Bleaching Miscanthus x giganteus Acetosolv pulps with hydrogen peroxide/acetic acid. Part 2: Behaviour in acetic acid media

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Blanqueo de las pastas Miscanthus x giganteus Acetosolv con peróxido de hidrógeno y ácido acético. Parte 2: Comportamiento en medio ácido acético
Blanqueig de les pastes Miscanthus x giganteus Acetosolv amb peròxid d'hidrogen i àcid acètic. Part 2: Comportament en medi àcid acètic

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RESUMEN

Se han blanqueado pastas de *Miscanthus x giganteus* obtenidas mediante el proceso Acetosolv, en condiciones optimizadas previamente, mediante el uso de peróxido de hidrógeno en medio ácido acético, como primera etapa de una secuencia de blanqueo. Se han cuantificado las influencias de las principales variables operacionales: concentración de peróxido de hidrógeno (1,6-8,4%), temperatura (48,2-81,8ºC) y pH (1,8-5,2) sobre el rendimiento en pasta, el número kappa, la viscosidad, el contenido en grupos saponificables y la blancura de la pasta. Para ello se llevó a cabo un diseño de experimentos de segundo orden que, además, permitió la identificación de las condiciones de operación óptimas. Los resultados experimentales fueron ajustados a modelos empíricos polinómicos que demostraron que la deslignificación puede llevar a pastas de número kappa inferior a 15. La composición química y las propiedades de la pasta blanqueada son adecuadas para las etapas de blanqueo posteriores. También se analizó el uso de agentes quelatantes en la etapa de peróxido de hidrógeno y los efectos del pH y el tiempo fuera de los límites del diseño experimental.

Palabras clave: Acetosolv, blanqueo, peróxido de hidrógeno, ácido acético, agentes quelantes, diseño factorial, *Miscanthus x giganteus.*

SUMMARY

Miscanthus x giganteus bark samples subjected to fractionation by Acetosolv process under optimal conditions were bleached using hydrogen peroxide in acetic acid medium. The influences of the main operational variables in the bleaching of Acetosolv pulps of *M. x giganteus* (i.e. hydrogen peroxide concentration (1,6-8,4%), temperature (48,2-81,8ºC) and pH (1,8-5,2), have been assessed on pulp yield, kappa number, viscosity, saponifiable groups and brightness of pulps. In order to identify the optimum operating conditions, a rotatable and orthogonal second-order factorial design of experiments was used. Results from the fitting experimental data to empirical mathematical models demonstrate that in general the delignification was extensive, and pulps can achieved with kappa number below 15. The chemical composition and properties of the bleached pulps fulfilled the requirements for forthcoming bleaching stages. Moreover, the use of chelating agents in the hydrogen peroxide stage along with the study of pH and time effects outside limits of the experimental design was studied.

Keywords: Acetosolv, bleaching, hydrogen peroxide, acetic acid, chelating agents, factorial design, *Miscanthus x giganteus*.

RESUM

Es blanquegen pastes de Miscanthus x giganteus obtingudes mitjançant el procés Acetosolv, en condicions optimitzades prèviament, emprant peròxid d'hidrogen en medi àcid acètic, com a primera etapa d'una seqüència de blanqueig. Es quantifiquen les influències de les principals variables operacionals: concentració de peròxid d'hidrogen (1,6-8,4%), temperatura (48,2-81,8ºC) i pH (1,8-5,2) sobre el rendiment en pasta, el número kappa, la viscositat, el contingut en grups saponificables i la blancor de la pasta. A aquest efecte, es realitza un disseny d'experiències de segon ordre que, a més, permet la identificació de les condicions d'operació òptimes. Els resultats experimentals s'ajusten a models empírics polinòmics que demostren que la deslignificació pot portar a pastes de número kappa inferior a 15. La composició química i les propietats de la pasta blanquejada són apropiades per a les etapes de blanqueig posteriors. També s'analitza l'ús d'agents quelants en l'etapa de peròxid d'hidrogen i els efectes del pH i el temps fora dels límits del disseny experimental.

