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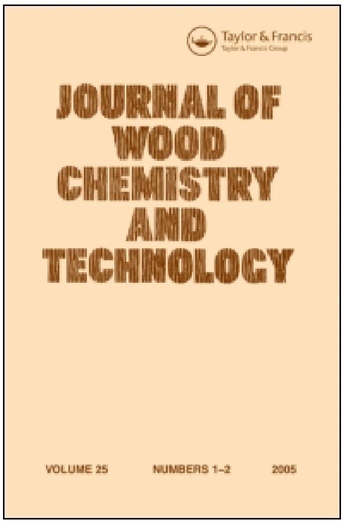

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JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 17(1&2), 135-146 (1997)

# MOLECULAR WEIGHT DISTRIBUTION STUDY OF DELIGNIFICATION OF SPRUCE WOOD MEAL WITH CHLOROACETIC ACIDS

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## ABSTRACT

The amount of lignin removed from spruce wood meal at 50°C to 110°C with mono-, di-, and trichloroacetic acid, as well as its molecular weight (MW) distribution was studied. Trichloroacetic acid gives rise to the lowest $M_n$ (2,000-4,000), the lowest $M_w$ (4,500-8,000), the lowest upper MW limit (~40,000), and the lowest polydispersity (1.5-3.0) of lignin. The removed lignin is split by the tested acids to different extents.

## INTRODUCTION

In recent years, considerable research has been carried out on organosolv delignification. Organosolv processes seem to have a big advantage over the Kraft process in terms of pulp bleachability exploited in the continuing development of organosolv processes towards a totally effluent-free operation[1]. Organic solvents exert a significant role not only in the yield and bleachability of fibres but also in the chemical composition and molecular weight of extracted lignin.

Besides the organic solvent and the catalyst, the temperature and the reaction time are decisive parameters of organosolv processes[2,3]. A special emphasis is given in this respect to organic acids, formic and acetic acid, as delignification agents[4,5]. Organic acids are important solvents in organosolv processes as they give rise to hydrolysis of linkages in lignin and they are also good solvents for the lignin fragments produced. Owing to their strength and structure, haloacetic acids are an efficient medium for wood delignification at mild cooking conditions[6].

Several studies dealing with the characterisation of organosolv lignin molecular weight (MW) and its distribution (MWD) have been reviewed[2,3,7-10]. High performance size-exclusion chromatography (HPSEC) using tetrahydrofuran as eluent, polystyrene standards for calibration and UV detection has become a widely used technique for determining the MWD of lignins. For improved calibration the use of lignin model compounds has been proposed[11]. Recent advances in HPSEC and detectors based on differential viscometry have made it possible to determine absolute molecular weights of several commercially and semi-commercially available lignins[12].

In our previous papers we presented the MWD of lignin obtained on the delignification of spruce chips with trichloroacetic acid for 4 hours at 90°C[13] and compared it to the MW of several acid organosolv lignins[14]. To obtain a better insight into what is going on during trichloroacetic acid delignification we studied the influence of temperature and the time of delignification of spruce wood meal with mono-, di- and trichloroacetic acid on the MWD of dissolved lignin.

## EXPERIMENTAL

### Materials

Spruce (Picea abies) chips were obtained from the mill Goričane, Medvode. They were prepared according to the Tappi standard T 264 om-82 (1982) and ground in the "Micro-Hammer-Cutter" grinder (Spex). The fraction of 100 - 200 Mesh was used as spruce meal.

Monochloroacetic (MCA), dichloroacetic (DCA), trichloroacetic (TCA) acid, and HPLC grade tetrahydrofuran (containing no antioxidant) were obtained from Aldrich and used as received.

### Methods

The spruce meal/acid ratio was 1:10 w/w. No catalyst was added. The components were pre-warmed to working temperature. Delignification was stopped by addition of 100 parts of cold tetrahydrofuran and filtration. The filtrate was used for high performance size exclusion chromatographic (HPSEC) analysis without any further treatment.

