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Internet: SASSUS, F., M. FOURNIER, AND B. THIBAUT. 1995. Longitudinal growth strains and drying shrinkage in tension wood of poplars (*Populus euroamericana* cv 1214) IUFRO XX World Congress, Tampere, Finland http://www.metla.fi/conf/iufro95abs/d5pos13.htm. (8 June 1998).

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CHANGES IN THE CHEMICAL COMPOSITION AND SPECTROSCOPY OF LOBLOLLY PINE MEDIUM DENSITY FIBERBOARD FURNISH AS A FUNCTION OF AGE AND REFINING PRESSURE

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ABSTRACT

Loblolly pine wood between the ages of 5–35 was refined into medium density fiberboard furnish at steam pressures from 2 to 18 bar. The effect of age and processing conditions on the properties of the fibers was assessed by wet chemical analyses, Near Infrared Spectroscopy (NIR) and powder X-ray diffraction (XRD). In general, the percentages of extractives and glucose increased, while the xylose, galactose, and mannose decreased with increasing refining pressure. There were no consistent changes in chemical composition of the refined fibers as a function of the age of the wood. The crystallinity of the refined fibers increased with both age and refining pressure. The spectroscopic and XRD data were analyzed using multivariate statistical methods, indicating a strong relationship between the spectral patterns and refining pressure.

Keywords: Medium density fiberboard, (MDF), near infrared spectroscopy, X-ray diffraction, partial least squares.

INTRODUCTION

Medium density fiberboard is a nonstructural panel product, with densities of 31–50 pounds per cubic foot that are uniform throughout the panel, generally glued with urea-formaldehyde resins, and used in applications including furniture underlayment, molding and door skins (USDA 1999). The panel furnish is manufactured by subjecting wood chips to a thermomechanical process, in which the wood is subjected to high pressure steam and then reduced to fibers by shearing the wood through a set of refiner plates. Adhesives and waxes are added to the fibers, which are subsequently pressed to specified thickness and density.

Recent studies have examined the impact of processing conditions and location within the

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tree from which the chips originated on the fundamental material properties of the fibers. These results have also been compared to the properties of the finished boards.

In a preliminary study, chips representing juvenile wood (rings 1–10) and mature wood (rings 20 and above) of a loblolly pine were processed at steam pressures of 4, 8, and 12 bar. These fibers have been analyzed with scanning electron microscopy, atomic force micrcoscopy (Snell et al. 2001), Fourier transform infrared spectroscopy, and X-ray photoelectron spectroscopy (Rials et al. 2001). The microscopy experiments indicated an increase in surface roughness with refiner pressure, with juvenile wood fibers exhibiting a higher degree of roughness than mature ones. Quantitative measures of roughness showed that surface roughness is greatest for both tissue types at the 8 bar pressure. These results are interpreted as indicating the occurrence of different failure modes in juvenile and mature wood at differing pressures. Fiber lengths were also found to be maximized at 8 bar, with the fibers refined at 4 and 12 bar exhibiting about equal fiber lengths (Rials et al. 2001). This behavior, in which the samples refined at 8 bar differ markedly from the others, can also be observed through the determination of surface energy by inverse gas chromatography (Elder et al. 2002). Furthermore, these differences in surface level properties are consistent with the stiffness of panels made from these fibers, which were also found to be at a maximum at 8 bar (Rials et al. 2001).

The chemical composition and physical properties of wood and a variety of biomass materials have been measured with NIR spectroscopy (Hoffmeyer and Pedersen 1995; Kelley et al. 2004; McLellan et al. 1991; Newman et al. 1994; Raymond et al. 2001; Schimleck et al. 1997; Tygesen 1994; Thumm and Meder 2001). These studies have shown that all of the individual wood components, lignin, extractives, and individual sugars can be measured with NIR. Physical properties such as density, mechanical strength, and microfibril angle can also be measured with NIR (Hoffmeyer and Pedersen 1995; Kelley et al. 2004; Thumm and Meder 2001). The bending and internal bond properties of MDF panels have also been correlated with NIR spectra (Rials et al. 2001). All of these results suggest that NIR should be useful for characterization of these MDF fibers.

