FIBERBOARD MANUFACTURED WITHOUT RESIN USING THE FENTON REACTION

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ABSTRACT

Resin-free fiberboards were manufactured using industrial fiber from Pinus radiata activated by an oxidative treatment using the Fenton reaction (H2O2 / Fe(II)). A multivariate analysis was used to study the effect of fiber moisture content (MC), press temperature (T), and the H2O2/Fe(II) ratio on the board internal bond strength (IB). Using response surface methodology, a set of maximum IB conditions was obtained. Validation of these conditions which included 25% MC, 170ºC press temperature and a H2O2/Fe(II) ratio of 25 produced an optimal board with an IB strength of 0.888 MPa. Without the addition of sizing agents or other additives, the dimensional stability properties were 16% of thickness swell and 40% of the water absorption of control boards.

Keywords: Fenton reaction, Fiberboard, multivariate analysis

INTRODUCTION

Wood based panels are traditionally manufactured via the application of thermosetting resins to fibers, particles or strands under pressure and temperature.1-5. Boards consolidated with urea formaldehyde (UF)-type resins are characterized by their high mechanical strength, dimensional stability, hardness, resistance to microorganisms and abrasion.6-9. However, because synthetic resins are produced from high demand non-renewable resources, such as petrochemicals, bonding mechanisms for wood and lignocellulose composites using bio-based chemicals could be an attractive alternative.

Considering environmental concerns with the use of formaldehyde-based resin, studies have been conducted to determine if self-bonding of wood fibers, without synthetic resins, can be achieved.10-12. Most of these self-bonding processes are based on the generation of free radicals on the fiber surface so that the fiber can be pressed into panels without additional adhesives. Some of the applications involve thermosetting binder applications using oxidoreductases, such as laccases and peroxidases, for polymerization or cross-linking of wood components to promote binding.13-15. Direct bonding of wood surfaces with inorganic chemical oxidants has been studied.16-18. As a complement to an added oxidant, ultrasound or photo- or electro-Fenton reactions (in situ generation of hydroxyl radicals by radiation or electric currents) can be used.19 The chemical reactions involved in these self-bonding systems are not fully understood, although the oxidative coupling of phenolic and non-phenolic lignin units contained in wood is either the principal, or at least one of the predominant, reactions leading to self-adhesion of lignocellulosic materials.20-23. Phenolic free radical formation and subsequent coupling probably occurs precisely when the surfaces to be bonded are in close contact.24 Some polysaccharide-to-polyascaride or lignin-to-polyascaride bonding may also occur during oxidation.25-27

The Fenton Reaction [eqn.(1)] has been proposed as an oxidative treatment for the self-bonding of material containing lignocellulose particles for the non-conventional manufacturing of restituted wood boards.28. When wood fibers are treated with hydrogen peroxide and a ferrous salt (Fenton reaction), fiberboard panels with enhanced internal bond strength can be produced due to the increase in interfiber bonds formed by hydroxyl radicals. In addition, other reactive groups, and bonding generated by the Fenton reaction, may develop within the fiber under elevated pressure temperature conditions.29-31

\[ \text{H}_2\text{O}_2 + \text{Fe}^{II} \rightarrow \text{Fe}^{III} + \cdot \text{OH} + \text{OH}^- \] (1)