Mots clau: Acetosolv, blanqueig, peròxid d'hidrogen, àcid acètic, agents quelants, disseny factorial, Miscanthus x giganteus.

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INTRODUCTION

Within the efforts made in the idea of sustainable development, the interest of the scientific community in plant biomass is growing significantly. More and more industries turn their attention to biomass as a potential powerhouse of products of interest, due to the scarcity of woody fibers and to the development of biomass related policies implemented by many governments. Among the available ways of exploitation of plant biomass, biorefineries will play a major role in the development of an integral use of many species.

Specifically, cellulose produced by LCF type (Lignocellulose Feedstocks) biorefineries (Kamm and Kamm, 2004) can probably be the most important raw material in a future bio-based economy due through production of bulk chemicals, new materials, fuels and energy. Such biorefineries divide biomass by chemical fractionation into its main components (cellulose, hemicelluloses, lignin and extracts) for ulterior processing, at the same time as it is a more environmental friendly technology than kraft process. The organosolv fractionation technology is not new, but the revived interest for biorefineries also rekindles the attention to these systems with organic solvents. The Acetosolv process achieves the fractionation of fibrous materials by the use of mixtures of acetic acid, water and small quantities of hydrochloric acid, at atmospheric pressure. The fractionation proceeds by partial depolymerisation of lignin and hemicelluloses which produce lignin and carbohydrate fragments soluble in the reaction medium (Abad et al., 2001; Ligero et al., 2005; Villaverde et al., 2010).

In order to prepare organosolv pulps for subsequent uses, such as paper or dissolving pulp production, unbleached pulps must be purified (bleached) by removing its residual lignin content. To maximize the environmental benefits of organosolv processes, pulp bleaching should be accomplished with totally chlorine free processes (TCF). Oxygen, hydrogen peroxide and ozone are commonly used in TCF sequences (Ramos et al., 2008). Alkaline hydrogen peroxide improves brightness, while oxygen and ozone contribute mainly to delignification. The search for new TCF agents which are both more potent and selective is not over yet; peroxyacids are attracting attention as bleaching agents, and peroxyacetic acid is among the most widely used (Jääskeläinen et al., 2000). Depending on pH, peroxyacetic acid will act in a very different way. In acid medium, peroxyacetic acid, an electrophile, is the main product. In alkaline conditions, the peroxyacetate anion is dominant, and obviously these species will react very differently (Pérez et al., 2006; Jiménez et al., 2008; Villaverde et al., 2009).

The aim of this work was to develop a detailed mathematical study of the influence of independent variables in peroxyacetic acid bleaching of Acetosolv *M. x giganteus* pulps (viz. concentration of hydrogen peroxide, temperature and pH) on pulp yield, kappa number, saponifiable groups, viscosity and brightness. A rotatable and orthogonal second-order factorial design was used, with the aim of identifying the optimum operating conditions.

MATERIALS AND METHODS

Raw material

M. x giganteus from an experimental plantation near Santiago de Compostela (Spain), established as part of the UE AIR *Miscanthus* Productivity Network, was used in this study. The plant was harvested, manually stripped of leaves and core, air-dried for two weeks and ground to pass through a sieve of 1 cm. Once in the laboratory was allowed to reach its equilibrium moisture content, and finally stored in sealed polypropylene containers.

Acetosolv fractionation

A mixture of ground *M. x giganteus* bark, water and acetic acid (percentage by weight with respect to liquor = 90%, liquid/wood weight ratio = 12) was heated to boiling point in a 3000 cm^3 glass reactor. Hydrochloric acid (percentage by weight with respect to the cooking liquor = 0.15%) was added when boiling started, and the mixtures were refluxed, with stirring, at atmospheric pressure for 55 minutes. The pulp was filtered, treated four times with 85% acetic acid (in w/v ratios of 0.4, 0.4, 0.2 and 0.2 with respect to the initial dry weight of *M. x giganteus*), and washed repeatedly times with distilled water until neutrality. The process and reaction conditions mentioned have been optimized in a previous work (Ligero et al., 2005).

