the cooking temperatures. For Y, LK and C the higher values are observed for the lower temperature and all temperatures are statistical different.

For the hemicelluloses content the higher value are also for the lower temperature but the higher temperatures present behaviour similar. For the hexenuronic acids the value found for the cooking temperature of 150 was statistical different and very different from the others. The difference between 150 and 160-170 is almost o the double. For the ERA the higher values are found for 160 and 150 temperatures.

Table 2. Statistical differences, made by ANOVA using the Tukey HSD test, presented for the coking time in the second plateau for the studied parameters. First colon represent the point time where were collected the sample.

Yield (%)	Lignin (%)	Cellulose (%)	Hemicelluloses (%)	Hexenuronic acids (µmol/g)	Residual effective alkali (g/L)
0(a)	0(a)	0(a)	0(a)	0(a)	0(a)
1(b)	1(b)	1(b)	1(a,b)	1(a,b)	1(b)
2(c)	2(c)	2(c)	2(a,b)	2(b)	2(c)
3(d)	3(c,d)	3(c)	3(a,b)	3(a,b)	3(c,d)
4(d)	4(d,e)	4(d)	4(b)	4(a,b)	4(d,e)
5(e)	5(e,f)	5(d,e)	5(a,b)	5(a,b)	5(e,f)
6(e,f)	6(f)	6(e,f)	6(a,b)	6(a,b)	6(f,g)
7(f)	7(f,g)	7(e,f,g)	7(a,b)	7(a,b)	7(f,g)
8(f,g)	8(f,g)	8(f,g)	8(a,b)	8(a,b)	8(g,h)
9(g)	9(g)	9(g)	9(a,b)	9(a,b)	9(h)

The different temperatures used on the cooking sequence (150 ºC, 160 ºC and 170 ºC) present for the first two point of removal time statistical similarities for all the wood species, at all temperatures.
For yield, Lignin content, cellulose content and residual effective alkali it appears to present a statistical difference for between the removal times, but in the case of the Hemicelluloses contents and the hexenuronic acids it seems that the present a similar statistical behaviour.

CONCLUSIONS

This study presents an exhaustive comparison of the behaviour of different wood species used for kraft cooking. The first important point shown by this study is that the kinetic approach chosen has a certain importance in the estimation of the activation energies for the bulk phase (although this part of the study is not presented here). This approach corresponds to superimposed kinetic phases that correspond better to the case of fast-cooking species.

The initial delignification concept was validated, however, instead of using a plateau of 110ºC, a plateau of 130ºC was carried out, it would be preferable, in this way we would be shore that the initial delignification it would be complete [1, 13, 14].

The yield loss is observed in a range between the 50 and 40% of pulp, depending n the temperature. The behaviour of polysaccharides was studied separately. In the case of the hemicelluloses content, xylans are better preserved than glucommans during the cooking sequence, but the degradation is gradual.

Hexenuronic acids present always an increase until a certain point, around the 60% of yield loss, and then present a decrease until the end of the cooking sequence.

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