

EFFECTS OF DELIGNIFICATION STRATEGIES ON PRODUCTION AND QUALITY OF EUCALYPT KRAFT PULP

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ABSTRACT

In this study, the effects of different pulping strategies on process parameters and pulp quality were evaluated in laboratory trials using industrial chips of eucalypt wood. Cooking and oxygen delignification yields, chemical requirements, wood consumption estimates and production capacities were compared for continuous (reference, constant temperature profile and low concentration profile) and displacement batch processes. Pentosan, DCM extractives, viscosity, fiber anatomical characteristics and PFI beating curves of oxygen delignified pulps were considered in this evaluation.

Operational parameters caused only small differences on results obtained for the different pulping strategies. Anatomical and chemical fiber characteristics were also similar. Differences were observed for viscosity and some specific pulp strength properties, basically those used to estimate fiber intrinsic strength and paper machine runnability. In addition, no effect of pulp viscosity on pulp strength properties was observed.

INTRODUCTION

The majority of the world's pulp production is manufactured using the kraft process. Since its discovery, in 1879, this process has remained basically the same. In recent decades, however, some process modifications and optimization have been introduced due to economical, quality and environmental reasons. The combined effects of several process modifications have been cost reduction, higher delignification yield, lower chemical requirements, more uniform pulp quality, better pulp properties and improved environmental protection [1-10].

Modern modified kraft cooking followed by oxygen delignification effectively decreases bleaching chemical demand. The oxygen delignification stage significantly decreases the amount of lignin to be sent to the bleaching plant, reduces the total demand of bleaching chemicals and improves environmental protection [10-19].

A typical modern kraft pulp bleaching facility includes an oxygen stage as a pre-delignification stage before bleaching or during the bleaching sequence. Newest technologies such as ozone, acidic pre-treatment, and pressurized hydrogen peroxide stages can also be found in some mills.

In an MCC process the relative flow rates of the cooking liquors re-circulation allow adjustments of chemical charges and temperatures. The lignin is removed faster and more efficiently than in conventional cooking. It is possible to reduce pulp kappa number and bleaching chemical requirements without sacrificing bleached pulp quality [7-9, 20-23].

Further modifications of the MCC process allow additional improvements. Use of hi-heat washing zone as a counter-current cooking phase was probably the most important modification. This modification, first characterized as Extended Modified Cooking Cycle (EMCC), was later used in Iso-thermal Cooking (ITC) and in LoSolids Cooking systems. Maintenance of a constant temperature throughout the digester is the basic characteristic of ITC. It was introduced in 1984 as an optimization of MCC cooking by addition of a new cooking zone in the traditional digester washing zone by increasing its temperature to the same level as the other cooking zones [8, 24-26].

Another modification of kraft pulping is the LoSolids process. Its strategy is a reduced dissolved solids concentration during the bulk delignification phase, a low concentration of cooking chemicals and dissolved lignin combined with low temperature during the cooking phases [22, 26-28].

The batch cooking technology has shown dramatic improvement in steam economy and flexibility, giving the opportunity to optimize pulp kappa number according to wood and bleaching costs, pulp quality requirement and environmental regulations [4, 29-32]. SuperBatch and RDH (Rapid Displacement Heating) processes have the same basic operational principles. Differences occur in the cooking liquor and temperature profiles in each digester [33, 34].

The objective of this study was not to compare different commercial kraft processes but to evaluate the effects of different concepts used in various modern modified kraft processes on unbleached pulp characteristics related to production parameters and pulp quality.

EXPERIMENTAL

The laboratory cooking cycles were simulated using operational conditions of modified kraft commercial processes. Continuous and batch simulations were carried out to obtain a target kappa number of 18.0 ± 0.5 . For each pulping strategy the alkali charge was established experimentally to reach the target kappa number.

