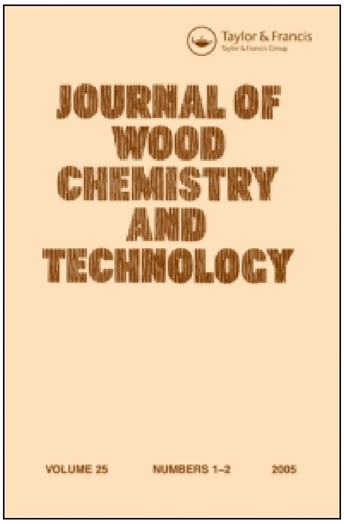

**Journal of Wood Chemistry and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# Effect of Chemical Pretreatment on Chemical Characteristics of Steam Explosion Pulps of Aspen

Yuxia Ben[a]; Bohuslav V. Kokta[b]; Jacques Doucet[a]; Serge Kaliaguine[c]
[a] Département des sciences du bois, Faculté de Foresterie, Université Laval, Québec, CANADA [b] Centre de recherche en ptes et papiers, Université du Québec à Trois-Rivières Trois-Rivières, Québec, CANADA [c] Département de génie chimique, Faculté de Science et Génie, Université Laval, Québec, CANADA

**To cite this Article** Ben, Yuxia , Kokta, Bohuslav V. , Doucet, Jacques and Kaliaguine, Serge(1993) 'Effect of Chemical Pretreatment on Chemical Characteristics of Steam Explosion Pulps of Aspen', Journal of Wood Chemistry and Technology, 13: 3, 349 — 369

**To link to this Article: DOI:** 10.1080/02773819308020522

**URL:** http://dx.doi.org/10.1080/02773819308020522

JOURNAL OF WOOD CHEMISTRY AND TECHNOLOGY, 13(3), 349-369 (1993)

# EFFECT OF CHEMICAL PRETREATMENT ON CHEMICAL CHARACTERISTICS OF STEAM EXPLOSION PULPS OF ASPEN

Yuxia Ben*, Bohuslav V. Kokta***, Jacques Doucet* and Serge Kaliaguine**

* Département des sciences du bois, Faculté de Foresterie

** Département de génie chimique, Faculté de Science et Génie

Université Laval, Ste-Foy, Québec, G1K 7P4 CANADA

*** Centre de recherche en pâtes et papiers, Université du Québec à Trois-Rivières

Trois-Rivières, Québec, G9A 5H7 CANADA

## ABSTRACT

The effect of chemical pretreatment on the chemical characteristics of steam explosion pulps was studied by ESCA, FTIR and other chemical methods. 18 different chemical solutions, which were the combination of following chemicals $Na_2SO_3$, NaOH, $NaHCO_3$, $Na_2CO_3$, $MgCO_3$, $MgCl_2$, $ZnCl_2$, $Na_2S$ or $H_2O_2$, were used as pretreatment agent. The chemical characteristics of pulps with different pretreatment including hydrophilic group content, surface composition of the fibers, bulk chemical composition as well as physical and optical properties were compared. Compared to $Na_2SO_3$ alone or to other chemical pretreatment systems, a presence of NaOH, $NaHCO_3$ or $MgCO_3$ led to a higher hydrophilic group content, more carbohydrates exposed on the fiber surface as well as to a higher degree of lignin sulfonation, which may explain their high physical strength. A lignin analysis showed little difference in their bulk lignin contents. The presence of NaOH in impregnation solution led to xylan partially dissolving during the steam explosion cooking process. Furthermore, controlling the impregnation solution's initial pH in the range 9-10 normally led to high pulp yield.

## INTRODUCTION

The effect of chemical impregnation pretreatment on the pulp and paper properties of SEP (Steam Explosion Pulping) of aspen was reported in a previous publication[1]. The results showed that the presence of NaOH, $NaHCO_3$ or $MgCO_3$ led to lower relative specific refining energy consumption and higher physical strength when compared to $Na_2SO_3$ alone or to other chemical systems ($Na_2SO_3$+$MgCl_2$; $Na_2SO_3$+$Na_2CO_3$; $Na_2SO_3$+$ZnCl_2$; NaOH+$Na_2S$; NaOH+$MgCl_2$ or $H_2O_2$ as an impregnation solution). The presence of $NaHCO_3$ or $MgCO_3$ resulted in higher brightness and yield.

A change in the impregnation solution led to a considerable difference in pulp and paper properties. However, little is known about the effect of the chemical pretreatment of wood chips on the chemical characteristics of fibers after steam explosion pulping, which in turn affect pulp and paper properties.

The present study is aimed at establishing correlations:

1. between the chemical pretreatment of wood chips and the chemical characteristics of the fibers after steam explosion pulping;
2. between fiber chemical characteristics and pulp and paper properties.

Steam explosion pulps are ultra-high-yield pulps. Their fiber bonding depends on both fiber flexibility and the chemical nature of the fiber surface. Therefore, one may expect the pulp and paper properties to significantly depend on the surface composition of the fibers and on the hydrophilic group content of the pulp[2,3].