The HPSEC analysis was performed on a series of μStyragel columns, 30 cm in length, 7.8 mm i.d., particle size 10 μm, pore diameters of $10^6$, $10^5$, $10^4$, $10^3$, 500, and 100 Å, with tetrahydrofuran, 1.5 mL/min, as eluent and UV (254 nm) detection. The system was calibrated with polystyrene standards obtained from TSK Toyo Soda Manufacturing Co. (MW= 43900, 10300, 2800, 526), a dilignol (MW= 300), and veratryl alcohol (MW= 168).

Several samples of lignin were isolated after delignification of spruce chips or of approx. 2 mm particles obtained from the chips or of spruce meal, with trichloroacetic acid at 90°C for 8 and 240 min, respectively. The delignification was stopped by addition of 2 v/w of acetone and filtration. After removing the majority of acetone in vacuo, lignin was precipitated by pouring its solution into 20 times greater quantity of water. The precipitate was filtered off, washed with water to pH 4 and vacuum dried at 40°C. The HPSEC analysis of these lignins was performed on column Pl gel mixed D with tetrahydrofuran, 1 ml/min, as eluent. The detector was Perkin Elmer DAD LC-235 and the calibration was performed with polystyrene standards.

## RESULTS AND DISCUSSION

The crude lignins dissolved from comminuted spruce wood by monochloroacetic, dichloroacetic or trichloroacetic acid are denoted in this paper as chloroacetic lignins. The results of HPSEC analysis of chloroacetic lignins obtained from spruce wood meal without isolation are presented in Fig. 1 through Fig. 4. The HPSEC chromatogram of lignin isolated by precipitation after 8 or 240 min of delignification is presented in Fig. 5. The number average molecular weights ($M_n$) of chloroacetic lignins are comparable to or higher than $M_n$ of a number of (semi-) commercial lignin preparations determined by Glasser et al.[12], whereas the weight average molecular weights ($M_w$) of chloroacetic lignins are comparable to the $M_w$ of these lignins. The polydispersity of chloroacetic lignins is somewhat lower.

Fig. 1 presents the changes of $M_n$ and of polydispersity of dissolved lignin as a function of delignification time at fixed delignification temperatures of 50, 70, 90, and 110°C. The $M_n$ of dissolved lignin is in most cases the lowest, using trichloroacetic acid as the delignification solvent. In most cases, $M_n$ does not change much with time of delignification. The polydispersity of lignin isolated with trichloroacetic acid is around 2, and with monochloroacetic acid around 3, whereas the polydispersity of lignin isolated with dichloroacetic acid is more variable. The dependence of $M_n$ and of polydispersity on delignification temperature is presented in Fig. 2. The patterns observed at higher delignification times are similar to that presented for $t = 60$ min. Using monochloroacetic acid as the solvent, $M_n$ and polydispersity increase slightly if at all with increasing delignification temperature. Increase in polydispersity of trichloroacetic lignin is slightly higher and its $M_n$ peaks at 90°C. The data for dichloroacetic acid are more variable. At short delignification times they increase with temperature, especially from 50 to 70°C, and at longer delignification time they peak at 90°C. At any temperature, the delignification rate is TCA > DCA > MCA[6]. The trends of MW or polydispersity vs. the amount of dissolved lignin are similar to the trends presented in Fig. 1. Fig. 3 presents the data extrapolated to delignification time zero. These zero-time $M_n$ values are between 2,000 and 4,000 using trichloroacetic acid, and between 3,000 and 5,000 using dichloroacetic acid as well as monochloroacetic acid. The zero-time $M_w$ values span between 4,000 and