All cooking simulations were carried out using industrial chips (seven year old eucalypt clonal trees) and a Selective Delignification System available at Federal University of Viçosa - Pulp and Paper Laboratory. This system consists of a regular MK lab digester connected to a set of vessels equipped with heating and pressurizing systems allowing liquor displacement during cooking phases. The vessels were connected to the digester by two separate pipes, leading to great flexibility during the liquor displacement steps. Two high pressure precision dosing pumps were used for liquor displacements during cooking simulation. The operational conditions used for laboratory cooking simulations are reported in Table 1.

Table 1 – Operational variables used for laboratory cooking

Continuous Cooking				Batch Cooking	
	Reference	Cont-A	Cont-B		
Direct Steaming Phase					
Wood Chips, g (oven dried)	800	800	800	Wood Chips, g (oven dried)	1280
Steam Pressure, atm	1.5	1.5	1.5	Steam Pressure, atm	1.5
Time at Open Down Flow, min	10	10	10	Time at Open Down Flow, min	10
Time with Bottom Valve Closed, min	10	10	10	Time with Bottom Valve Closed, min	10
Condensed Steam Drainage	yes	yes	yes	Condensed Steam Drainage	yes
Chip Impregnation					
Alkali Charge, % EA **	75	58	48	Alkaline Charge, % EA **	7.5
Liquor to Wood Ratio	4 : 1	4 : 1	4 : 1	Cooking Liquor, g EA (NaOH)/L	5.0
Temperature, °C	160	155	110	Initial N ₂ Pressure, kg/cm ²	6.5
Time to Temperature, min	12	13	15	Liquor to Wood Ratio	4.8 : 1
Time at Temperature, min	-	-	30	Temperature, °C	90
Initial N ₂ Pressure, kg/cm ²	6.5	6.5	6.5	Time at Temperature, min	10
Co-current Cooking Phase				Cooking Liquor Replacement, mL	3800
Liquor to Wood Ratio	4 : 1	4 : 1	-	Alkaline Charge, % EA **	12.5
Temperature, °C	160	155	-	Cooking Liquor, g EA (NaOH)/L	10.0
Time at Temperature, min	65	60	-	Temperature, °C	125
Counter-current Cooking Phase				Liquor to Wood Ratio	4.8 : 1
Alkaline Charge, % AE **	25	25	31	Time to Temperature, min	25
Liquor to Wood Ratio	4 : 1	4 : 1	4 : 1	Cooking Liquor Replacement, mL	3800
Temperature, °C	160	155	155	Alkaline Charge, % EA **	74.0
Time to Temperature, min	-	-	17	Cooking Liquor, g EA (NaOH)/L	60.0
Time at Temperature, min	60	60	45	Liquor to Wood Ratio	4.8 : 1
Liquor Displacement, mL/min	-	53.3	11.8	Temperature, °C	165
Co-current Cooking Phase				Time to Temperature, min	35
Liquor to Wood Ratio	-	-	4 : 1	Time at Temperature, min	44
Temperature, °C	-	-	155	Cooking Liquor Replacement, mL	3800
Time at Temperature, min	-	-	60	Alkaline Charge, % EA **	3.0
Counter-current Cooking Phase (Washing Zone)				Cooking Liquor, g EA (NaOH)/L	2.0
Alkaline Charge, % AE **	-	17	21	Liquor to Wood Ratio	4.8 : 1
Liquor to Wood Ratio	-	4 : 1	4 : 1	Cooking Liquor Recirculation, min	15
Temperature, °C	-	155	155	Cooking Liquor Replacement, mL	3800
Time at Temperature, min	-	180	180	Alkaline Charge, % EA **	3.0
Liquor Displacement, mL/min	-	25.5	7.9	Black Liquor, g EA (NaOH)/L	2.0
Number of Replicates	4	4	4	Liquor to Wood Ratio	4.8 : 1
Remarks:				Final Temperature, °C	70
* White Liquor Sulfidity = 25 %				Time to Temperature, min	15
** % Total Effective Alkali (EA) required to obtain the target kappa number				Number of Replicates	4

The chips moisture content was 55.4% after steaming. After cooking the cooked chips were washed (45 L of hot water) followed by a final washing step (room temperature water) to completely remove black liquor. A 25 liter

laboratory hydropulper was used for fiber separation and the pulps obtained were screened using a 0.2 mm slot screener.