Characterization of the raw material and cellulose pulps

For all experiments, kappa numbers (KN), intrinsic viscosity (VIS) and %ISO brightness (BR) were measured in duplicate in accordance with TAPPI standards (T236, T230 and T525, respectively). Pulp yields (PY) were determined gravimetrically after oven drying to constant weight. Saponifiable groups content (SG, as NaOH equivalents) was determined by KOH-ethanol saponification (Abad et al., 2002; Dapía et al., 2002; Villaverde et al., 2010).

Bleaching

Before Paa-stages, the pulps were soaked with a solution of 85% acetic acid with the same pH as the one established for the experiment (pH was adjusted with a solution of NaOH 10 M), and filtered to remove excess liquid. This was repeated three times to achieve the adequate pH.

Paa-stages were performed in sealed polyethylene bags submerged in a thermostatic water bath at the desired temperature. Samples were treated at 10% consistency, and the rest of variables were changed as follows: time, 15-180 minutes; temperature, 48.2-81.8ºC; hydrogen peroxide concentration, 1.6-8.4% (peroxyacetic acid was generate in situ with the acetic acid medium with this concentrations of peroxide (Jääskelainen et al., 2000)); and pH, 1.8-5.2. The samples were kneaded several times during the reaction.

After each bleaching treatment, the pulps were washed with a solution of acetic acid (85% by weight) and then neutralized with water.

Experimental design

A rotatable orthogonal second-order factorial design (Akhnazarova and Kafarov, 1982) was used to fit the experimental data to polynomial equations and quantify the effects of independent variables (IV) on the parameters that define the progress of bleaching. Factorial designs have been used extensively to examine the behaviour of bleaching organosolv pulps (Jiménez et al., 2008; López et al., 2002 and 2003). In accordance with standard procedures in experimental design construction and analysis, the independent variables were standardized in accordance with

$$X_j = \frac{Z_j - \overline{Z_j}}{\Delta Z_j}$$

where Z_j, is the value of the variable j in a specific experiment; $\overline{Z}_j$ is the arithmetic mean of the minimum and the maximum values applied to the variable j, and ΔZ_j is the mid-point of the variation range of each variable, that is

$$\Delta Z_j = \frac{Z_{j_{max}} - Z_{j_{min}}}{2}$$

This way the different standardised variables are restricted between the values –1 (which corresponds to the lowest treatment value) and +1 (corresponding to the highest value).

The following experimental results were analysed as dependent variables: PY, KN, SG, VIS, and BR of the resulting pulps; and submitted to multivariate regression against the independent variables using polynomial fit functions such as:

$$DV = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i<j} b_{ij} X_i X_j + b_{123} X_1 X_2 X_3$$

where DV represents each one of the dependent variables (system responses) examined in this study; and X_i and X_j are the normalised independent variables. The different values of b_0, b_i and b_{ij} represent the fitting parameters by which, due to normalisation, we can determine and compare the effects of each of the independent variables on the dependent variables (experimental results).

All calculations were performed with a statistics module of Excel.

RESULTS AND DISCUSSION

Unbleached Acetosolv pulps presented the next characteristics: PY: 59.1%, KN: 19.9, SG = 8.0%, VIS: 1033 cm^3/g and BR: 36.2%. Several authors have identified the acetylation of the pulp as a significant reaction taking place in Acetosolv pulping (Saake et al., 1998; Abad et al., 2001 and 2002; Dapía et al., 2002 and 2003). The acetylation is recognized as a problem in the early stages of bleaching due to the alkaline demand resulting from the inevitable alkaline saponification that occurs in many stages of TCF bleaching. Moreover, as SG content increases, the determination of VIS in cupriethylenediamine solution provides lower values than the actual (Saake et al., 1998). *Miscanthus Acetosolv* unbleached pulp showed a relatively high content of these groups (8.0%, measured as NaOH equivalents), which increased after several Paa-treatments (up to 14.8%). Also are evident in the FTIR spectra of pulps, which have an intense band at 1740 cm-1 that disappears after an alkaline treatment (E-stage). For this reason, analysis of saponifiable group contents of pulps was performed after each treatment with peroxyacetic acid.

