

LO-SOLIDS KRAFT PULPING OF EUCALYPTUS WOOD

Gomide, J.L.¹, Pimenta, L.R.¹, Colodette, J.L.¹, Shin, N.H.²

¹Universidade Federal de Viçosa; jlgomide@ufv.br

² Andritz Inc.

ABSTRACT

The objective of this study was to evaluate the behavior of eucalyptus wood chemical components during Lo-Solids kraft cooking. All cooks were carried out in duplicate to obtain pulp of 16 ± 0.5 kappa number. Semi-delignified chips, pulp and cooking liquors were collected from five different zones of a laboratory digester. Wood delignification (97%) occurred in five phases with the “bulk delignification” made up of three steps. Overall, 14.2% of the cellulose and 53.9% of the hemicelluloses were removed at the end of the cook. Lignin richer in guaiacyl units was removed during the impregnation while during bulk delignification the lignin removed was progressively richer in syringyl units. There was a rapid formation of hexenuronic acids in the “Impregnation Zone” but their concentration decreased toward the middle of the “Upper Cooking Zone” and from this point on they increased until the end of cook. Solids content and alkali concentration in cooking liquor were relatively constant during the whole cook. A large viscosity drop (31.8 cP) occurred during the final cooking phase, despite the small yield loss (1%) coupled to a considerable kappa reduction (5.5 units).

INTRODUCTION

Over the past few years various modifications in the kraft process technology have occurred, mainly with regard to more intensive delignification, developed in response to the need to increase pulp process delignification levels in order to permit reduction in bleaching reagent consumption. Although the initial developments led to large advances in pulping processes it has been found that in certain situations intensive delignification can harm pulping yield.

Almeida (1), citing various authors, stated that pulp produced by a modified process presents lower bleaching chemical consumption than conventional pulp of the same kappa number. He also stated that these pulps could be cooked to a lower kappa number, while maintaining or improving viscosity and strength properties. Cooking to low kappa number reduces bleach plant pollution because of the lower bleaching reagent demand.

Even at optimal kappa numbers, hardwood kraft pulps present significant variations in yield, bleachability and quality. According to Gomide et al. (2), much of this variation can be related to variability in wood quality, but some is certainly related to the pulping operations and conditions. The pulping conditions affect the chemical nature of residual lignin, the constitution of the carbohydrate fraction and the pulp hexenuronic acids (HexA's) content.

Pulp mills are currently directing research efforts towards alternatives that increase process yield without harming pulp bleachability or loss in product quality. Increases in process yield lead to productivity gains and are important in reducing specific wood consumption and the quantity of solids sent to the recovery boiler, often a production bottleneck in Brazilian pulp mills.

Although many studies exist on modified eucalypt pulping, few contain a thorough analysis of the phases of delignification, including carbohydrate dissolution, and especially the behaviour of HexA's and lignin structural alterations during the process. Knowledge of wood chemical composition modifications during pulping may permit pulp producers to identify problems, propose improvements and make operational adaptations for different production schedules or bleaching sequences.

One way to seek improvements leading to increased process yield and product quality is through careful monitoring of chemical modifications of wood in different cooking phases. According to diverse authors (1,3, 4, 5, 6), the best way to increase yield is through retention of hemicelluloses. Another advantage of retaining hemicelluloses is their positive affect on strength properties and fiber-water chemical interactions.

Lo-Solids Process: Principles and Objectives

Current commercial pulping processes are based on the principles of selective delignification (7) through different configurations of modern industrial digesters.

Careful laboratory studies have revealed that the dissolved solids content of the cooking liquor pulping is very important. Wood components (lignin, cellulose, hemicelluloses, and extractives) dissolved in the cooking liquor significantly contribute to increased white liquor consumption and decreased viscosity, pulp strength, unbleached pulp brightness, pulp bleachability and final pulp brightness (8, 9).

Improvements in pulping performance and pulp quality were achieved by decreasing the dissolved solids retention time in the digester and cooking liquor concentration. This is the basis of the Lo-Solids cooking (10). The main objective of this cooking process is to minimize the quantity and concentration of dissolved wood solids in the bulk and final delignification stages (9). As in other types of continuous modern kraft processes, it is also necessary to guarantee uniform temperature and pulping reagent distributions, a constant alkali profile throughout the cooking vessel, a minimum concentration of dissolved lignin at the end of the cook, a minimum of temperature peaks during the cook and a sufficient alkali concentration during bulk and residual delignification.

The basic principle of Lo-Solids pulping involves multiple cooking liquor extractions. Reposition and dilution with preheated white liquor and washing liquor follows each extraction. The combined reposition liquor flows (white liquor + washing liquor) afford low dissolved solids concentrations. The reposition liquor flows also increase the liquor/wood ratio, helping to dilute subproducts formed during cooking, thereby decreasing the concentrations of these products in the bulk and residual delignification stages (9).

MATERIAL AND METHODS

Material

Industrial, screened *Eucalyptus* sp. chips and white liquor from a pulp and paper company in São Paulo, Brazil were used in this study.

Methods

The analytical methods used in this study are listed in Table 1.

Table 1 – Methods of analysis used in the study

Analysis	Method
Chip classification	SCAN-CM 40:95
Pulp viscosity	TAPPI T230 om-94
Kappa number	TAPPI T236 cm-85
Black liquor residual alkali	SCAN N33:94
Soluble lignin content	Goldschimid (11)
Insoluble lignin content	Gomide and Demuner (12)
Carbohydrate content	TAPPI T249 cm-00
Acetyl group content	Solar et al. (13)
Uronic acids	Englyst and Cummings (14)
Hexenuronic acids	Vuorinem et al. (15)
Dichloromethane extractives	TAPPI 204 cm-97
Syringyl/Guaiacyl ratio	Lin and Dence (16)

Process Simulation

Cooks were run in duplicate to obtain pulp of kappa number 16 ± 0.5 . Wood chemical components were monitored during the different steps of the cook, simulating the different regions of the digester, as shown in Figure 1. Pulping conditions used are described in Table 2. Temperatures in the cooking zones and the alkali charges applied were defined in

preliminary cooks to obtain the desired residual alkali at the end of each zone. The effective alkali residual target was within the range pre-established for this pulping process.

Table 2 – Pulping conditions

Pulping parameters	Impregnation	Upper cooking	Lower cooking
Heating time (min.)	15	15	-
Time at temperature (min.)	30	60	120
Temperature (°C)	110	155	156
Total alkali charge (EA, % wood)	-----17,5-----		
Alkali split (% total EA)	50	30	20
Liquor/wood ratio	3.5	3.5	3.5

Collection and Preparation of Samples for Analysis

Process monitoring was performed as previously described by Fantuzzi Neto (17) and Almeida (1), and consisted of interrupting the cooks at different phases to collect semi-delignified chips, pulp and spent black liquor. The samples were collected at five points in the process (Figure 1):

- The end of the Impregnation Zone (IMP) after 45 minutes of pulping,
- The middle of the Upper Cook Zone (mid-UCZ), after 90 minutes of pulping,
- The end of the Upper Cook Zone (end-UCZ), after 120 minutes of pulping,
- The middle of the Lower Cook Zone (mid-LCZ), after 180 minutes of pulping,
- At the end of the cook (End), after 240 minutes.

Upon interrupting the cook, polyethylene bottles were completely filled with drained black liquor for posterior analysis. Unbleached pulp was washed, defibered, screened, dewatered in a centrifuge to a consistency of 30-35% and stored in polyethylene bags. The pulp was weighed and samples withdrawn for moisture determination and yield calculation.

Samples containing fractions of pulp and rejects were air dried and then weighed for yield calculations. Samples were then milled in a cyclone type mill (100 mesh) and pulp and rejects fractions were mixed after milling in the proportions based on screened pulp and rejects yields. Milling with a low screen mesh was done to permit uniform mixing of the fractions, and to avoid future sample analysis errors.

RESULTS AND DISCUSSION

Lignin Behavior

The behavior of lignin during the cooking process is shown in Figure 2. As can be observed, delignification occurred in four phases. “Initial Delignification” phase occurred in the impregnation step with low lignin removal (9.2% of initial content). Low molecular weight and more readily accessible lignin fractions in the fiber wall were probably removed in this phase. Lignin behavior in this phase is very important because it can influence behavior during the bulk phase, as well as the quantity of residual lignin (Teder and Olm, cited by Lindgren and Lindstrom, 18).

Intense delignification occurred in the Upper Cooking Zone (155°C) in the first 30 minutes. The highest process delignification rate (56.6%) occurred in this period, followed by two periods of lower lignin removals of 9.5 and 18.9%. These first three steps in the Lo-Solids digester cooking zone (the two steps in the Upper Cooking Zone and the first half of the Lower Cooking Zone) characterize the “Bulk Delignification”. Differently from what has been reported by other authors for eucalypt wood (17, 1), in Lo-Solids cooking a bulk delignification phase was formed by three phases, bordered by the lignin removal curve. The lower delignification rate in the second half of the upper cooking zone was probably caused by the decrease in alkali concentration in this phase. Overall, 66.1% of the original wood lignin present occurred in the Upper Cooking Zone of the digester.

In the final cooking step, corresponding to the second half of the Lower Cooking Zone (156°C), a small amount of lignin was removed (2.8%) as compared to the rest of the process, characterizing the “Residual Delignification” phase. Lignin structures in this phase were probably condensed, with a greater proportion of carbon-carbon bonds not easily broken by

the action of pulping reagents. Another explanation found in the literature for lignin resistance in the residual delignification phase is the formation of lignin-carbohydrate complexes, mostly between lignin and xylan chains and their side chains containing HexA's and 4-O-methylglucuronic acids.

Kappa Number

Kappa number analysis was carried out in the steps where fiber separation occurred, from the mid-Upper Cooking Zone onward. In the second half of the Upper Cooking Zone, the kappa number fell 29 units. The first half of the Lower Cooking Zone showed similar delignification intensity and a 24.6 kappa number unit reduction. The intense kappa number drop in the initial cooking zone was a result of high lignin removal in the "Bulk Delignification" phase of the Lo-Solids process. Kappa reduction was less intense (5.5 units), in the final cooking phase, associated to the "Residual Delignification" phase.

Syringyl/Guaiacyl Ratio (S/G)

During Lo-Solids pulping of *Eucalyptus* wood, the ratio between syringyl and guaiacyl lignin structures did not show a defined trend (Figure 3).

Lignin with a greater proportion of guaiacyl units was removed in the impregnation phase (initial delignification phase), evidenced by an increase in S/G ratio after the impregnation step. Pinto et al. (19) also found that highly condensed lignin rich in p-hydroxyphenol and guaiacyl units and containing many lignin-carbohydrate (mostly xylose units) bonds was extracted during the initial phase of *Eucalyptus globulus* wood pulping. According to the authors, the reason for the greater removal of these units is that the pulping reagents initially penetrate and act on the fiber vessel walls and the middle lamella, regions known to possess guaiacyl-rich lignins. The liquor later penetrates the secondary fiber region rich in syringyl lignin. This explanation appears unsatisfactory since the cooking liquor reaches the middle lamella after diffusion into the secondary wall. Another more plausible explanation is that low molecular weight, and possibly more guaiacyl rich lignin molecules are removed in the beginning of the cook.

Lignin removed in the bulk delignification phase was progressively richer in syringyl units and the S/G ratio decreased, similar to what was reported by Pinto et al. (19).

It was not possible to establish the S/G ratio of the unbleached pulp at the end of the cook due to its low lignin concentration which did not permit lignin extraction and chromatographic analysis.

Carbohydrate Behavior

The behavior of carbohydrates during the cook is presented in Figure 4. Intense mannan (77.6%) and acetyl group (87.4%) degradation occurred in the Impregnation Zone. Galactans (26.7%), xylans (7.6%), glucans were removed to a lesser extent. Arabinans exhibited the greatest resistance in this step and practically, undergoing almost no degradation.

More intense xylan (17.4%) and arabinan (22.3%) degradation and complete hydrolysis of acetyl groups occurred midway through the Upper Cooking Zone after reaching the cooking temperature (155°C). Mannans were degraded to a lesser extent (14.1%) in this phase. Glucans underwent slightly more severe (6.4%) degradation than in the impregnation phase because of the increase in cooking temperature.

Carbohydrates showed more stability in the second half of the Upper Cooking Zone, undergoing little degradation. When compared to the first half of this zone, galactans underwent the most degradation (7.4%), followed by the arabinans (3.4%). Mannan and glucan contents remained stable, with only small reductions in each (0.4% and 0.7%, respectively). Xylans were practically not removed (0.1% loss) in this phase.

There was an increase in galactan and arabinan removal in the first half of the Lower Cooking Zone (156°C). Galactans presented the highest degradation (13.6%) in this phase. Arabinans (8.6%), glucans (2.7%) and xylans (2.1%) were more degraded than in the previous step while mannans underwent little degradation (0.9%).

Xylan content increased (1.7%) during the final cooking step probably due to lower alkali concentration, confirming that a fraction of these hemicelluloses can be deposited in the fibers at the end of the cook. Galactans (5.3%) and arabinans (1.7%) were slightly degraded while glucans (0.5%) were quite resistant to the final cooking step.

Cellulose and hemicellulose contents were determined by considering a 1:1 ratio between glucose and mannose belonging to the glucomannans. The hemicellulose content in the pulp included the HexA's content.

Intense reduction in hemicellulose content occurred (25.4%) and less intense degradation of cellulose (3.9%) occurred during impregnation, as shown in Figure 5. A greater reduction in cellulose content (6.3%) occurred after reaching the Upper Cooking Zone, where 23.5% of the hemicelluloses had already been removed. Little cellulose was degraded (0.5%) in the final cooking step and hemicelluloses contents were not reduced, which can be explained by xylan precipitation during this step that compensated the degradation of other hemicelluloses. At the end of the cook total cellulose content reduction was 14.2%, evidence of this polysaccharide's greater resistance to pulping than the hemicelluloses that presented a removal of 53.9%.

Behavior of Hexenuronic Acids (HexA's)

Figure 6 shows the behavior of HexA's during Lo-Solids cooking. The majority of uronic acids are composed of 4-O-methylglucuronic acids that can be converted to HexA's during kraft pulping. Therefore loss of uronic acids can be explained in part by degradation and in part by conversion to HexA's.

In contrast to monitoring of other wood chemical components, the reference HexA's content was not that of the original wood sample, since this component is formed during pulping. The reference point was therefore chosen as that stage which presented the highest HexA's concentration, the end of the impregnation zone. This artifice was used to better illustrate the true dynamics of these acids during the cook, considering the yield in the different zones and not its absolute concentration in the sample.