Oxygen delignification was simulated using screened pulps and a high-shear mixer operated with 300 g (b.d.), 10.8 % consistency, 100 °C, and 6.0-kg/cm² oxygen pressure for 70 minutes. The chemical charge was modified to obtain the same target kappa number (10.0±0.5) for all pulps. Soda and oxygen were applied 1:1 ratio. For each pulping strategy three replicates at the target kappa number were performed.

The unbleached pulps were evaluated according to their yield and viscosity. After oxygen delignification the parameters analyzed were viscosity, pentosan content, DCM extractives content, fiber dimensions, and physical-mechanical properties. TAPPI or SCAN standard methods were used for pulp characterization.

RESULTS AND DISCUSSION

Pulping

The average results from all pulping strategies simulated in this study are shown in Table 2.

Table 2 – Average Laboratory Cooking Results

Process or Pulp Characteristics		Cooking Strategies			
		Reference	Continuous A	Continuous B	Displacement Batch
Cooking Simulation					
Alkaline Charge (as NaOH)	Added as White Liquor, %	21.9	22.8	21.0	24.2
	Consumed, %	10.8	9.3	11.3	9.9
H Factor		844	1300	1246	622
Unbleached Pulp Kappa Number		18.3	17.7	18.0	17.9
Cooking Yield, %		47.9	49.3	49.7	50.6
Residual Liquor Solids	Organic, %	38.4	40.5	40.4	42.7
	Inorganic, %	61.6	59.5	59.6	57.3
Pulp Viscosity, dm ³ /kg		1020	1140	1100	980
Oxygen Delignification					
Chemical Charges	Oxygen, kg/t	35.0	30.0	32.0	45.0
	NaOH, kg/t	35.0	30.0	32.0	45.0
Chemical Consumption, kg NaOH /t		46.0	42.6	44.2	36.0
Final pH		12.4	12.4	12.4	12.6
Pre-bleached Yield, % (unbleached pulp basis)		98.1	97.9	97.7	97.5
Pre-bleached Yield, % (wood basis)		47.0	48.3	48.6	49.3
Total Solids to Recovery System, t/admt		1.69	1.63	1.59	1.64
Specific Wood Consumption, m ³ /admt		4.25	4.14	4.12	4.06
Oxygen Bleached Pulp – Basic Characteristics					
Kappa Number		10.0	10.3	10.2	10.6
Viscosity, dm ³ /kg		888	1006	969	844
Brightness, % ISO		58.4	57.5	57.4	57.8
Pentosans Content, %		14.7	14.8	14.8	14.8
DCM Extractives Content, %		0.07	0.10	0.07	0.08
Average Fiber Length, mm		0.66	0.65	0.66	0.65
Average Fiber Coarseness, mg/100m		7.7	7.9	7.9	7.8
Number of Fibers per Gram, million		24.2	23.3	23.5	23.8

Although there was no specific difference of alkali consumed by continuous and batch processes, it was necessary to use higher alkali charges for the batch process probably due to the higher cooking liquor displacement in this type of simulation (Table 2). Since in an industrial operation part of the chemicals are added as black liquor, remaining in the cooking cycle for liquor replacement in the next cook, the chemical balance in this study was done considering only the alkali consumed. Alkali requirement is an important operational parameter for mills that have limited causticizing capacity.

The chemical charges required to produce one ton of oxygen bleached pulp were higher for the batch strategy. Nevertheless, only part of these chemicals were consumed. Considering the chemicals consumed (effective alkali plus soda in the oxygen delignification stage) the batch strategy showed an intermediary consumption (195 kg/admt). The chemical consumptions varied from 185 kg/admt (strategy Cont-B) to 222 kg/admt for strategy Cont-A and reference cook (Figure 1).