Changes in the crystallinity of cellulose (Segal et al. 1959; Hu and Hsieh 1996; Hindeleh and Johnson 1972; Bang et al. 1999) and wood pulps as a function of processing conditions (Ramos et al. 1999; Goswami et al. 1996) have been reported by several authors. In work directly related to the current paper, Ahtee et al. (1980, 1983) have used X-ray diffraction to determine the crystallinity of thermomechanical pulps. Beating to various freeness levels seems to have little impact on the crystallinity, while as might be expected, it is reported that grinding in a ball mill for increasing lengths of time dramatically decreases the crystallinity.

Based on this body of prior work, the current study was undertaken to relate changes in the chemical composition and spectra of refined fibers to the refining conditions and the age of the original wood chips. The chemical composition of a subset of the fibers was measured with standard wet chemical techniques. NIR spectra of these fibers were collected to investigate the potential for using NIR to measure the chemical composition of MDF fibers and to see if the spectra could be related to processing conditions. XRD patterns were collected on a larger set of fibers to investigate the effects of the age of the wood chips and the refining conditions on the fibers.

METHODS

Production of refined fibers

Loblolly pine was collected from the Crossett Experimental Forest, and individual trees were divided into four age groups representing tissue from the pith to ring 8, rings 9–16, 17–24, and 25 and above. The wood was chipped and pressure-refined at the BioComposites Center in Bangor, Wales (Snell et al. 2001; Rials et al. 2001). The refining conditions included pres-

sures of 2, 4, 5, 6, 7, 8, 10, 12, 14, and 18 bar, providing a total of 40 samples for evaluation.

Chemical analysis

All samples were milled using a Standard Wiley knife mill with a 2-mm screen (ASTM 1999). All samples were analyzed using ASTM standard methods for whole biomass analysis (ASTM 1999). NIST Pine Standard Reference Material # 8493 was used as a reference for the determination of extractives, lignin, and carbohydrates. Analysis errors for softwood composition using these traditional wet chemical analysis methods are 0.5% for lignin and ash, 1.0% for glucose and extractives, and 1.5% for all other sugars (Milne et al. 1992).

NIR measurements

The NIR spectrometer used for method development was a Foss NIR Systems model 6500 Forage Analyzer with a sample transport module and a standard reflectance detector array that measures between 400–2500 nm. Natural product sample compartment cells in 1/4 cup size and ring cups (4-mm diameter) for small samples were used as sample holders in the transport module. This instrument has a maximum resolution of 2 nm. The fiber samples were ground using a small coffee grinder to homogenize the sample and to minimize differences in particle size. Each sample was sub-sampled three times, and the sub-sample spectra were averaged; the samples were also run in duplicate and the duplicate spectra were averaged. This provided a thoroughly representative spectrum that was used for the analysis.

XRD measurements

Powder X-ray diffraction measurements were taken on each sample, at 20 angles from 3 to 90°, using a Rigaku Miniflex X-ray Powder Diffractometer, with Cu Kα radiation (1.54056 Å) Crystallinity indices were calculated by I(22°)-I(18°)/I(22°) (Segal et al. 1959). The complete XRD patterns, containing more than 8,500 data-points each, were averaged along the angle axis by a factor of 20 to produce a file with 425 points for each pattern. The PLS (partial least squares) models were constructed with these averaged data sets.

PLS analysis

The spectra and XRD patterns were converted to an Unscrambler ® file (The Unscrambler 7.6, 2000). The reflectance spectra were converted to absorbance spectra in Unscrambler ®. All the data sets were subjected to Multiplicative Scattering Correction (MSC) using the Unscrambler algorithms Averaging the spectral data reduces the size of the matrix and significantly reduces the time required to compute the projection to Latent Structures (PLS) models without decreasing the quality of the models.