ESCA (Electron Spectroscopy for Chemical Analysis) recently revealed itself to be a powerful method of analyzing wood fibers and paper surfaces[4-14,16-18]. It is based on the measurement of kinetic energies and intensities of photoelectrons ejected at a given level of atomic energy and submitted to a monoenergetic X-ray beam. The binding energy of the photoelectron is calculated from its kinetic energy and the X-ray (impinging photon) energy. The binding energies characterize the elements present on the sample surface. The intensity of the signal depends on the number of atoms present in the surface layer. Therefore, it provides information on the elemental composition, electronic structure and bonding of molecules of a very thin surface layer( about 5 nm)[8].

Dorris and Gray[7-9] interpreted the $C_{1s}$ peak using a deconvolution method and studying the chemical shift of the peak. The carbon atoms in the paper surface were classified into three groups, $C_1$, $C_2$ and $C_3$. $C_1$ corresponds to carbon only linked to hydrogen or to carbon ( -C-H, -C-C ), $C_2$ has one link to a single oxygen ( -C-O ), whereas $C_3$ bonds to two non-carbonyl oxygen ( $-C<^{O}_{O}$ ) or to a single carbonyl oxygen ( -C=O ). It is believed that $C_1$ came from lignin and extractives on the fiber surface since cellulose only contributes to $C_2$ and $C_3$ peaks. The authors also measured the oxygen to carbon atomic ratio O/C on fiber surface, which related to the surface composition of the fiber. A higher content of the O/C atomic ratio reflects a relatively higher carbohydrate content and lower lignin and extractive contents on the fiber surface. The sulfur to carbon atomic ratio S/C on the fiber surface of sulfonated pulps were studied by X. Hua[19]. A higher S/C atomic ratio means greater level of surface lignin sulfonation.

FTIR (Fourier Transform Infrared Spectrometry) spectroscopy also revealed itself to be a powerful tool for studying the chemical composition changes in pulp and paper[20-23]. The principle of FTIR and its applications in paper science have been reviewed[24]. FTIR can identify chemical functional groups from vibrational spectra and characterize the chemical structure of paper. In present study, FTIR was used to examine the chemical composition of steam explosion pulps. The lignin content was also measured in order to compare the difference between the surface chemical composition and the bulk chemical composition.

## EXPERIMENTAL

### Impregnation of Chips

150g aspen chips (50% dryness) were mixed in plastic bags along with 150g of a solution made up of different concentrations of chemical products, such as $Na_2SO_3$ alone or with NaOH, $NaHCO_3$, $MgCO_3$, NaOH with $MgCl_2$ or with $Na_2S$ or $H_2O_2$ alone. The liquor/chips ratio was 3:1. The time of impregnation was 24 hours and the temperature of impregnation 60 °C. Chemical compositio of the impregnation solutions appears in the Table 1. The impregnation of two other samples was divided into two steps. First step: 150g chips (50% dryness) were mixed in plastic bags with 150g of a solution made up of 2% $H_2O_2$, 1% NaOH, 2.5% $Na_2SiO_3$, 0.25% $MgSO_4$, 0.025% DTPA (diethylenetriaminepentaacetic acid). Pretreatment lasted 6 and 24 hours; second step: samples were neutralized with a $Na_2SO_5$ solution to pH5.5, washed 3 times with deionized water, and then were mixed with 6% $Na_2SO_3$. This step lasted 18 and 24 hours. The temperature was 60 °C for both steps. In all cases, 0.5% DTPA was used for cooking liquors. To compare the effect of the chemicals, only $H_2O$ was used as an impregnation solution for one sample.

## Cooking

Explosion pulping was carried out with saturated steam in a laboratory batch reactor of 300 ml built by Stake Tech. Company. Cooking temperature was 190°C for 4 minutes. Cooking was proceeded by steam flushing for one minute at atmospheric pressure. After cooking, the pressure was instantaneously released and the chips were exploded into the release vessel and washed with tap water. The chips were then stored in a cold room. Yield was measured as follows: the explosion chips (75g) were washed with tap water and later defibrated in a laboratory domestic blender OSTERIZER B-8814 at a 2% consistency level. The resulting pulp was washed again and dried at 105 °C to constant weight. The dried weight was compared to initial O.D. weight of chips.

## Evaluation of Properties

Paper sheets were prepared and tested on the basis of standard CPPA testing methods[25]. Brightness was evaluated on 3 g paper sheets made from distilled water.

## Determination of Lignin in Aspen Chips and Pulps

Total lignin content is the sum of acid insoluble and acid soluble lignin. They are determined separately according to TAPPI test methods[26], T222 om-88 and UM 250.

## Sulfonate and Carboxylate

The content of sulfonate and carboxylate groups was measured by the conductive titration method[15].

## ESCA Experiments

The ESCA spectrometer was an ESCALAB MK II spectrometer fitted on a microlab system from V. G. Scientific and equipped with a dual Mg-Al anode X-ray source, non-monochromatized.

Kinetic energies were measured using a hemispherical electrostatic analyzer with 150 mm radius working in the constant pass energy mode (20 eV for $C_{1s}$ and $O_{1s}$ peak, 50 eV for $S_{2p}$ and survey spectra). No flood gun was used. The vacuum in the test chamber was maintained at a pressure of $10^{-8}$ Torr. Liquid nitrogen was used for cooling the sample.