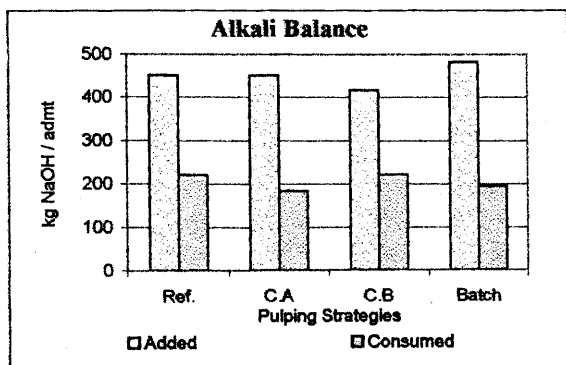


Figure 1– Alkali requirement to produce one air dried metric ton of oxygen delignified pulp.

Organic solids in cooking liquor react with alkali increasing the effective alkali consumption. Therefore, solids content in cooking liquor could affect the alkaline charge required to meet a target kappa number, the cooking yield and the way cooking liquor inside the digester should be managed (i.e. cooking strategy).

It can be seen in Table 2 that the simulation based on the laboratory continuous reference cook resulted in the lowest yield, as has been reported elsewhere [20, 25, 27, 28].

The highest cooking yield was obtained for the batch displacement technology. For continuous cooking the best yield was obtained for the strategy using low solids concentration profile (strategy Cont-B).

After oxygen delignification the total yield ranking of the different pulping strategies remained the same although the absolute differences were reduced. If a pulp mill is limited by its digester feeding system, higher pulping yields allow increased production.

Lower cooking yield or higher effective alkali charge contribute to higher solids content in black liquor, and also the filtrate from oxygen delignification is added to the black liquor increasing the recovery load. The recovery system is the most frequent bottleneck in kraft pulp mills. The amount of solids generated to produce one ton of pulp is a more accurate prediction of the production capacity potential than the process yield itself. More pulp can be obtained for the same recovery capacity by lowering this relationship.

Figure 2 shows the amount of solids in black liquor per admtr of oxygen bleached pulp produced. All cooking strategies produced lower solids than the continuous reference cook. The lowest value was determined for continuous cooking with low solids concentration profile (strategy Cont-B), 5.9 % lower than reference, meaning a potential pulp production increase of 6.3 % if the recovery boiler is assumed to be the mill production bottleneck.

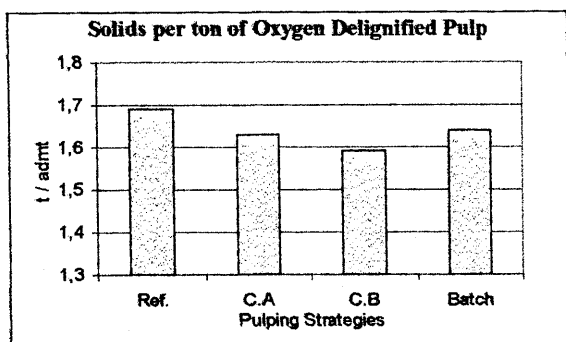


Figure 2– Total solids generated to produce one ton of pulp (admtr) as a function of the pulping strategies evaluated.

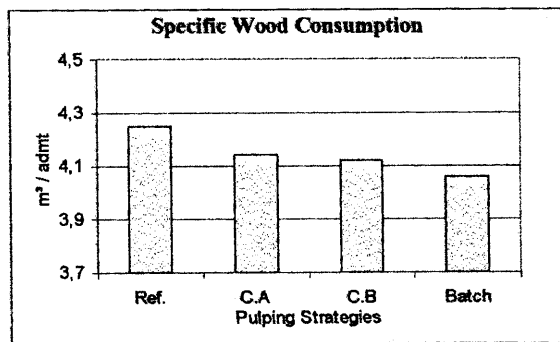


Figure 3– Specific wood consumption as a function of the pulping strategies evaluated.

If mill capacity is limited by washing, screening or bleaching, decrease in solids per ton of pulp allows reduction of wood consumption for the same production level (Figure 3). The lowest specific wood consumption was observed for the batch strategy, for which a 4.5 % lower wood requirement per ton (admtr) of oxygen bleached pulp was estimated. In this case, the higher solids content in black liquor for the batch technology was probably related to the higher alkaline charge used for this cooking simulation.