Considering that board adhesion using fiber activation by the Fenton reaction does not involve a resin curing process, traditional manufacturing process conditions could potentially be altered to reduce energy and costs associated with bonding. However, at present, there is little information on conditions required for appropriate bonding to occur. Experimental process conditions such as press temperature and fiber moisture content at the press entry must be determined for Fenton reaction activated fibers. Stofko et al.32 patented a plywood bonding process employing a mixture of oxidants in solution, using a wide range of the press temperatures, between 80º and 200ºC. Recent studies16,17 used temperatures between 170º and 200ºC to produce fiberboard activated by the Fenton reaction and by a synthetic chelator mediated free radical system (CMFR), respectively. A patented process by Westermark et al.33 employed press temperatures between 120º and 200ºC. The manufacture of fiberboards via an oxidative enzymatic process also used press temperatures between 180º and 200ºC, to obtain acceptable mechanical strength properties34-36. There are no studies on Fenton reaction fiberboard production that define the moisture content at the time of press entry. In traditional resin curing processes, a moisture content of 10% to 13% is used for an optimal transfer of mass and energy.7 These conditions permit heat transfer to the center layers of the fiber mat while limiting strength loss as material compression and fiber deformation occurs.15 In earlier research18 with wet process fiberboard production, high moisture contents (70% to 400%) were tested. The authors of this work proposed that and the CFMR system rapidly penetrated into fiber wall interior, producing free radicals in fiber’s cellulosic core, decreasing the internal bond strength.17 They suggested that lower MC fiber may help to eliminate this effect as the free radical reaction could be limited to the fiber exterior where high lignin fractions were located. Westermark et al.33 patented the manufacture of composite lignocellulosic materials activated with an oxidant treatment that employing a wood particle moisture content between 3% and 9% before hot pressing. In fibers activated with oxidative enzymes, no difference in internal bond strength was observed between boards that were pre-dried at 50ºC and those flash dried before hot pressing, although they suggested that forced air drying may have decreased the dimensional stability properties of the final boards produced.

The objective of this study was to determine experimental process conditions for the production of fiberboard with sufficient internal bond strength for general use in dry end-use environments. The influence of MC, T and the H2O2/Fe(II) ratio were evaluated to determine the optimal interaction conditions appropriate for maximal IB strength in thin fiberboards as defined by EN 622-5.

Materials and Methods

Chemicals

In all the experiments, nanopure distilled water and industrial external mould release agent (Wurzt) were used. All reactants were grade p.a. 30% (w/w) H2O2, ferrous sulfate heptahydrate FeSO4·7H2O were purchased from Merck. The Fe(II) solutions were adjusted to pH 3.5 with HCl. All the solutions were prepared immediately before each experiment.

Multivariate Analysis

Response surface modeling (RSM) was used for the multivariate analysis.29,30 The model was based on a two-level factorial design with three central points and their respective star points (central composite model). The data were analyzed using Modde 7.0 software. The variables were coded and normalized using unitary values where -1 was defined as the variable with the lowest value and +1 as the one with the highest value. With these external values for the variables, central points (coded as 0) were established and the analyses

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performed in triplicate. The star points were distributed at a distance of -2 and +2 from the central point. The influence of the following three variables was studied: fiber moisture content ($X_1$), press temperature ($X_2$), and the $H_2O_2/Fe(II)$ ratio ($X_3$). The response evaluated was internal bond strength ($Y$) expressed in MPa. The variable range was as follows: $X_1$ between 10% and 20%, $X_2$ between 140°C and 180°C, and $X_3$ between 10 and 20.

A second-order function describing the behavior of the system was determined using a multiple linear regression (MLR). The optimized values of the variables analyzed were obtained from the SIMPLEX algorithm. Statistical validation was performed using ANOVA at a 95% confidence level.

The different values of MC, T, and the $H_2O_2/Fe(II)$ ratio are provided in Table 1. The $H_2O_2$ charge was added to provide a final concentration of 4.5% based on dry fiber. The $Fe(II)$ amount (%) was changed according to the experimental design.

**Defibering and Fiber Treatment with the Fenton Reaction**

*Pinus radiata* wood fibers produced by an Asplund Sunds process were obtained from an industrial board manufacturing plant (MASISA S.A. Chile). For pulping, the wood chips were preheated for 5 minutes, reaching a temperature of 160°C. The fibers were collected from a start up cyclone with 120% moisture content and dried in a forced air oven (100°C) until reaching 10% MC. The fibers were placed in a batch reactor and agitated to prevent clumping. The $Fe(II)$ solution was injected followed by $H_2O_2$ following the experimental sequence used by Pino et al. Following treatment, the fiber consistency was 55%. The fiber activated by the Fenton reaction was then agitated about 2 minutes and dried in an oven at 75°C.