Given that 19 samples were subjected to wet chemical analysis, the NIR and PLS correlation models for the chemical composition were based on full cross validation, with one sample removed at a time (Gabrielsson et al. 2002; Martens and Naes 1991). The correlation coefficient and root mean square error of prediction are generated by the full cross-validation procedure. For the analyses of refining pressure and total crystallinity, 40 samples were analyzed, and the data sets were randomly divided into two groups. One group was used to construct a calibration model, using full cross-validation, and this calibration model was used to predict the properties of the second set of samples that were not included in the original model. The correlation coefficient and root mean square error of prediction are from the validation set.

RESULTS AND DISCUSSION

Changes in chemical composition

The results of the wet chemical analysis are shown in Fig. 1a–1f. While it is well known that the chemical composition of juvenile pinewood and mature pinewood is different, there were no consistent changes in the chemical composition

for the different age classes. Thus, the four different age classes at five different refining pressures were averaged to show trends in the chemical composition as a function of refining pressure. There is a significant increase in the extractives content (Fig. 1a), and a less dramatic increase in the glucose content (Fig. 1b), with increasing refining pressure. There is a corresponding decrease in the hemicellulose sugars, xylose (Fig. 1c), galactose (Fig. 1d), and mannose (Fig. 1e) at the higher refining pressures. The lignin content remains the same as a function of refining pressure, although there is a large amount of variation between the different samples.

As expected, there are changes in the chemical composition as a function of refining pressure. The higher refining pressures depress the glass transition temperature of the lignin and can initiate hydrolysis of labile carbohydrate bonds. The decrease in the hemicellulose sugars starts above 8 bar, which corresponds to a temperature of 170°C. Below 8 bar, there is no significant change in the amount of hemicellulose sugars, and only minor changes in the extractive content, suggesting limited hydrolysis of the sugars at the lower pressures.

The relationship between the total crystallinity and refining pressure is shown in Fig. 2a. There was a great deal of scatter in the crystallinity measured with XRD, but there is a general trend of increasing crystallinity with increasing refining pressure. These results are consistent with increased refining pressure leading to a decrease in the concentration of the amorphous cellulose and hemicellulose components, and thus a relative increase in the crystallinity of the fibers. The wet chemical analysis shows a clear loss in the hemicellulose sugars (Fig. 1c–1e). Higher refining pressures are also known to decrease the relative amount of earlywood fibers and ray cells, which can also lead to an increase in the relative crystallinity (Rials et al. 2001). There were also differences in the crystallinity of the fibers based on the age of the original wood (Fig. 2b). Refined fibers from mature wood, average age of 35 years, were more crystalline than fibers from juvenile wood average age 8 years. Fibers from the transition region, average age 20 years, were also more crystalline than the fibers from juvenile wood. These trends are consistent with prior results (Wang and Chiu 1990).

NIR spectroscopy

Representative NIR spectra of fibers refined at different pressures are shown in Fig. 3. As expected, the absorbance in the visible region of the spectra increases, which is consistent with a darkening of the fibers as the refining pressure increased. However, there are few, if any, obvious changes in the overtone and combination regions of the near infrared spectrum that can be assigned to chemical changes in the samples.

The NIR spectra were also used to predict the chemical changes in the fibers. The results from these predictions are shown in Table 1. In general, there is a good correlation between the NIR spectra and the chemical composition of the fibers. The notable exception is the poor correlation between the NIR spectra and measured lignin content. In prior work, the correlation between the measured lignin content and the NIR spectra has been reported to be very strong, generally above 0.85 (Kelley et al. 2004; McLellan et al. 1991; Newman et al. 1994; Raymond et al. 2001; Schimleck et al. 1997).