Intense formation of HexA's in the Impregnation Zone was accompanied by a 16% reduction in uronic acid content. A 32% reduction in HexA's and a 20% reduction in uronic acids contents were observed between the end of the Impregnation Zone and the first half of the Upper Cooking Zone. According to some authors (20, 21, 22), two mechanisms may lead to a decrease in HexA's content. One mechanism is alkaline hydrolysis and elimination of these groups from xylan chains. The other mechanism is their dissolution together with the xyloans. The quantity of HexA's was calculated per 100 xylose monomers to determine which mechanism caused the decrease in HexA's content as shown in Figure 7. The greatest value of HexA's/100 xyloses occurred at the end of impregnation, similar to what was reported by Dahlman (22) and Buchert et al. (23). This value then decreased which can be explained by the elimination of HexA's groups from the xylan chains as the predominant mechanism. It is not possible to affirm that this was the only mechanism since some of the HexA's were also possibly eliminated with the xylan chains. The results of this study however demonstrate that the decrease in HexA's in the first half of the Upper Cooking Zone was caused by elimination of the acids from the xylan chains. Similar results were found by Al-Dajani (20) and Dahlman (22) who showed that the rate of dissolution/degradation of HexA's is greater than of xylan, although some HexA's are still linked to xylan chains dissolved in residual black liquor.

The rate of HexA's formation increased 9.6% from the second half of the Upper Cooking Zone to the end of the cook (Figure 6), which also led to an increase in the HexA's/xylose ratio (Figure 7).

The behavior of HexA's during cooking is complex since it is governed by dynamic processes of formation and degradation of varying intensities in the different digester zones. HexA's formation and degradation processes depend on pulping parameters, mainly alkali concentration and temperature.

Some mills face serious restrictions in unbleached pulp HexA's levels because of bottlenecks in production of bleaching reagents or use of inefficient bleaching sequences. As previously demonstrated for the Lo-Solids process, the HexA's content increased after reaching a minimum in the middle of the Upper Cooking Zone. Prolonging the cook in order to reduce the kappa number can result in pulps with higher HexA's concentrations. This is true within the limits of kappa number commercially used for bleached eucalypt pulp but is not valid for very severe cooks that produce very low kappa number pulps. It should also be remembered that wood type can influence this trend.

Lipophilic Extractives

Extractives that can be extracted with dichloromethane (DCM) are denominated lipophilic. Lo-Solids cooking efficiently leached these extractives that are potential sources of pitch deposits (24), that are harmful to equipment and can form dirt and specks in bleached pulp, compromising its quality. Behavior of these extractives is presented in Figure

8. These extractives were intensely removed from chips until halfway through the Upper Cooking Zone after which their residual fraction proved resistant to pulping conditions.

Global Analysis of Cooking

Averages for the pulping process are detailed in Table 3.

Table 3 – Overall results of Lo-Solids cooking of eucalypt

Analyses and Results	Cooking phase				
	IMP*	mid-UCZ*	end-UCZ*	mid-LCZ*	End*
Kappa number	---	75.4	46.5	21.9	16.5
Kappa number per HexA*	---	3.5	3.8	4.4	4.8
Corrected kappa number	---	71.9	42.7	17.5	11.7
Screened yield (%)	0	32.5	51.4	56.1	55.3
Rejects (%)	89.6	34.2	13.4	0.2	0
Total yield (%)	89.6	66.6	63.7	56.3	55.3
Viscosity (cP)	---	---	102.5	100.1	68.5
H factor	2	160	280	561	839

* 11.6 mmol HexA/unit kappa number; IMP = Impregnation Zone; mid-UCZ= Middle of Upper Cooking Zone; end-UCZ = End of Upper Cooking Zone; mid-LCZ= Middle of Lower Cooking Zone; End = End of Cook.

Process Yield

Despite the loss of about 10% of the wood weight at the end of the impregnation step, fiber individualization was only observed to begin in the middle of the Upper Cooking Zone. From this point on an intense reduction in reject content and increase in screened yield occurred. In the middle of the Lower Cooking Zone the quantity of rejects was very low, evidence of an efficient wood impregnation step. Efficient impregnation results in uniform distribution of cooking reagents in the interior of the chips, guaranteeing delignification of all the wood, resulting in efficient fiber individualization and fewer rejects.

Final process yield in was high (55.3%) compared to other laboratory studies on modified continuous cooking of eucalypt wood (17, 1).

Wood weight fell 10.4% in the impregnation zone mainly due to carbohydrates dissolution since lignin removal was low in this zone. Behaviors of lignin and carbohydrates are shown in Figure 11. Greater loss (22.9%) occurred in the middle of the Upper Cooking Zone, the region in which intense lignin, carbohydrate and extractives dissolution occurred. Total yield decreased less intensely in the both following steps: 2.9% at end of the Upper Cooking Zone and 7.4% in the middle of the Lower Cooking Zone. Little carbohydrate degradation (3.9%) occurred in these digester zones. In the last cooking step (final 60 minutes) only a slight drop in total yield occurred (1%) which can be explained by the greater carbohydrate stability resulting in lower dissolution of these compounds in this final phase (0.4%). At the end of the Lo-Solids process only 44.7% of the wood was degraded, leading to a low specific wood consumption (1.81 ton wood/adt pulp).

Viscosity

Pulp viscosity during the process was analyzed only at three points due to difficulty in solubilizing the sample from the middle of the Upper Cooking Zone in cupric ethylene diamine solvent used to carry out the analysis (Tappi standard T230 om-94).

As shown in Figure 9, little pulp viscosity loss occurred in the Lower Cooking Zone (drop of 2.2 cP) indicating that the carbohydrate chains, mostly cellulose, did not undergo much chemical fragmentation in this phase. Intense cellulose chain fragmentation occurred in the “Residual Delignification” phase corresponding to the final 60 minutes, evidenced by the high viscosity drop of 31.8 cP. This phase thus constituted a critical step in the process since despite the low yield loss (1%) and considerable kappa drop (5.5 units) extending the cook sacrificed viscosity. To reach the pre-established level of delignification (kappa 16 0.5) while maintaining low residual alkali it was necessary to increase the temperature

to 156°C in the Lower Cooking Zone. Although this did not harm yield it probably caused a decrease in viscosity. Similar results was reported by Shin and Stromberg (25) who performed laboratory simulations of this process and showed that the increase in cooking temperature for a constant H factor negatively affected pulp viscosity although it did not affect process yield.

It can be observed that the decrease in alkali concentration in the Lower Cooking Zone leads to gains in process yield. However, low alkali concentration can compromise the delignification rate. According to Axelsson et al. (26) residual lignin is difficult to remove in cooking without severe cellulose and hemicellulose degradation resulting in loss of yield and, or pulp strength. A similar result was found by Fantuzzi Neto (17), who reported a severe viscosity loss in the residual delignification phase that also corresponded to the final 60 minutes of the cook.

Although the unbleached pulp viscosity of 68.5 cP is relatively high, an attractive option to minimize viscosity loss in pulp quality would be to end the cook at a higher kappa. The viscosity gains in cooking could make the bleaching step more flexible and result in a higher quality bleached pulp. On the other hand, extending the cook in order to reach a lower kappa number affects the chemical nature of residual lignin, the leachable lignin content and the lignin carbohydrate compounds, factors that affect pulp bleachability and bleaching reagent consumption.

Process Selectivity

Highly selective processes effectively attack lignin without however degrading carbohydrates to great extent, preserving yield. Selectivity was calculated as the ratio between percent lignin removed and percent carbohydrates degraded. Figure 10 presents the selectivity values and Figure 11 the lignin and carbohydrate removal profiles in the different phases of the process.

The Impregnation Zone had low selectivity due to the low lignin removal rate compared to the carbohydrate (mostly hemicelluloses) degradation rate. Selectivity increased in the first half of the Upper Cooking Zone due a proportionally higher increase in the lignin removal rate (56.5%) than in carbohydrate degradation (11.4%). The highest selectivity was observed in the second half of the Upper Cooking Zone where significant delignification occurred coupled with low carbohydrate loss. In the final 60 minutes of the cook (middle of the Lower Cooking Zone) the process was also quite selective, and could therefore be extended to obtain greater lignin removal without harming the carbohydrate content.

It should be pointed out that the greater reductions in lignin and carbohydrates shown in Figure 11 at the end of the impregnation and the end of the Upper Cooking Zone were preceded by injections of alkali. This demonstrates the effect of the increase in alkalinity on delignification kinetics and degradation of carbohydrates in the cooking process.

These results together with information on the influence of hydroxyl ion concentration on kinetics of the bulk delignification phase (18, 27, 28) and the quantity and structure of lignin in the residual phase (18, 28) indicate a possibility of increasing delignification efficiency, which could be achieved by keeping the hydroxyl ion concentration constant during the entire bulk phase from the end of impregnation to the middle of the Lower Cooking Zone. Injection of additional alkali at an intermediate point in the Upper Cooking Zone may guarantee a more homogeneous alkali concentration during the main delignification phase. Homogeneity of hydroxyl ion concentration might also favor selectivity in the bulk phase since it would avoid localized high alkali concentrations and thus decrease the rate of carbohydrate degradation.

Spent Liquors

Results of the analysis of black liquor in the different phases of the process are presented in Table 4.

Table 4: Spent black liquor characteristics in different phases of cooking

Analysis/Result	Cooking phase				
	IMP	mid-UCZ	end-UCZ	mid-LCZ	End
Effective alkali (g/L)	4.7	5.9	4.0	5.9	4.5
pH	12.9	13.2	12.9	13.0	12.9
Organic solids (%)	2.7	6.2	7.1	8.1	8.4
Inorganic solids (%)	4.3	6.4	6.5	7.4	7.2
Total solids (%)	7.0	12.6	13.6	15.5	15.6
Alkali consumed (%)	38.0	31.0	9.2	15.1	6.8

Liquor solids concentration is very important in the process since this is the basic principle of the process. The quantity and concentration of organic and inorganic solids, particularly in the bulk and residual delignification steps have diverse effects on process performance and final product quality.

The solids profile did not undergo abrupt alterations after the Impregnation Zone as shown in Figure 12. One of the objectives of this process is to guarantee a low and uniform dissolved solids concentration in the bulk and residual delignification stages. A total of 987.3 kg solids per ton of dry pulp were generated during the cook.

Another important parameter in this process control is the concentration of residual alkali, which can be an indication of process efficiency. According to some published studies low and well controlled residual alkali guarantees greater carbohydrate conservation, resulting in process yield benefits (4, 25) and final product strength (28).

Lo-Solids cooking presented low residual alkali concentrations throughout the whole process, proportioning a low applied alkali charge (17.5% EA, as NaOH) but a sufficient H factor (839) to allow effective consumption of the alkali applied. The low alkali concentration resulted in a high yield (55.3%) for the relatively low kappa (16.5) usually produced in mills that use eucalypt wood. For a constant H factor, increases in pulping temperature do not negatively affect Lo-Solids process yield, however high residual alkali at the end of the second cooking zone lead to yield losses (25).

Sufficient residual alkali must be present at the end of the cook to avoid precipitation of lignin structures dissolved in the liquor. Precipitated lignin structures affect pulp bleachability since they are difficult to remove during the bleaching operation. The liquor pH has to be sufficiently high to guarantee good wood delignification and avoid lignin precipitation at the end of the cook. According to Gomes et al. (29) and Gomide (30), under normal pulping conditions, lignin precipitation begins at pH below 12 and is considerable at pH below 11.

Residual effective alkali at the end of the cook was 4.5 g/L and pH was 12.9, values that do not favor lignin precipitation. On the other hand, the relatively low residual alkali may have favored xylan precipitation onto fibers at the end of the cook. According to Gomide et al. (6) cooking with low residual alkali results in high xylan and HexA's contents, which was confirmed in the present study, since the concentration of these components was high in the unbleached pulp at the end of the cook.

The alkali and temperature profiles during the Lo-Solids cook are presented in Figure 13. Alkali concentration remained stable during the whole process due to injections of alkali in the cooking zones. Maintenance of level alkali concentration through white liquor injections during cooking is one of the principles of selective delignification in modern kraft pulping processes. Furthermore, large variations in spent liquor alkali concentrations are not acceptable to the industry since they would compromise materials balances and recovery unit efficiency.

Alkali Consumption

As can be observed in Table 4, about 69% of total applied alkali in the cook was consumed by the middle of the Upper Cooking Zone. This high consumption was caused by the high lignin, carbohydrate and extractives degradation rates and by the complete hydrolysis of acetyl groups. Alkali consumption was lower in the final pulping, accompanying the lower lignin and carbohydrates degradation rates.

CONCLUSIONS

The results presented in this study demonstrated that:

1. Lo-Solids cooking delignification occurred in five steps. The "Initial Delignification" phase of low lignin removal (9.2% of the initial content) occurred in the impregnation step. The three first steps in the digester zones characterized the "Bulk Delignification" phase where 85% of the lignin was removed. The bulk delignification phase was formed by three sub-phases, bordered by the slope of the lignin removal curve. In the "Residual Delignification" phase during the final cooking period only a small amount of lignin was removed (2.8%) compared to the rest of the process.
2. Lignins with a higher proportion of guaiacyl units were removed in the initial delignification phase. Lignin removed in the bulk delignification phase had progressively more syringyl units, and the syringyl/guaiacyl ratio decreased.

The syringyl/guaiacyl ratio increased in the final phase of the process, indicating that more guaiacyl-rich lignin fractions were removed in this phase.

3. An intense reduction in hemicellulose content (25.4%) and a lower reduction in cellulose (3.9%) occurred during impregnation. The greatest reduction in cellulose (6.3%) occurred in the middle of the Upper Cooking Zone, when 23.5% of the hemicelluloses had already been removed. Little cellulose degradation (0.5%) occurred and no hemicellulose reduction was observed in the final cooking phase. Xylan precipitation probably occurred during this step that compensated the loss of other hemicelluloses. A total reduction of 14.2% of cellulose and 53.9% of hemicelluloses was observed at the end of the cook.
4. Hexenuronic acids formed rapidly in the Impregnation Zone. In the first half of the Upper Cooking Zone the HexA's content decreased mainly due to their hydrolysis and elimination of xylan chains. Thereafter, HexA's content increased until the end of the cook.
5. The Impregnation Zone had low selectivity due to the low lignin removal rate relative to the carbohydrate (mostly hemicelluloses) degradation rate. The highest selectivity was observed in the second half of the Upper Cooking Zone where significant delignification and low carbohydrate loss occurred.
6. Black liquor analyses demonstrated that both the solids content and alkali concentration remained uniform throughout the process.
7. Despite the low yield (1%) and considerable reduction in kappa number (5.5 units) a large drop in viscosity occurred (31.8 cP) at the end of the process (final 60 minutes).
8. When the middle of the Upper Cooking Zone was reached, 69% of the total applied alkali in the cook had already been consumed. This high consumption was caused by the high rate of degradation of lignin, carbohydrates, and extractives and by the complete hydrolysis of acetyl groups. Alkali consumption was lower in the final cooking phase, as were the rates of lignin and carbohydrate degradation.