Preliminary experiments were conducted to determine the possibility of using black liquor as a reaction medium, simply adding the necessary amount of hydrogen peroxide, or the need to replace it by fresh acetic acid before the Paa-stage. A number of variables were fixed in these experiments: consistency, 8%; acetic acid concentration, 89% by weight; hydrogen peroxide concentration, 5% o.d. pulp; temperature, 70ºC; time, 60 minutes. The results showed that when the cooking liquor was replaced for fresh acetic acid, a kappa number of 12.0 (a 17% lower) and viscosity of 745 cm^3/g (18% higher) was obtained. Therefore, hereafter, black liquor was filtered and removed after pulping.

An experimental design (Table 1) was performed to quantify the effects of hydrogen peroxide concentration (in the range 1.6-8.4%), temperature (48.2-81.8°C), and pH (1.8-5.2) on pulp yield (PY), kappa number (KN), %ISO brightness (BR), intrinsic viscosity (VIS), and saponifiable groups of pulps (SG). In these experiments consistency and time were fixed to 10% and 1 hour, respectively.

H_2O_2 conc. (% o.d.p.)	**T (°C)**	**pH**	**PY (% o.d.p.)**	**KN**	**BR (%ISO)**	**VIS (cm^3/g)**	**SG (% o.d.p.)**
3	55	2.5	88.8	16.4	37.9	972	14.8
7	55	2.5	88.4	16.9	34.1	963	5.6
3	75	2.5	87.9	16.1	42.1	961	10.1
7	75	2.5	87.4	14.9	43.6	992	9.8
3	55	4.5	55.8	18.6	32.7	1056	6.9
7	55	4.5	59.6	17.0	27.0	1092	3.3
3	75	4.5	61.0	16.4	16.5	880	6.5
7	75	4.5	60.1	17.2	33.7	991	9.8
1.64	65	3.5	78.6	15.8	43.0	903	13.1
8.36	65	3.5	78.7	16.5	41.3	962	10.0
5	48.2	3.5	79.6	17.6	35.9	948	9.5
5	81.8	3.5	79.3	14.8	43.9	914	12.4
5	65	1.82	92.2	16.3	40.4	964	6.6
5	65	5.18	53.3	16.9	34.1	1001	8.4
5	65	3.5	79.1	18.6	39.4	967	6.4
5	65	3.5	77.1	16.4	40.1	963	8.0
5	65	3.5	77.5	17.2	37.4	936	8.4

Table 1. *Experimental design structure and results of the peroxyacetic treatment of Acetosolv M. x giganteus pulp.*

Fitting experimental results afforded the results presented in Table 2, where it can be seen different parameters of the model, their significance and several statistical values indicating the goodness of fit of the mathematical models that, in general, were acceptable.

		PY	KN	BR	VIS	SG
Factor	Name	Coefficient	Coefficient	Coefficient	Coefficient	Coefficient
b_0		78.11*	17.37*	39.38*	952.8*	7.716*
b_1	H_2O_2	0.159	-0.024	0.464	19.64**	-1.099
b_2	T	0.241	-0.660*	1.293	-23.15**	0.767
b_3	pH	-13.28*	0.433	-4.276*	14.15	-0.789
b_{12}		-0.600	0.088	3.525	14.38	1.975*
b_{13}		0.475	-0.013	1.725	15.63	1.150
b_{23}		0.950	0.038	-2.900	-36.88*	0.825
b_{123}		-0.575	0.513	2.200	4.375	-0.250
b_{11}		-0.460	-0.345	-0.288	0.832	0.998
b_{22}		-0.177	-0.327	-1.083	0.302	0.786
b_{33}		-2.546*	-0.186	-2.020	18.51	-0.434
R		0.9871	0.8585	0.8523	0.9061	0.8817
Std Error		3.3173	0.8678	5.9061	35.305	2.2300
F		22.747	1.6817	1.5936	2.7524	2.0951
Sig F		0.0005	0.2709	0.2938	0.1138	0.1890
F_{LOF}		14.238	0.4111	26.150	6.0756	6.1599
Sig F_{LOF}		0.0667	0.7964	0.0372	0.1463	0.1445

