ALTERNATIVE TECHNIQUE FOR EVALUATING YIELD LOSS IN MODERN BLEACH PLANTS

Dalton Longue Júnior[1], Jorge Luiz Colodette[2], Marcela Freitas Andrade[3]

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ABSTRACT: In this study an alternative technique is presented and discussed for measuring yield loss based on the analysis of total organic carbon (TOC) in bleaching filtrates. Oxygen predelignified eucalyptus kraft pulp was subjected to the D_{HT}(EP)D, D(EP)DD and D(EP)DP bleaching sequences and the gravimetric yield of each stage was determined, with 10 replicates. Then the filtrates were analyzed for TOC and COD. Correlations were established among the three measurement methods (gravimetric, COD and TOC). Yield losses in the D_{HT} stage were more accentuated than in the D_0 stage, these losses being recovered in subsequent stages of the bleaching sequence. Yield loss decreased with each advancing stage of the bleaching sequences (D_0,D_{HT}>(EP)>D_1>P>D_2). Yield loss increased with higher kappa factors in the first bleaching stage and with higher temperature in the (EP) stage. The final P stage resulted in greater yield losses than the final D stage. Yield loss intensifies with gain in brightness from bleaching. Yield losses as measured by the TOC method revealed a narrower range of variation in relation to the gravimetric and COD methods, and the linear equation derived for the TOC *vs.* gravimetric yield relationship provided the best fit (R^2=97.27%). Overall yield losses throughout were in the range of 4-5%, depending on the bleaching sequence and operating conditions.

Key words: TOC, COD, yield, bleaching.

TÉCNICA ALTERNATIVA PARA AVALIAÇÃO DE PERDA DE RENDIMENTO EM PLANTAS MODERNAS DE BRANQUEAMENTO

RESUMO: *Neste estudo, uma técnica alternativa de medição de perda de rendimento, baseada na análise do carbono orgânico total (COT) dos filtrados do branqueamento, é apresentada e discutida. Polpa kraft de eucalipto pré-deslignificada com oxigênio foi branqueada pelas sequências D_{HT}(EP)D, D(EP)DD e D(EP)DP, sendo os rendimentos gravimétricos de cada estágio determinados com 10 repetições. Os filtrados de tais tratamentos foram analisados quanto ao COT e DQO. Correlações foram estabelecidas entre os três métodos de medição de rendimento (gravimétrico, DQO e COT). As perdas de rendimento no estágio D_{HT} foram mais acentuadas que no estágio D_0, sendo que essas perdas são recuperadas nos estágios subsequentes da sequência de branqueamento. As perdas de rendimento nas sequências de branqueamento diminuem com o avanço dos estágios (D_0,D_{HT}>(EP)>D_1>P>D_2). A perda de rendimento aumentou com o aumento do fator kappa no primeiro estágio de branqueamento e com aumento da temperatura do estágio (EP). O estágio P final resultou em maiores perdas de rendimento que o estágio D final. A perda de rendimento aumenta com o ganho de alvura no branqueamento. As perdas de rendimento medidas pelo método COT apresentaram menor amplitude de variação em relação aos métodos gravimétricos e DQO, e a equação linear obtida da relação funcional COTxgravimétrico apresentou o melhor ajuste (R^2=97,27%). As perdas totais de rendimento durante o branqueamento foram da ordem de 4-5%, dependendo da sequência e condições operacionais do branqueamento.*

Palavras-chave: COT, DQO, rendimento, branqueamento.

1 INTRODUCTION

Bleaching can be defined as a physicochemical treatment intended to improve cellulose pulp properties such as brightness, chemical purity and clarity (ALMEIDA 1988). More simply, bleaching is meant to remove or transform chromophore groups present in pulps so that the final product attains the desired brightness. According to Pan & Yuan (2004), while on the one hand bleaching increases pulp brightness, it also leads to inevitable yield loss on the other. Ala-Kaila et al. (2002) discussed the possibilities and difficulties of estimating kraft pulp yield losses in an industrial oxygen delignification process.

Yield is an important indicator of the selectivity (brightness gain *vs.* carbohydrates removal) of the bleaching process and is crucial for economic assessment of the process. Lower yield means increased consumption of wood for a given cellulose pulp output (PAN & YUAN 2004).

