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EVALUATION OF KRAFT-PS COOKING FOR EUCALYPT AND PINE WOOD CHIP MIXTURES

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The purpose of this study was evaluating polysulfides (PS) as additives in kraft cooking of wood mixtures eucalypt (E) and pine chips (P) wood mixtures, namely: 50E/50P, 70E/30P, and 90E/10P. Bleaching (O(D/A)(EP)D) and refining of pulps were also investigated. The PS addition (1.5 or 3.0%) to the kraft cooking preserved the hemicelluloses resulting increased pulp yield and reduced H-factor. The oxygen delignification was more efficient for chip mixtures containing higher proportion of pine chips, but was not largely affected by the addition of PS. The bleach chemical consumption was not significantly influenced by PS dosage or by the wood chip mixture. The burst and tear indexes were improved by increasing the proportion of pine chips to the mixture, but an opposite effect was observed for refinability, tensile index, and opacity. The kraft-PS pulps showed increased refinability, tensile, and burst strengths in relation the standard pulps, but lower opacities.

KEYWORDS. Eucalypt, pine, polysulfides charge, pulp chemistry, pulp strength

INTRODUCTION

Within the Brazilian forest sector, pulp and paper segment has excelled significantly. Of the 7,740,000 hectares of trees planted in Brazil, 34% is dedicated to the pulp and paper industry. According to report of the Brazilian Tree Industry Association, Brazil occupies the 4th place worldwide in the ranking of pulp producers, with over 19 million tons produced in 2017, being the largest eucalypt pulp producer in the world. The expectation is that for 2020, pulp production will reach 22 million tons.^[1] These impressive numbers, stimulate research and development aimed at improving not only the raw material, but also the variables associated with the process of producing pulp.

Pulp production is achievable by different processes, of which the chemical processes are the most prominent, whereby acid, neutral, alkaline and organic solvent systems may be used for fiber individualization. Although the acidic processes have been used in the past, currently they have little significance. Neutral processes are used in small scale in the production of unbleached semi-chemical pulps. Organic solvent-based processes are of no importance commercially. The commercial pulp production nowadays is largely based on alkaline processes, mainly the kraft process.

Since its initial development in 1879, the kraft process has gone through several improvements in order to enhance delignification rates and pulp yield. In addition to

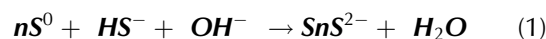
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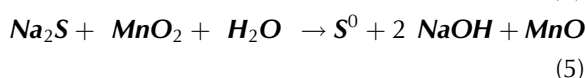
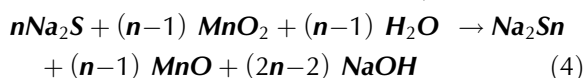
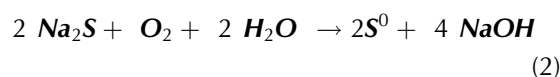
important gains in the equipment side that allowed for realization of kinetically modified cooking, other improvements in reaction efficiency involving the use of additives were also put into place. In the early 1970, a class of additives called polysulfides (PS) were introduced and have been widely studied ever since.^[2–10] In fact, there are a reasonable number of pulp mills worldwide currently using PS as additives to their cooking processes. The PS action in kraft cooking is well-documented and their positive effect on yield is largely attributable to minimization of the endwise depolymerization reaction that occurs on cellulose and hemicellulose polymer chains.^[8–10] By oxidizing the reducing end group on these polymer chains, to stable carboxylic acid groups (aldonic acids), the PS minimize pulp yield losses during kraft cooking.^[2,11] The increase in yield caused by PS is affected by its concentration in the impregnation and cooking liquors and the pulping process conditions,^[12] and it results from minimized peeling reaction of polysaccharides.^[5–7,13,14] For eucalypt wood, yield gains of 0.9, 1.1, and 2.2% have been reported with doses of 1.0, 2.5, and 4.0% PS on wood weight, and for pine wood these gains were 0.9, 2.9, and 4.2%, for the same PS doses.^[7] In another study with eucalypt wood, Robles reported yield gains of 1.8, 1.5, and 0.8% with application of 1.8% PS for kappa number targets of 13, 18, and 25, respectively.^[6] Viscosity gains of 6.1, 6.4, and 13.8 mPa.s, for PS applications of 1.0, 2.5, and 4.0%, respectively, were reported for eucalyptus.^[7] For pine wood, viscosity increases of 4.5, 9.3, and 13.5 mPa.s, were obtained for the same dosages of PS.^[7] One inconvenient of PS addition in kraft cooking is the potential odor increase due to the formation of non-condensable gases, especially methyl mercaptan (CH₃SH) and dimethyl sulfide (CH₃SCH₃).^[15,16] A number of strategies have been suggested to circumvent this problem, including black liquor oxidation, gas burning and ozone oxidation.^[15] However, the best strategy is probably the proper control of the

cooking conditions. According to Kleppe, by applying elemental sulfur loads under 2% on dry wood weight, sufficient amount of effective alkali and controlling the final cooking pH, a reduction in the cooking time is achieved, which in turn decreases the formation of non-condensable gases to levels similar to those observed in conventional kraft process.^[16]

The kraft white liquor containing PS, also designated orange liquor, can be obtained by different methods. The simplest method consists of the addition of elemental sulfur to the white liquor, in temperatures between 90 and 110 °C. According to Grace *et al.* this method has the disadvantages of reducing the alkalinity of the white liquor,^[3] since hydroxyl ions are consumed in the formation of PS (reaction 1) and, consequently, increasing the sulfur/sodium ratio in white liquor, which is undesirable to the recovery system.

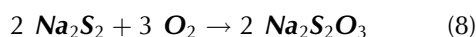
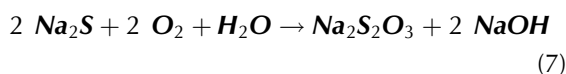


An alternative method for PS production is the MOXY process, which was developed in 1973 by Mead and Chiyoda International Companies. In this technology part of the sodium sulfide present in the white liquor is converted into PS by oxidation in the presence of air (reactions 2 and 3) or of a catalyst such as MnO₂ (reactions 4–6).^[7]