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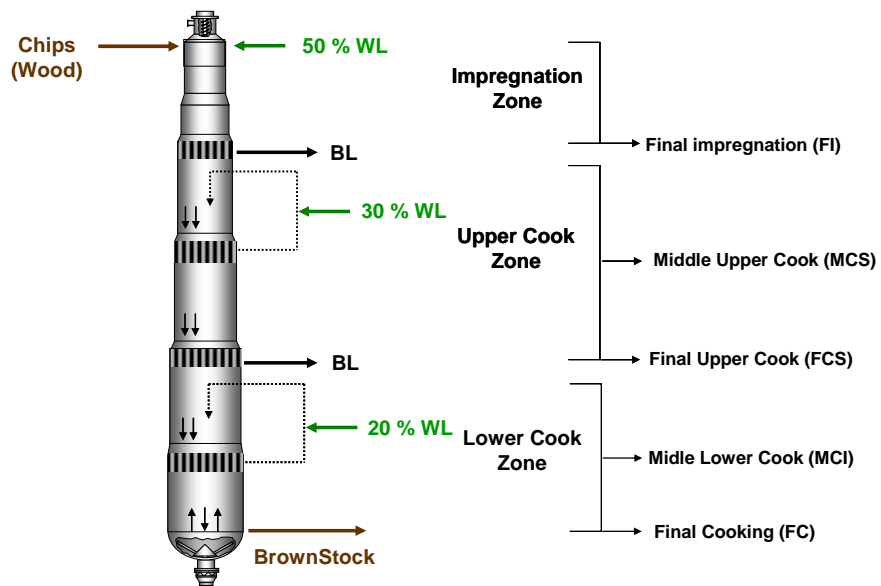


Figure 1 – LoSolids digester showing sampling points.

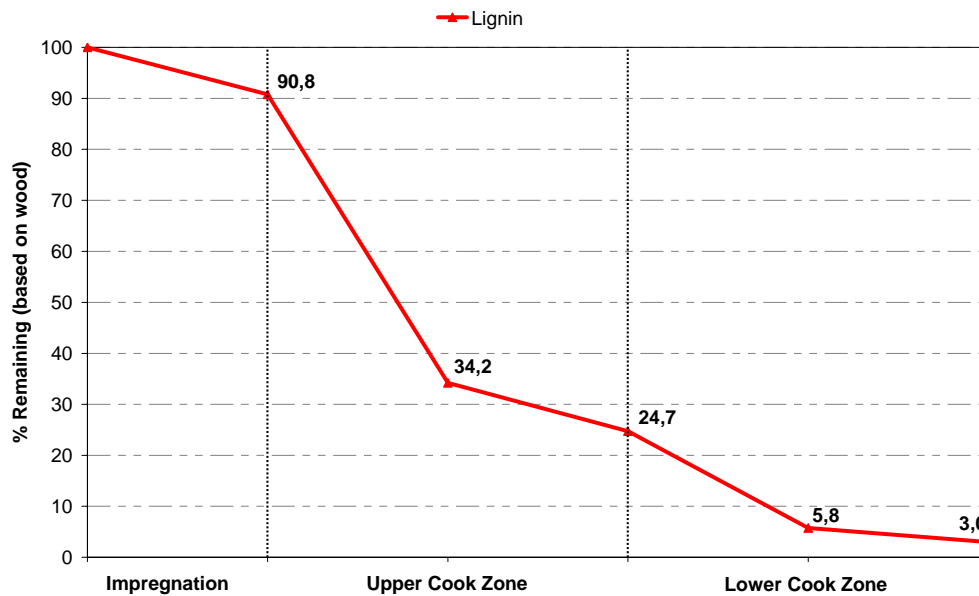


Figure 2 – Lignin behavior during pulping.

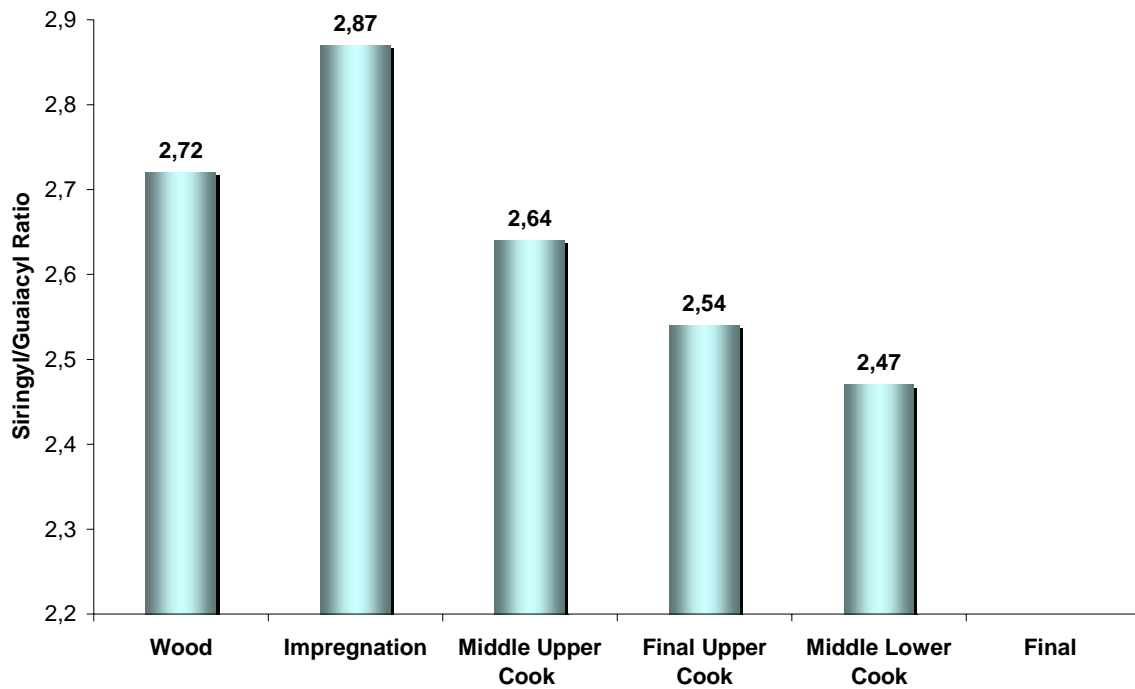


Figure 3 – Syringyl/guaiacyl ratio during pulping.

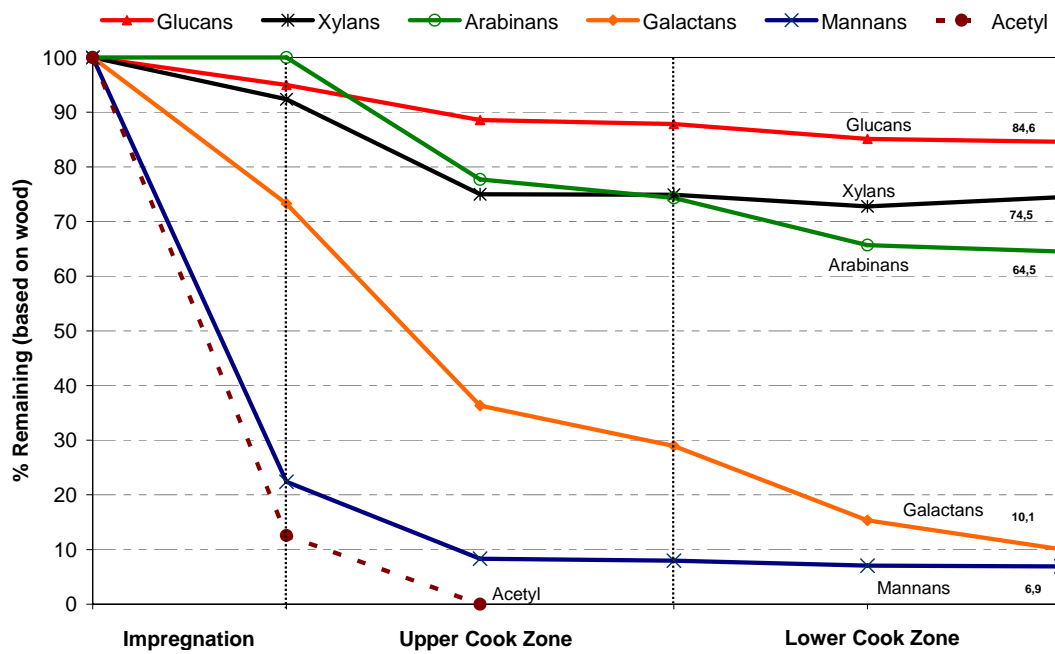


Figure 4 – Carbohydrates behavior during pulping.

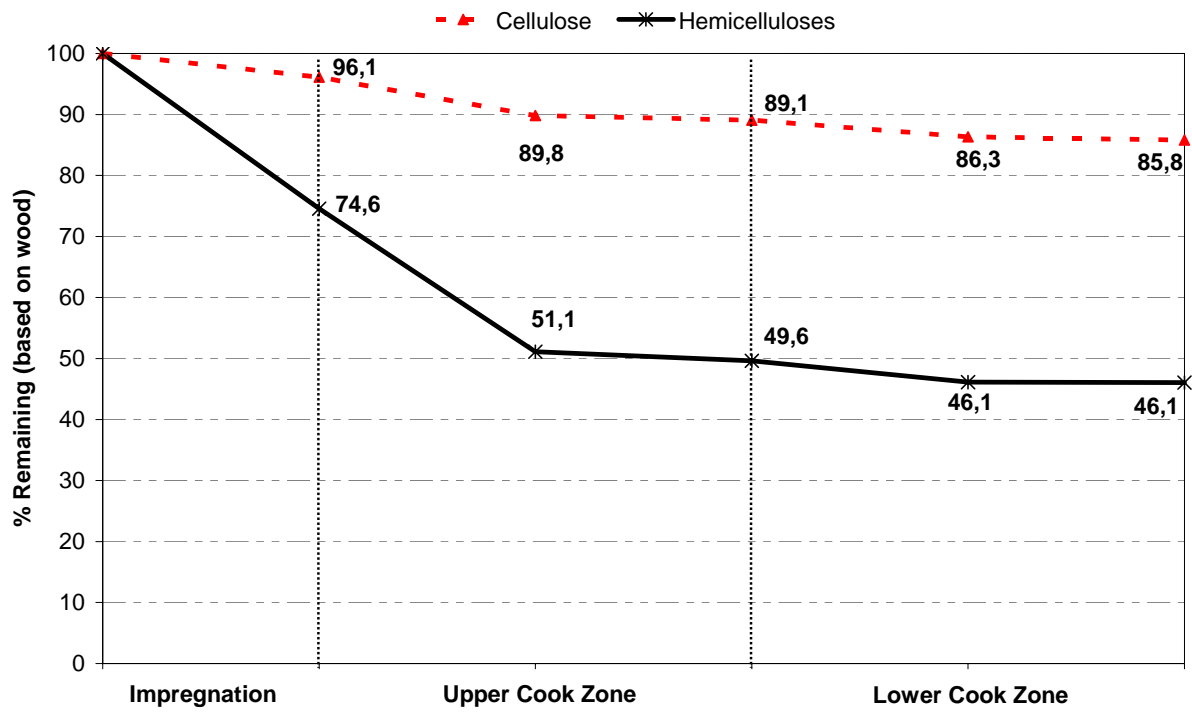


Figure 5 – Cellulose and hemicelluloses behavior during pulping.

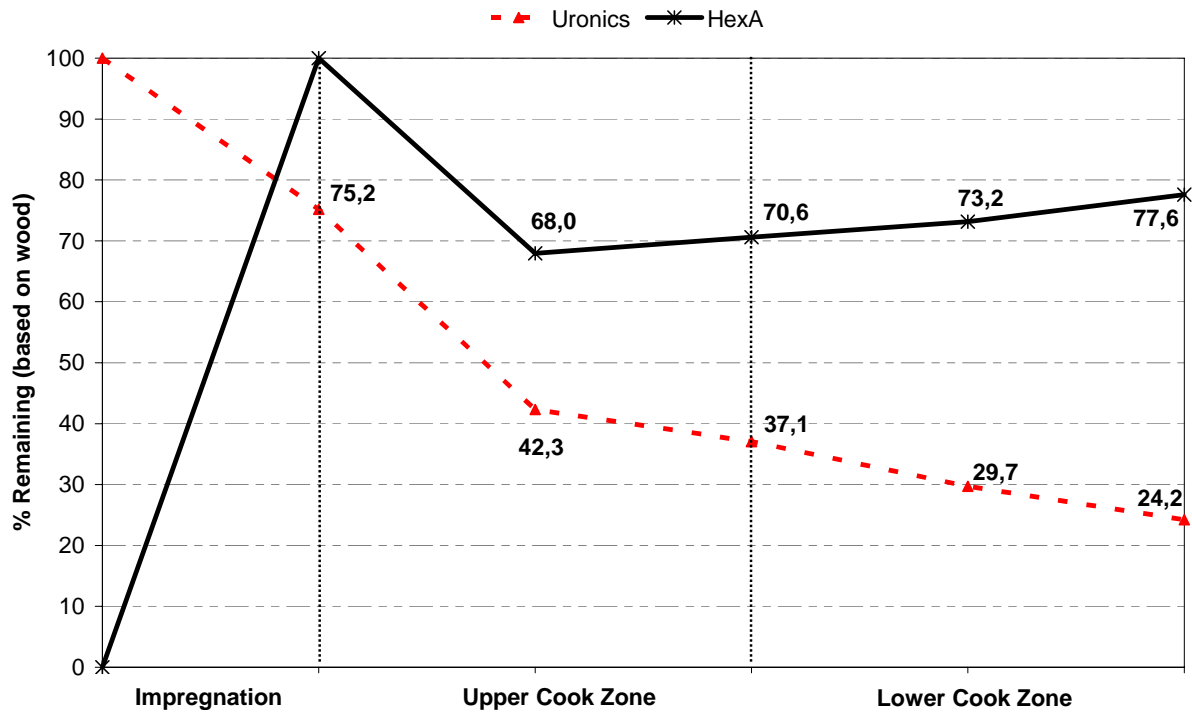


Figure 6 – Behavior of uronic and hexenurônico acids during pulping.

