Highly purified pulps from Miscanthus x giganteus. A comparative study of a new TCF bleaching sequence applied to organosolv pulps

Juan José Villaverde, Pablo Ligero, Alberto de Vega
Department of Physical Chemistry and Chemical Engineering, University of A Coruña, A Coruña 15071, Spain.

RESUMEN

Se ha utilizado una nueva secuencia alcalina de blanqueo (EPabO(PO)P) sobre tres pastas organosolv (Acetosolv, Formosolv y Milox). Los resultados demuestran que esta secuencia puede ser una buena alternativa para el tratamiento del Miscanthus x giganteus como fuente de celulosa de alta pureza. La eficacia de esta secuencia en cada una de las pastas ha sido analizada en función de los equivalentes de oxidación (OXE).

Palabras clave: Miscanthus x giganteus, Acetosolv, Formosolv, Milox, TCF blanqueo, protectores de carbohidratos.

SUMMARY

A new sequence (EPabO(PO)P) in alkaline medium was used on three acid organosolv pulps (Acetosolv, Formosolv and Milox). The results showed this sequence is a good alternative to exploit Miscanthus x giganteus stems as cellulose source in applications where high purity is necessary. The effectiveness of this sequence was analysed in terms of oxidation equivalents (OXE) for each pulp.

Keywords: Miscanthus x giganteus, Acetosolv, Formosolv, Milox, TCF bleaching, carbohydrate protectors.

RESUM

S’ha utilitzat una nova seqüència alcalina de blanqueig (EPabO (PO) P) sobre tres pastes organosolv (Acetosolv, Formosolv i Milox). Els resultats demostren que aquesta seqüència pot ser una bona alternativa per al tractament del Miscanthus x giganteus com a font de cel·lulosa d’alta pureza. L’eficàcia d’aquesta seqüència en cada una de les pastes ha estat analitzada en funció dels equivalents d’oxidació (OXE).

Paraules clau: Miscanthus x giganteus, Acetosolv, Formosolv, Milox, TCF blanqueig, protectors de carbohidrats.
INTRODUCTION

Cellulose consists of polydisperse linear glucose polymer chains which form hydrogen-bonded supramolecular structures. Cellulose is the most abundant bio-renewable material and represents a vast potential feedstock. Derivatised products have many important applications in the fibre, paper, membrane, polymer and paints industries. Today, researchers are developing methods to isolate cellulose from wood and non-wood fibres. Cellulose isolation requires the removal of other substances, such as hemicelluloses and lignin. Organic acids have been proposed as agents for fractionation. Among them, acetic acid pulping has proven to be an effective method for fractionating lignocellulosic materials (Ligero et al., 2007a, 2008a). Acetic acid is advantageous because it can be followed immediately by bleaching. The addition of hydrogen peroxide to acetic acid generates peroxy-acetic acid. Formic acid has also received attention as a solvent for fractionation, and can be used in aqueous solution with hydrochloric acid as a catalyst (for short, Formosolv) (Ligero et al., 2007b, 2008a) or in combination with hydrogen peroxide (Milox) (Ligero et al., 2008b).

These organic acid-based fractionation processes are good options for dissolving pulps to manufacture feedstock for cellulose derivatives and cellulosic fibres.

For years, Miscanthus species were considered to be invasive grasses in Europe. However, in the last 20 years, European authorities have regarded them as excellent biomass sources (Lewandowski, et al., 2000). Among them, “Miscanthus x giganteus” Greer Deuter ex Hodkinson and Renvoize (Hodkinson and Renvoize, 2001), a sterile hybrid recognised for its controlled propagation, has been the subject of numerous research efforts in different areas (Barba et al., 2002; El Mansouri and Salvadó, 2006; Lundquist et al., 2004; Michel et al., 2006; Salvadó et al., 2003; Vega et al., 1997; Villaverde et al., 2009a, 2009b, 2009c; Ye et al., 2005; Yuan et al., 2008). Large economical benefits can be obtained from dissolving pulps obtained from TCF sequences at Lignocellulosic Feedstock (LCF) organosolv biorefineries (Fernando et al., 2009a, 2009b, 2009c). M. x giganteus, with a productivity of 30 tons d.m. ha⁻¹ year⁻¹ in plantations in southern Europe (Lewandowski, et al., 2006), could be a remarkable raw material for these industries using organic acids as fractionation reagents and TCF sequences as purification technologies.