According to Jiang, when the orange liquor produced by the addition of elementary sulfur is compared to liquor generated by the MOXY process, the latter contains lower percentage of PS (wood base) and sulfidity, which results in lower pulping selectivity.^[17] Dorris states that an alternative to the use of

the manganese dioxide as catalyst, is the addition of activated charcoal, previously treated with polytetrafluoroethylene.^[4] The use of activated charcoal improves the rate of oxidation of sodium sulfide, resulting in more substantial formation of PS. The most recent development for producing orange liquor, the PAPRICAN method, consists of a simplified improvement of sodium sulfide oxidation process in the white liquor, which does not use the activated carbon as catalyst. This process uses air or oxygen in the presence of particles of lime mud (CaCO_3), which are responsible for increasing the production of PS. The lime mud particles support and accommodate the manganese dioxide catalyst, thus expanding its contact with the white liquor.^[4] Lime mud particles (CaCO_3) represent an alternative source and are beneficial relative to activated carbon, because it is an integral part of the kraft recausticizing cycle.^[11] During the white liquor oxidation process for production of PS there occurs parallel and undesirable reactions (reactions 7 and 8), which results in the formation of sodium thiosulfate.^[3]



In Brazil, the main raw materials used for pulp production are woods from genus *Eucalyptus* (eucalypt) and *Pinus* (pine). These woods present distinct physical, chemical, and morphological characteristics. Ideally, they should be processed individually using appropriate conditions for each. However, the reality of some pulp mills equipment-wise makes it difficult the processing of those raw materials separately. Mills equipped with a single continuous digester and with deficient pulp storage capacity, sometimes for lack of investment, may cook eucalypt and pine together, even though the disadvantages of the mutual processing on the final product yield and quality are known. The wood components that are more penalized when pine and eucalypt are cooked together (co-

processing) are the hemicelluloses. Thus, techniques that result in greater preservation of these polymers during co-processing are desirable, for improving pulp yield and quality. The use of PS as additive to kraft pulping is one such technique, and this is the main goal of this research as applied to eucalypt and pine wood mixtures of different proportions. To the best of our knowledge, a study of this nature has not yet been published.

MATERIAL AND METHODS

Samples Preparation and Characterization

Industrial wood chips from eucalypt and pine both coming from commercial plantations at harvesting age were used. The chips were air-dried to uniform and stable moisture content and classified in a set of sieves according to SCAN-CM 40:94 standard procedures.^[18] Subsequently, the materials were homogenized in a chip blender and stored in polyethylene bags to preserve the moisture content. The chips basic and bulk densities were determined according to SCAN-CM 43:95 and SCAN-CM 46:92 standard procedures, respectively.^[18] For the chemical characterization of the materials, 500 g chips were sampled and milled in a knife mill for sawdust production. The sawdust was classified in accordance with TAPPI T257cm-85 standard and maintained in a room with controlled temperature and moisture content ($23 \pm 1^\circ\text{C}$, $50 \pm 2\%$ RH) until equilibrium moisture of $\sim 10\%$ was achieved. The sawdust total extractives, acid soluble and acid insoluble lignin contents were determined according to TAPPI T264 cm-97, T222 om-98, and UM200 standard procedures, respectively.^[19] The content of polysaccharides was determined in accordance with the SCAN-CM 71:09 standard procedures.^[18] The contents of uronic acids and acetyl groups were determined according to procedures described by Scott and Solar *et al.*, respectively.^[20,21]

Pulping Conditions and Pulp Characterization

The liquor containing PS (orange liquor) was prepared by addition of elemental sulfur to the white liquor, which was heated in a water bath at the temperature of 80 °C, until complete dissolution of the sulfur. Subsequently, the liquor was titrated to quantify the PS generated, following TAPPI T694 om-90 standard procedure, with replacement of mercury chloride by silver nitrate.^[19] Kraft cooking was performed in duplicate in a 7-L MK digester with 500 g of chips, dry mass, of the different proportions of eucalypt (E) and pine (P), which were: 50E/50P, 70E/30P, and 90E/10P, using PS charges of 1.5 and 3.0% on dry wood basis. Reference cooks without PS addition were also performed. The cooks were carried out with a liquor/wood ratio of 4 L:1 kg, 30% sulfidity, active alkali charge of 23.5–26% as NaOH and H-factor of 707–1457. The values of kappa number and residual effective alkali were set at 19 ± 0.5 and 7 ± 1 g/L, respectively, through the variation of H-factor and active alkali charge for each cook. For the kraft-PS cooks an impregnation step was carried out at 90 °C for 60 min to avoid PS decomposition, which may occur in temperatures >100 °C.

At the end of each cook, the pulps were discharged into a washing device equipped with 150 mesh stainless steel wire and washed with plenty of water in order to remove the residual liquor. The individualization of the fibers, post-washing stage, was carried out in a 25-L laboratory hydropulper. The pulp screening was carried out in a Voith laboratory screener, equipped with plates having 0.25-mm slit openings, and at the end of this stage, the rejects were collected. The screened pulps were dewatered by centrifugation to a consistency of ~30%, stored in polyethylene bags and then analyzed for kappa number (TAPPI T236 cm-85), hexenuronic acids (HexA; TAPPI T282 pm-07), viscosity (SCAN-CM 15:99), sugar composition (SCAN-CM 71:09), and brightness (ISO 2470).^[18,19] From the values of kappa number and HexA, the corrected

kappa number values (only lignin) were determined according to the procedure described by Li and Gellerstedt.^[22] Spent black liquor was analyzed for residual effective alkali (SCAN-N 33: 94).^[18]

Bleaching Conditions and Bleached Pulp Characterization

The pulps resulting from kraft and kraft-PS cooks were submitted to ECF bleaching, using the sequence O(D/A)(EP)D, to obtain a brightness of 85.0% ISO in the final pulp, where: O = oxygen delignification; (D/A) = bleaching with chlorine dioxide at high temperature; (EP) = oxidative extraction enhanced with hydrogen peroxide; D = bleaching with chlorine dioxide. The O-stage was performed at a consistency of 11.5%, 60-min, 100 °C, 750 kPa, 2.0% NaOH and 1.7% O₂. The (D/A)-stage was performed at 11% consistency, 120-min, 90 °C, pH 3.0, and 0.21 kappa factor. The (EP)-stage was performed at 11% consistency, 75-min, 85 °C, 0.8% NaOH, and 0.4% H₂O₂. The D-stage was performed at 11% consistency, 90-min, 80 °C, pH 5.0, and variable load of ClO₂ aiming at 85% ISO brightness. The pH adjustments for each bleaching stage was carried out with H₂SO₄ or NaOH. Oxygen delignification was performed in a Mark V reactor/mixer (Quantum Technologies, USA), with 250 g oven dried pulp sample. The (D/A)-, (EP)-, and D-stages were carried out in polyethylene bags in a temperature-controlled steam bath. At the end of the bleaching reactions, a filtrate sample was collected for pH and residual reactant analysis and the pulps were washed with the equivalent to 9 m³ of distilled water per ton of pulp. The pulps from each bleaching stage were analyzed for kappa number (TAPPI T236 cm-85), viscosity (SCAN-CM 15:99), brightness (ISO 2470), and brightness reversion (TAPPI UM200).^[18,19]

Refining and Mechanical Tests

The bleached pulps were beat in a PFI mill, according to TAPPI T 248 wd-97 standard procedure, using the equivalent of 30 g

absolutely dry pulp at 10% consistency at levels 1000, 2000, and 3000 revolutions.^[19] Subsequently, unbeaten and PFI beaten pulp samples were made into handsheets of 60 g/m² in a Tappi sheet former, and they were used to evaluate pulp physical properties according to TAPPI T220 sp-96 standard procedure.^[19] These handsheets were conditioned at 23 ± 1 °C and 50 ± 2% relative humidity, for a minimum of 12 h, after which their physical properties were determined.