**Preparation and Evaluation of the Fiberboards**

Activated fiber furnish was placed in a 30 cm x 30 cm frame and cold pressed at low pressure for a two-minute period. The fiber mat was then transferred to a stainless steel caul plate in a Dieffenbacher press. All boards were pressed using a closure rate of 20 s mm$^{-1}$. Target thickness and density of the boards were 6mm and 850 kg m$^{-3}$, respectively. The boards were conditioned for three days at 60% relative humidity (RH) and 25°C before evaluating their IB strength according to EN- 319. Thickness swell and water absorption were determined according to the European board standard EN- 317.

Table 1 shows that the treatment with 15% MC, T of 160°C, and a $H_2O_2/Fe(II)$ ratio of 25, presents the highest internal bond strength value. For a better understanding of the importance of each variable, their coefficients in the polynomial were plotted in decreasing order (see Fig. 1). Considering the first-order and the interaction coefficient of each variable in Eqn. (2) and Fig. 1, it can be seen that, the main effects are due to the MC-$H_2O_2/Fe(II)$ ($X_1X_3$) interaction, which is more important than the effect of moisture content ($X_1$) and the $H_2O_2/Fe(II)$ ratio ($X_3$) by themselves. The positive coefficients of these factors mean that they improve the IB strength as the value of these variables increase. The negative coefficient of second-order of MC ($X_1^2$) indicates a maximum region described by a parabola. The $X_1X_3$ interaction terms were omitted in the polynomial (reduced model), because its coefficients were not significative with $P=0.5$ and $P=0.1$ respectively. This imply that the interaction MC-$T$ and $T-H_2O_2$ are not important for IB in the studied range. In this way T is only important as independent variables and do not modified the behavior of the other studied variable.

**RESULTS AND DISCUSSION**

**Polynomial Response**

From the results of the experimental design (Table 1), a polynomial function was obtained [eqn (2)] for the internal bond strength, which considers the relative importance of the different variables and their interaction. The coefficients were normalized according to codified variables value.

$$Y\% = 1.5 (\pm 0.2) + 0.14X_1 (\pm 0.07) + 0.3X_2 (\pm 0.1) + 0.49X_3 (\pm 0.07) - 0.23X_1^2 (\pm 0.07) - 0.4X_2^2 (\pm 0.1) + 0.36X_3^2 (\pm 0.07) + 0.6X_1X_2 (\pm 0.1)$$

Where Y is the IB strength, $X_1$ is the moisture content of the fiber mat, $X_2$ is the press temperature, and $X_3$ is the $H_2O_2/Fe(II)$ ratio. The error with a confidence level of 95% is also indicated.

Table 1 shows that the treatment with 15% MC, T of 160°C, and a $H_2O_2/Fe(II)$ ratio of 25, presents the highest internal bond strength value.

Fig. 2 shows a proportional relation of the polynomial predicted values and the experimental values. The linear correlation coefficient ($R_2$) was 0.992 indicating a good prediction by the model. The ANOVA test results over the regression (table 2) shows the validity of the regression.
Fig. 2 Graph of predicted vs. observed responses.

Table 2 Analysis of variance for suggested model

<table>
<thead>
<tr>
<th>Source</th>
<th>d.f</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
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</thead>
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<tr>
<td>Regression</td>
<td>7</td>
<td>0.406</td>
<td>0.0581</td>
<td>133</td>
<td>0.000</td>
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<tr>
<td>Residual</td>
<td>8</td>
<td>0.00349</td>
<td>0.000436</td>
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<td></td>
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<tr>
<td>Lack of fit</td>
<td>6</td>
<td>0.0022</td>
<td>0.00036</td>
<td>0.561</td>
<td>0.753</td>
</tr>
<tr>
<td>Pure error</td>
<td>2</td>
<td>0.0013</td>
<td>0.00066</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>16</td>
<td>1.27</td>
<td>0.0793</td>
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</table>