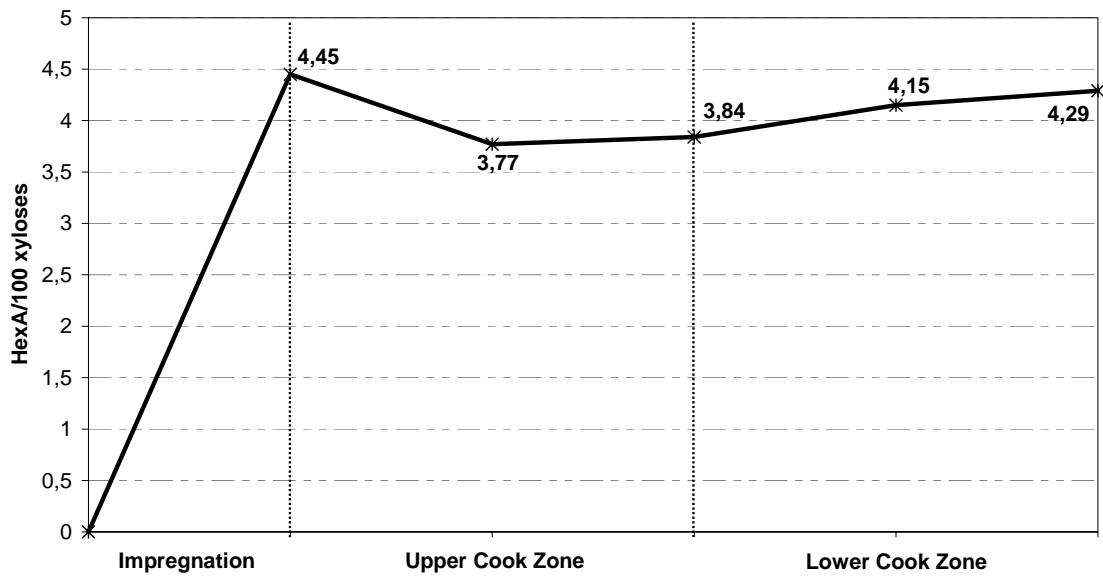


Figure 7 – Hexenuronic acid groups for 100 xylose monomers.

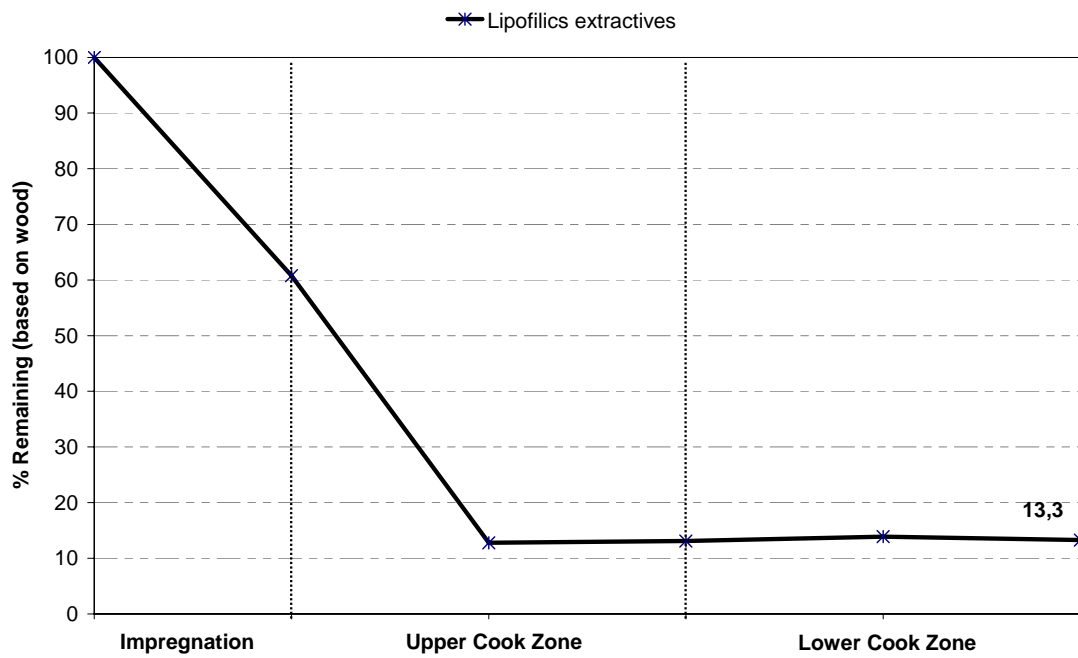


Figure 8 – Removal of lipophilic extractives during pulping.

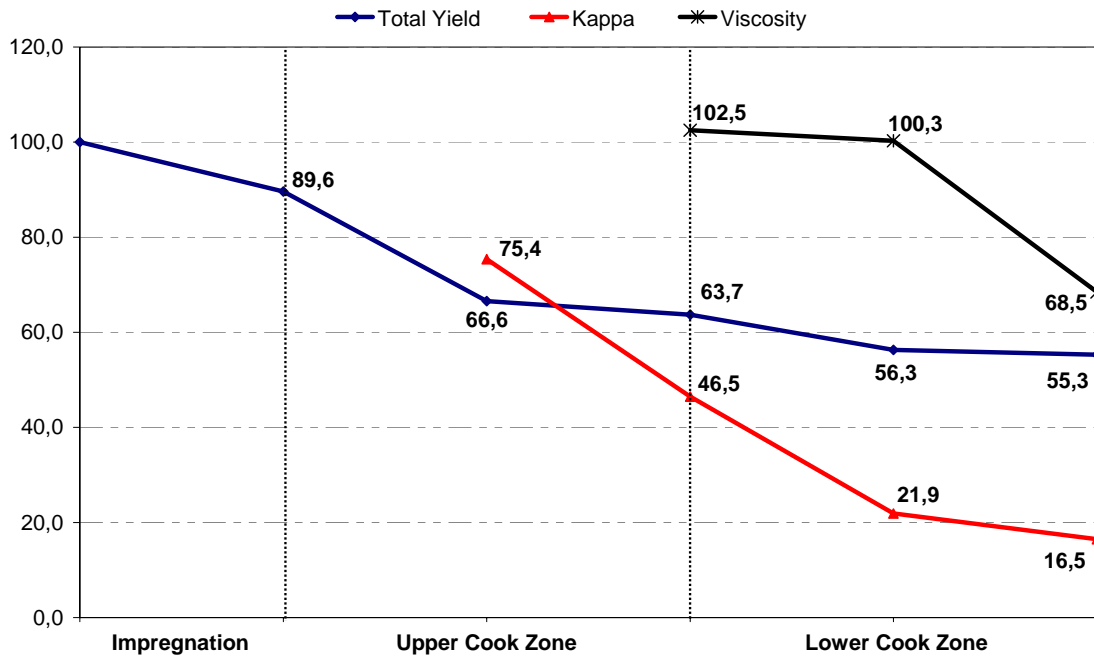


Figure 9 – Pulp modification during pulping.

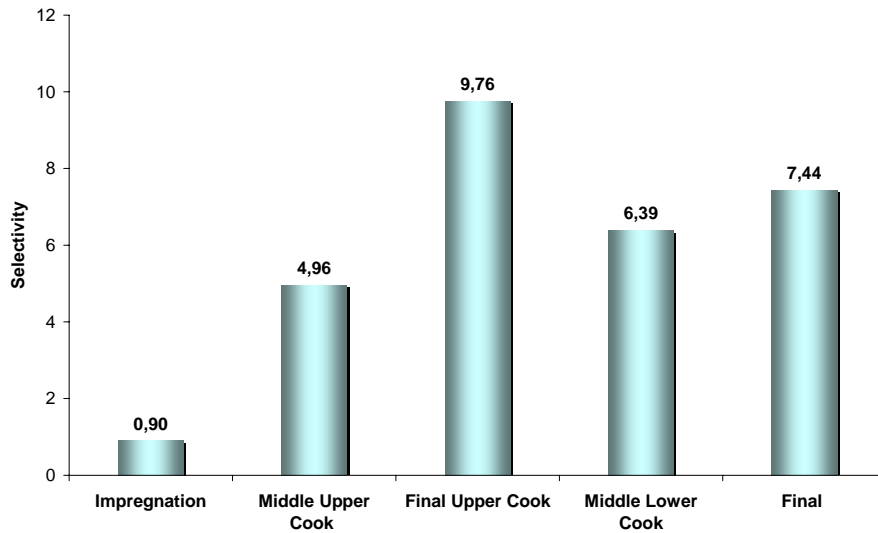


Figure 10 – Selectivity of digester cooking zones.

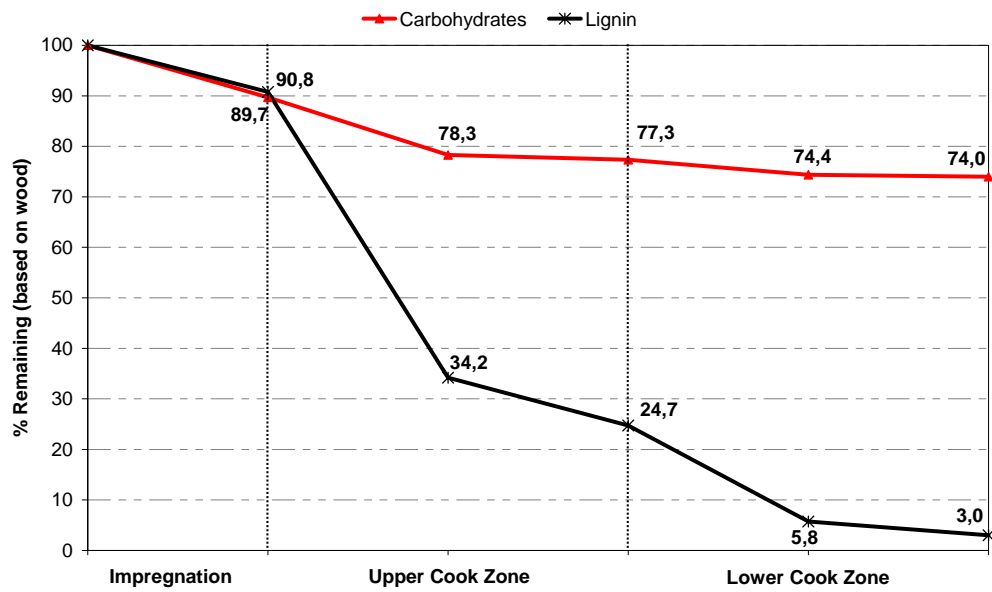


Figure 11 – Lignin and carbohydrates behavior during pulping.

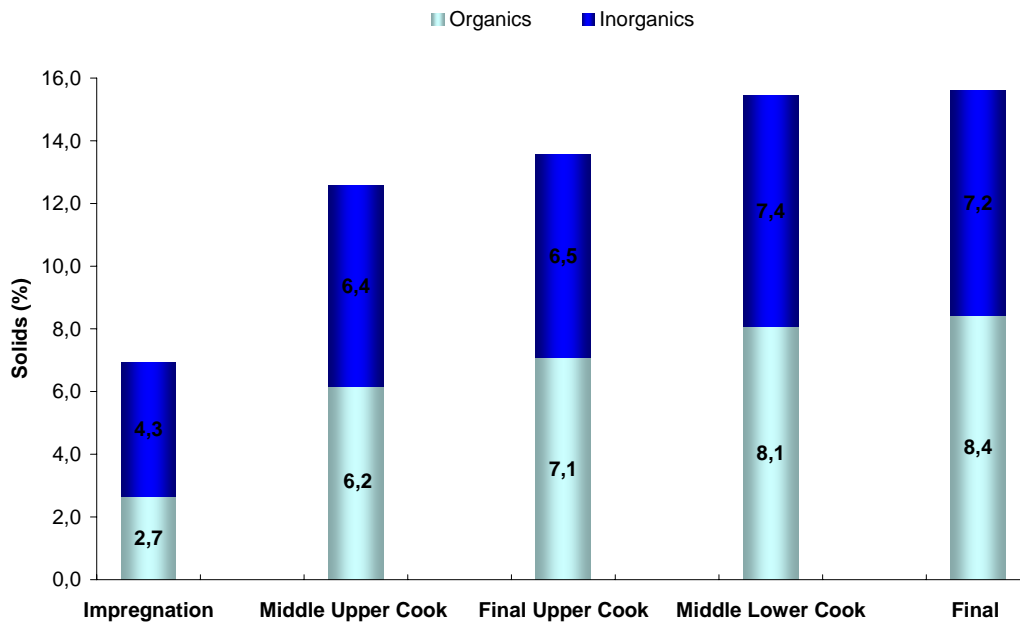


Figure 12 – Solids content of cooking liquor during pulping.

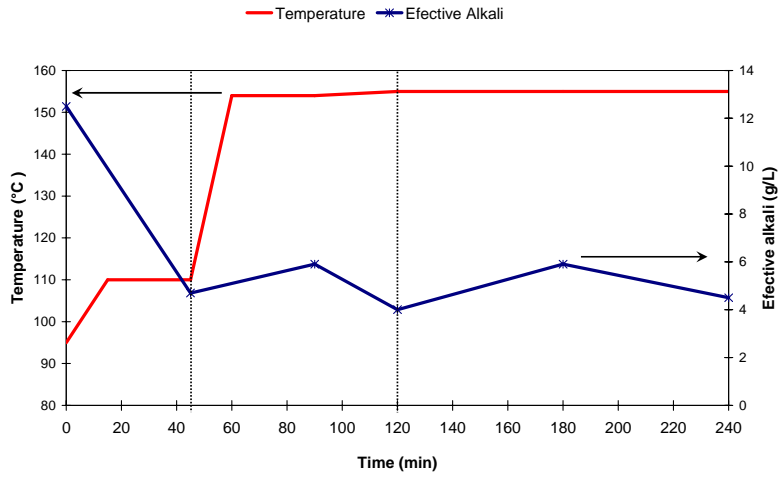


Figure 13 – Temperature and alkali profiles during cooking.



**FEDERAL UNIVERSITY OF VIÇOSA
PULP AND PAPER LABORATORY**



Lo-SOLIDS® KRAFT PULPING OF EUCALYPTUS WOOD

***Autors: Prof. José Lívio Gomide - UFV
Leonardo R. Pimenta - UFV
Prof. Jorge Colodette – UFV
Nam Hee Shin – Andritz Inc.***

TAPPI PULPING CONFERENCE – Jacksonville, Fl, USA – Oct. 21-24/ 2007.