RESULTS AND DISCUSSION

Wood Characterization

Cooking is largely influenced by wood quality, which is determinant of process efficiency and pulp quality, thus affecting overall pulp production performance.^[23] Table 1 shows the mean results of wood densities and chemical compositions of eucalypt and pine woods. The basic density is an important wood quality trait, as it directly relates to the performance of the pulping process as well as the quality of the final product.^[24] The bulk density is a simple and direct parameter, widely used by the pulp industry, since it relates to the density of chip pile and the basic density of the wood. The values of basic and bulk density obtained for eucalypt and

pine are consistent with those found in the literature. Gomide *et al.* studied various different commercial clones of eucalypt and found basic densities in the range of 465–510 kg/m³.^[24] Barrichelo *et al.* found basic densities varying in the range of 354–404 kg/m³ for *Pinus taeda* from different origins.^[25] The large density differences between eucalypt and pine may affect significantly the co-processing of these two woods, especially regarding the chip impregnation phase during kraft cooking. The different densities affect the PS additive performance, which is added in the impregnation step. Low-density woods will impregnate faster than the high-density ones and, potentially, will gain more benefits from PS cooking.

Among the various wood chemical components, the most significant weight fraction is the polysaccharides, mainly celluloses and hemicelluloses. The results of Table 1 show higher levels of glucose and xylose for the eucalypt in relation to pine wood. However, there is more mannose in pine than in eucalypt wood. These results are in agreement with other studies on the same subject and are explained by the intrinsic nature of the two different wood genders.^[26]

Lignin and extractives are considered undesirable to the pulping process because they directly affect effective alkali demand and, consequently, pulp yield. Moreover, high levels of extractives are undesirable for they cause pitch" problems.^[26] The levels of lignin and extractive present in eucalypt and pine woods (Table 1) may be considered low in relation to values reported in the literature. Extractives and lignin values of 4.5% and 29.7%, respectively, have been reported for *Pinus taeda*,^[27] while 1.76 and 27.5%, respectively, have been reported for *Eucalyptus grandis*.^[24] Bassa found total lignin values of 28.5% and 31.2% for the hybrid *Eucalyptus grandis* × *Eucalyptus urophylla* and *Pinus taeda* woods, respectively.^[28] The rule of thumb is that wood containing high levels of lignin and extractives requires large charge of effective alkali for cooking and, as

TABLE 1. Density and detailed chemical composition of eucalypt and pine woods expressed on extractive-free dry wood weight.

Parameter	Eucalypt	Pine
Bulk density (kg/m ³)	187	130
Basic density (kg/m ³)	489	347
Arabinose (%)	0.2	1.3
Galactose (%)	0.8	2.1
Glucose (%)	45.2	42.7
Xylose (%)	10.2	5.9
Mannose (%)	0.8	9.7
Klason lignin (%)	25.0	28.6
Acid soluble lignin (%)	4.2	0.6
Total lignin (%)	29.2	29.2
Lignin S/V ratio (mole/mole)	2.9/1	–
Total uronic acids (%)	3.5	2.7
Acetyl groups (%)	3.0	1.4
Total extractives (%)*	3.9	2.0
Ash (%)*	0.23	0.34

*Percent on total dry wood weight.

a consequence, result low pulp yield. However, pine lignin is comprised of guaiacyl moieties only, which is of low reactivity, whereas eucalypt wood contains both guaiacyl and syringyl moieties, the latter being of high reactivity.^[29] Therefore, the eucalypt lignin is more reactive in kraft cooking, especially considering that the ratio of syringyl to guaiacyl was 2.9 for the eucalypt wood under investigation (Table 1).

The uronic acids of the wood, consisting mainly of 4-*O*-methylglucuronic and galacturonic acids, represent a fraction of about 3–5% of their weight. While the units of glucuronic acid predominate in the xylans, those of galacturonic acid are usually present in pectin; the value of uronic acids found for eucalypt in this work is in agreement with the values reported elsewhere.^[29,30] in the range of 3–4.1%. As expected, the content of uronic acids found for pine was lower than that for eucalypt, which is explained by the quantitative and structural differences between the xylans of the two genders. Hardwood xylans, although having an average ratio of 1 unit of 4-*O*-methylglucuronic acid to every 10 xylose units, represents about 20–35% by weight of the wood; those of softwoods, have on average 2 units of acid per 10 units of xylose, but only 5–10% of its weight is represented by this hemicellulose.^[26]

The acetyl groups present in the hemicelluloses are easily hydrolyzed by the alkaline conditions used in kraft cooking process, a mechanism known as deacetylation. The content of acetyl groups found in eucalypt was typical and corroborates the data published elsewhere (1.6–3%) for this specie.^[26] The pine acetyl group content was lower than that of eucalypt, which is justified by the lower acetylation of the softwood hemicelluloses. While the softwood galactoglucomannan (G:M) have a ratio of 2–3 acetyl units for every 10 units of G:M, the hardwood hemicelluloses, of the 4-*O*-methylglucuronoxylan acetate type, contains a ratio of 6–7 acetyl groups for every 10 units of xylose. The ash contents of both eucalypt

and pine woods were quite low and pose no potential threat to the co-processing of the two woods in kraft cooking.

The aforementioned discussions relating to the pine and eucalypt chemical compositions (Table 1) suggest significant differences in reactivity between the two woods, which in principle should pose a significant challenge to their co-processing, particularly during kraft cooking. It is anticipated that more drastic conditions (effective alkali load and temperature) will be required for pine and, hence, cooking the mixture of the two woods would lead to excessive degradation of the eucalypt wood constituents, mainly the hemicelluloses. The use of PS as additives in kraft cooking may be a potential solution to minimize these hemicelluloses losses. However, the action of the PS in kraft cooking of eucalypt and pine wood mixtures is not well known, particularly in regard to their potential to protect eucalypt xylans and pine mannan. This very matter is discussed in the next sessions.