* indicates significant at a 0.05 level
** indicates significant at a 0.10 level

Table 2. *Regression parameters for each variable, goodness of fit and signification of regression equations.*

PY was strongly influenced by pH, being the only experimental variable highly significant, both for first and second order terms of regression equation (Table 2). As pH increased, PY diminished. Figure 1 shows the behaviour of

PY with pH and temperature, at a constant hydrogen peroxide concentration of 3%. The mathematical model predicts the minimum PY (58.6%) at this peroxide concentration and at 55°C and pH = 4.5; being the rest of responses: KN = 18.2, VIS = 1030 cm^3/g, BR = 36.9%, and SG = 8.4%.

KN only depended significantly on temperature (Table 2), diminishing with increasing T. pH wears an effect not as important, but near to be significant at a 0.10 level, what is reflected in steep slopes in the graph T-pH-KN, especially in the zone of high temperatures and low pH (Figure 2). Minimum KN predicted by regression is 14.9 (when hydrogen peroxide concentration = 7%, temperature 75°C, and pH = 2.5), while other responses were: PY = 87.6% (51.8% accumulated), VIS = 986 cm^3/g, BR = 44.5%, and SG = 9.8%.

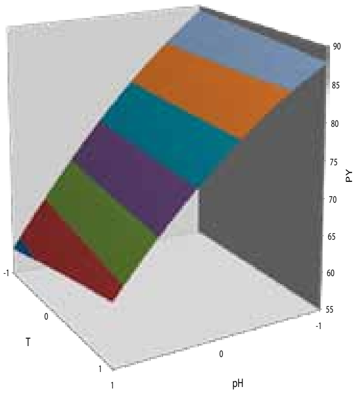

Figure 1. *Effects of temperature and pH on PY at a constant hydrogen peroxide concentration of 3%*

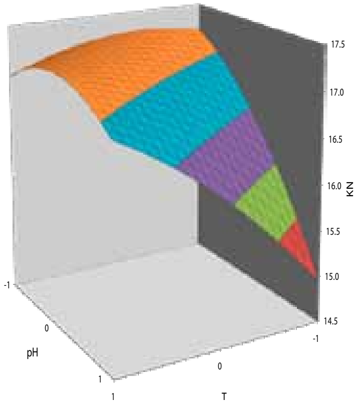

Figure 2. *Effects of temperature and pH on KN at a constant hydrogen peroxide concentration of 7%*

BR only depended significantly on pH: results showed that BR increases as pH decreases (Figure 3). This result may be explained in terms of reaction mechanisms, because as the pH decreases more conjugated structures, responsible for the color of the pulp, are destroyed by a number of reactions among which it can be remarked those of electrophilic addition.

VIS mainly decreases with increasing temperature, as expected of a hydrolytic process. But the amount of peroxide present also has significant influence in the opposite direction: VIS increases with increasing peroxide (Figure 4). The best VIS (1063 cm^3/g) is predicted when peroxide and pH values are the highest within the variation range (7% and 4.5, respectively), and the temperature the lowest (55°C). The rest of responses being: PY = 62.3%, KN = 16.9, BR = 29.8%, and SG = 5.0%.