In the case of these refined fibers, there are two possible explanations for the poor correlation between the NIR spectra and lignin content. Both explanations involve changes in the structure lignin caused by the refining process. Changes in the lignin structure that make the lignin more heterogeneous generally decrease the quality of the correlations since there are more chemical features in the NIR spectra that must be accommodated in the PLS model. This trend has been seen though generally lower correlations between the measured and predicted lignin content in hardwoods versus softwoods. The second explanation involves the actual measured lignin content used for the calibration model. The lignin content measured by the tradi-

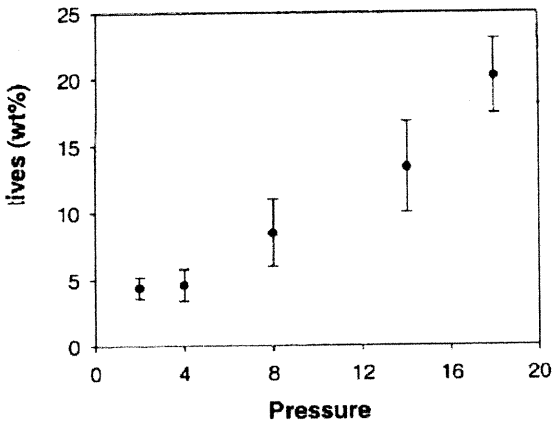


Figure 1a.

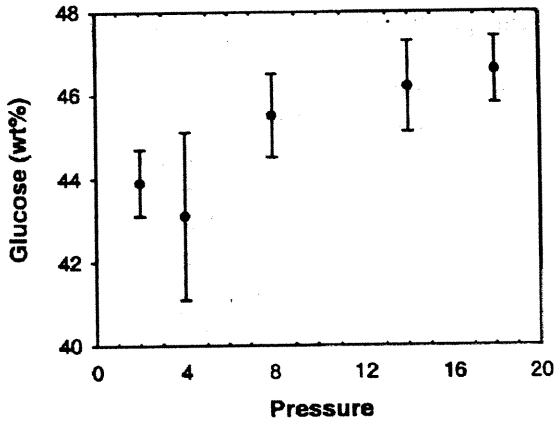
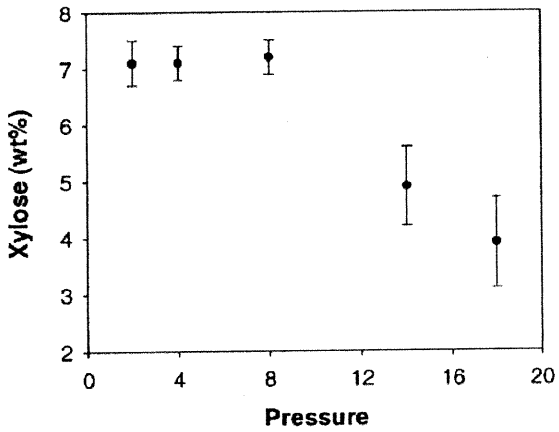


Figure 1b.



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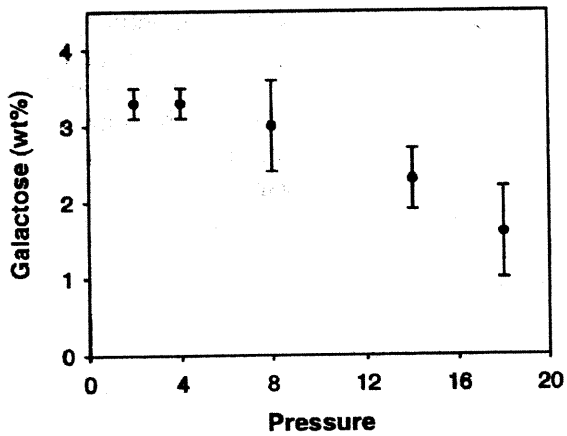

Figure 1d.

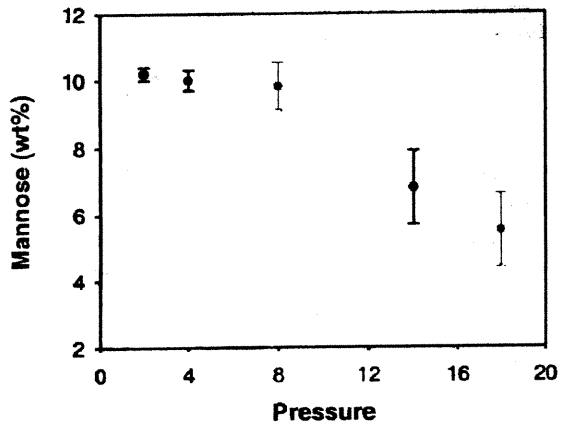

Figure 1e.