Fig. 3 illustrates the contour prediction graphs showing two variables, while the other are kept constant at a maximum value. The contour graphs are predicted by the polynomial function [eqn. (2)], where the area of the experimental domain is within the circle formed by the dotted line. In this area the validity of the model is guaranteed at confidence level 95%, but outside this it must be considered with caution. The maximum IB strength regions are shown by a 0.9 MPa, and the values chosen for each variable are shown by black points in their respective area (see Fig.3).

In Plot A of Fig. 3, which presents IB strength as a function of MC and T, a maximum region with MC ranging from 22% to 38% and T ranging from 145º to 190º C can be observed.

For moisture contents above 20%, the IB strength is above the European board standard EN 622-5 and coincides with the moisture content values used by other researchers11. However, increases in MC would improve the IB strength, which would cause a time increase in the press cycle for degasification23.

However, in all the experimental treatments, the same rate of 20 mm s⁻¹ was used, although press cycle times needed to be redistributed for the different moisture contents, avoiding possible delaminating and “blown” boards. Yelle et al.17 used a rate of 76 mm s⁻¹ for a dry thin fiberboard production in order to obtain similar values for internal bond strength.

In Plot B of Fig. 3, the internal board strength is illustrated as a function of T (X₂) and the H₂O₂/Fe(II) (X₃) ratio. The model predicted the press temperatures between 160º and 180ºC increased the IB strength for a H₂O₂/Fe(II) ratio of 25.

Model Validation

The suggested conditions from the SIMPLEX optimization to maximize IB strength correspond to the two treatments shown in table 3. In treatment A, a higher MC (25%) is required, although this value is lower than the MC of 40% used by Yelle et al.17 for fiberboard elaboration in the “dry process” with a CMFR system. Additionally, the H₂O₂/Fe(II) ratio equal to the one used by Widsten et al.15 with an acceptable IB strength.

In condition B, a higher T (180ºC) is required, value below the temperature traditionally used for resin curing in board industry24.

After analyzing the experimental data, the best suggested conditions for the IB strength are shown in table 3, also in this table the experimental value of IB is shown.
Table 3 Model Validation Results

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Variables</th>
<th>Responses</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>25</td>
<td>0.962 (±0.004)</td>
</tr>
<tr>
<td>B</td>
<td>20</td>
<td>0.743 (±0.050)</td>
</tr>
</tbody>
</table>

The improved IB strength is explained by the superficial oxidation of the fibers with the Fenton Reaction preventing their diffusion to fiber interior due to the low MC. These results are in agreement with the conclusions obtained by Yelle et al. and Qian et al. in similar systems.

Finally, the optimized boards were evaluated for thickness swell and water absorption according to European board standard EN 317, reaching values within the range indicated by standard EN 622-5 with respect to thin fiberboards for general use in a dry environment. These values were reached without sizing agent or other additives like that were used by Widsten.

CONCLUSIONS

The multivariate analysis presented a statistically validated response surface that identifies conditions to improve the IB strength in fiberboards activated by oxidative treatment with the Fenton reaction with a 95% confidence level. These experimental conditions resulted in a board at lower press temperatures (170ºC and 180ºC) than used industrially (200ºC to 220ºC) and furthermore using fiberwood obtained at defibration temperature allowed to obtain below than those used routinely. The polynomial response indicates an important synergic interaction between MC and the $\text{H}_2\text{O}_2/\text{Fe(II)}$ ratio with respect to the effects of the remaining variables. Fiberboards without resin, having IB strength according to standard EN 622-5, were obtained through fiberwood activation using the Fenton reaction.

Further studies should be performed to verify if the same conditions for maximum IB strength in $P. \text{radiata}$ wood fiberboards activated with the Fenton reaction are valid in pilot plant.

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