Pulp Quality

Besides wood characteristics, the cooking process strongly affects both pulp properties and paper machine runnability as well as the quality of the final paper [4, 20, 35-40]. Considering that the same wood was used in all cooking simulations, any variation in pulp quality parameters can be related to the pulping strategy adopted.

DCM extractives and pentosan content are considered important quality parameters for eucalypt pulps. Results in Table 2 illustrate that pulp characteristics did not vary significantly with the cooking strategies simulated in laboratory. Since the refining behavior of a certain chemical pulp is defined by its cellulose and hemicellulose

contents [1, 41-43], these results indicate that any variation in refining (beating) from these pulps can not be related to their hemicellulose contents.

Alkaline reactions cause carbohydrate degradation which reduces the degree of polymerization and intrinsic fiber strength during kraft cooking and oxygen bleaching. When different processes are compared, the relationship kappa number/viscosity (cooking selectivity) is not a precise parameter to evaluate pulp quality [20]. However, pulp viscosity is a traditional quality property for market pulps and was also considered in this evaluation. The effects of the different cooking strategies and oxygen delignification on pulp viscosity are shown in Figure 4.

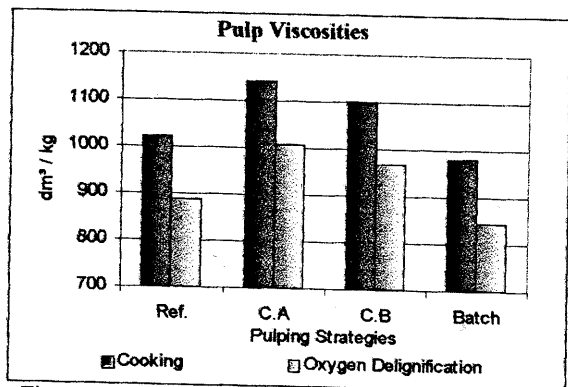


Figure 4 - Effect of pulping strategy on pulp viscosity.

It was possible to identify a critical effect of the cooking strategies on pulp viscosity. The highest viscosity values were observed for the continuous cooking strategies (Cont-A and Cont-B) and the lowest value for the batch displacement process. In addition, the results illustrate that the cooking processes were the main factor involved in viscosity variation. Viscosity reductions due to oxygen delignification were almost the same (131-136 dm³/kg) for all pulps and no relationship with pentosan content could be detected.

Results indicate that viscosity variation was related with the intensity of cellulose degradation during the cooking process. For cooking, no relationship was found between viscosity reduction and H-factor or chemicals added or consumed chemicals. Lowest viscosity values were found for cooking at higher temperature.

The effects of these viscosity differences on physical and mechanical pulp properties will be discussed latter.

Fiber morphology, pulping and bleaching are of fundamental importance for pulp quality. During cooking the cell wall components and medium lamella are dissolved, allowing fiber separation. Removal of cell wall components leads to pore formation in the fiber cell wall. Water is adsorbed by these pores hydrating the cell wall and decreasing intrinsic strength. Fibers become flexible producing paper of higher density, smoothness, tensile index and burst index. For pulps with similar kappa numbers, reduction of fiber strength or fiber length decreases sheet strength properties. In other words, the way the pulp is produced can affect the pulp behavior during the refining process as well as the final quality of dried paper [1, 24, 35, 37-39, 44-51].

Fiber coarseness and fiber length are used to estimate number of fibers per gram which is an important parameter to define optical and other paper properties related to fiber bonding ability [24, 41, 48, 52-62]. As a general rule, for the same pulping process the number of fibers per gram increases with pulp kappa number reduction [24, 38].

Fiber characteristics of the five pulping strategies evaluated are shown in Table 2. As expected [39, 63], the pulping strategies did not show any significant difference in fiber length. The laboratory reference cook was the only process to present a slightly lower coarseness and therefore its number of fibers per gram was slightly higher.