A small piece of pulp pad was pressed in an indium disk with maximum care to prevent sample contamination. Spectra were produced using a Mg anode at 300 W with typical accumulation time of 225 - 300 seconds for $S_{2p}$ peak, 270 - 300 seconds for carbon $C_{1s}$ peak, 130 - 210 seconds for oxygen $O_{1s}$ peak and 288 seconds for survey spectra. To check the stability of the fiber surface with exposure time, repeated spectra acquisitions were performed.

For peak synthesis, a computer with VGS 1000 software was used. The ratio of Gaussian to Lorentzian function was 60%. The FWMH (Full Width at Middle Height) of component peaks was 2.0 $\pm$ 0.1 ev.

For the spectrometer and conditions used in this study, the atomic ratios of oxygen to carbon $N_O/N_C$ and sulfur to carbon $N_S/N_C$ were estimated from their

TABLE 1
Pulp and Paper Properties

| Impregnation Solution | Yield % | CSF* ml | Brightness % | Brust Index $kPam^2/g$ | Tear Index $mNm^2/g$ | Breaking Length km |
|---|---|---|---|---|---|---|
| $8\%Na_2SO_3$ | 90.3 | 103 | 61.8 | 3.28 | 7.16 | 5.91 |
| $8\%Na_2SO_3+1\%NaOH$ | 87.0 | 110 | 58.8 | 4.91 | 7.30 | 7.10 |
| $2\%H_2O_2$--$6\%Na_2SO_3$** | | 86.1 | 110 | 67.3 | 4.91 | 7.508.66 |
| $8\%Na_2SO_3+1\%MgCl_2$ | 90.4 | 125 | 63.9 | 3.33 | 6.50 | 6.27 |
| $8\%Na_2SO_3+1\%Na_2CO_3$ | 88.2 | 140 | 63.1 | 4.81 | 7.02 | 6.94 |
| $8\%Na_2SO_3+1\%ZnCl_2$ | 91.4 | 135 | 61.9 | 2.83 | 6.09 | 5.50 |
| $8\%Na_2SO_3+1\%NaHCO$ | 90.4 | 100 | 65.5 | 4.63 | 7.27 | 7.75 |
| $2\%H_2O_2$--$6\%Na_2SO_3$*** | 91.0 | 106 | 71.1 | 3.89 | 6.75 | 7.65 |
| $2\%H_2O_2$ | 92.2 | 142 | 46.8 | 2.64 | 6.85 | 4.91 |
| $4\%Na_2SO_3+4\%NaHCO_3$ | 90.5 | 110 | 67.2 | 3.77 | 6.82 | 5.83 |
| $2\%Na_2SO_3+6\%NaHCO_3$ | 91.7 | 129 | 59.8 | 3.40 | 7.09 | 5.50 |
| $8\%NaHCO_3$ | 91.8 | 140 | 46.8 | 2.80 | 6.99 | 4.98 |
| $3\%NaOH+1\%NaCl$ | 88.3 | 103 | 45.6 | 3.34 | 7.25 | 5.43 |
| $8\%Na_2SO_3+1.5\%NaHCO_3$ | 90.3 | 136 | 65.7 | 4.60 | 7.37 | 7.67 |
| $8\%Na_2SO_3+0.5\%NaHCO_3$ | 90.3 | 137 | 62.9 | 3.75 | 6.20 | 6.54 |
| $2.5\%NaOH+1\%Na_2S$ | 88.7 | 106 | 41.5 | 3.67 | 7.52 | 7.24 |
| $8\%Na_2SO_3+1\%MgCO_3$ | 93.0 | 110 | 64.2 | 4.61 | 7.26 | 7.46 |
| $H_2O_2$ | 87.9 | 105 | 34.3 | 2.09 | 5.92 | 3.31 |

* Canadian Standard Freeness

** Two-step impregnation: the first step with 2% $H_2O_2$ for 24 hours, the second step with 6% $Na_2SO_3$ for 24 hours.

*** Two-step impregnation: the first step with 2% $H_2O_2$ for 6 hours, the second step with 6% $Na_2SO_3$ for 18 hours.

respective peak intensity according to the following equations[10-14]:

$$N_O/N_C = I_O / 2.85\ I_C \quad \text{------------------------}(1)$$

$$N_S/N_C = 0.523\ I_S / I_C \quad \text{------------------------}(2)$$

where $I_O$ is the normalized integrated area of $O_{1s}$ peak,
$I_C$ is the normalized integrated area of $C_{1s}$ peak,
$I_S$ is the normalized integrated area of $S_{1s}$ peak.