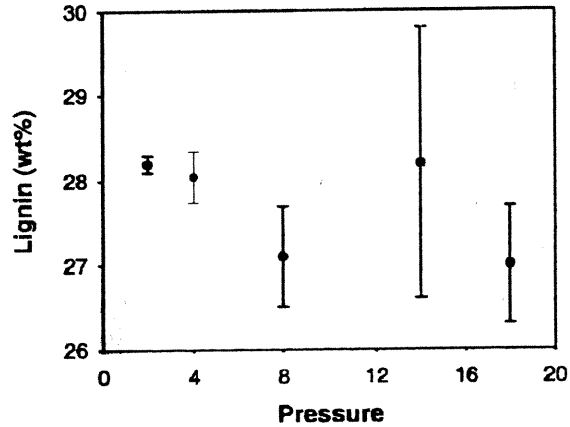

Figure 1f.

FIG. 1. Changes in chemical composition as a function of refining pressure (a) extractives, (b) glucose, (c) xylose, (d) galactose, (e) mannose, (f) lignin.

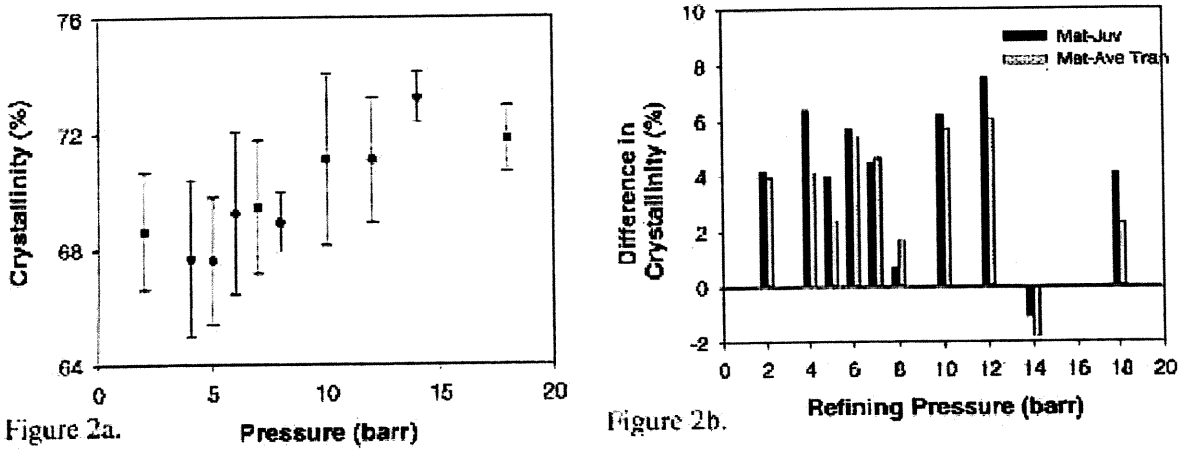

FIG. 2. Changes in (a) XRD measured crystallinity for all samples as a function of refining pressure and (b) difference in crystallinity between mature wood (greater than 35 years) and juvenile wood (less than 8 years) and mature wood and transition wood (average age 20 years) with refining pressure.