Objective of this study

Laboratory simulation of a LoSolids digester zones to analyze the behavior of Eucalyptus wood chemical constituents during pulping

METHODOLOGY

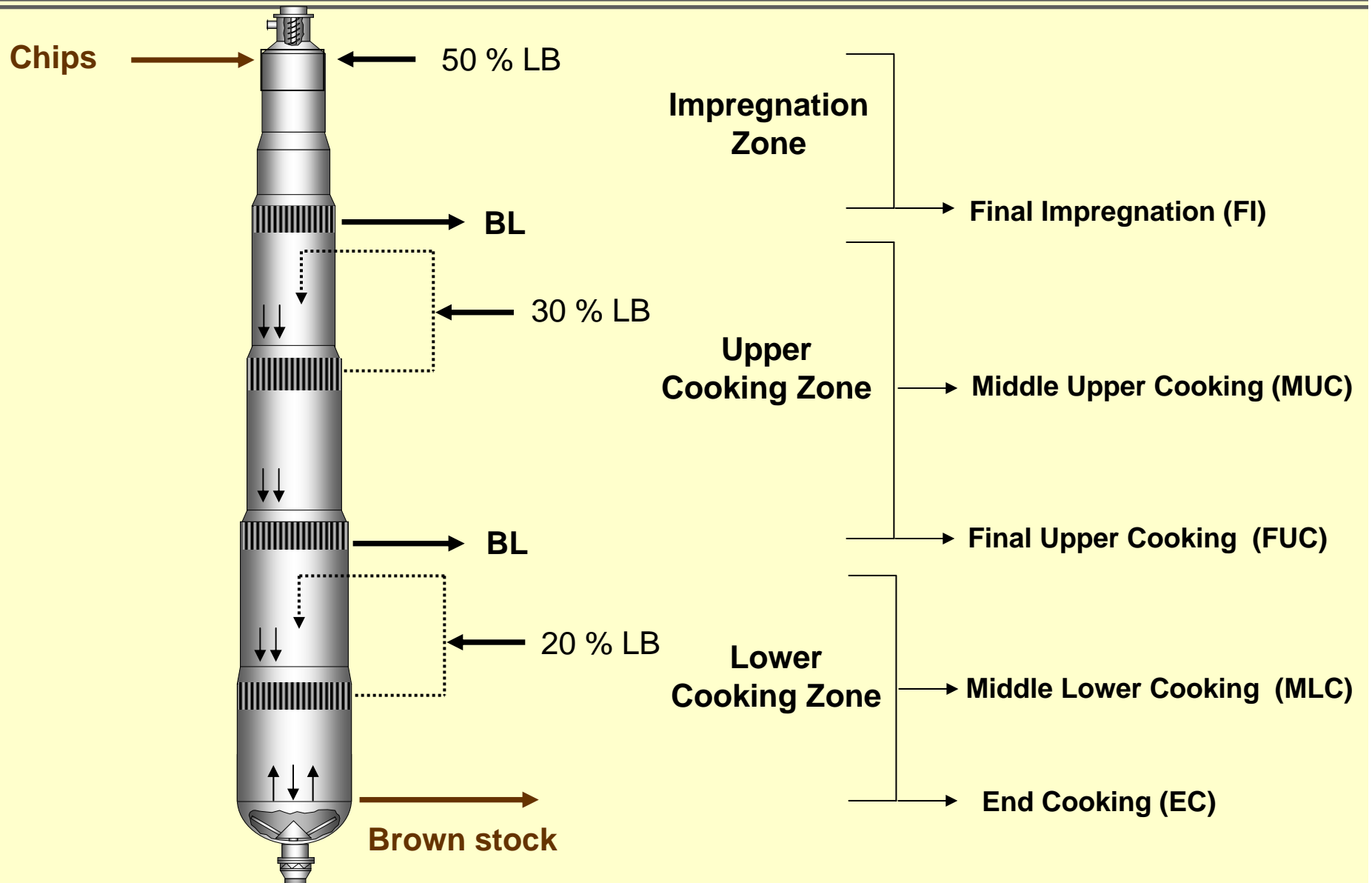
Methodology



Methodology

- ✓ Use of industrial chips and cooking liquors
- ✓ Simulation of Lo-Solids[®] ⇒ MK digester and accumulator vessels
- ✓ Stopping cooking cycle at following points:
 1. After impregnation zone (45 min)
 2. Middle of upper cooking zone (90 min)
 3. Final of upper cooking zone (120 min)
 4. Middle of lower cooking zone (180 min)
 5. Final of cooking zone (240 min)

Methodology



Methodology

Cooking Parameters	Impregnation	Upper Cooking	Lower cooking
Heating time, min.	15	15	---
TAT, min.	30	60	120
Temperature, °C	110	155	156
Effective Alkali Charge, %	17.5	17.5	17.5
Alkali split, %	50	30	20
Liquor/wood ratio	3.5	3.5	3.5

White Liquor: 104 g/L AE as NaOH; S = 30,5%

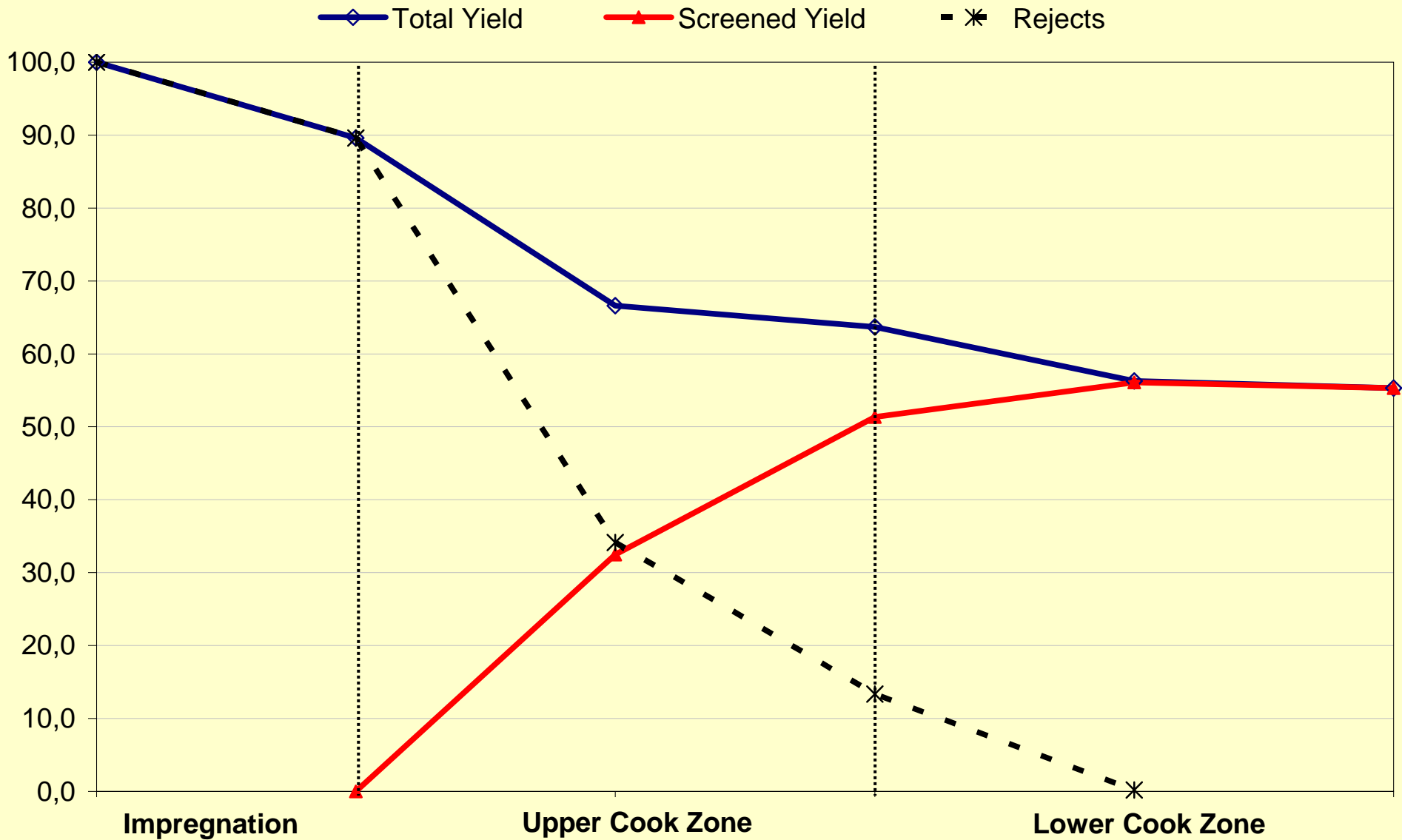
Pre-steaming: 105-110°C; 1.5 bar; 10+20 min

RESULTS

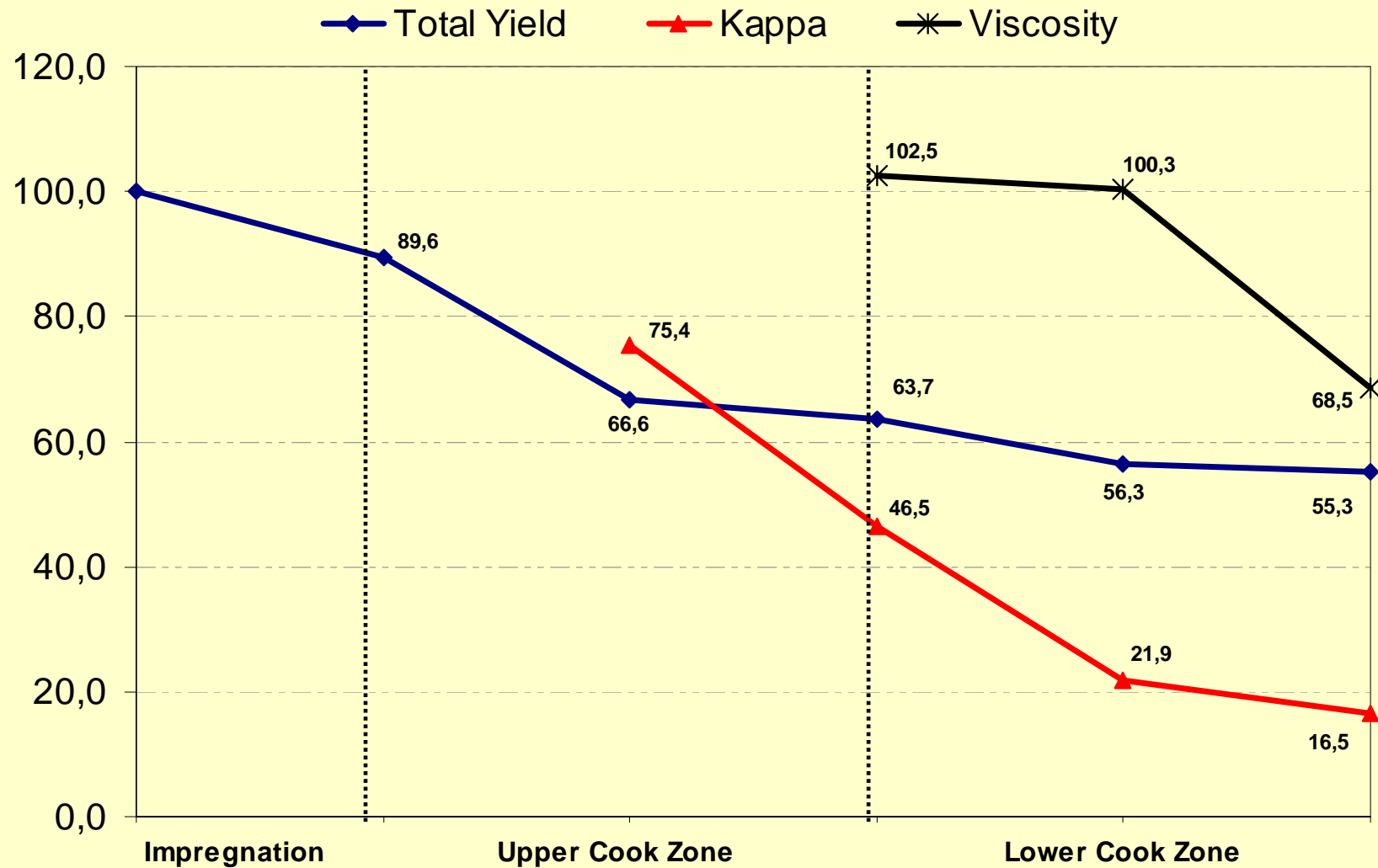
Pulping Results

Parameters	Impregnation Zone	Upper Cook	Final Upper Cook	Lower Cook	End of Cook
Kappa number	---	75.4	46.5	21.9	16.5
Kappa – HexA	---	3.5	3.8	4.4	4.8
Kappa – correct	---	71.9	42.7	17.5	11.7
Screened yield, %	---	32.5	51.4	56.1	55.3
Rejects, %	86.6	34.2	13.4	0.2	0.0
Total Yield, %	89.6	66.6	63.7	56.3	55.3
Viscosity, cP	---	---	102	100	68.5
H-factor	2	160	280	561	839