The fractional contributions to $C_{1s}$ peak were estimated from their respective peak areas. The fractional areas $I_{C1}/I_{C1s}$, $I_{C2}/I_{C1s}$ and $I_{C3}/I_{C1s}$ are equal

TABLE 2
Chemical Analyses Results

| Impregnation solution | Initial pH | Sulfonate (mmol/kg) | Carboxylate (mmol/kg) | Lignin Content(%) |
|---|---|---|---|---|
| 8%$Na_2SO_3$ | 9.1 | 41.9 | 127.0 | 19.3 |
| 8%$Na_2SO_3$+1%NaOH | 12.0 | 47.6 | 136.6 | 19.4 |
| 2%$H_2O_2$--6%$Na_2SO_3$* | 9.8, 8.8 | 36.6 | 145.5 | 18.2 |
| 8%$Na_2SO_3$+1%$MgCl_2$ | 9.1 | 47.0 | 116.8 | 18.8 |
| 8%$Na_2SO_3$+1%$Na_2CO_3$ | 10.4 | 54.7 | 124.2 | 19.0 |
| 8%$Na_2SO_3$+1%$ZnCl_2$ | 8.1 | 37.6 | 110.0 | 19.0 |
| 8%$Na_2SO_3$+1%$NaHCO_3$ | 9.4 | 59.0 | 121.2 | 18.4 |
| 2%$H_2O_2$--6%$Na_2SO_3$** | 9.8, 8.8 | 34.2 | 124.9 | 18.4 |
| 2%$H_2O_2$ | 9.8 | 0 | 123.4 | 19.1 |
| 4%$Na_2SO_3$+4%$NaHCO_3$ | 9.2 | 41.3 | 120.2 | 18.5 |
| 2%$Na_2SO_3$+6%$NaHCO_3$ | 9.1 | 34.2 | 120.4 | 19.3 |
| 8%$NaHCO_3$ | 9.0 | 0 | 118.9 | 19.6 |
| 3%NaOH+1%NaCl | 12.0 | 0 | 118.9 | 20.0 |
| 8%$Na_2SO_3$+1.5%$NaHCO_3$ | 9.3 | 59.9 | 123.2 | 18.3 |
| 8%$Na_2SO_3$+0.5%$NaHCO_3$ | 9.4 | 46.0 | 112.5 | 18.6 |
| 2.5%NaOH+1%$Na_2S$ | 11.9 | 0 | 119.5 | 20.4 |
| 8%$Na_2SO_3$+1%$MgCO_3$ | 10.8 | 56.1 | 121.9 | 18.6 |
| $H_2O$ | 7 | 0 | 79.0 | 20.2 |

* Two-step impregnation: the first step with 2% $H_2O_2$ for 24 hours, the second step with 6% $Na_2SO_3$ for 24 hours.

** Two-step impregnation: the first step with 2% $H_2O_2$ for 6 hours, the second step with 6% $Na_2SO_3$ for 18 hours.

to the fraction of the surface carbon atoms $C_1/C_{1s}$, $C_2/C_{1s}$ and $C_3/C_{1s}$ in each of the three chemical classes[9].

## FTIR Spectroscopy Experiments

Thin handsheets (10 $g/m^2$) were prepared. Circular specimens of 10 mm in diameter, cut from the handsheets, were covered with potassium bromide powder on two sides to form a sandwich, and the sandwich was pressed to 1565 kPa.

Infrared spectra were recorded in absorbance units in the frequency range of 4000 - 400 $cm^{-1}$ at a resolution of 2 $cm^{-1}$ with a FTS-60 Digilab spectrometer. The spectrometer was equipped with a nitrogen-cooled source, a computer control (IRIS) and a DTGS detector. Two hundred scans of both the sample and reference were signal averaged to improve the signal-to-noise ratio.

## RESULTS AND DISCUSSION

Table 1 and 2 present some pulp and paper properties and chemical analysis results.

### Lignin Content of Aspen Chips and Pulps

The lignin content of raw aspen material is 19.6%, while the lignin content of the pulps does not show much difference, between 18.3 - 20.4%. The pulps, prepared with 8% $Na_2SO_3$ + 1% NaOH and 3% NaOH + 1% $MgCl_2$ as impregnation solution, have a slightly higher lignin content, 20% and 20.4% respectively. This may be due to the partial dissolution of hemicellulose, especially xylan, during impregnation and steam cooking at a higher pH value, which led to a decrease in the carbohydrate content of the pulps.

### Effect of Initial Impregnation pH

Varying the composition of the impregnation solution directly influenced the initial pH value of the wood chips. Yields and lignin contents are plotted in Fig. 1 as a function of the initial pH of the impregnation solution. While the yield of the explosion pulps decreased, the lignin content of SEP pulps slightly increased with a rise in the initial pH of the impregnation solution in the range under study. When the initial pH are less than 9 (i.e. when using 8% $Na_2SO_3$ + 1% $ZnCl_2$ or $H_2O$ as an impregnation solution), SEP pulps have weak mechanical properties or/and brightness. On the other hand, when initial pH are above 10 (i.e. when using 3% NaOH + 1% NaCl or 8% $Na_2SO_3$ + 1% NaOH as an impregnation solution), the SEP pulps have a low yield or/and low brightness or/and mechanical properties (see Table 1). The impregnation agent