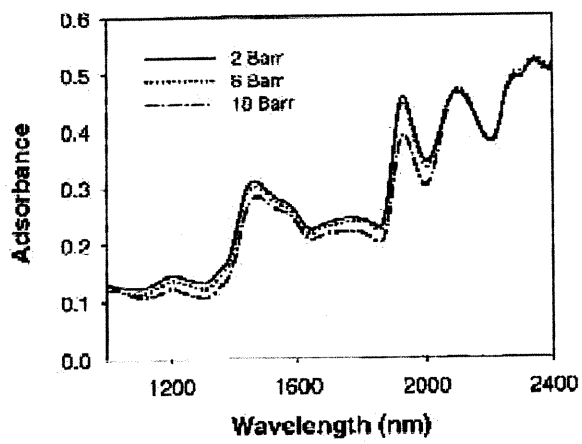

FIG. 3. NIR spectra of mature wood refined at 2, 8, and 18 bar.

TABLE 1. *Correlations and normalized RMSEP for PLS models predicting the chemical composition, crystallinity and refining pressure of the fibers from NIR spectra, and XRD patterns.*

Component	R	Normalized RMSEP	PCs
From NIR spectra			
Extractives	0.92	0.19	2
Glucose	0.88	0.02	4
Mannose	0.95	0.08	4
Galactose	0.78	0.07	4
Xylose	0.91	0.12	5
Lignin	0.25	0.25	2
Refining Pressure	0.93	0.18	2
Crystallinity	0.52	0.15	2
From XRD Patterns			
Refining Pressure	0.91	0.13	5
Crystallinity	0.94	0.02	5

tional wet chemical methods covers a very narrow range of values (26.2 to 28.3, with one sample above 29.8). These Klason lignin analyses used in this study are optimized for a standard softwood lignin, and the refining process may generate non-soluble or soluble lignin structures with uncommon chemical features, that complicate the wet chemical analysis.

Table 1 also shows the results of a PLS model for refining pressure based in the NIR spectra. There is a strong relationship ($r = 0.93$) between the measured refining pressure and the refining pressure predicted from the NIR spectra. Given the well-defined changes in the chemical composition as a function of refining pressure (Fig. 1), it is not surprising that the NIR spectra also indicate the effects of refining pressure. The relationship between the total crystallinity and NIR spectra is also shown in Table 1. The poor correlation between the NIR spectra and percent

cystallinity was also somewhat surprising. Prior work has shown a good correlatión between NIR spectra and the microfibril angle of the cellulose crystallites (Kelley et al. 2004). Microfibril angle of the cellulose crystallites and total crystallinity are different features but similar enough that we had anticipated that the NIR spectra would contain some information on the total crystallinity.

The regression coefficients for the PLS models of refining pressure and crystallinity are shown in Fig. 4. The regression coefficients for both the refining pressure and crystallinity are very similar, indicating that changes in the physical and chemical features observed with the NIR are very similar. These regression coefficients are consistent with changes in carbohydrate hydrogen bonding patterns, but it is impossible to assign these changes to specific carbohydrates.

XRD patterns

The crystallinity index of cellulose and wood fibers is commonly measured with XRD, and the XRD patterns for the refined fibers in the current study are shown in Fig. 5. There are two major peaks in the XRD patterns corresponding to the 101 and 002 crystal planes, at 17 and 22°, respectively.

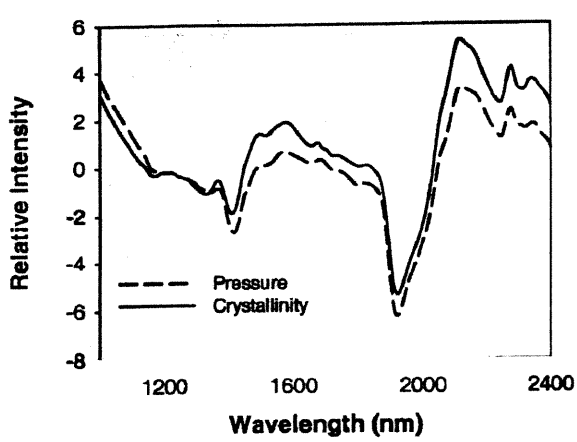

FIG. 4. Regression coefficients from PLS models based on NIR spectra for refining pressure and crystallinity.