Paper properties are defined by fiber bonding ability and how fibers collapse. These depend on fiber chemical and anatomical characteristics. These fiber characteristics are related to wood species and pulping procedures [39, 45, 46, 60, 64-77]. For high degrees of delignification it is possible to observe a reduction of intrinsic fiber strength and, therefore, lower pulp strength. In this study the kappa number of all pulps were very similar and, therefore, the way pulps were produced would affect their refining behavior as well the final quality of paper [1, 24, 35, 39, 50, 51].

In Figure 5 the effect of pulping strategy on fiber cell wall collapsability (aparent density) and interfiber bonding (tensile index) is evaluated. All cooking strategies produced pulps with the same tendency of property evolution with beating energy. Only small differences in energy requirement were observed for the cooking simulations. The low solids concentration (Cont-B) and batch displacement strategies produced slightly more flexible fibers.

The laboratory continuous reference cook presented the highest tear strength. This suggests [35, 44, 67] that this process produced pulp with higher intrinsic fiber wall strength. This was probably the main reason for the higher beating energy requirement for this process.

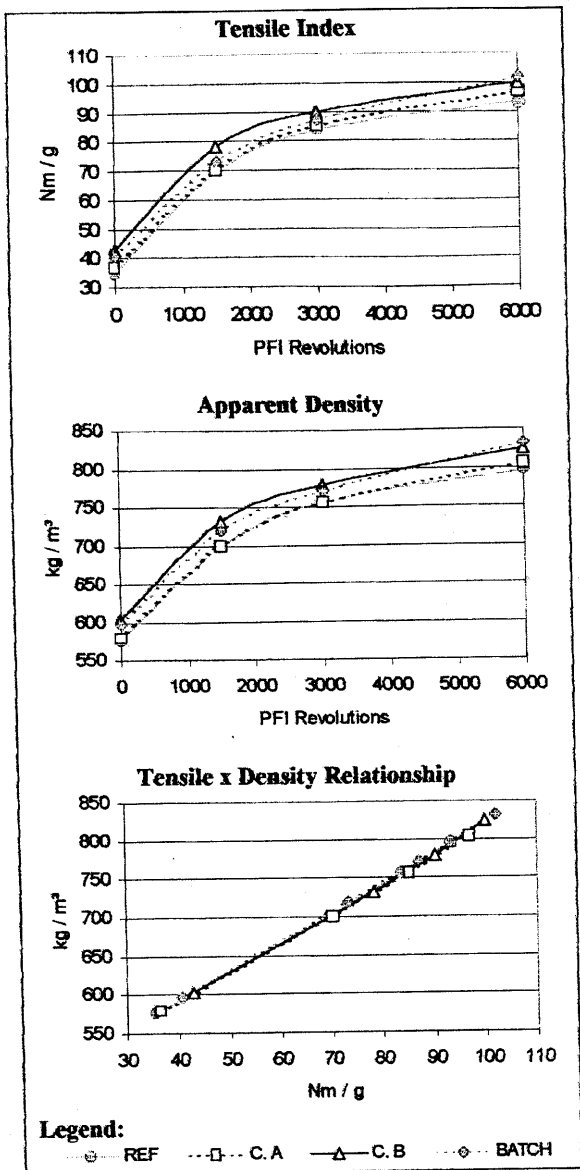


Figure 5 - Tensile-density relationship for oxygen delignified pulps from the different cooking strategies evaluated.