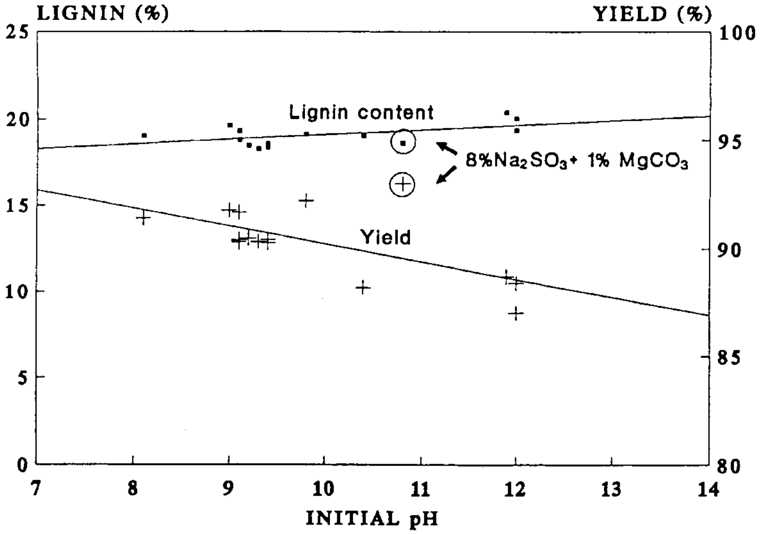

FIGURE 1. Pulp Yield and Lignin Content versus Initial pH of Impregnation Solution.

should be chosen to provide the impregnation solution with an initial pH in the range of 9 - 10, which normally leads to a high yield of SEP pulps. The pulps produced with 8% $Na_2SO_3$ + 1% $MgCO_3$ as an impregnation solution had a higher yield, even though the initial pH of the impregnation solution was above 10 (Fig. 1). This is because magnesium carbonate can protect carbohydrate against hydrolysis, oxidation and degradation.

## Effect of Sulfonate and Carboxylate

A recent study has shown that the sulfonate and carboxylate contents are the major factors in determining physical strength and optical properties of conventional chemimechanical pulps[3]. Fig. 2-4 show an improvement in breaking length, burst index, tear index and brightness following an increase in the sulfonate and carboxylate contents of the pulps. This is consistent with the results obtained by C. Heitner et al[3]. When using 8% $Na_2SO_3$ + 1% NaOH,

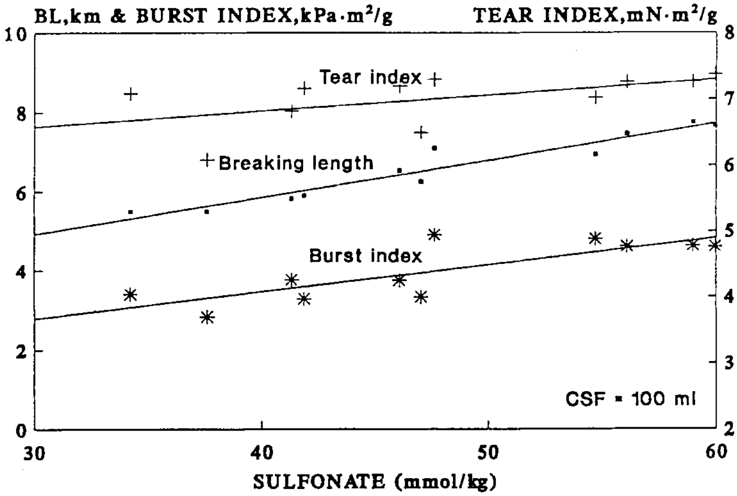

FIGURE 2. Breaking Length, Burst Index and Tear Index versus Sulfonate Content.

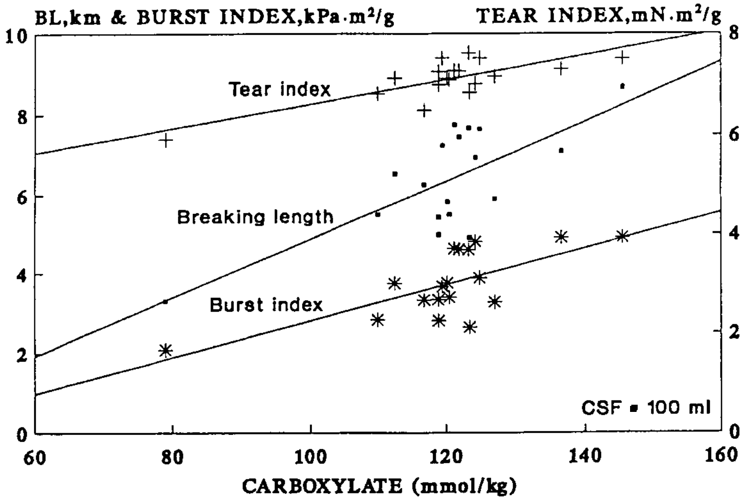

FIGURE 3. Breaking Length, Burst Index and Tear Index versus Carboxylate Content.