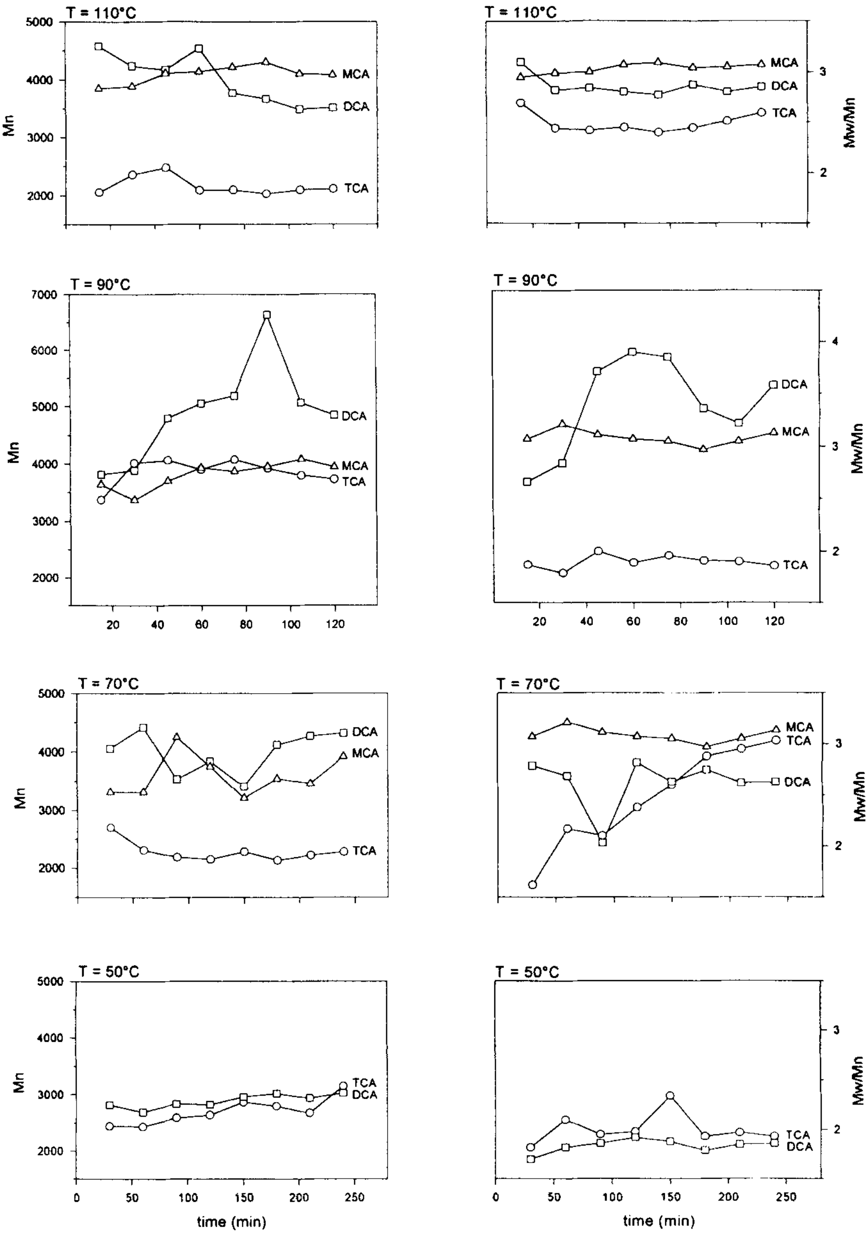

FIGURE 1. $M_n$ and polydispersity of lignin isolated from spruce wood meal with chloroacetic acids at 50°C to 110°C as a function of delignification time.