PS Cooking of Wood Mixtures

The main purpose of chemical cooking is to remove lignin, which acts as bonding substance among the wood fibers, to obtain individual fibers with high yield and adequate properties.^[31] The results presented in Table 2 indicate a significant influence of the different proportions of eucalypt and pine and of PS charge on kraft cooking performance. For all wood proportions, there was an increase in the active alkali demand with the addition of PS to the cooking up to a charge of 1.5% of PS. Increasing the PS charge to 3% had no additional effect on alkali demand. For the 3% PS charge, it is apparent that the increase in alkali consumption caused by the decomposition of PS was counterbalanced by the lower alkali consumption necessary to neutralize isosaccharinic acids; it is anticipated that lower quantities of these acids was produced with the high dose of PS (less peeling reactions). In general, the need for higher alkali charges during cooking in the presence

TABLE 2. Results of conventional kraft and kraft-PS cooking for the different proportions of eucalypt and pine woods (the sulfidity of 30% was used for all the cookings).

Parameter	Wood MIX 50E/50P			Wood MIX 70E/30P			Wood MIX 90E/10P		
	Ref.	1.5% PS	3.0% PS	Ref.	1.5% PS	3.0% PS	Ref.	1.5% PS	3.0% PS
Total Kappa No.	19.0	18.8	18.6	19.4	19.3	18.5	19.2	19.5	19.5
HexA-free Kappa No.	16.4	15.8	15.6	15.4	15.3	14.5	14.0	13.8	13.9
Active Alkali, % NaOH	25.0	26.0	26.0	24.5	26.0	26.0	23.5	24.5	24.5
Temperature (°C)	171	171	171	170	170	170	169	169	169
H-Factor	1457	1414	1348	1190	1150	1074	814	778	707
Residual effective alkali, g/L NaOH	6.9	7.1	6.6	7.7	7.3	6.8	7.3	6.3	6.3
Total Yield (%)	45.2	46.6	47.3	46.8	47.8	48.0	47.9	48.8	49.4
Screen Yield (%)	45.1	46.6	47.3	46.6	47.7	47.9	47.6	48.7	49.3
Screen Rejects (%)	0.1	0.0	0.0	0.2	0.1	0.1	0.3	0.1	0.1
Viscosity (dm ³ /kg)	763	810	804	813	834	847	931	934	943
HexA (μmoles/g)	30.5	34.7	35.0	46.1	46.3	46.7	60.1	66.7	65.5
Brightness (% ISO)	30.8	31.1	31.0	31.4	31.9	32.8	32.1	32.4	32.7
Arabinose (%)	0.3	0.3	0.3	0.3	0.3	0.2	0.1	0.2	0.2
Galactose (%)	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Glucose (%)	85.6	84.7	84.9	85.2	85.2	84.9	85.6	84.8	85.0
Xylose (%)	10.8	11.2	10.8	12.3	12.4	12.3	13.3	13.9	13.7
Mannose (%)	3.1	3.5	3.7	1.9	1.9	2.4	0.8	0.8	0.9
Hemicelluloses contribution to lignin- and HexA free screen yield, % wood	6.6	7.3	7.3	6.9	7.1	7.3	6.8	7.3	7.3
Cellulose contribution to lignin- and HexA-free screen yield, % on wood	37.2	38.0	38.6	38.3	39.3	39.3	39.5	40.0	40.6
Calculated lignin- and HexA-free yield	43.8	45.3	46.0	45.2	46.3	46.6	46.2	47.3	47.9
Cellulose contribution to yield gain due to PS (%)	0	0.8	1.5	0	1.0	0.9	0	0.5	1.1
Hemicelluloses contribution to yield gain due to PS (%)	0	0.7	0.7	0	0.1	0.4	0	0.5	0.5
Total yield gains due to PS (%)	0	1.5	2.2	0.0	1.1	1.3	0.0	1.0	1.6

of PS is due to the fact that PS undergoes decomposition at temperatures above 100 °C, and the reaction requires three molecules of hydroxide for each molecule of PS.^[7]

It is also observed in Table 2 that the increase in the proportion of eucalypt wood results in decreased demand for active alkali to reach the target kappa number. This result is explained by the better pulpability of eucalypt wood in relation to pine – eucalypt contains a fraction of syringyl lignin, which is of higher reactivity than the guaiacyl lignin present in pine. The H-factor required to reach the kappa number 19 was slightly reduced in the cooks assisted with PS, regardless of the wood mix ratio, as a consequence of the slightly higher active alkali charge used in

kraft-PS cooks. When comparing the three wood proportions evaluated, the H-factor is lower for the blend containing more eucalypt and less pine, regardless of the PS dose. According to Bugajer *et al.*, the H-factor required for eucalypt wood is in the range of 30–50% lower in relation to that for pine wood.^[32]

The use of the additive PS caused a yield increase in the order of 1.0–2.2% on dry wood weight, depending on the dose of PS and the wood mix proportion (Table 2). The highest yield gain (2.2%) was obtained for the 50E/50P wood mix with the 3.0% PS charge, while the lowest gain (1.0%) was obtained for the 90E/10P wood mix, with the 1.5% PS dose. Hence, the largest yield gains due to

PS addition occurred for the wood mix containing more pine, in line with results reported by other workers who claimed better performance of PS additive in cooking of softwood chips.^[7,14] However, the highest overall pulping yields were achieved for the wood mixtures containing higher proportion of eucalypt because of its better pulpability in relation to pine, regardless of the use of PS. Oliveira *et al.* studied the production of kraft pulp with mixtures of *Pinus strobus var. chiapensis* and *Eucalyptus urophylla* and concluded that the highest yields were obtained for 100% eucalypt, and as the proportion of pine wood in the mixture increased, the screen yield decreased appreciably.^[33]

The yield gains caused by PS addition to kraft cooking can in one hand be explained by lowering H-factor, which inarguably improves yield.^[13,34] Nevertheless, there are also chemical aspects of carbohydrate preservation by PS, especially hemicelluloses, which need to be considered.^[8–10] The results in Table 2 shows that there is, in general, a greater preservation of the hemicelluloses in the pulps for the PS assisted cooking, although this trend is not so clear when the charge of PS is increased from 1.5 to 3.0%. The PS brought more significant benefits for the wood chip mixture containing larger proportion of pine chips, which is explained by the PS protection of the mannans, which are labile during kraft pulping and exist in larger quantities in the softwoods. Preservation of cellulose was also proven very important when PS was used as additive to kraft cooking. For example, the total yield gain due to 3.0% PS addition was 2.2% for the 50E/50P wood mix, with the cellulose preservation representing 1.5% of that value and the remainder 0.7% due to hemicelluloses preservation. Remarkable preservation of mannans and cellulose in kraft-PS cooking of Scots pine was also reported elsewhere.^[9] Similar trends were seen for the other wood mixtures, thus indicating that PS preserves both cellulose and hemicelluloses, but the benefit is larger for cellulose. The action of the PS

occurs through the protection of the carbohydrates (cellulose and hemicelluloses) against the reaction of terminal depolymerization, which occurs during alkaline cooking.^[6] The PS, therefore, oxidize the reducing end group of the wood polysaccharides to aldonic acids, stabilizing them against the terminal depolymerization reaction, thus decreasing their degradation.^[11] It is worth noting that the pulps xylans content increased with increasing proportion of eucalypt in the mixture, in detriment to the mannans contents, a result explained in one hand by the low content of mannans present in the original eucalypt wood, and in the other hand by the higher stability of the xylans in relation to the mannans across kraft cooking.