[1]Forest Engineer, MSc in Forest Science – Laboratório de Celulose e Papel – Departamento de Engenharia Florestal/DEF – Universidade Federal de Viçosa/UFV – Avenida Peter Henry Rolfs, s/n – Campus Universitário – 36570-000 – Viçosa, MG – daltonufv@yahoo.com.br
[2]Forest Engineer, Professor, PhD in Forest Sciences – Laboratório de Celulose e Papel – Departamento de Engenharia Florestal/DEF – Universidade Federal de Viçosa/UFV – Avenida Peter Henry Rolfs, s/n – Campus Universitário – 36570-000 – Viçosa, MG – colodett@ufv.br
[3]Forest Engineer, Technical Master's Degree Student in Pulp and Paper Technology – Laboratório de Celulose e Papel – Departamento de Engenharia Florestal/DEF – Universidade Federal de Viçosa/UFV – Avenida Peter Henry Rolfs, s/n – Campus Universitário – 36570-000 – Viçosa, MG – andrade-marcela@hotmail.com

Pan & Yuan (2004) proposed methods of improving yield measurement techniques in bleached pulps, as well as methods of improving the repeatability and precision of such techniques, particularly gravimetric techniques. Typically, yield is obtained by using the gravimetric method in laboratory simulation, though this type of method requires lengthy intervals and is unsuitable for industrial practice (EGAS & SIMÕES 2004).

The Brazilian wood pulp sector has seen the construction of new pulp plants and expanded production through plant modernization. Currently wood pulp plants have been operating at high capacity, which makes precise yield loss estimation during bleaching even more difficult to attain. This work aims to compare techniques for measuring yield loss in bleach plants, with emphasis on a new technique of analysis of bleaching filtrates known as TOC (Total Organic Carbon).

2 MATERIAL AND METHODS

The experiment used industrial eucalyptus kraft pulp previously delignified with oxygen (11.4 kappa, 47.4% ISO brightness and 33.6 cP viscosity), and subjected to the D_{HT}(EP)D, D(EP)DD and D(EP)DP bleaching sequences, to a 90% ISO brightness, where: D_{HT} = chlorine dioxide stage at high temperature (ClO_2); D_0, D_1 and D_2 = conventional chlorine dioxide stages (ClO_2); (EP) = oxidative extraction with hydrogen peroxide (H_2O_2); P = hydrogen peroxide stage (H_2O_2). General conditions of bleaching as used in each stage are illustrated in Table 1. All bleaching stages were performed in duplicate.

The chlorine dioxide bleaching stage was performed in polyethylene bags with oven dry samples weighing 300 grams (D_0 and D_{HT}), 100g (D_1) and 50g (D_2) under the conditions described in Table 1. The bleaching liquor containing ClO_2, H_2O, NaOH or H_2SO_4 was added to the pulp at room temperature. Requirement for NaOH or H_2SO_4 as pH control agents was determined in a previous study with mini samples of pulp. After being manually mixed in polyethylene bags, the material was microwave heated to the desired temperature, and transferred to a temperature controlled steam bath, where it was kept for the preset time interval. Once the reaction was complete, samples were extracted from the residual liquor for analysis of pH and residual chlorine dioxide, as well as for analysis of TOC, COD and gravimetric yield, after which the pulp was washed with distilled water in the proportion of $9m^3$ / oven dry ton. The (EP) stage was performed in a temperature controlled steam bath with oven dry samples weighing 100 grams, under the conditions described in Table 1. The pulp was placed in polyethylene bags at the appropriate consistency and preset charges of H_2O_2 and NaOH were added, being microwave heated to the desired temperature. Once the reaction was complete, samples were extracted from the residual liquor for analyses of pH, residual peroxide, TOC, COD and gravimetric yield, and subsequently the pulp was washed with distilled water in the proportion of $9m^3$ / oven dry ton.

Table 1 – General conditions of bleaching.

Tabela 1 *– Condições gerais de branqueamento.*

General Conditions	Bleaching Stage					
	D_0	D_{HT}	(EP)	D_1	D_2	P
Consistency (%)	10	10	10	10	10	10
Time (min.)	30	120	60	60	90	90
Temperature (°C)	60	95	50, 70, 90	85	85	85
Kappa factor	0.10, 0.14, 0.18, 0.22, 0.26, 0.30					
ClO_2 (kg/odt)	-	-	-	**	3.0	3.0
H_2O_2 (kg/odt)	-	-	3.0	-	-	1.5
H_2SO_4 (kg/odt)	*	*	*	*	*	*
NaOH (kg/odt)	*	*	10	*	*	*
final pH	3.0	3.0	11-11.5	3.5-4.0	3.5-4.0	10.5

* Dosages for pH adjustment

** Dosage required for completing a total active chlorine charge set at 51.47 kg / ton of oven dry pulp, changeable as a function of the kappa factor used in the first stage (D_0 or D_{HT})

The final hydrogen peroxide bleaching stage (P) was performed in polyethylene bags, with oven dry samples weighing 50 grams, and peroxide charges (Table 1) sufficing to attain 90% ISO brightness. The bleaching liquor containing H_2O_2, H_2O and NaOH was added to the pulp, at room temperature. After being manually mixed, the pulp was microwave heated to the desired temperature and transferred to a temperature controlled steam bath, where it was kept for the preset time interval. Once the reaction was complete, samples were extracted from the residual liquor for analyses of pH and residual hydrogen peroxide, as well as for analysis of TOC, COD and gravimetric yield, and subsequently the pulp was washed with distilled water in the proportion of $9m^3$ / oven dry ton. Analyses were performed for pulp brightness, viscosity and kappa number, following TAPPI test procedures.