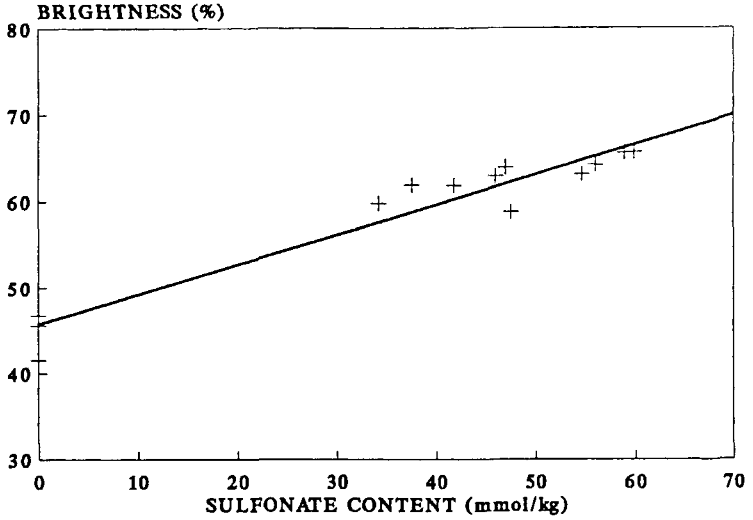

FIGURE 4. Brightness versus Sulfonate Content.

1%$NaHCO_3$ or 1% $MgCO_3$ as an impregnation solution, the pulp contains higher total ionic content than if only $Na_2SO_3$ is used. The higher hydrophilic group content facilitates hydrogen bonding during paper formation as well as increases fiber flexibility, which in turn improves fiber bonding properties and results in greater paper strengths.

## ESCA Results

The surface characteristics of some SEP pulps were studied by using the ESCA technique. Table 3 shows the three components of $C_{1s}$ and O/C, S/C atomic ratios of a selection of seven steam explosion pulps. The $C_1$ peak area fraction was lower for the three pulps using the 8% $Na_2SO_3$ + 1% $MgCO_3$, 8% $Na_2SO_3$ + 1% NaOH and 8% $Na_2SO_3$ + 1% $NaHCO_3$ as an impregnation solution, i.e. 27.6%, 32.4% and 33.8% respectively. As previously mentioned, it is believed that $C_1$ comes from lignin and extractives on the fiber surface,

TABLE 3
Atomic Ratios of Each Component

| Impregnation solution | $C_{1s}$ area (%) $C_1$ | $C_2$ | $C_3$ | O/C | S/C x100 |
|---|---|---|---|---|---|
| 8%$Na_2SO_3$ | 39.8 | 55.5 | 4.7 | 0.466 | 0.23 |
| 8%$Na_2SO_3$+1% NaOH | 32.4 | 61.4 | 6.2 | 0.511 | 0.25 |
| 2%$H_2O_2$--6%$Na_2SO_3$* | 41.7 | 53.8 | 4.5 | 0.436 | 0.20 |
| 8%$Na_2SO_3$+1%$NaHCO_3$ | 33.9 | 60.5 | 5.6 | 0.506 | 0.26 |
| 8%$Na_2SO_3$+1%$MgCO_3$ | 27.6 | 64.7 | 7.7 | 0.561 | 0.28 |
| 3%NaOH+1%$MgCl_2$ | 46.1 | 46.2 | 7.7 | 0.416 | ---- |
| No chemicals | 42.7 | 51.1 | 6.2 | 0.438 | ---- |

* Two-step impregnation: the first step with 2% $H_2O_2$ for 6 hours, the second step with 6% $Na_2SO_3$ for 18 hours.

since cellulose only contributes to $C_2$ and $C_3$. From the empirical formula, for pure cellulose, $C_1/C_{1s}$, $C_2/C_{1s}$ and $C_3/C_{1s}$ should be 0, 0.833 and 0.167 respectively. According to the Freudenberg formulation for spruce milled-wood lignin, these three ratios should be 0.492, 0.488 and 0.02 respectively. A lower $C_1$ peak area fraction means that for these three samples there was less lignin and extractives and more cellulose exposed on the fiber surface.

Table 4 shows the theoretical and experimental O/C atomic ratios of some pulp, cellulose, lignin and extractive samples. For pure cellulose, the O/C atomic ratio was 0.83; for spruce milled wood lignin and spruce dioxane lignin, it was 0.33 and 0.36 respectively; the O/C atomic ratio for abietic acid was 0.10. Consequently, the O/C atomic ratios reflect the content of lignin and extractives on the fiber surface. For the three pulps using the 8% $Na_2SO_3$ + 1% $MgCO_3$, 8% $Na_2SO_3$ + 1% NaOH and 8% $Na_2SO_3$ + 1% $NaHCO_3$ as an impregnation solution, the O/C atomic ratios (0.561, 0.511 and 0.506 respectively) were higher than those of the other samples under study. This indicates again that for these three pulps, more cellulose was exposed on the fiber surface and less lignin and extractives, confirming the result from the area fraction of $C_{1s}$ peak. This suggests that fiber separation which took place during the SEP process might be different and depend upon the nature of the impregnation solution used. The presence of NaOH, $NaHCO_3$ or $MgCO_3$, when compared to $Na_2SO_3$

TABLE 4
Theoretical and Experimental Oxygen-Carbon Atomic Ratios[4-14]

| Samples | O/C (theoretical) | O/C (experimental) |
|---|---|---|
| Cellulose | 0.83 | |
| Spruce milled wood lignin | 0.33 | |
| Spruce dioxane lignin | 0.36 | 0.36 |
| Whatman filter paper | | 0.80, 0.83, 0.79 |
| Bleached kraft pulp | | 0.72, 1.14, 0.62 |
| Bleached sulfite pulp | | 0.73 |
| CTMP (chemithermomechanical pulping) | | 0.46 |
| TMP (thermomechanical pulping) | | 0.44 |
| Kraft pulp | | 0.49 |
| Abietic acid | 0.10 | |

alone or other chemical systems, may lead to a fiber separation closer to the secondary wall of the fiber cell.