This work is a comparative study of the responses of three organosolv pulps (Acetosolv, Formosolv and Millox) that have kappa numbers suitable to obtain bleached pulps by a novel TCF sequence, EPabO(PO)P. This sequence was optimised for Acetosolv pulps and the aim of this work was to explore its ability to efficiently bleach other Miscanthus organosolv pulps.

MATERIAL AND METHODS

Raw material and pulping

Depithed M. x giganteus stems were used to produce pulps for the bleaching experiments. A detailed description of the characteristics of this material has been reported elsewhere (Hodkinson and Renvoize, 2001). Acetosolv, Formosolv and Millox pulps, with kappa numbers around 20, were prepared in a 3 L batch reactor using experimental procedures described previously (Villaverde et al., 2009b, 2009c).

Bleaching

All pulps were bleached under identical conditions with an EPabO(PO)P sequence. Epsom salt (magnesium sulfate) and DTPA (diethylenetriaminepentaacetic acid) were used as chelating chemicals (both 1% by weight with respect to oven dry pulp) to minimise radical degradation reactions of the carbohydrates (Villaverde et al., 2009b).

The bleaching tests with alkaline treatments (E-stages), peroxyacetate treatments (Pab-stages) and peroxide bleaching (P-stages) were carried out at the desired consistency in sealed polyethylene bags. The bags were immersed in a thermostatic water bath at the desired temperature and the samples were kneaded several times during the reaction (Villaverde et al., 2009c).

Bleaching with oxygen (O-stages) and oxygen-presurised hydrogen peroxide (PO-stages) were performed in a 500 cm³ stainless steel Parr high-pressure reactor (Model 4560, Parr Instrument Company, Moline, IL) under oxygen pressure at the chosen consistency. A helicoidal rod was used to adequately stir the reaction mixtures. The reactor pressure was measured with a pressure gauge and the temperatures were controlled by a Parr controller (Model 4842). After each bleaching treatment, the pulps were washed with an aqueous solution at pH 11 to keep the pH alkaline and prevent lignin precipitation. The specific bleaching conditions of each stage are listed in Table 1.

Table 1. Bleaching conditions in each stage

<table>
<thead>
<tr>
<th>Bleaching stage</th>
<th>E</th>
<th>Pab</th>
<th>O</th>
<th>(PO)</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Consistency (%)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Time (min)</td>
<td>60</td>
<td>30</td>
<td>40</td>
<td>30</td>
<td>60</td>
</tr>
<tr>
<td>T (°C)</td>
<td>70</td>
<td>55</td>
<td>80</td>
<td>90</td>
<td>60</td>
</tr>
<tr>
<td>Sodium hydroxide (%)</td>
<td>6.0</td>
<td>5.0</td>
<td>2.5</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Hydrogen peroxide (%)</td>
<td>11.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>-</td>
<td>4.0</td>
<td>4.0</td>
<td>-</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>MgSO₄ (%)</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>DTPA (%)</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Pulp analysis

For all experiments, kappa number (KN) and ISO brightness (BR) were measured according to TAPPI standards (T 236, and T 525, respectively), and viscosity according to UNE-039-92. Pulp yields (PY) were determined gravi-
metrically after oven drying until a constant weight was obtained.

**Oxidation equivalents (OXE) and effectiveness of bleaching**

The utilisation of oxidation equivalents (OXE) allows for comparison among the different oxidative bleaching stages. The chemicals can be converted to oxidation equivalents and be expressed as OXE per metric ton of bleached pulp. An OXE is defined as “the quantity of substance which receives 1 mol of electrons when the substance is reduced” (Grundellius, 1993).