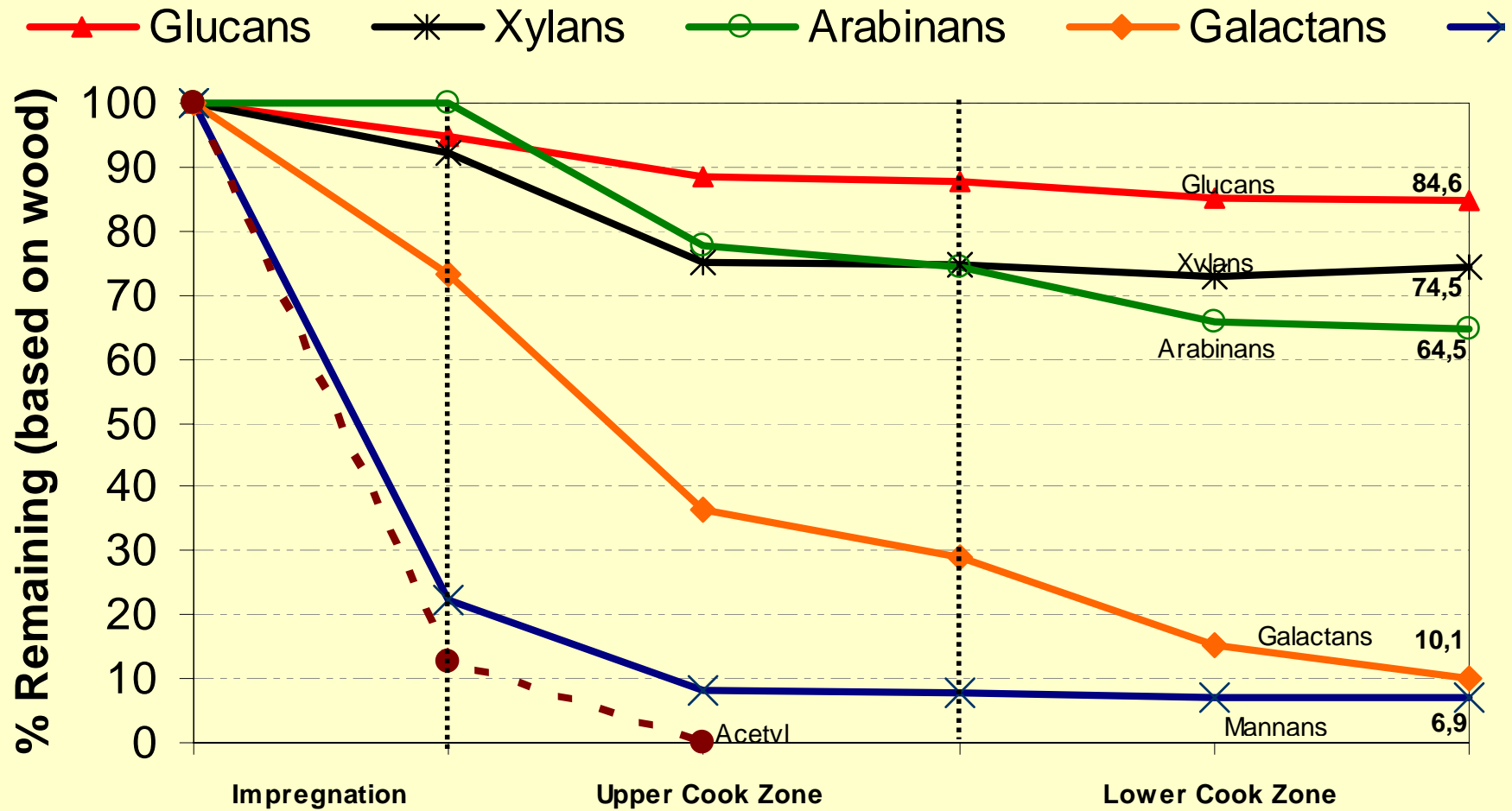
Yields and Rejects



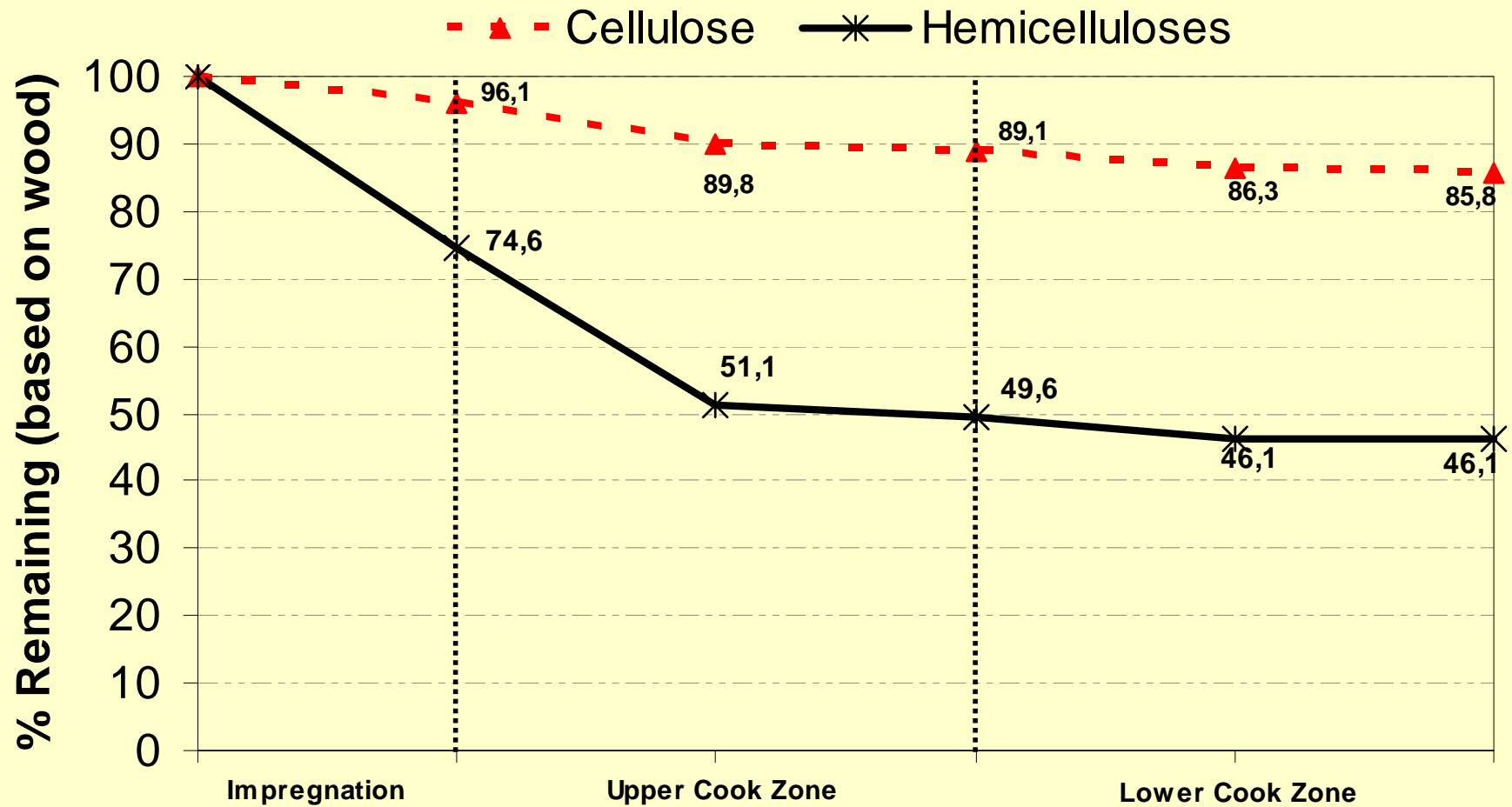
Yield, Kappa, Viscosity



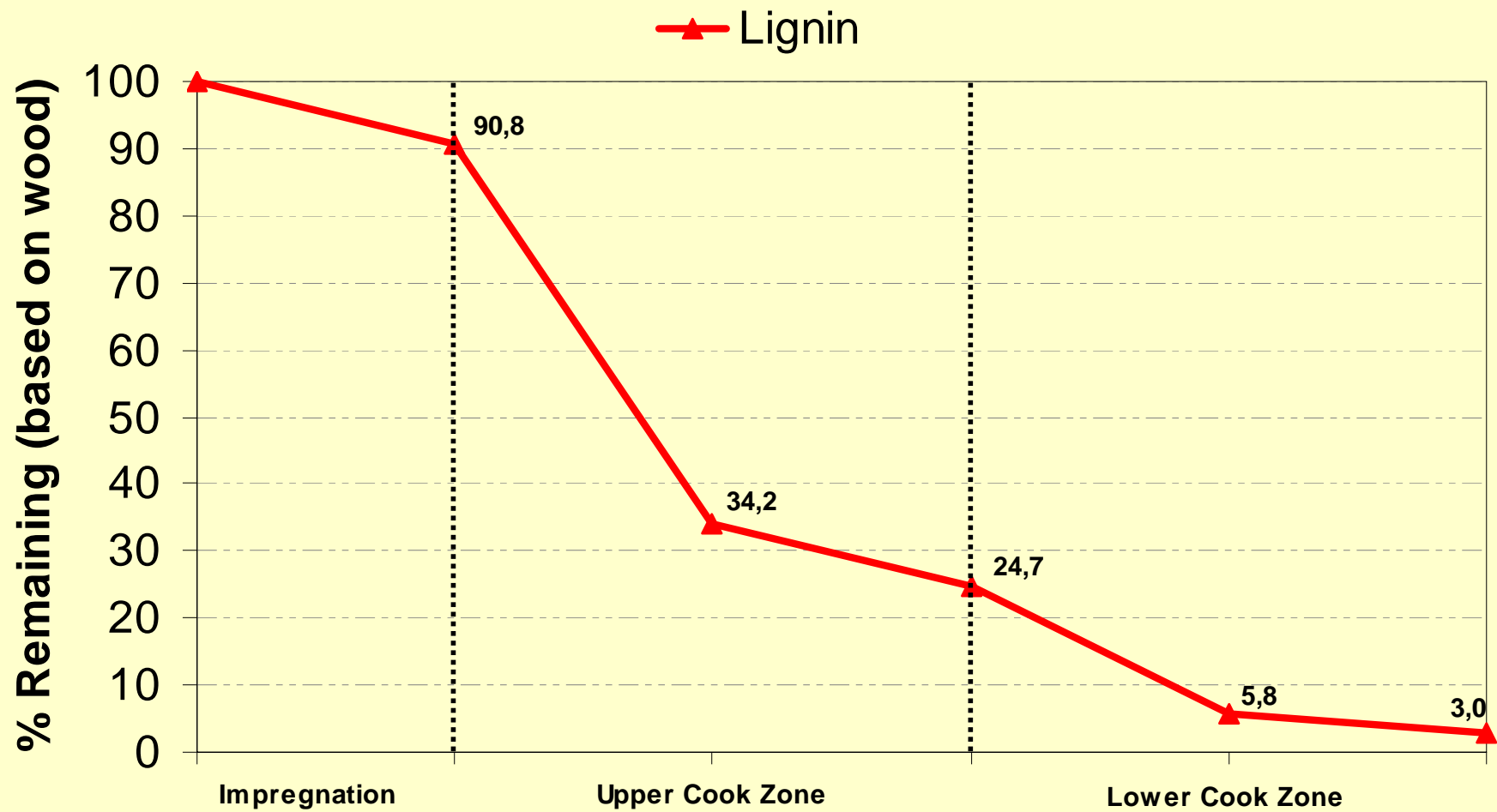
Carbohydrates



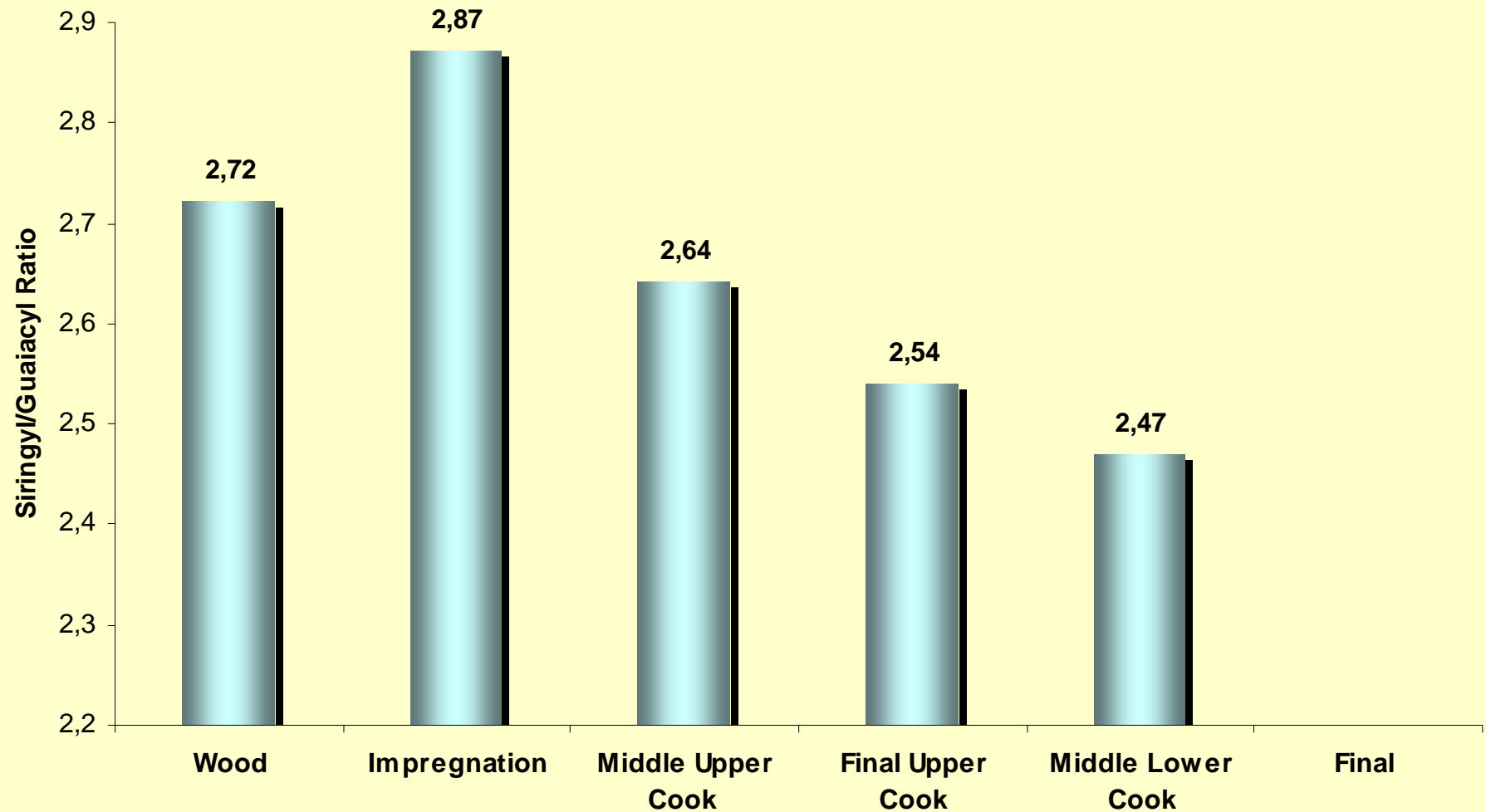
Cellulose and Hemicelluloses



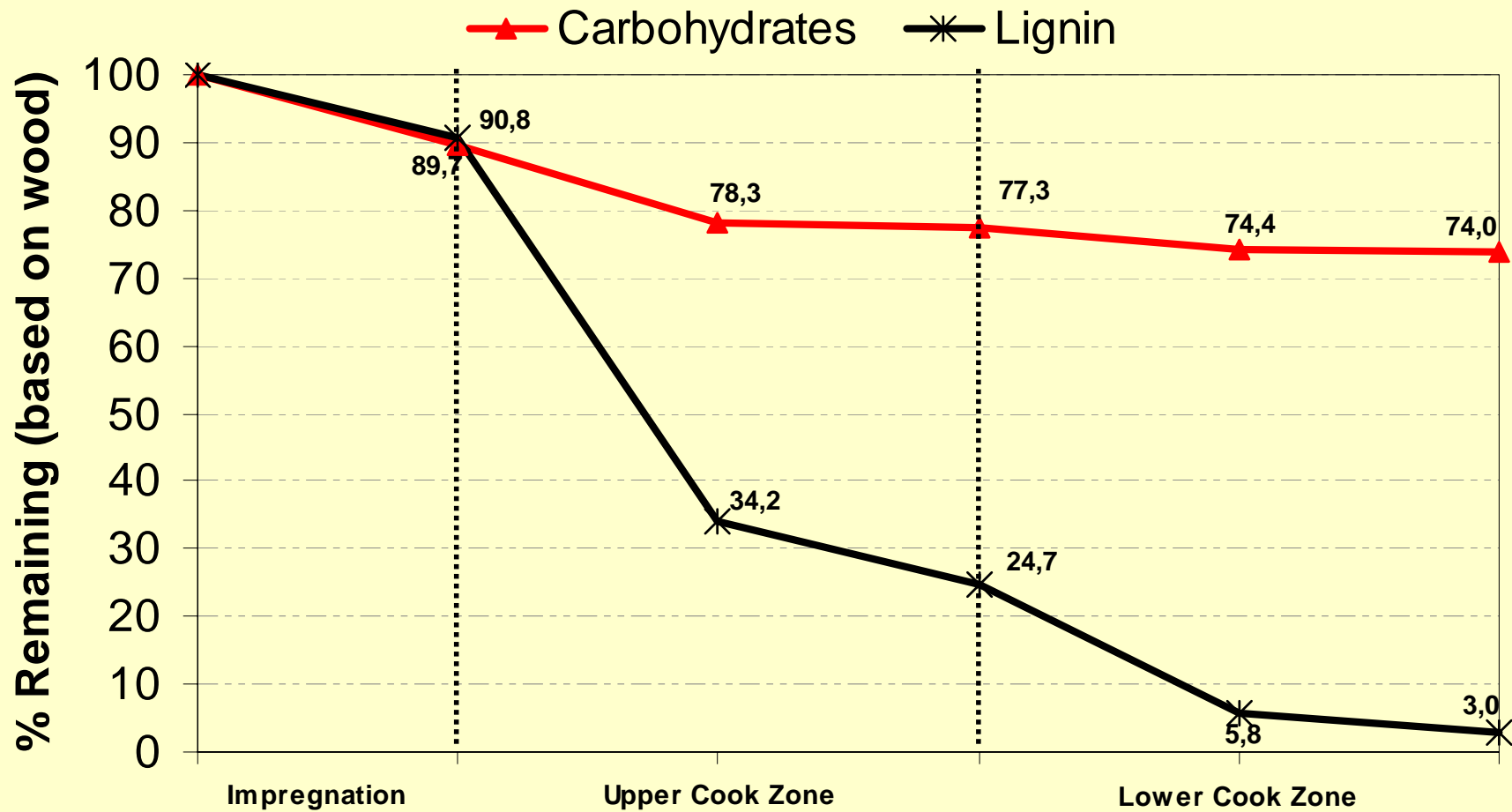
Lignin



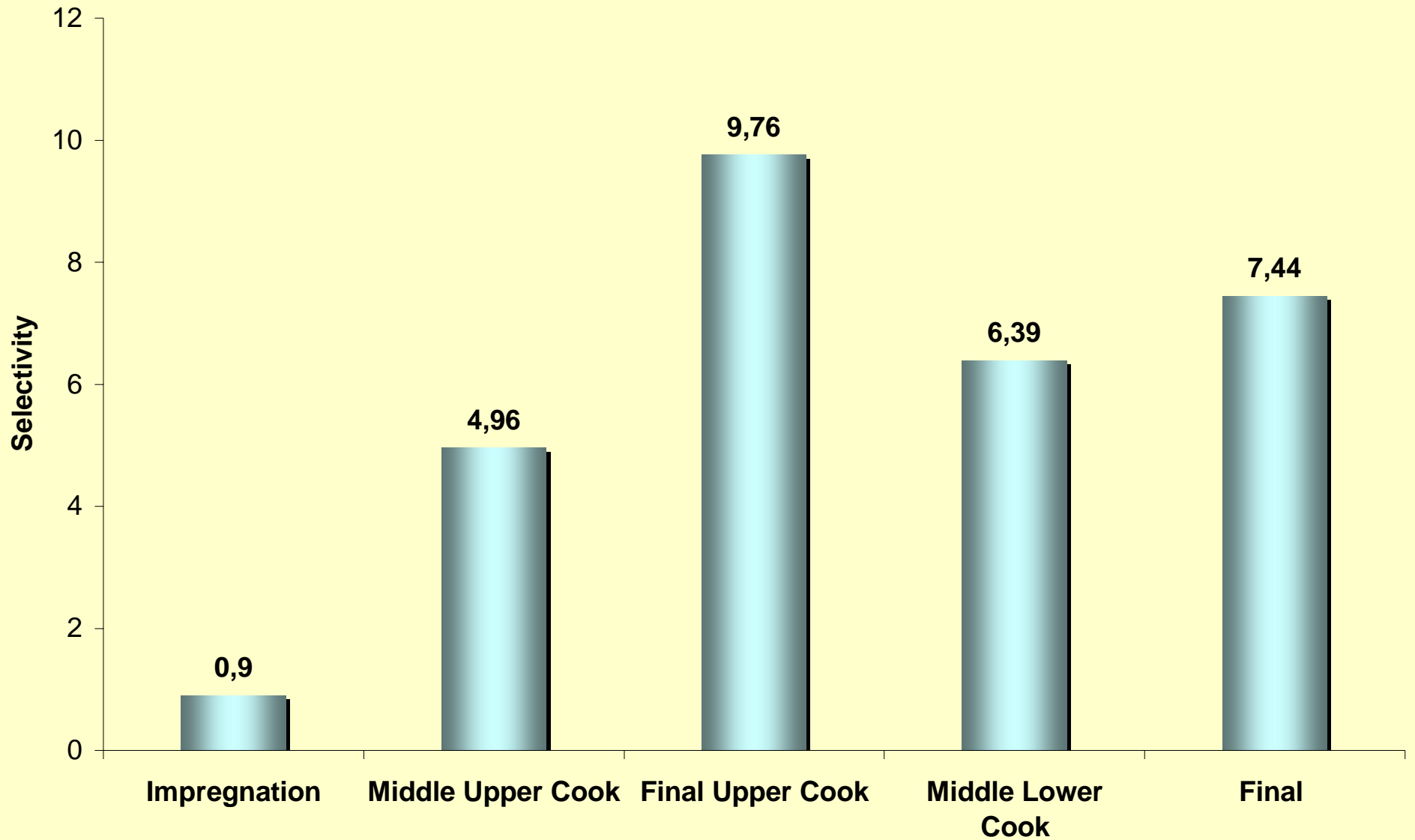
Siringyl/Guaiacyl Ratio



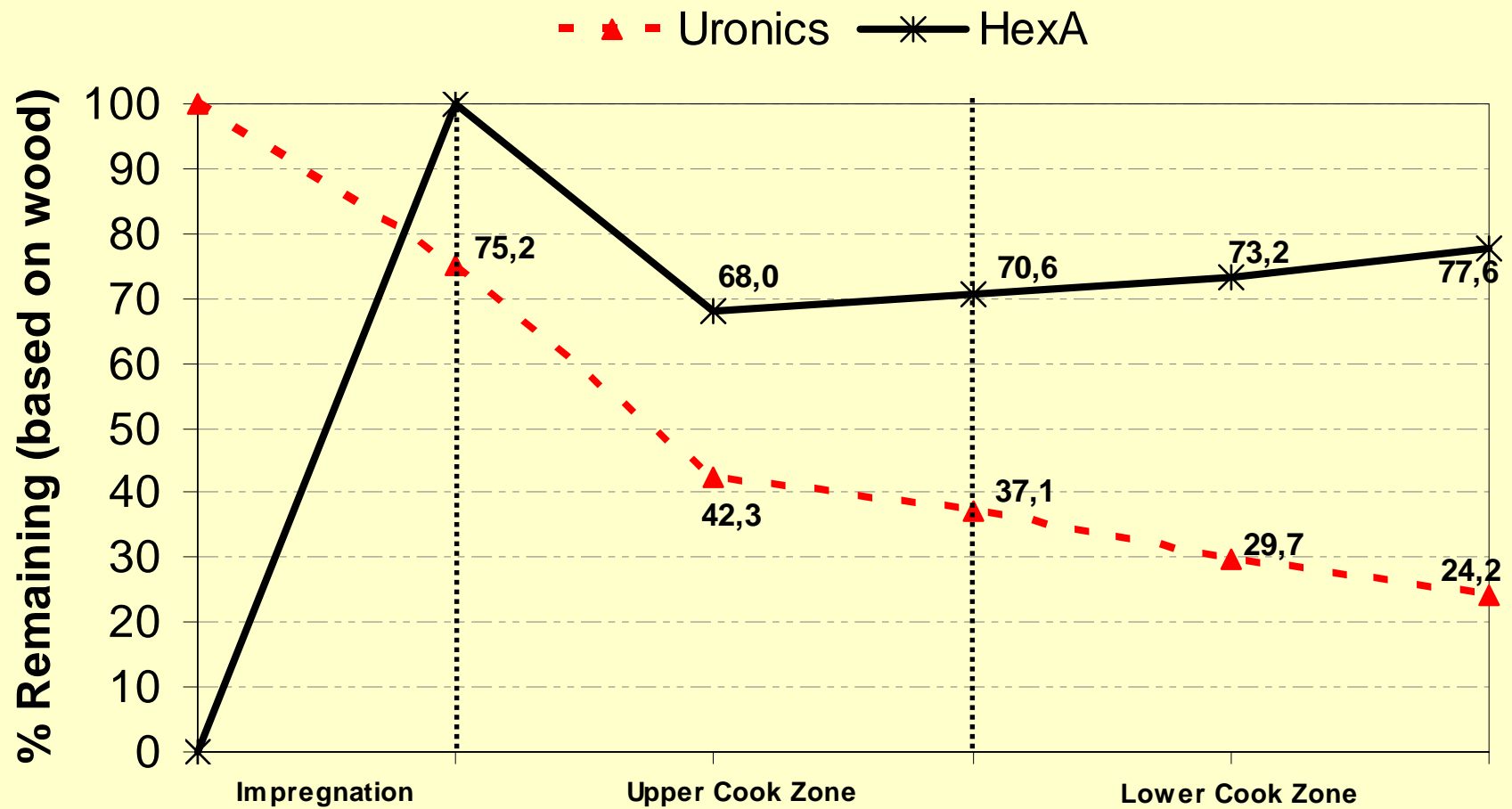
Carbohydrates and Lignin Removal



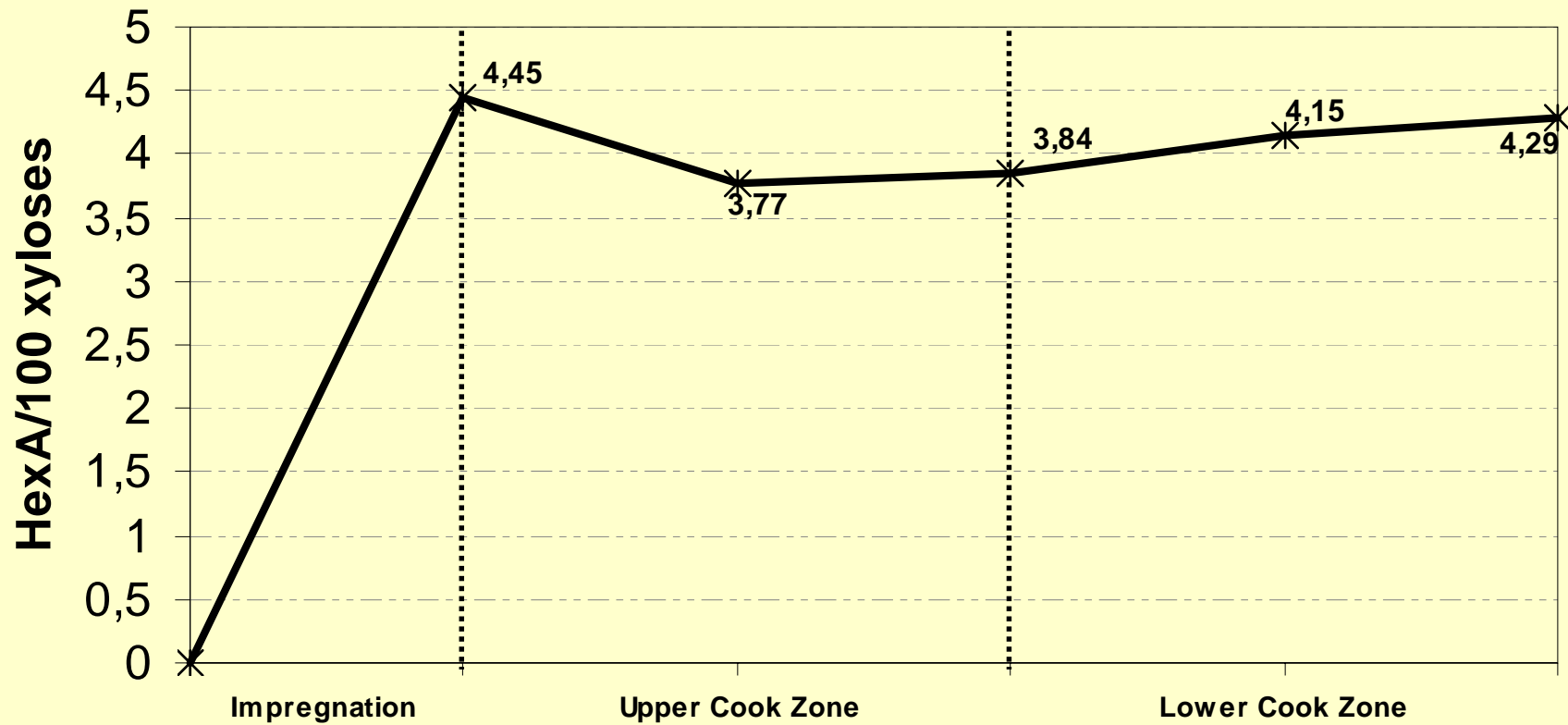
Pulping Selectivity