The sulfur content in all the samples was very small, which is reflected by the sulfur to carbon ratios shown in Table 3. It is hard to resolve $S_{2p}$ with a synthesis technique. The binding energy of $S_{2p}$ for all samples was 168.9±0.1 eV, which indicates the sulfur in the form of sulfonate group[19,27]. For the pulps using 8% $Na_2SO_3$ + 1% $MgCO_3$, 8% $Na_2SO_3$ + 1% NaOH and 8% $Na_2SO_3$ + 1% $NaHCO_3$ as an impregnation solution, the S/C atomic ratios are greater than those of the other pulps appearing in the Table. This means that the lignin reached a higher degree of sulfonation, which increased its hydrophilicity. This is also consistent with the bulk sulfonate content.

The mechanical properties (burst index, tear index and breaking length) are plotted in Fig. 5-7 as functions of $C_1$ peak area fraction, O/C atomic ratio and S/C atomic ratio. Breaking length and burst index decreased with a rise in the $C_1$ peak area fraction and moved upwards with an increase in the O/C and S/C atomic ratios. As previously mentioned, a lower content of $C_1$ peak area fraction and a higher content of O/C and S/C atomic ratios indicate greater carbohydrate content exposure on the fiber surface and better lignin sulfonation. This enhances the exposure of hydrophilic groups on the fiber surface and facilitates hydrogen bonding during paper formation, which in turn increases fiber bonding

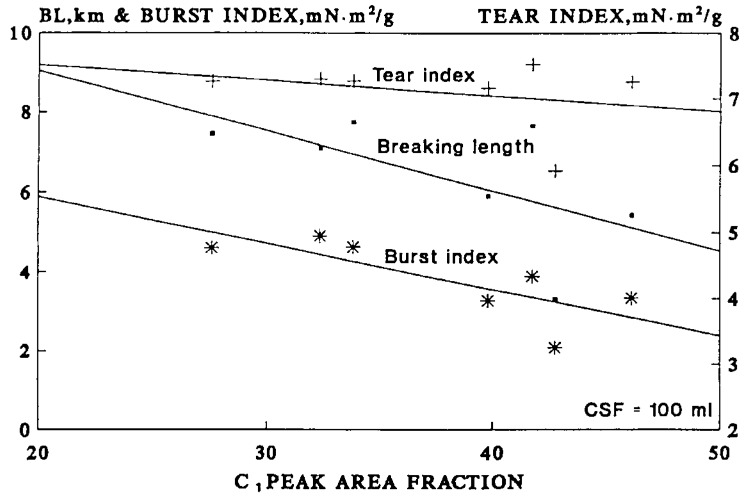

FIGURE 5. Breaking Length, Burst Index and Tear Index versus $C_1$ Peak Area Fraction.

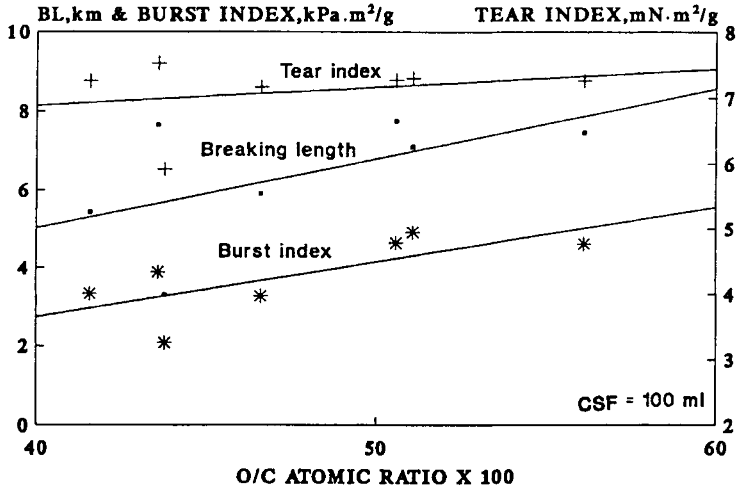

FIGURE 6. Breaking Length, Burst Index and Tear Index versus O/C Atomic Ratio.