Gravimetric yield loss is based on determination of the mass of organic substances solubilized in the filtrates during bleaching. At the end of each bleaching stage, the samples were filtered to separate fibers (which are regarded as process losses rather than yield losses), and a portion of these filtered samples was weighed in preweighed Griffin beakers and then placed in an oven at 105°C for around 24 hours. The gravimetric yield loss from bleaching stages was then determined using the formula YL=(M1-M2)/P*100, where YL = gravimetric yield loss from bleaching stages, in %; M1 = mass of Griffin beaker containing dry sample; M2 = initial mass of Griffin beaker without sample; P = mass of moist sample (approximately 50g).

Yield by the TOC method was obtained by infrared detection of organic CO_2, generated after combustion at 680°C in a Shimadizu total organic carbon analyzer. This combustion occurred in the absence of vapors (moisture trap) and halogens (halogen scrubber). Before burning, the samples were filtered for removal of fibers, also having their pH adjusted (pH~2-3) with addition of HCl 2N, for subsequent elimination of inorganic carbon. Inorganic carbon was removed by sparging the sample with oxygen in an acidified solution (inorganic CO_2 release), it being ignored for purposes of yield analysis.

Yield by the COD method was obtained by determination of amount of organic matter contained in the filtrates of each bleaching stage, using oxidation with a known amount of potassium dichromate ($K_2Cr_2O_7$) in a highly acidified solution. After 2 hours of reaction at 148°C (thermoreactor), the samples were read in a spectrophotometer and absorbances were determined. A calibration curve relating absorbance and COD (mg O_2/l) was previously fitted.

Regression equations were developed relating yield losses in each bleaching stage, quantified by the three methods (gravimetric, TOC and COD), using MSO Excel software.

3 RESULTS AND DISCUSSION

3.1 Yield loss per stage (D_{HT}(EP)D, D(EP)DD and D(EP)DP bleaching sequences)

Yield losses tend to increase as the bleaching stages progress. This tendency was observed for all three methods (TOC, COD and gravimetric) and for the three bleaching sequences: D_{HT}(EP)D - Figures 1 (A, B and C), and also D(EP)DD and D(EP)DP - Figures 2 (A, B and C). The TOC *vs.* gravimetric yield relationship revealed greater linearity (better point distribution) for different treatments than the COD *vs.* gravimetric yield relationship. The four-stage sequences showed slightly higher yield losses than the three-stage sequences, particularly the one ending with a final P stage.

3.2 Effect of kappa factor and time / temperature on the 1st stage (D_0 and D_{HT})

Yield losses for the three methods were assessed at three different kappa factors (KF) in the D_0 and D_{HT} stages. Results in Figures 3 (A, B and C) indicate that yield losses increase with higher kappa factors in the D_0 or D_{HT} stages. It was noted that yield losses are greater in the D_{HT} stage, which is explained by the harsher time and temperature conditions used in this stage (Table 1).

3.3 Effect of temperature on the second stage (EP)

Figures 4 (A and B) depict yield losses in the (EP) stage at three temperature levels (50°C, 70°C and 90°C), as measured by the gravimetric method. Figures 5 (A and B) and Figures 6 (A and B) depict yields losses as measured by the COD and TOC methods respectively. The increase in temperature to a range of 50°C to 90°C in the (EP) stage increased yield losses, for sequences starting with a D_0 or D_{HT} stage, yet yield losses were more accentuated in pulps emerging from a D_0 stage. This is explained by the fact that, as far as oxidation and extraction of oxidized materials is concerned, the D_0 stage is less efficient than the D_{HT} stage. The D_0 stage leaves more potentially soluble materials in the pulp, which are eliminated in the (EP) stage, resulting in higher yield loss in that stage.