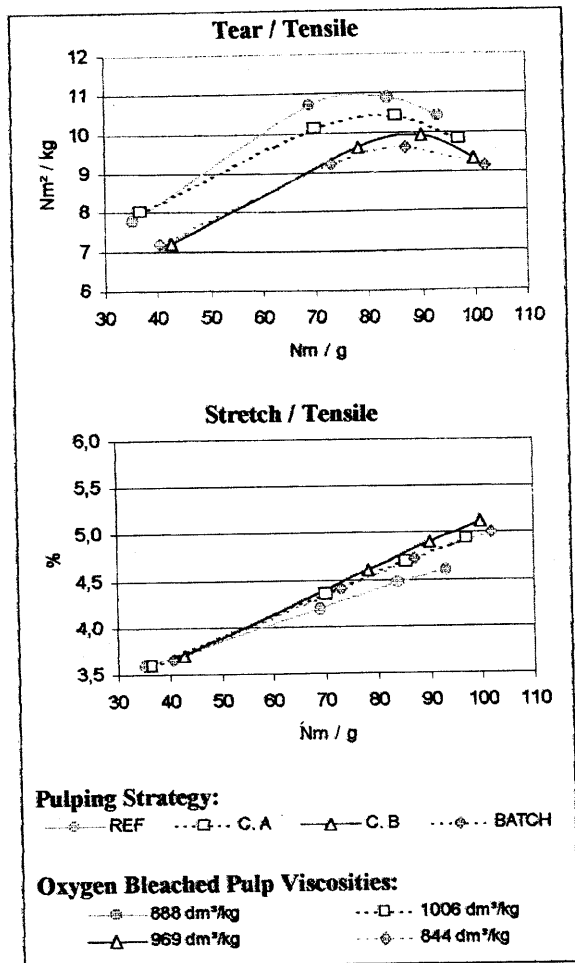


Figure 6 - Tear-tensile (fiber strength) and stretch-tensile (wet-web strength) relationships as a function of viscosity after cooking and oxygen delignification.

The tensile-tear strength relationship is a recommended way for pulp quality evaluation since it is a good indicator of cell wall intrinsic strength and structural modifications of cell wall fibers. As refining increases, both fiber bonding and cell wall damage increase simultaneously. The tear resistance increases with the tensile resistance up to a certain level and after this point the tear strength decreases despite increases in tensile strength. The tear-tensile relationship is traditionally reported as a predictor of paper strength and in association with the tensile-elongation relationship is used as a wet web strength indicator [67, 82-89].

It is possible to estimate the paper machine runnability for different kinds of pulps using the results in Figure 6. The lab reference cook and the continuous constant temperature strategies produced the highest tear-tensile relationships (curves) indicating that stronger cell wall fibers are present in these pulps.

The effect of pulp viscosity on strength properties can also be observed in Figure 6. Although large variations in viscosity were observed as a function of pulping strategy, the strength properties were not affected by viscosity variations. These results confirm literature data [20, 62, 78-81].

CONCLUSIONS

The following conclusions could be drawn based on the results obtained.

Although higher alkali charges were used for the batch process there was not a specific difference in alkali consumed by continuous and batch processes. The higher cooking liquor displacement was identified as the main factor increasing the chemical charge in the batch cooking strategy.

All cooking strategies had lower chemical consumptions and produced lower solids per ton of oxygen delignified pulp than the laboratory continuous reference cook. The lowest (7%) chemical consumption was observed for the continuous strategy adopting a low concentration profile. In addition, due to the lower solids in the black liquor to recovery system, all the cooking strategies presented potential to increase mill daily production capacity when compared to the reference.

The lowest specific wood consumption was estimated for the batch cooking strategy.

No effect on DCM extractives or pentosan content was observed as a function of cooking strategy. Therefore, any difference in refining (beating) behavior could not be related to hemicellulose content.

The cooking strategy was the main factor controlling pulp viscosity. The highest values were observed for the continuous cooking strategies (Cont-A and Cont-B) and the lowest value for the batch displacement process. Batch and continuous reference cooks used the highest cooking temperature. Despite the large variation in viscosity no effect was observed on pulp strength properties. In addition, viscosity reduction due to oxygen delignification was practically the same for all cooking strategies.

No significant difference was observed in fiber anatomy as a function of cooking strategy.

Only small differences in energy requirement were observed for the cooking simulations. The low solids concentration (Cont-B) and batch displacement strategies produced slightly more flexible fibers. Batch and continuous cooks with the same temperature strategies produced pulps with the lowest predicted fiber cell wall strength. In addition, the best paper machine runnability potencial was found for the reference continuous cooking strategy.

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