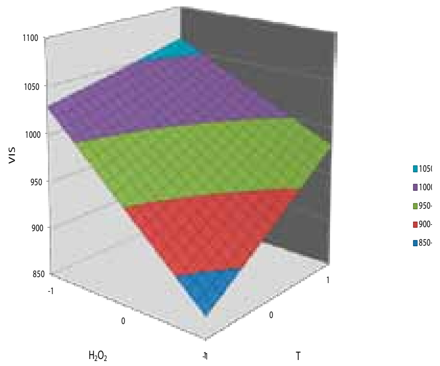

Figure 4. *Effects of temperature and hydrogen peroxide concentration on VIS at a constant pH of 4.5*

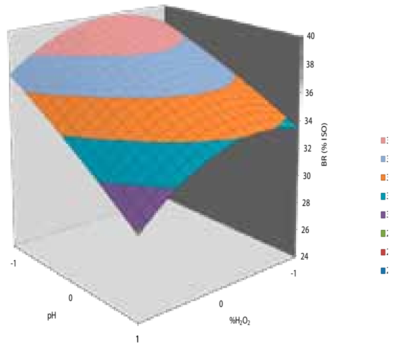

Figure 3. *Effects of pH and hydrogen peroxide concentration on BR at a constant temperature of 55℃*

For SG, the only significant coefficient was that of interaction between peroxide concentration and temperature (none of first order was significant) and results are difficult to explain quantitatively. Nevertheless, the signs of first order coefficients agree with the influences expected from an esterification reaction, that is: SG are formed in greater proportion by increasing T and decreasing pH (acid catalyzed) and peroxide load (reagents concentration). The results can be explained as follows: SG proportion increased with temperature due to kinetic reasons because the rate of any reaction increases with temperature. The proportion of SG decreased as peroxide concentration and pH increased; this could be related with the chemical equilibria taking place in solution. Specifically, it is known that decomposition reactions of peroxide and peracetic acid are more important as pH increases, with a maximum at around pH = 8.2. Assuming this, a lower proportion of the esterification agent (formate ion) should be available.

In short, results show that low kappa numbers and high viscosities can be achieved with a 7% of hydrogen peroxide, but in relation to temperature and pH, the effects are opposite. In order to calculate the most suitable conditions for the Paa-stage, the statistical software was utilised for optimization. Restrictions for simultaneous conditions of minimum KN and maximum VIS were introduced with the same weight. Thus, the best pulp that could be obtained would be subject to the following conditions: H_2O_2 = 7%, 75ºC and pH = 2.5; with the results listed below: PY = 87.2% (51.5%

accumulated), KN = 14.9, VIS = 986 cm3/g; BR = 44.5%, and SG = 9.8%. This means that pulps after the Paa treatment can be obtained in 51.5% global yield, with kappa number reduced by 25.1%, brightness improved by 22.9%, and a low reduction of pulp viscosity (4.5%). Although the proportion of SG not decreased at all, even increased by 12%, is expected that next stages of the TCF sequence, probably a Z stage, could reduce this content significantly.

Figure 5 shows the results of a set of experiments in which pH were varied even outside the limits of the design. As can be seen, both the viscosity and kappa number worsen progressively with increasing pH. Therefore, 2.5 was adopted as the best among all the pH tested experimentally.

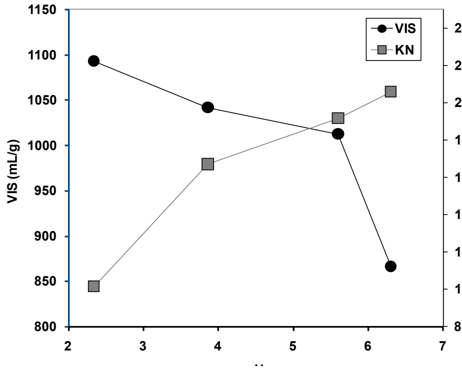

Figure 5. *Effect of initial pH on the properties of pulps obtained after Paa processing at 10% consistency, 5% peroxide load and 75°C for 60 min.*