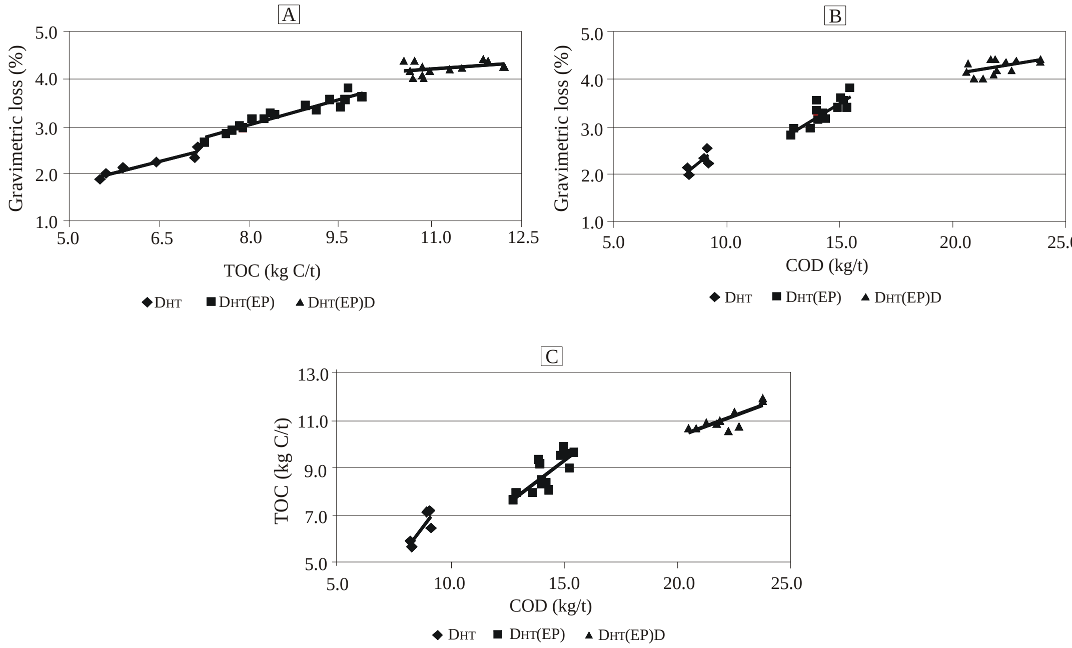

Figure 1 – Yield loss for the three methods, stage by stage of bleaching with the D_{HT}(EP)D sequence. (A, B and C)

Figura 1 *– Perda de rendimento pelos três métodos, estágio por estágio do branqueamento com a sequência D_{HT}(EP)D. (A, B e C)*

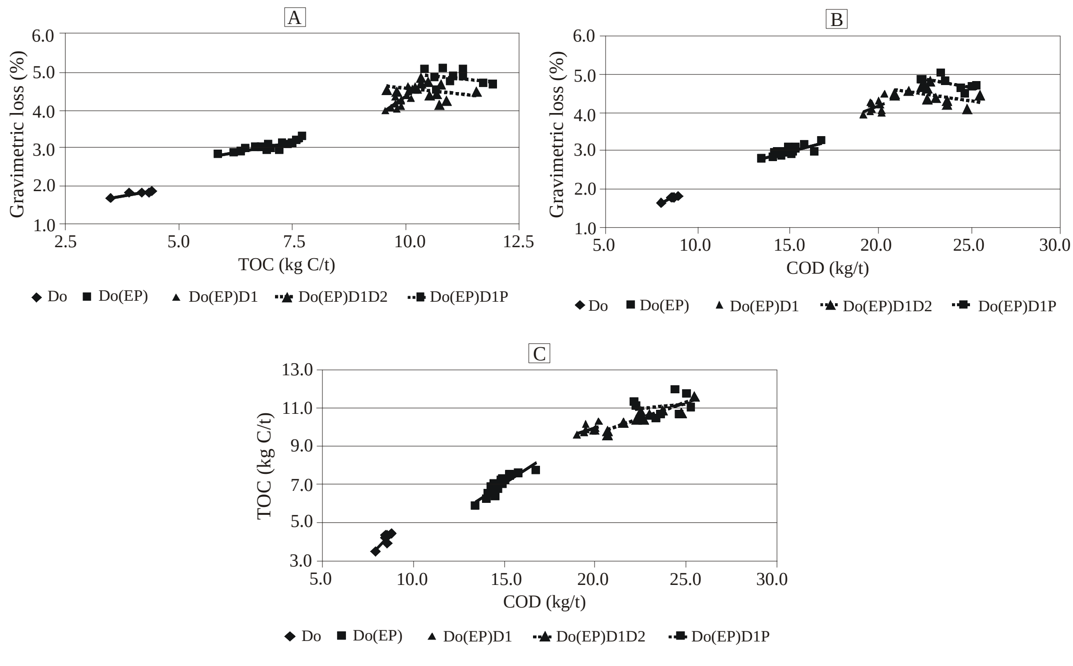

Figure 2 – Yield loss for the three methods, stage by stage of bleaching with the D(EP)DD and D(EP)DP sequences. (A, B and C)

Figura 2 *– Perda de rendimento pelos três métodos, estágio por estágio do branqueamento com as sequências D(EP)DD e D(EP)DP. (A, B e C)*