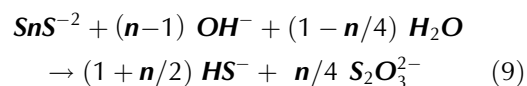
Chemical reactions during cooking occur between solid (wood) and liquid (white liquor) phases, which requires uniform impregnation of the chips with liquor so that an efficient delignification occurs.^[35] When this impregnation is not uniform, and the delignification process is not homogeneous, part of the wood is not delignified, and as a consequence rejects are observed in the end of the cook. The pulp rejects contents shown in Table 2 indicate, however, that there is no difference among the reject values of the pulps produced with and without the PS additive, regardless of the dosage of additive employed and the wood mix used. Potucek *et al.* reported that cooking of softwoods and hardwoods with PS causes reduction of the pulp reject content.^[36]

Pulp viscosity measurements are used for determining, indirectly, the average degree of polymerization and corresponding molecular weight of the cellulose and hemicelluloses polymers chains present in the pulp. Indirectly, viscosity results can be used for estimation of carbohydrate degradation and pulp quality potential.^[28,37] The viscosity data shown in Table 2, indicate that the addition of PS to the kraft cooking, irrespective of the dosage applied, increased the pulp viscosity. Other studies corroborate the positive impact on viscosity derived from the use of PS in the

kraft cooking of eucalypt and pine.^[6,7] The viscosities of pulps derived from different wood mixtures increased with decreasing pine proportion. This result can be explained by the greater ease of cooking of the eucalypt in comparison to the pine.^[33]

HexA are compounds formed during alkaline pulping by the modification of 4-O-methylglucuronic acids (MeGlcA) present in xylans, through the mechanism of β -elimination of the methoxy group.^[38] The conditions that most influence the formation of HexA during the pulping process are effective alkali and temperature.^[38,39] The presence of these compounds in the pulp affects the bleaching process, since they do consume electrophilic chemical reagents and they may cause pulp brightness reversion when left in the bleached pulp.^[40,41] The differences in pulp HexA contents observed in this study (Table 2), caused by variation in the wood mix, can be explained by the chemical differences between the original woods. There is significant correlation between the content of MeGlcA in the wood and the content of HexA in the kraft pulp.^[42] Kraft pulps from coniferous woods contain less HexA than hardwoods, since the MeGlcA content is lower in the former.^[26] From the analysis of the results presented in Table 2 it is possible to conclude that when compared to the references (Ref.), the treatments that used the PS additive resulted pulps containing higher amounts of HexA. This result can be explained by the fact that the PS preserves more hemicelluloses in the pulp. As the amount of xylan is higher in the hardwoods, with the increase of the eucalypt proportion, there was an increase in the amount of HexA present in the pulp. Therefore, the cooks of the 90E/10P wood mixtures were the ones that resulted in pulp with greater amount of HexA. In contrast, the 50E/50P cooks resulted pulps with the lowest HexA contents. In comparison to the reference, the PS cooks, resulted pulps with significantly higher HexA contents, but no significant differences were observed in the treatments with 1.5 and 3.0% PS.

Although the target kappa number was 19 ± 0.5 , the pulps derived from different wood mixes cooked in the presence and absence of PS had different amounts of lignin, as can be seen by the HexA-free kappa values shown in Table 2. These values were calculated considering that an HexA value of $11.6 \mu\text{mol/g}$ pulp is equivalent to one kappa number unit.^[22] The so-called HexA-free kappa values roughly correlates with the pulp lignin content, although it may contain some other minor amounts of other oxidizable materials. The treatments with higher proportion of pine resulted pulps with higher values of HexA-free kappa number, that is, pulps containing more lignin at a given kappa number. This fact can be explained by two ways: (1) the pine wood contains less MeGlcA and tend to produce less HexA, resulting in a greater contribution of lignin to a given kappa number; (2) the lignin present in pine wood is of the guaiacyl type, in contrast to that of the eucalypt that contains both guaiacyl and syringyl moieties. Guaiacyl lignin is more susceptible to form condensed structures, which are difficult to cleave during cooking, and hence it remains in large proportion in the pulps derived from pine wood. Therefore, the tendency was that with increasing proportion of pine wood in the chip mixture, an increase of the HexA-free kappa number was observed due to the increased amount of lignin. However, there was a trend of decreasing pulp HexA-free kappa numbers when PS were used as additive to kraft cooking. The use of the PS additive results in better delignification, because when the PS decomposes, thiosulfate and HS^- (reaction 9) are formed. The anion HS^- acts specifically in the reactions of degradation of lignin, allowing for greater delignification.^[43]



Pulp brightness is an optical property of cellulosic pulp, being a measure of blue visible light, at 457 nm wavelength, under standardized conditions. The method uses an

absolute scale, where blackness is 0% (non-reflective material) and the brightness of a perfect reflection of light is considered 100%.^[44] The pulp brightness results shown in Table 2 indicate that an increase of pine in the wood mix results decreased pulp brightness, in line with the increase in pulp true lignin content (HexA-free kappa number). A side-effect of the different scattering coefficients between pine and eucalyptus fibers on brightness values is also probable, but it was not assessed in this study. In addition, the positive effect on pulp brightness of the PS addition to kraft cooking is evident, particularly for the wood mixes containing more eucalypt.

Table 3 shows the percentages of sugar losses across cooking, on a wood weight basis, for the cooks of different wood mixtures with different PS charges. It is observed that galactose is the sugar lost in largest proportion across cooking, followed by arabinose and mannose. Among the sugar components of wood hemicelluloses, the xylose is the most stable one, and overall the glucose is the sugar most resistant to kraft cooking. Since mannose and xylose are the most prominent hemicellulose sugars in pine and eucalypt, respectively, the weight losses (yield losses) were larger for the wood mixes containing more pine. In general, the use of PS additive decreased the sugar losses across cooking and the increase in PS charge from 1.5 to 3.0% was also beneficial in most cases.