Since the quantities of oxidizing agents used in each stage are in stoichiometric excess, there are always enough bleaching medium and active chemicals to produce the reaction, and a comparison among the four systems can be done in terms of “OXE effectiveness”; defined as a function of consecutive values of brightness and kappa number (de la Rosa, 2003):

\[
\text{Eff}_{\text{BR}}^{\text{OXE}} = \frac{\text{BR}_{n} - \text{BR}_{n+1}}{\text{OXE}} \times 100
\]

\[
\text{Eff}_{\text{KN}}^{\text{OXE}} = \frac{\text{KN}_{n} - \text{KN}_{n+1}}{\text{OXE}} \times 100
\]

**RESULTS AND DISCUSSION**

In this paper, we examined the ability of the TCF sequence EPabO(PO)P to produce highly purified pulps of dissolving grade from *M. x giganteus* organosolv pulps. The E- and Pab-stages for Acetosolv pulp were studied previously (Villaverde et al., 2009c). A significant acylation was observed in the unbleached pulps of the three organosolv methods. Therefore, in order to remove saponifiable groups, an initial alkaline treatment was implemented. Later, we have included and optimise a peroxiacetate stage (Pab) which caused simultaneously important delignification and brightness development. A final kappa number of 10 was attained after peroxyacetate bleaching. To improve the brightness, the introduction of one O-, (PO)- and P-stage within the TCF sequence was studied (Ramos et al., 2008). The sequence with and without carbohydrate protectors in the last two stages of the Acetosolv pulp is presented in order to illustrate the beneficial effects of chelating chemicals when radical mechanisms are present (Villaverde et al., 2009c).

Several pulps were selected, including an acetic acid pulp (Acetosolv) for which the sequence was optimised, a formic acid pulp (Formosolv) and a peroxyformic acid pulp (Milox). Table 2 shows the characteristics of these pulps. Kappa number values were around 20 and the intrinsic viscosities were above 900 mL/g. Their brightness (mainly that of Milox pulp) was high compared to typical bleachable kraft pulps (around 26% ISO), and the pulp yields were similar to those obtained in kraft pulping of wood (i.e., eucalyptus and pine). Therefore, they were suitable for bleaching.

**Table 2. Properties of unbleached organosolv pulps from *M. x giganteus*.**

<table>
<thead>
<tr>
<th>Pulping process</th>
<th>Acetosolv</th>
<th>Formosolv</th>
<th>Milox</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pulp yield (%)</td>
<td>55.2</td>
<td>48.7</td>
<td>55.0</td>
</tr>
<tr>
<td>Kappa number</td>
<td>17.9</td>
<td>23.0</td>
<td>19.0</td>
</tr>
<tr>
<td>Intrinsic viscosity (cm³/g)</td>
<td>1005</td>
<td>1197</td>
<td>915</td>
</tr>
<tr>
<td>Brightness (% ISO)</td>
<td>33.6</td>
<td>30.6</td>
<td>40.8</td>
</tr>
</tbody>
</table>

**Assessment of the bleaching effectiveness**

Figure 2 shows the effectiveness of the oxidative stages in the EPabO(PO)P sequence for each organosolv pulp. Among the effectiveness values for KN and BR, in regards to OXE, stands out the O-stage, for which higher Eff_{oxe} have been obtained, and also high values of Eff_{oxe}. Although to a lesser extent, the Pab- and PO-stages were also effective in increasing brightness (the Pab-stage was most effective for Acetosolv/Milox pulps and the PO-stage for Formosolv pulps). The PO- and P-stages showed their effectiveness as brightness developers rather than as delignifying agents.

![Figure 2. Kappa number (a) and brightness (b) effectiveness of each stage of the EPabO(PO)P sequence in terms of oxidation equivalents (OXE).](image-url)
Figure 1. Changes in pulp yield (a), kappa number (b), intrinsic viscosity (c) and brightness (d) of *M. x giganteus* stem organosolv pulps during the bleaching sequence.

The three pulps were submitted to the bleaching sequence (EPabO(PO)P). Fig 1 summarises the changes during the bleaching sequence. The accumulated pulp yields (compared to the initial dry weight of Miscanthus) remained relatively high (above 45%) along the whole sequence. The exception was the Formosolv system, which solubilised more materials during pulping than the others (Fig 1a).