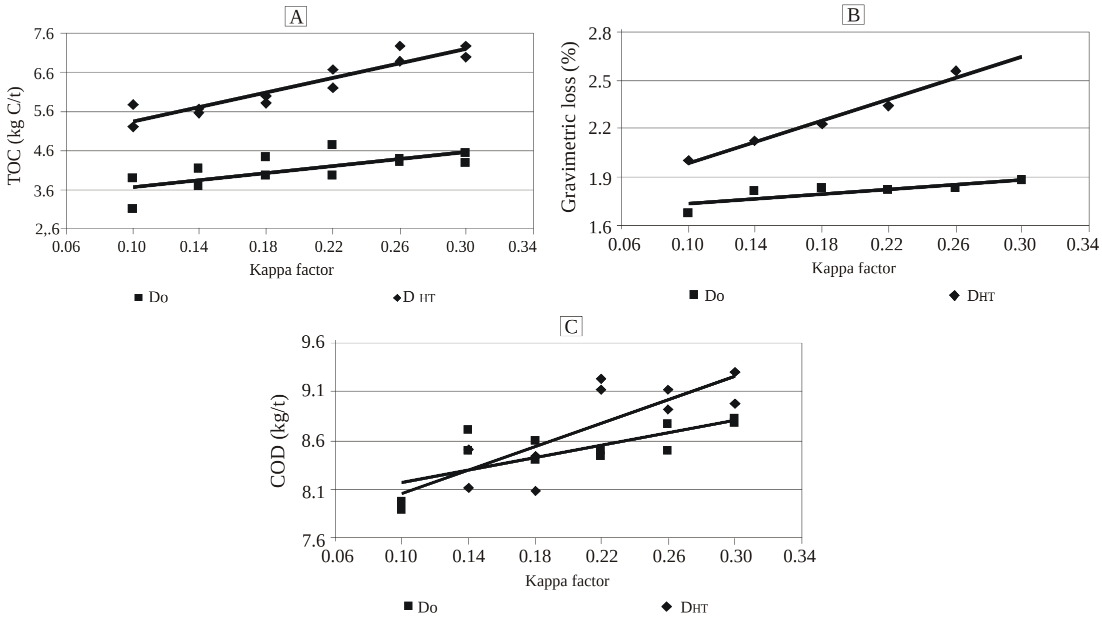

Figure 3 – Yield losses for the three methods, D_0 or D_{HT} stages, at different kappa factors. (A, B and C)

Figura 3 *– Perdas de rendimentos pelos três métodos, para os estágios D_0 ou D_{HT}, quando submetidos a diferentes fatores kappa. (A, B e C)*

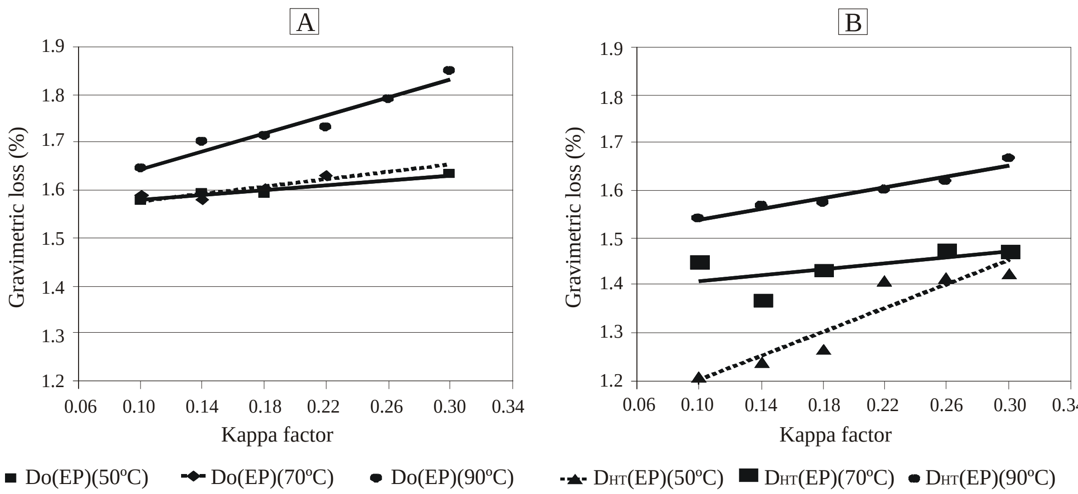

Figure 4 – Gravimetric yield loss in the (EP) stage at 50°C, 70°C and 90°C, of pulps previously treated with a D_0 or D_{HT} stage. (A and B)

Figura 4 *– Perda de rendimento gravimétrico no estágio (EP) a 50, 70 e 90 °C, de polpas previamente tratadas com estágios D_0 ou D_{HT}. (A e B)*