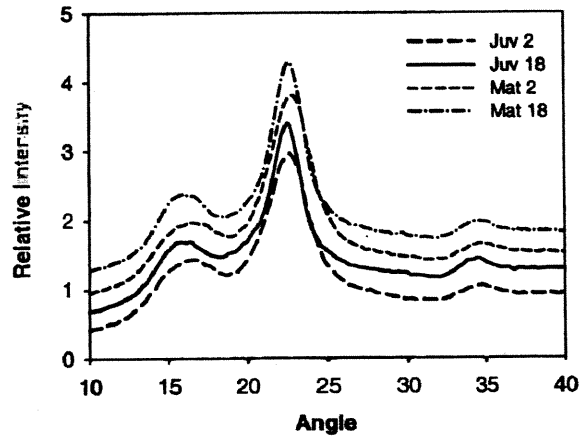

FIG. 5. XRD patterns for juvenile and mature wood refined at 2 and 18 bar.

PLS methods were used to correlate changes in the XRD patterns with the crystallinity index and refining pressure, and these results are also shown in Table 1. There is a high correlation between changes in the XRD patterns and the total crystallinity, which is not surprising. However, there is also a strong relationship between changes in the XRD patterns and the refining pressure used in the preparation of the fibers. So while there is only a modest relationship between the total crystallinity and refining pressure (Fig. 2a), a PLS analysis based on the raw XRD patterns is able to identify subtle shifts in the XRD patterns that are highly correlated with the refining pressure.

Again the PLS analysis also provides the regression coefficients that indicate the specific XRD features that are responsible for the correlations between the XRD patterns, and total crystallinity and refining pressure. The regression coefficients are shown in Fig. 6, along with the averaged XRD patterns for all the fibers refined at 2 and 4 bar, and all the fibers refined at 14 and 18 bar. The regression coefficients for both the crystallinity and the refining pressure show a clear shift in intensity to higher angles for the 002 peak. There is also a less pronounced shift in the regression coefficients of refining pressure to higher angles in the 101 peak.

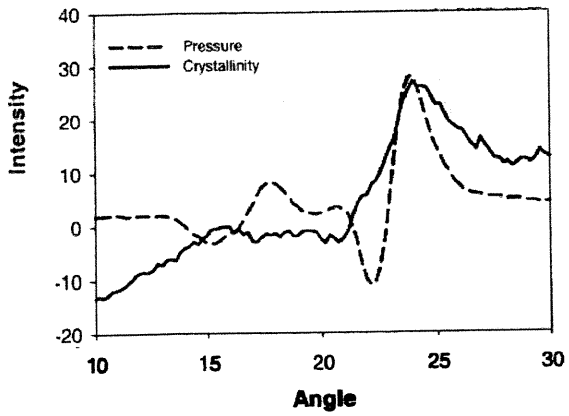

FIG. 6. Regression coefficients from PLS models based on XRD patterns for refining pressure and crystallinity.

CONCLUSIONS

A series of MDF fibers were prepared using different refining pressures and chips with different average ages. The chemical composition and crystallinity of the refined fibers changed as a function of the refining pressure. Specifically, the extractive and glucose contents increased, while the mannose, xylose, and galactose concentrations decreased with increased refining pressure. The average crystallinity of the fibers also increased with increasing refining pressure. All of these changes were more pronounced above 8 bar refining pressure. The measured lignin content was highly variable and did not shown any trends as a function of refining pressure. Across all of the refining pressures the crystallinity of the fibers generally increased with increasing age of the chips. The increase in crystallinity was greatest moving from fibers prepared from the juvenile wood (8 years old) to transition wood (16–24 years old).

NIR and XRD analyses were conducted on the refined fibers. These data were subjected to PLS analysis to monitor the effects of refining pressure, and changes in the chemical composition and crystallinity of the fibers. Both analytical tools could predict changes in the fibers as a function of refining pressure. NIR was effective for predicting the chemical composition, except lignin content. Only XRD was effective for predicting the overall crystallinity of the refined fibers.

ACKNOWLEDGMENTS

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