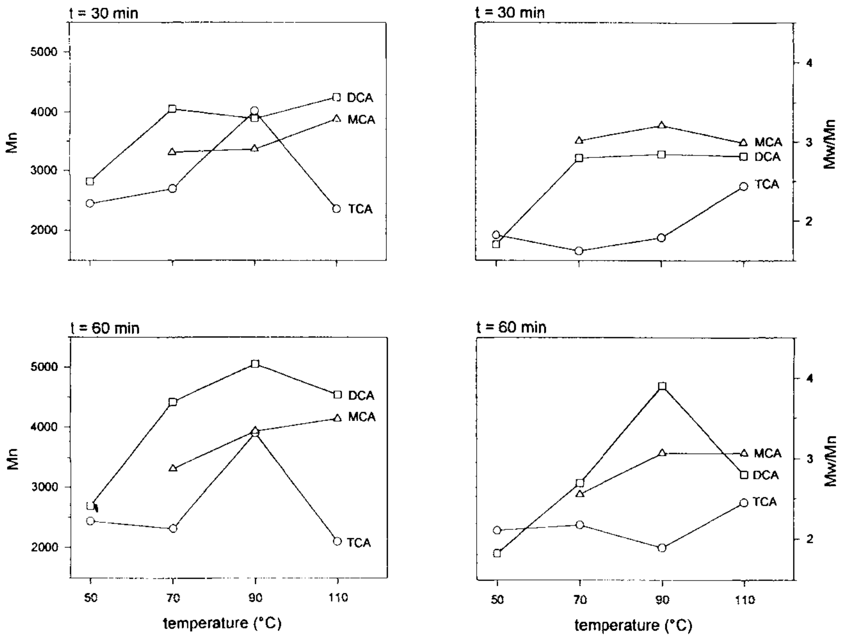

FIGURE 2. $M_n$ and polydispersity of lignin isolated from spruce wood meal with chloroacetic acids as a function of delignification temperature.

7,000 using trichloroacetic acid, between 5,000 and 14,000 using dichloroacetic acid, and between 9,000 and 12,000 using monochloroacetic acid. Zero-time polydispersity is around 2 using trichloroacetic acid, between 2 and 3.5 using dichloroacetic acid, and around 3 using monochloroacetic acid. Most of these zero-time data show a tendency to increase with increasing delignification temperature. The increase is DCA > MCA > TCA and only with TCA a peak value at 90°C is indicated. In Fig. 4 the changes in the upper limit of MW of dissolved lignin are presented. Not only $M_n$ but also the upper MW limit is the lowest on delignification with trichloroacetic acid and at least a slight increase with delignification time is observed. The value of the upper MW limit is by one order of magnitude higher than $M_n$. The temperature dependence of the upper

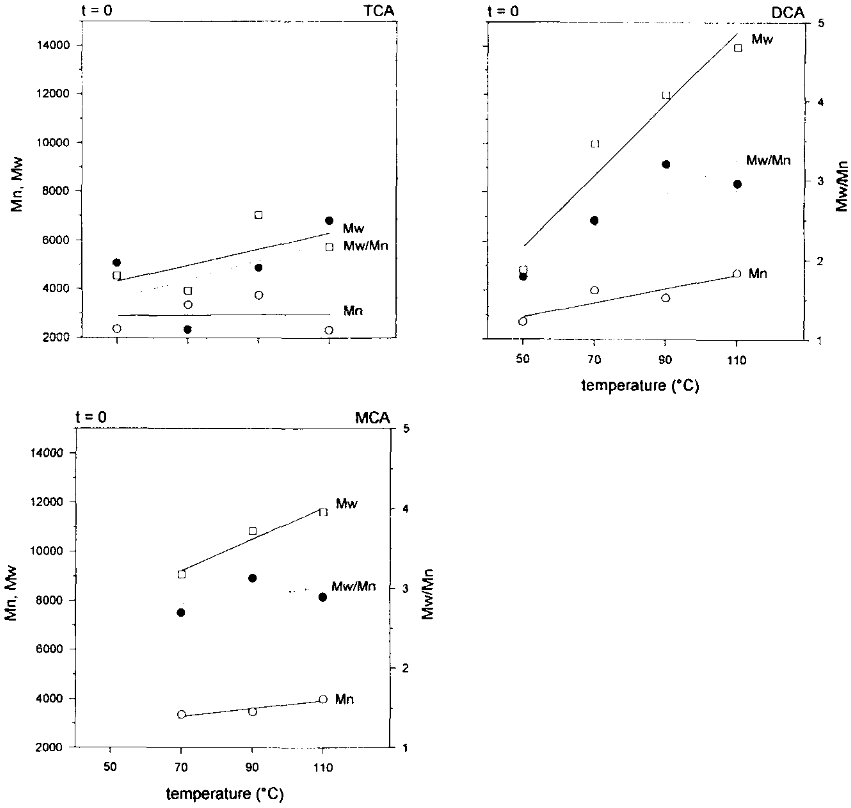

FIGURE 3. Zero-time (extrapolated) $M_n$ (o), $M_w$ (□) and poly-dispersity (●) of lignin isolated from spruce meal with chloroacetic acids as a function of delignification temperature.