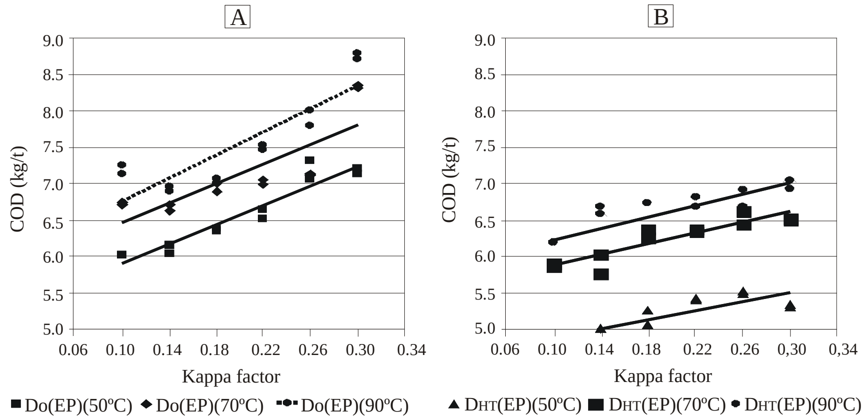

Figure 5 – Yield loss by the COD method in the (EP) stage at 50°C, 70°C and 90°C, of pulps previously treated with a D_0 or D_{HT} stage. (A and B)

Figura 5 *– Perda de rendimento DQO no estágio (EP) a 50, 70 e 90 °C, de polpas previamente tratadas com estágios D_0 ou D_{HT}. (A e B)*

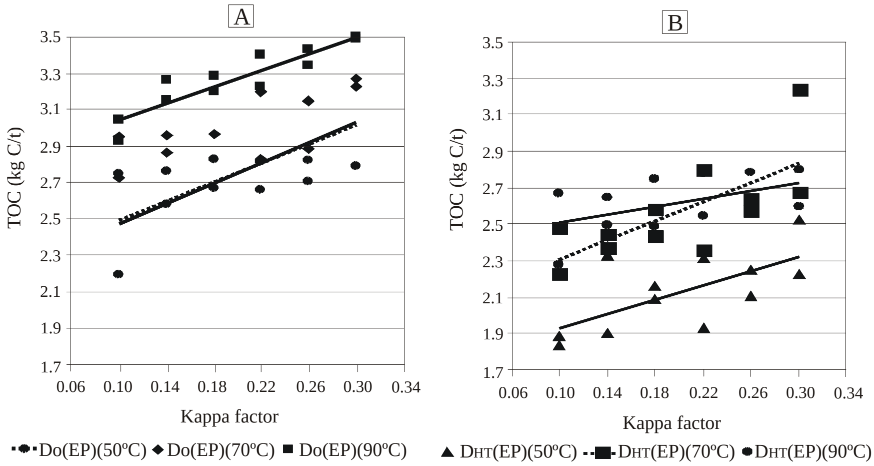

Figure 6 – Yield loss by the TOC method in the (EP) stage at 50°C, 70°C and 90°C, of pulps previously treated with a D_0 or D_{HT} stage. (A and B)

Figura 6 *– Perda de rendimento COT no estágio (EP) a 50, 70 e 90 °C, de polpas previamente tratadas com estágios D_0 ou D_{HT}. (A e B)*

3.4 Peroxide *vs.* dioxide in the last bleaching stage

In comparing the last stages of the D(EP)DD and D_{HT}(EP)DP sequences, it was noted that losses in the final P stage (Figure 7) were greater than losses in the final D stage (Figure 8). The greater loss in the final P stage is explained by the fact that the peroxide stage is conducted under alkaline conditions, which favor the extraction of materials from the fibers. The use of a final P stage in the processing industry is justified by its positive influence in stabilizing pulp brightness.

3.5 Correlations between the gravimetric, TOC and COD methods regarding yield losses

Figure 9 illustrates a functional relationship between gravimetric and TOC methods for yield loss. A high degree of fit was observed for the equation ($R^2 > 97\%$) relating these methods, for the three bleaching sequences, suggesting that it is possible to precisely estimate gravimetric yield loss through TOC measurement in the bleaching filtrates. The degree of fit (R^2 > 80%) between gravimetric yield loss and COD (Figure 10) was not as high as the previous one. An also lower degree of fit was observed for the equation relating yield losses as measured by the TOC and COD methods (R^2 ≅80%), as illustrated in Figure 11. COD estimation through TOC analysis is extremely valuable for predicting bleaching effluent treatability.

3.6 Relationship between bleaching yield and pulp brightness

In all sequences, it was noted that yield losses intensify with increasing pulp brightness, stage by stage (Figure 12). This tendency was expected, since increasing pulp brightness presupposes removal of materials from the pulp by oxidation and/or extraction.