Subsequently, a kinetic monitoring was conducted to determine whether longer treatments (up to 120 minutes) would improve the results. Figure 6 shows that a substantial improvement (almost 3 units) in KN can be achieved by prolonging the reaction to 120 min, time from which the reduction in KN is very small. Into this interval, the viscosity was not significantly affected, only a 4.6% decrease (from 934 to 891 cm^3/g). At the same time, BR increased almost linearly with time up to 33.1% after 60 minutes (BR of unbleached pulp = 24.1%). The prolongation of treatment up to 180 minutes resulted in an increase of only 2.5% units.

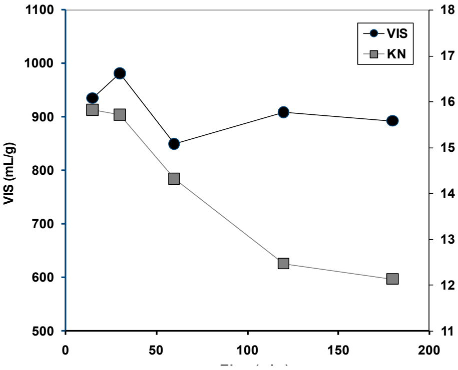

Figure 6. *Effect of time on the properties of pulps obtained after Paa processing at 10% consistency, 7% peroxide load, 75°C, and pH = 2.5*

Finally, the effect of some usual chelating agents was studied. A new series of experiments was performed, under the conditions deduced, adding diethylenetriaminepentaacetic acid (DTPA, 1% on dry pulp basis), $MgSO_4$ (1% on dry pulp basis) or both. Table 3 shows that no clear beneficial effect was observed derived from the addition of DTPA or $MgSO_4$. Although VIS was slightly improved, Kappa numbers were worse and no effect at all was observed in BR. Therefore, at least at these still relatively lignified pulps, the use of those cellulose protecting agents seems to be not justified.

Table 3. *Results of the addition of DTPA (1%) and $MgSO_4$ (1%) on the peroxyacetic (Paa) treatment of Acetosolv Miscanthus pulps (10% consistency, 7% peroxide, pH = 2.5, 60 min. and 75ºC).*

DTPA added	$MgSO_4$ added	PY (% o.d.p.)	KN	VIS (cm^3/g)	BR (%ISO)
No	No	91.0	14.3	849	33.1
No	Yes	96.5	13.9	819	31.6
Yes	No	92.8	15.2	926	29.9
Yes	Yes	94.3	15.5	911	30.8

CONCLUSIONS

This first stage was performed as an attempt to design an entirely acidic TCF bleaching sequence with the idea of taking advantage of the acid character of the Acetosolv pulps and, thus saving the costs of washings and pH changes between acidic and basic stages of a typical TCF procedure. This work is the first step in order to achieve it.

In this context, we have studied the effects of three operational variables (hydrogen peroxide concentration, 1.6-8.4%; temperature, 48.2-81.8°C; pH, 1.8-5.2), in a bleaching stage of a *M. x giganteus Acetosolv* pulp with hydrogen peroxide in acetic acid media, and quantified these effects using empirical polynomial models.

Within the range of values for each operational variable, PY and BR depend on the pH at a confidence level of 95%. Also, temperature is significant at a 95% confidence level for KN.

Additional experiments for values of pH and time beyond the limits of the experimental design and with the addition of chelating agents were conducted in order to try to improve the quality of pulps. The results showed that neither the addition of DTPA, nor that of $MgSO_4$, separately, or both simultaneously, produced improvements. This information, along with the mathematical optimization of the models, allowed the calculation of our best conditions for this stage (consistency = 10%, time = 120 min, hydrogen peroxide concentration = 7%, temperature = 75ºC and pH = 2.5) with the following results: PY: 87.2% (51.5% accumulated); KN = 14.9; VIS: 986 cm^3/g; BR: 44.5; and SG = 9.8%.

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