Delignification, as measured by kappa number, proceeded along an almost linear pathway (Fig 1b). During the first stages, Formosolv pulp was the most recalcitrant to this process, although later its O- and (PO)-stages induced the biggest delignification percentages among the four systems. In fact, the final kappa number obtained for this pulp was the minimum of all systems. Milox pulp also reached similar final kappa values. It seemed to be particularly activated, especially in the E-stage, during which it reduced its kappa number by ten units. The absence of chelating agents affected the Acetosolv pulp in the two last stages. In this system, the final kappa number was around three times that of the systems where agents were used. In addition, Fig 1c and Fig 1d demonstrate the beneficial effects of the agents. The viscosity and pulp brightness in this last system were seriously damaged in comparison to the other three. The final values were 1.3 for Acetosolv, 0.5 for Formosolv and 1.1 for Milox.

VIS (Fig 1c) tended to reduce slowly as the treatments proceeded (except as mentioned above). Although the starting viscosity of the Milox pulp was clearly inferior, it reduced in a smooth curve to a very favourable value (Acetosolv = 786 mL/g; Formosolv = 745 mL/g; Milox = 669 mL/g).

Figure 1d shows that the brightness increased to values near 90% (Formosolv, 89.2%; Acetosolv, 86.9%; Milox, 90.7%) in a similar way during the three procedures (except for Acetosolv without chelators, 66.4%). The Milox curve was always above the others.
Finally, the sequence without carbohydrate protectors showed differences during the P-stage. As expected, the brightening was around five times lower and ineffective. A surprising result was obtained for \( \text{EPabO(PO)P} \) since its value was very similar to the other processes. That means, delignification proceeded (although in a lesser extent) with a restrained brightness increase. This, together with an important viscosity loss which was also observable in the PO-stage, demonstrated the necessity of carbohydrate protectors in the last two stages of the EPabO(PO)P sequence (Bajpai, 2005).

CONCLUSIONS

Among the three organosolv pulps from \( M. \times \text{giganteus} \) considered in this work, the highest brightness obtained after a EPabO(PO)P sequence was with the Milox pulp (90.7% ISO). Meanwhile, the lowest gain was measured with the Acetosolv pulp (86.9% ISO). The high BR values and very low kappa numbers (between 0.5-1.3) measured from these bleached pulps demonstrate their appropriateness as feedstock for cellulose derivatives.

The use of an oxidation equivalent helped in the comparison of the bleaching stages in the four systems. The oxidation equivalents allowed for quantification of the kappa numbers and brightness variations. The results revealed that the O-stage was the most effective delignifying stage, followed by the other three stages. All stages contributed significantly to brightness gain, except in the sequence without cellulose protectors, where the P-stage effectiveness was drastically reduced due to the lack of chelating agents. The best effectiveness in the EPabO(PO)P sequence in regards to OXE was the Formosolv pulp for KN and to the Acetosolv pulp for BR.

This novel sequence could be used to exploit Miscanthus in coordination with an acidic organosolv fractionation process within the biorefinery concept. Furthermore, the basic medium is never removed during the sequence, which saves washing water that is typically used between the bleaching stages; especially in TCF sequences including acidic ozone stages which require exhaustive washing.

ACKNOWLEDGMENTS

The authors wish to thank “Xunta de Galicia” for their grant for the research project (PGIDIT04RF02659912PR: Obtención de biopolímeros de orixe vexetal a partir da biomasa do Miscanthus sinensis, en condicións de cultivo enenxético, por procedementos solvolíticos), Dr. D. Manuel Bao Iglesias from the University of Santiago de Compostela for the kind donation of a predoctoral fellowship to Mr. J.J. Villaverde. and the University of A Coruña for the kind donation of the Formosolv pulp for KN and to the Acetosolv pulp for BR.

This work was supported by the European Union (FP7-ENV-2010 Grant Agreement no. 262939). The authors wish to thank the reviewers for their valuable comments and suggestions to improve the quality of this paper.

REFERENCES


totally chlorine-free sequence and the effect of carbohydrate protectors». Industrial & Engineering Chemistry Research, 48, 9830–9836.