3.7 Range of coefficients of variation

Figure 13 illustrates coefficients of variation for yield loss, as measured in each stage of the three bleaching sequences. Greater variations occurred in yield loss measurements by the gravimetric method, showing considerable imprecision in this method. Smaller variations occurred by the COD method, although variations by the TOC method were even subtler, in all stages and sequences. Therefore, the TOC method proved the most reliable for predicting yield loss from bleaching.

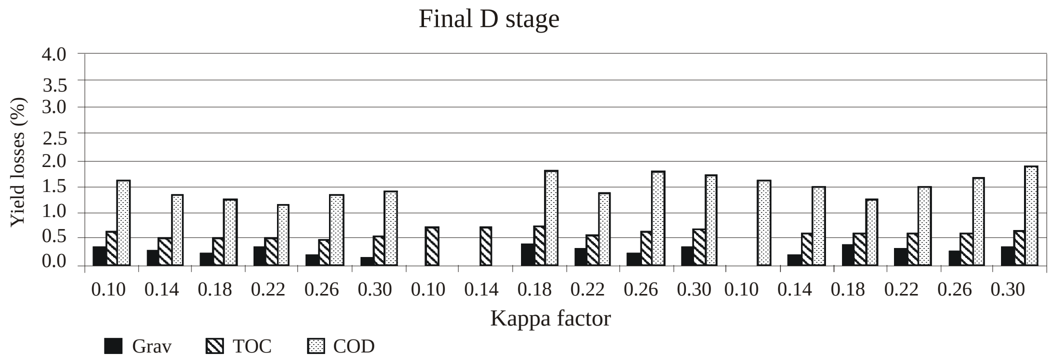

Figure 7 – Yield loss in the final D stage as measured by the gravimetric, TOC and COD methods.

***Figura 7** – Perda de rendimento no estágio D final pelos métodos gravimétrico, COT e DQO.*

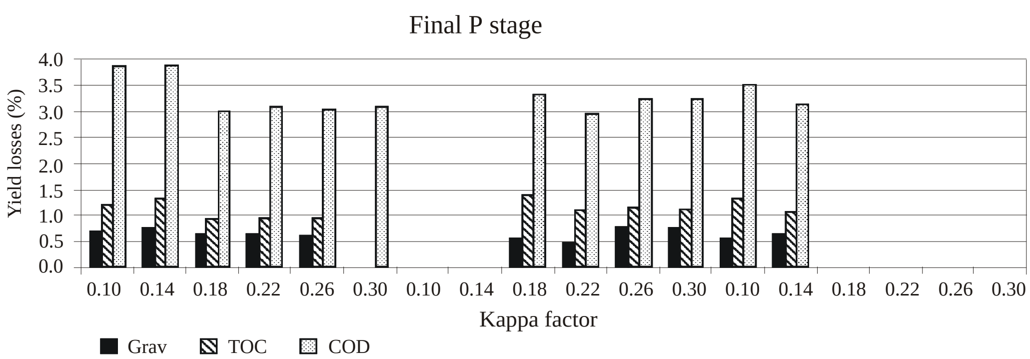

Figure 8 – Yield loss in the final P stage as measured by the gravimetric, TOC and COD methods.

***Figura 8** – Perda de rendimento no estágio D final pelos métodos gravimétrico, COT e DQO.*

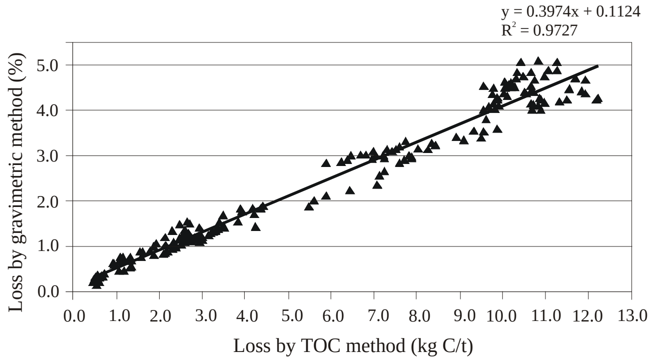

Figure 9 – Functional relationship for yield loss between the gravimetric and TOC methods, considering data from all stages of the D_{HT}(EP)D, D(EP)DD and D(EP)DP sequences.

Figura 9 *– Relação funcional entre perda de rendimento pelos métodos gravimétrico e COT, considerando dados de todos os estágios das sequências D_{HT}(EP)D, D(EP)DD e D(EP)DP.*

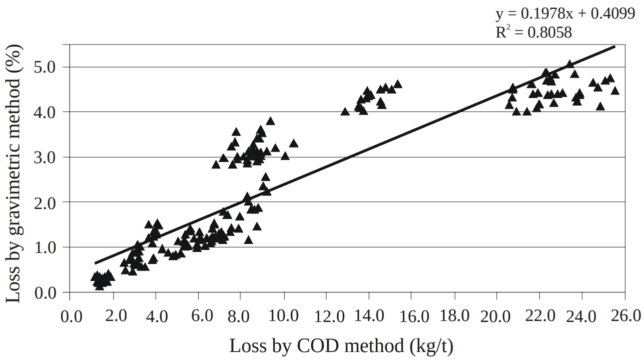

Figure 10 – Functional relationship for yield loss between the gravimetric and COD methods, considering data from all stages of the D_{HT}(EP)D, D(EP)DD and D(EP)DP sequences.