Thus, on the basis of the yield, viscosity and carbohydrate losses data for cookings carried out at approximately constant values of kappa number and residual effective alkali, it is possible to make the inference that PS

improves cooking selectivity regardless of PS charge and proportion of eucalypt and pine wood mixes. It is also possible to conclude that the cooking operation is more selective for eucalypt than for pine wood chips.

Oxygen Delignification (O-Stage)

A summary of the oxygen delignification (O-stage) results is presented in Table 4. Fixed operation conditions were used in the O-stage given that the kappa number of all pulps were in the range of 19. The oxygen delignification performance, measured by the kappa drop across the O-stage, was quite adequate for all pulps, but tended to be superior for the pulps derived from the wood mixtures containing more pine in the composition. This can be explained by the lignin/HexA ratio of the brown pulps. As shown previously (Table 2), as the proportion of pine wood increases, the kappa number becomes more influenced by the lignin content rather than HexA, and lignin is the main substrate for oxygen reactions. Under alkaline conditions oxygen reactions are largely nucleophilic and do not affect appreciably the pulp HexA groups.^[40]

It is worth noting that O-stage operating conditions were constant for all pulps, including the charges of alkali (2.0%) and oxygen (1.7%). The O-stage end pH values varied in the range of 11.4–11.8, with the higher values for the wood mix 90E/10P and the lower for the mix 50E/50P (Table 4). Since the kappa drop was higher for the 50E/50P wood mix, the lower end pH for this mix is logical. Regarding PS effect on O-stage performance there were no clear trends, except for the

TABLE 3. Sugar losses across conventional and kraft-PS cooking for different pine and eucalypt wood mixtures.

Sugar Losses (%)	Wood MIX 50E/50P			Wood MIX 70E/30P			Wood MIX 90E/10P		
	Ref.	1.5% PS	3.0% PS	Ref.	1.5% PS	3.0% PS	Ref.	1.5% PS	3.0% PS
Xylose	44.2	40.1	41.1	40.0	38.7	38.9	40.2	36.0	36.2
Glucose	18.6	16.7	15.2	17.4	15.4	15.3	16.3	15.1	13.9
Arabinose	81.2	80.9	80.7	81.6	76.9	81.0	84.1	75.2	70.6
Mannose	75.4	70.9	69.1	75.5	76.0	69.5	79.6	77.4	75.7
Galactose	93.5	93.3	93.2	91.8	91.6	91.6	89.4	89.1	89.0

TABLE 4. Performances of the oxygen delignification and (D/A)(EP)D bleaching to 85% ISO brightness for pulps produced from different eucalypt and pine wood mixtures in kraft cooking carried out in the presence and absence of PS.

Parameter	MIX 50E/50P			MIX 70E/30P			MIX 90E/10P		
	Ref.	1.5% PS	3.0% PS	Ref.	1.5% PS	3.0% PS	Ref.	1.5% PS	3.0% PS
End pH after O-stage	11.3	11.4	11.6	11.4	11.6	11.7	11.8	11.8	11.8
Kappa No. After O-stage	8.0	8.4	8.6	9.1	8.7	8.8	10.1	10.2	10.5
Viscosity after O-stage (dm ³ /kg)	615	654	662	671	681	698	781	803	854
Brightness after O-stage, % ISO	42.1	44.8	43	45.3	44.5	46.3	47.4	46.4	47.1
Kappa drop in O-stage (%)	57.9	55.3	53.7	53.1	54.9	52.4	47.4	47.7	46.2
Brightness gain in O-stage, % ISO	11.3	13.7	12	13.9	12.6	13.5	15.0	14.3	14.7
Viscosity drop in O-stage (dm ³ /kg)	148	156	142	142	153	149	150	131	89
ClO ₂ in D ₀ -stage, kg/odt pulp	6.4	6.7	6.9	7.3	6.9	7.0	8.1	8.1	8.4
H ₂ O ₂ in (EP)-stage, kg/odt pulp	4.40	4.40	4.40	4.40	4.40	4.40	4.40	4.40	4.40
Kappa No. After (EP)-stage	2.1	2.0	2.2	2.4	2.4	2.3	2.5	2.5	2.7
Brightness after (EP)-stage, % ISO	76.2	77.5	76.4	79.3	80.5	83.0	83.4	84.2	83.6
ClO ₂ in D ₁ -stage, kg/odt pulp	1.85	1.62	1.90	1.00	0.78	0.27	0.27	0.13	0.36
Total ClO ₂ to 85% ISO brightness, kg/odt pulp	8.2	8.3	8.8	8.3	7.7	7.3	8.3	8.3	8.7
TAC to 85% ISO brightness, kg TAC/odt pulp	30.9	31.1	32.3	30.9	29.5	28.4	31.1	31.0	32.2
O-D-(EPO)-D bleached pulp kappa No.	0.5	0.5	0.3	0.4	1.0	0.9	1.2	1.2	1.1
O-D-(EPO)-D bleached pulp reversion, % ISO	2.8	2.9	2.9	2.4	2.8	2.9	2.2	2.3	2.4
O-D-(EPO)-D bleached pulp viscosity (dm ³ /kg)	553	589	598	614	631	639	698	721	752

50E/50P wood mix whereby there was a trend for slightly lower kappa drops for the pulp samples cooked with PS as additive. In addition, no clear trends were visible for the brightness gains regarding the use of PS additive in the cooking, but pulp brightnesses were higher for the pulps derived from wood mixes containing more eucalypt, in the range of 11.3–15.0%. The kraft pulp brown coloration derives mainly from lignin since HexA are colorless.^[45] Lignin chromophores groups contains electrons capable of absorbing energy or visible light and excite to emit different colors.^[46]

The values of viscosity drop across O-stage showed no clear effect of PS addition to the kraft cooks for the 50E/50P and 70E/70P pulp samples but showed clear positive effect for the 90E/10P pulp sample, being lower for the samples cooked with PS. It is also visible that pulp viscosity after O-stage were in general higher for the wood mixes having more eucalypt in their composition and were positively affected by PS, reflecting the viscosities values after cooking. The mixtures containing higher proportion of eucalyptus were cooked under milder conditions (lower H-factor, active alkali, and temperature) in comparison with mixtures containing more pine, thus preserving the carbohydrate integrity and the

pulp viscosity after cooking (Table 2). The viscosity drops across O-stage, although different between the various pulps, tended to be lower for the wood mixtures containing more eucalyptus (Table 4). Hence, the higher viscosities of the pulps derived from wood blends containing more eucalypt result from the combined effects of higher viscosity values after cooking along with the lower viscosity drop in the O-stage. Oxygen delignification is more selective than kraft cooking regarding pulp yield,^[43] but can cause significant viscosity losses as observed in this study.