MW limit is slight when using trichloroacetic acid and more expressed when going from mono- to dichloroacetic acid, both giving rise to a maximum at 90°C.

The HPSEC chromatograms do not depend on the dimensions of spruce wood particles taken for delignification. The chromatograms of isolated trichloroacetic spruce meal lignins presented in Fig. 5 suggest bimodal distribution. The small low-MW peaks of $M_w/M_n$ 294/291 and 299/297 seem identical. The main peaks of $M_w/M_n$ 3849/2223 obtained after 8 min of delignification and 8778/4186 after

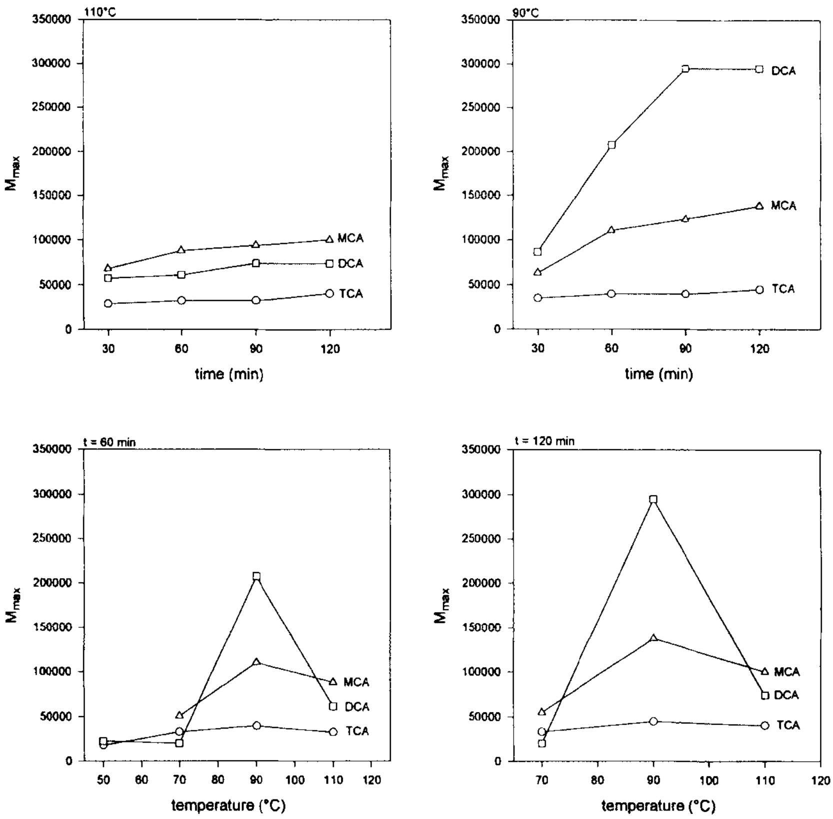

FIGURE 4. Upper limits of $M_W$ of lignin isolated from spruce wood meal with chloroacetic acids as a function of delignification time and temperature.

240 min of delignification indicate lower MW and polydispersity of lignin isolated after shorter delignification time. The data presented in Fig. 1 are between these values. The uniformity of peaks was tested by the spectral peak purity test as well as by derivation of curves. According to the spectral peak purity test, the main peak of 8 min lignin is uniform and the main peak of 240 min lignin is nearly uniform, too. The small peaks are not uniform. Second derivative curves suggest that the main peak of the 8 min lignin is composed of two peaks, whereas the main peak of the 240 min lignin may be a composed one, too.