Figura 10 *– Relação funcional entre perda de rendimento pelos métodos gravimétrico e DQO, considerando dados de todos os estágios das sequências D_{HT}(EP)D, D(EP) DD e D(EP)DP.*

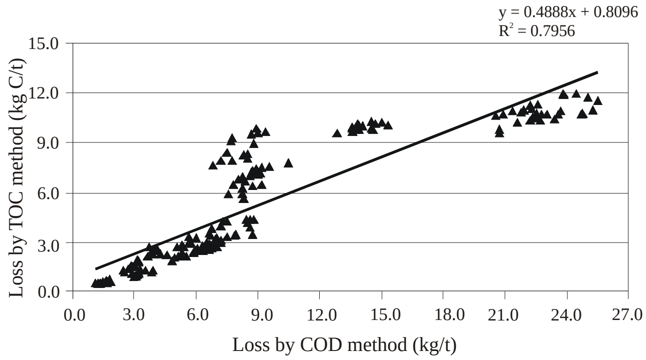

Figure 11 – Functional relationship for yield loss between the TOC and COD methods, considering data from all stages of the D_{HT}(EP)D, D(EP)DD and D(EP)DP sequences.

Figura 11 *– Relação funcional entre perda de rendimento pelos métodos COT e DQO, considerando dados de todos os estágios das sequências D_{HT}(EP)D, D(EP)DD e D(EP)DP.*

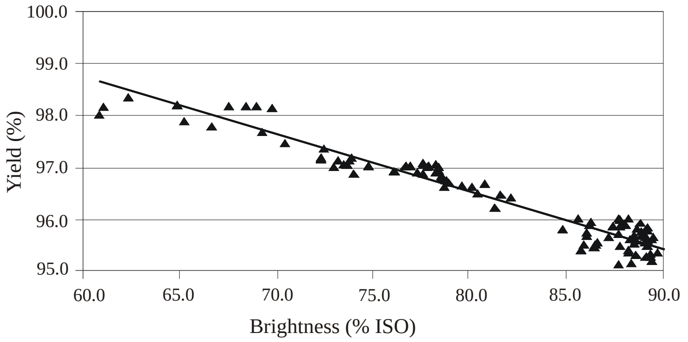

Figure 12 – Functional relationship between overall bleaching yield and pulp brightness, considering data from all stages of the D_{HT}(EP)D, D(EP)DD and D(EP)DP sequences.

***Figura 12** – Relação funcional entre rendimento geral do branqueamento e alvura da polpa, considerando-se dados de todos os estágios das sequências D_{HT}(EP)D, D(EP)DD e D(EP)DP.*

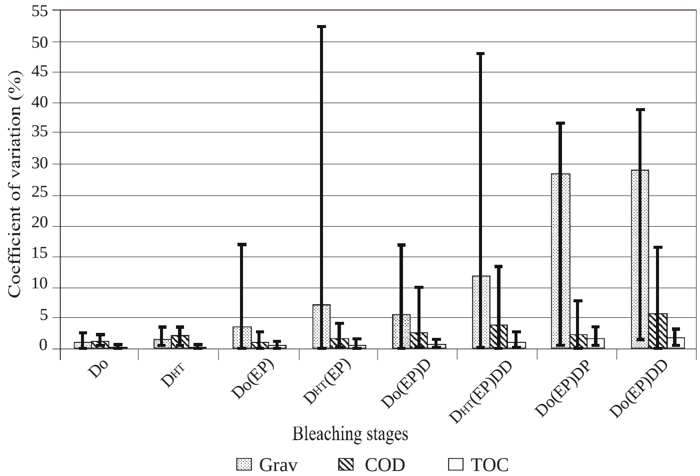

Figure 13 – Range of variation of yield loss measurements by the gravimetric, TOC and COD methods.

***Figura 13** – Amplitude de variação das medições de perda de rendimento pelos métodos gravimétrico, COT e DQO.*

4 CONCLUSION

Out of the three methods – gravimetric, COD and TOC –, the latter was found to be the most reliable for evaluating yield losses throughout the pulp bleaching process using the D_{HT}(EP)D, D(EP)DD and D(EP)DP sequences. The linear equation obtained for the TOC *vs.* gravimetric functional relationship provided the best fit (R^2=97.27%) in comparison to the other correlations.

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