ECF Bleaching

The ECF bleaching with the (D/A)(EP)D sequence was targeted to 85% ISO brightness. In the three-stages of the (D/A)(EP)D sequence all the conditions were kept constant, except for the chlorine dioxide charges applied to the (D/A)- and D-stage. In the (D/A)-stage a kappa factor of 0.21 was used for all samples, and the ClO₂ charge varied as a function of the O-stage incoming kappa number. In the D-stage, the ClO₂ charge was varied for each sample to meet the 85% ISO brightness target constraint. The (D/A)-stage was run at high temperature to remove the HexA. After the identification of HexA by Teleman et al.,^[38] it

has been common practice to remove them from the pulp, using the so-called hot acid hydrolysis (A-stage). The combination of the hot acid hydrolysis with chlorine dioxide bleaching, using the (A/D) and (D/A) (D_{HT}) technologies is quite usual these days for eucalypt pulps, allowing for the removal of small amounts of lignin and significant amounts of HexA at the same time.^[47] The ClO_2 charge in the (D/A)-stage varied in the range of 6.4–8.4 kg/odt pulp due to variations of the O-stage incoming kappa number of the various pulps, and these charges were totally consumed at 90 °C, 120 min, and pH 3.0.

The subsequent (EP) stage is run with 0.8% NaOH/0.4% H_2O_2 charges resulted pulp brightness in the range of 76.3–84.2% ISO for the various pulps at end pH in the range of 11.2–11.7, with H_2O_2 consumptions of 51.6–93.7%. The pulps containing more pine consumed more H_2O_2 . The highest brightnesses were achieved for the 90E/10P wood mix and the lowest ones for the 50E/50P blend, in spite of the lower end pH and higher H_2O_2 consumption occurring for the 50E/50P mix. The pulps that were cooked with 1.5% PS showed higher brightness than their references (Ref.) regardless of the wood mix. In alkaline media hydrogen peroxide reacts with the hydroxyl anion (OH^-) to form the perhydroxyl anion (HOO^-), which is responsible for the bleaching effect on the lignin.^[48] The higher H_2O_2 consumption and lower brightness gain of the 50E/50P pulp may be likely explained due to its higher content of true lignin in relation to the other pulps.

The end pH of the final D-stage varied in the range of 4.8–5.3 and the ClO_2 charges applied to this stage were 100% consumed during the reaction time of 90-min at 80 °C. The target brightness of 85% ISO was achieved for all pulps, by interpolation, but the total active chlorine (TAC) demand necessary to meet this brightness target varied slightly among the various treatments, in the range of 28.4–32.3 kg active Cl_2 . There was no clear effect of PS cooking on TAC demand. For the 50E/50P wood mix, the use of PS slightly increased TAC

demand but for the 70E/30P blend, the use of PS decreased it slightly and for the 90E/10P it showed no effect for the 1.5% PS charge and a small increase for the 3.0% PS charge. As a matter of fact, the slight changes in TAC demand were more due to a response to the kappa number after O-stage than anything else for within each one wood mix evaluated. It is worth noting that among the three wood mixes, the lowest TAC demands were achieved for the 70E/30P. In spite of the higher kappa numbers after the O-stage for the wood mix 90E/10P pulps, their TAC demands tended to be somewhat similar to those of the other wood mixes, a fact explained by the high HexA contents of these pulps.

The bleached pulp kappa numbers were in general very low, in the range of 0.3–1.2, and they increased with increasing the proportion of eucalypt wood in the wood mixture, because of the higher contents of HexA residuals of the bleached pulps containing more eucalypt fibers (Table 4). The use of PS additive in the cooking did not significantly influence this parameter, except for the 70E/30P where higher kappa values were seen for the pulps cooked with PS. The brightness reversion values of the various pulps were typical and varied in the range of 2.2–2.9% ISO but showed no clear trend regarding the effects of PS cooking and/or the composition of the wood mix. In fact, the pulps with higher kappa numbers (90E/10P) tended towards lower brightness reversion, which is rather unusual.

The bleached pulp viscosities were lower for the pulps derived from wood mixes containing large proportion of pine, following the same path observed for the brown and oxygen delignified samples. In addition, the pulps cooked with PS presented higher viscosities, regardless of the wood mix composition, also reflecting the trends observed after cooking and O-stage.

Pulp Refinability, Drainability, and Quality

Blends of eucalypt and pine fibers may have advantages in papermaking. Eucalypt

fibers produce papers with better formation and smoothness than pine ones and have acceptable strength properties. However, pine fibers produce paper with high strength properties, particularly tear and folding. In fact, pine fibers may deliver 10–15 higher folding endurance than the eucalypt counterparts. In addition, the pine fibers present better printing surface than the eucalypt ones because they do not contain vessel elements.^[49] The different morphological features of eucalypt and pine fibers enable their use in fiber blends in order to take advantage of the desirable and unique characteristics of each one. However, the pulp production from eucalypt and pine timber mixes is challenging regarding pulp properties because cooking these two materials together may cause some damage of pulp components, namely cellulose and hemicelluloses, with the eucalypt fibers suffering the most.^[33] The data presented in Figure 1 shows the effect of cooking pine and eucalypt wood chips together, in blends of 50E/50P, 70E/30P, and 90E/10P, and also the effect of PS cooking (1.5%), on pulp refinability, drainability, and strength properties.

The drainage resistance, expressed in °SR, is an important parameter for evaluation of fiber entanglement - the greater the pulp °SR value, the lower its ability to drain water. Figure 1(a,b) show results of refining energy consumption and drainage resistance, respectively. A similar linear trend was observed between PFI revolution and energy consumption, irrespectively to the wood mixture and absence or presence of PS (Figure 1(a)). Pulp drainage resistance increased with increasing PFI revolutions as anticipated (Figure 1(b)). There was a clear trend of increasing the resistance to drainage with increasing the proportion of eucalypt chips in the wood blend. However, no significant effect of PS cooking was observed on pulp drainage resistance.