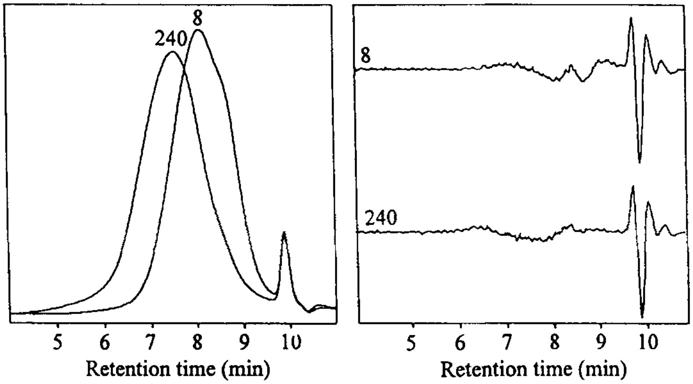

FIGURE 5. HPSEC chromatogram of crude lignins isolated after 8 and 240 minutes of delignification of spruce wood meal with trichloroacetic acid at 90°C (left) and its derivative (right).

The results can be explained in the following way. On the one hand, the dissolving power of the acids used for delignification increases with increasing temperature. This factor should not be limiting since at room temperature trichloroacetic lignin is well soluble even in acetic acid[14], which is an inefficient delignification solvent under our conditions. On the other hand, the dissolution of lignin is a degelation process[12]. The degelation depends on the ability of the solvent to induce degelation as well as on the susceptibility of the bonds keeping the gel together. The ability of chlorinated acetic acids to induce degelation can be expressed by the rate of lignin removal, (TCA > DCA > MCA)[6], or by the MW of dissolved lignin (TCA ≤ DCA / MCA, Fig. 1-4). It is to be correlated first of all to the acidity of the acid (TCA > DCA > MCA)[6]. The rate of lignin removal follows the acidity series and the most important factors in chloroacetic delignification are temperature and the acidity of the acid used as the solvent.

The MW and polydispersity of dissolved lignin, on the other hand, are not in a simple relation to the acidity series. This relationship seems to be more complex, reflecting not only the influence of the chlorinated acetic acids but also the properties of protolignin gel and of its fragments. Protolignin gel is not a

TABLE 1.
Molecular Weight of Lignin Obtained After Delignification with Acetic Acid and Chloroacetic Acids.

| Acid | $M_w$ | $M_n$ | P |
|---|---|---|---|
| acetic acid[16] (205°C) | 4600 | 1150 | 4.0 |
| MCA (110°C) | 11000 - 13000 | 3800 - 4300 | ~ 3.0 |
| DCA (110°C) | 10000 - 14000 | 3500 - 4600 | 2.8 - 3.1 |
| TCA (110°C) | 5000 - 6000 | 2000 - 2500 | 2.4 - 2.6 |

uniform polymer. It is kept together by a number of different bonds and the susceptibility of these bonds for the action of the acids can be reasonably expected to be different. These differences may be the reason for the departures of action of acids from what would be expected by relying only on their acidity. TCA seems to be strong enough to split fast[6] greater amounts of the protolignin gel into particles of MW and polydispersity lower than DCA and MCA do, as soon as the temperature is sufficiently above 50°C. DCA, on the other hand, splits higher amounts of lignin off the gel than MCA but the MW of dissolved lignin is higher than that dissolved by MCA. The simplest explanation for this observation would be that whereas DCA removes everything MCA does, it also removes additional lignin fragments but is unable to split them as profoundly as TCA does.

The MW data observed on the delignification of spruce meal with chloroacetic acids may be compared to those observed on trifluoroacetic acid[15] or acetic acid delignification[16]. Trifluoroacetic acid was used for total wood hydrolysis and the resulting lignin was largely insoluble.[15] The acetic acid delignification of pine wood[16] was performed at 205°C with 37 mol% of water in delignification liquor. These conditions are quite different from those of our chloroacetic delignification. The MW of the resulting lignins are presented in Table 1.

At a lower temperature (110°C) and using chloroacetic acids, higher $M_w$ and $M_n$ but lower polydispersities are observed than using acetic acid at higher temperature (205°C[16]).

## ACKNOWLEDGEMENT

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