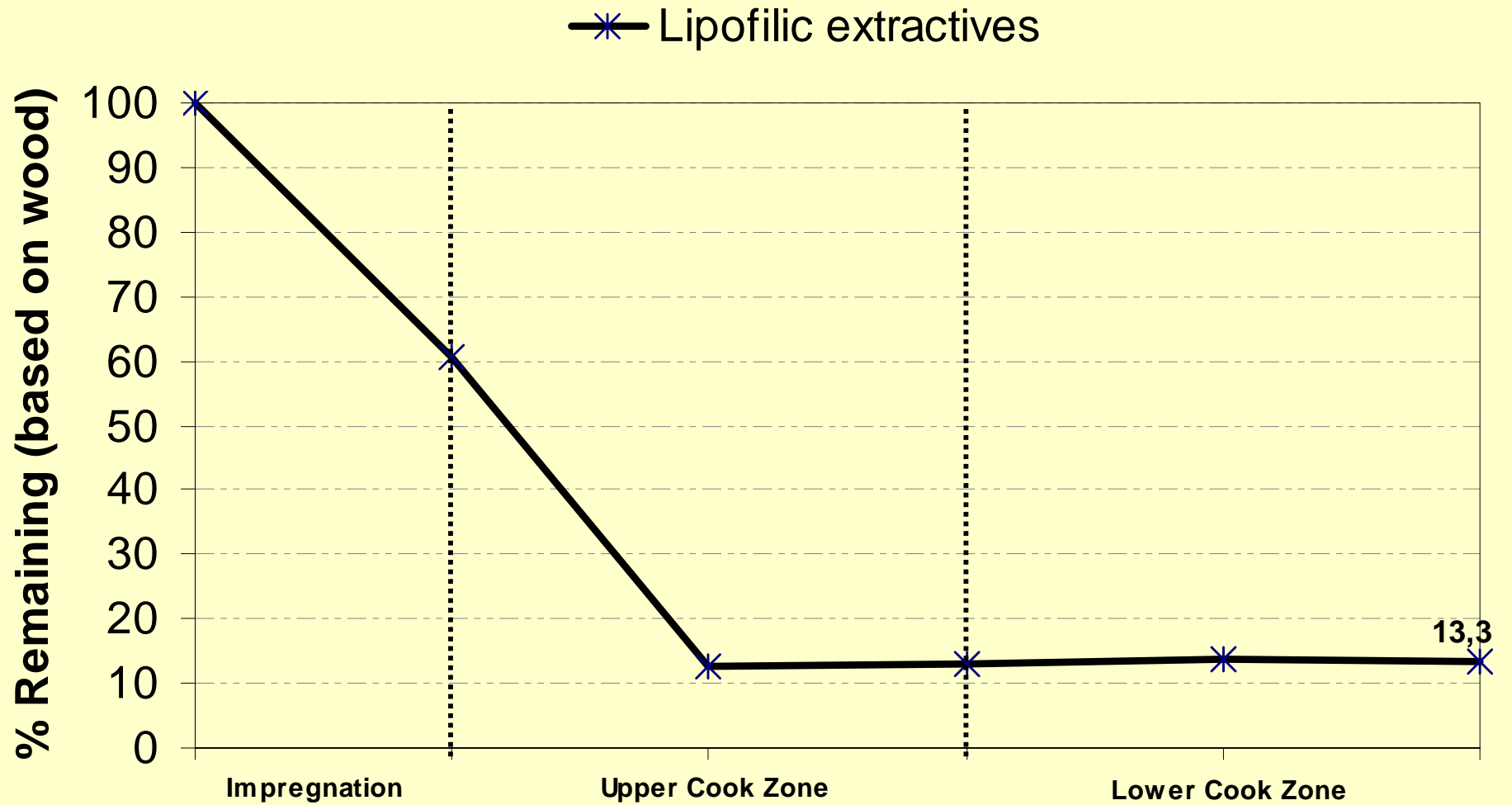
Uronic and Hexenuronic Acids



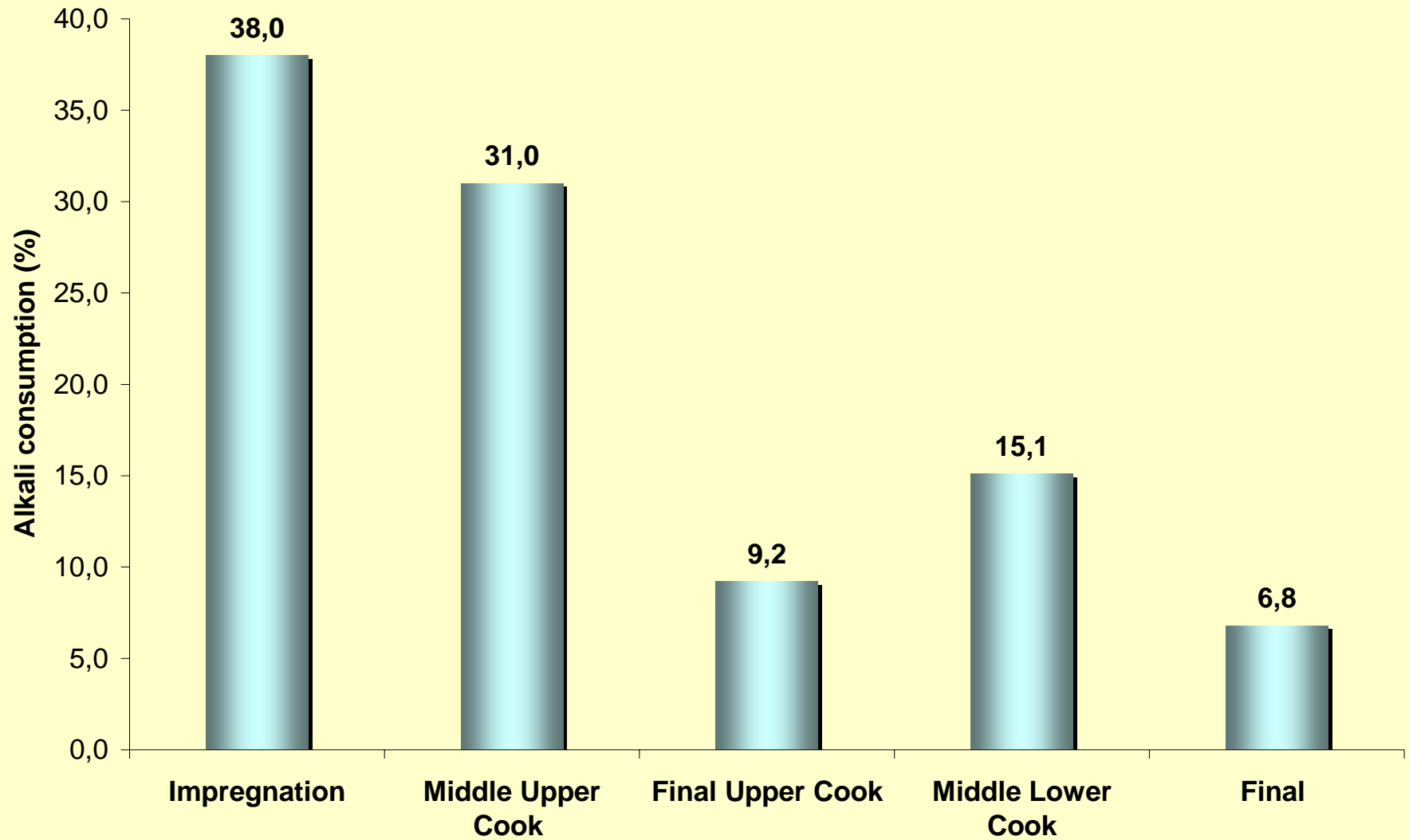
HexA/100 xyloses



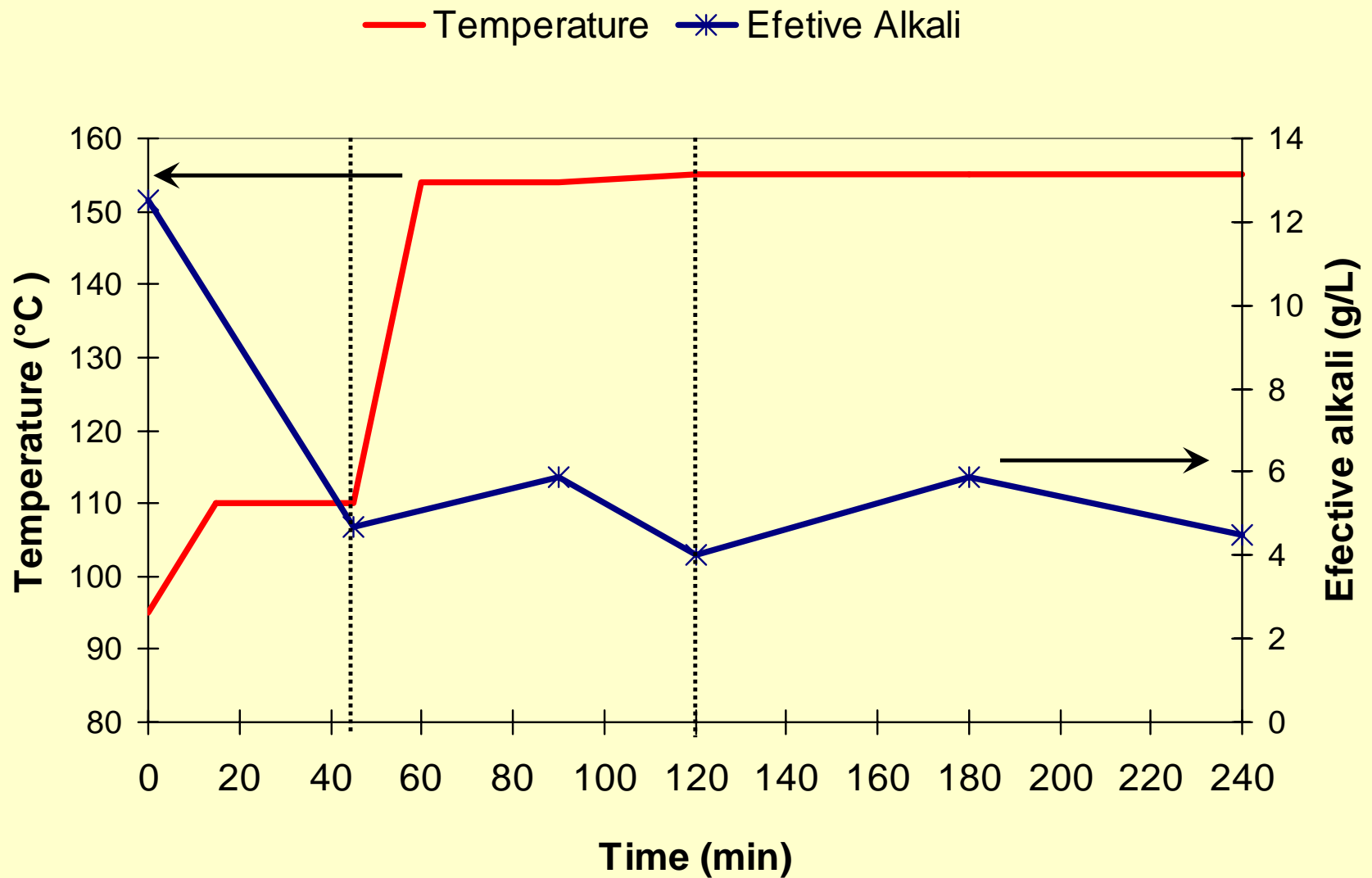
Lipofilic Extratives



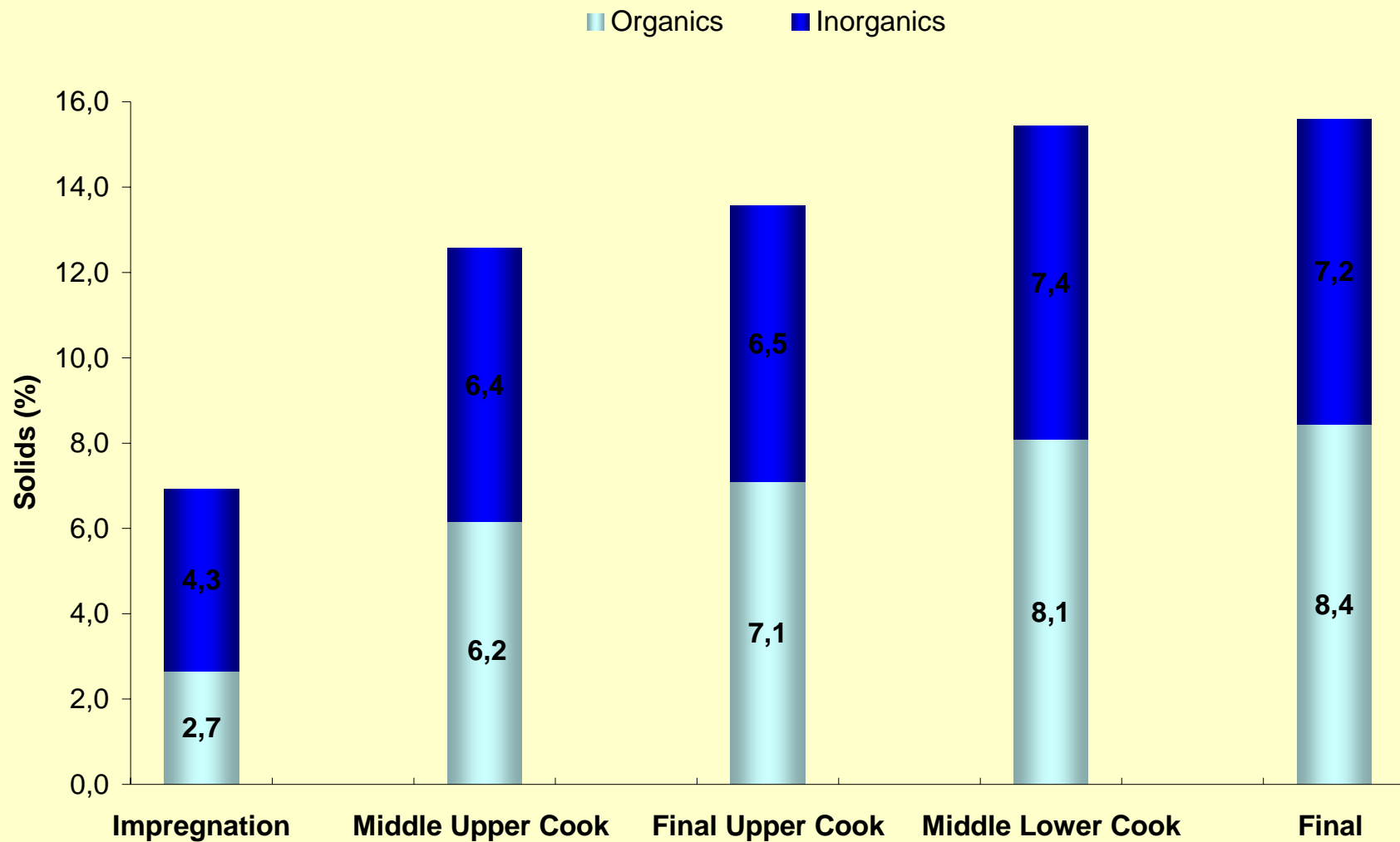
Alkali Consumption



Cooking Liquor



Cooking Liquor



Conclusions

1. During final cooking stage (60 min.) there was a small decrease in yield (1%), a considerable kappa reduction (5.5 units) and a significant decrease in viscosity (31.8 cP).
2. Five delignification stages could be detected in LoSolids cooking.
3. At the end of cook 14.2% of cellulose and 53.6% of hemicelluloses were removed from wood.

Conclusions

5. Impregnation zone presented lower selectivity and the highest selectivity was observed in upper cooking zone.
6. In impregnation zone there was a rapid formation of HexA but it decreased in the following zone (initial upper cooking zone).
7. Solids and alkali concentrations were quite homogeneous along the cooking cycle.

**Thank you Very
Much for Your
Attention !**