The bulk of the different pulps decreased with increasing refining energy as anticipated but was not significantly affected either by wood blend or by the use of PS additive in

cooking (Figure 1(c)). The pulp tensile index is a very relevant property for papermaking since it indicates the probability of sheet rupture during paper manufacturing, as well as the quality of the final product. Figure 1(d) shows tensile index results for various levels of refining energy consumption. There was no significant effect of the wood mix on tensile strength values. Other studies revealed a decrease in tensile strength with increasing the proportion of pine chips in the blend with eucalypt.^[28] The use of PS additive in cooking resulted in increased tensile strength for the lower levels of refining. However, for the higher levels of refining lower values of tensile index were observed for pulps that were cooked with PS additives. This result may be explained by the higher hemicelluloses contents of the pulps derived from kraft-PS cooking. Our results corroborated with those from Rahman *et al.*,^[10] which observed an increasing in tensile index for spruce pulp due to the use of PS as additive in kraft cooking, especially at lower refining degrees. It is worth noting that the well-known correlation between tensile and burst strength did not hold true when the proportion of pine fibers in the furnish increased. We currently do not have a good explanation for this finding. One possible explanation would be the softwood fiber cutting during beating with production of fines, which affected burst and tensile in different fashion, but we cannot prove that since pulp fiber morphology was not measured in this study.

Regarding burst strength, there was a clear trend of increasing this property with increasing proportion of pine wood in the mix (Figure 1(e)). The same trend has been observed by Oliveira *et al.* who explained the trend based on the morphological differences between pine and eucalypt fibers, particularly regarding fiber length.^[33] The use of PS additive in cooking had only a slight positive effect on burst strength. Regarding tear index (Figure 1(f)), there was no clear trend regarding the composition of the wood mix, in agreement with results reported elsewhere.^[33]

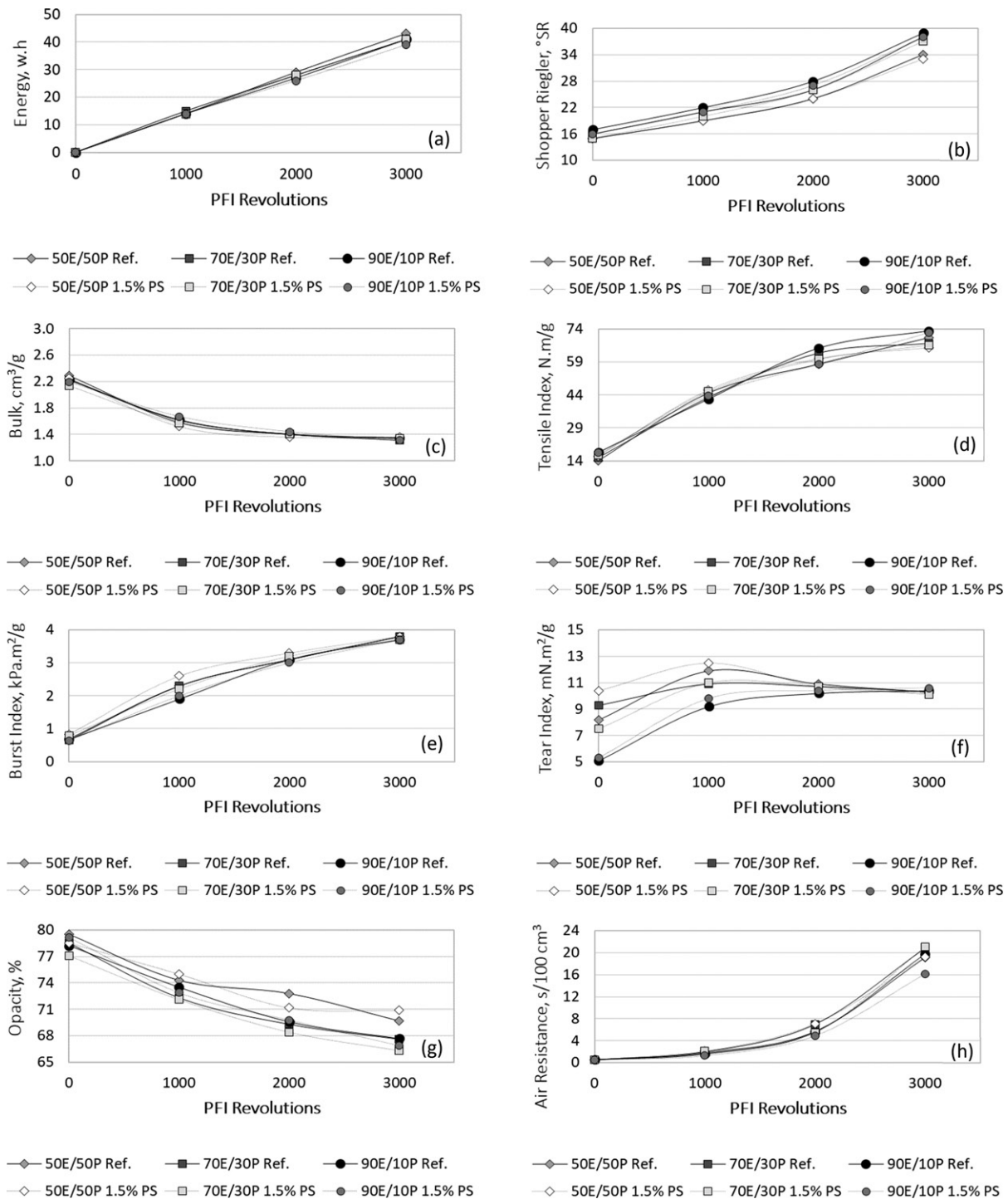


FIGURE 1. Energy consumption (a), drainability (b), bulk (c), tensile index (d), burst index (e), tear index (f), opacity (g), and air resistance (h) as a function of PFI revolutions for bleached pulps produced from different eucalypt and pine wood mixtures in kraft cooking carried out in the absence and presence of 1.5% PS.

The use of 1.5% PS in cooking slightly improved tear strength only for the 50E/50P and 70E/30P wood mixes.

Pulp opacity decreased with refining due to improved fiber-to-fiber bonding area and reduced air-fiber interface area, leading to a

lower light scattering (Figure 1(g)). This tendency was observed for all wood proportions used in this study, regardless of using PS additive in cooking. It was observed that an increase of eucalypt wood in the blend resulted in lower values of opacity. Regarding the use of the PS additive, there was a trend to lower pulp opacity values when this additive was used. Air resistance increased with increasing PFI revolutions as anticipated, but no clear trends were seen regarding different wood mixes and the use of PS in cooking (Figure 1(h)).

CONCLUSIONS

The different proportions of eucalypt and pine chips, as well as the use of PS additive significantly influenced kraft cooking performance. The use of PS additive for cooking pine and eucalypt wood blends is feasible to improve yield (up to 2.2%), preserving significant amounts of cellulose (up to 1.5%) and hemicelluloses (up to 0.7%) in the pulp. The maximum benefit of PS additive (1.5% PS) in cooking was achieved with the 50E/50P wood blend but it was beneficial for all wood chip blends.

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