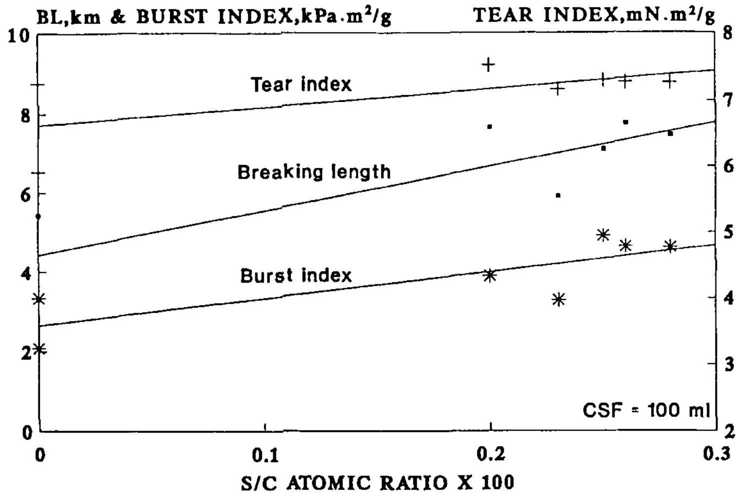

FIGURE 7. Breaking Length, Burst Index and Tear Index versus S/C Atomic Ratio.

properties. This is one of the reasons why SEP pulps increase their physical strength when using 8% $Na_2SO_3$ + 1% $MgCO_3$, 8% $Na_2SO_3$ + 1% NaOH and 8% $Na_2SO_3$ + 1% $NaHCO_3$ as an impregnation solution. Compared to breaking length and burst index, tear index does not show an obvious change with regard to $C_1$ fraction, O/C and S/C atomic ratio. This may be because tear index does not depend as much on the bonding properties among fibers (it mainly depends on fiber length and strength).

## FTIR Results

Fig. 8 shows the FTIR spectra of some SEP pulps. When comparing the spectra, some differences in relative intensity were observed particularly in the case of band at 1735 $cm^{-1}$ (see Fig. 9) due to C=O stretching vibration of acetyl and carboxyl in xylan which is characteristic of hemicellulose[28-32]. The intensity of the bands are much weaker for pulps using 8% $Na_2SO_3$ + 1% NaOH and 3% NaOH + 1% $MgCl_2$ as an impregnation solution, compared with that of other

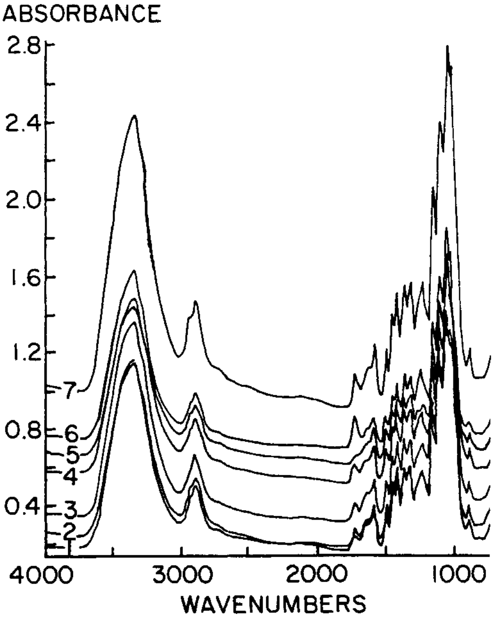

FIGURE 8. FTIR Spectra of SEP Pulps (500 to 4000 cm$^{-1}$) with Various Impregnation Solutions: 1) 8% $Na_2SO_3$; 2) 8% $Na_2SO_3$ + 1% NaOH; 3) $Na_2SO_3$ + 1% $NaHCO_3$; 4) 2% $H_2O_2$ -- 6% $Na_2SO_3$; 5) 3% NaOH + 1% $NaCl_2$; 6) No Chemicals; 7) 8% $Na_2SO_3$ + 1% $MgCO_3$.

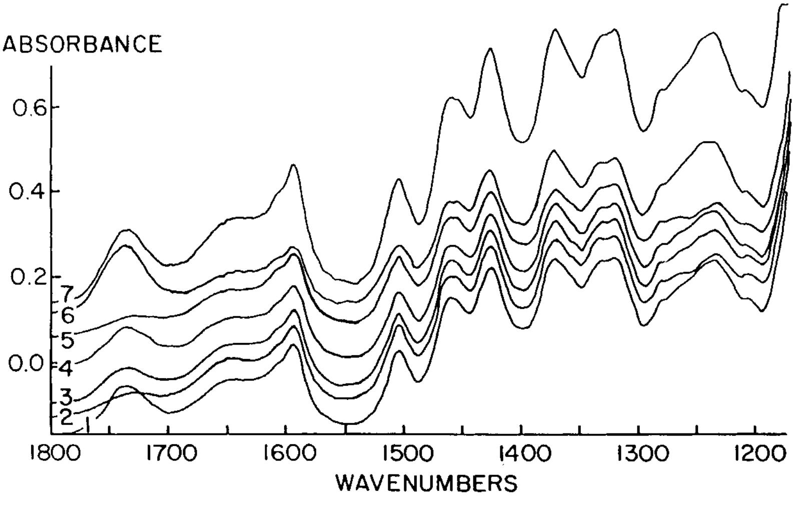

FIGURE 9. FTIR Spectra (in range from 1200 to 1800 cm$^{-1}$) of SEP Pulps with Various Impregnation Solutions: 1. 8% $Na_2SO_3$; 2. 8% $Na_2SO_3$ + 1% NaOH; 3. $Na_2SO_3$ + 1% $NaHCO_3$; 4. 2% $H_2O_2$ -- 6% $Na_2SO_3$; 5. 3% NaOH + 1% $NaCl_2$; 6. No Chemicals; 7. 8% $Na_2SO_3$ + 1% $MgCO_3$.

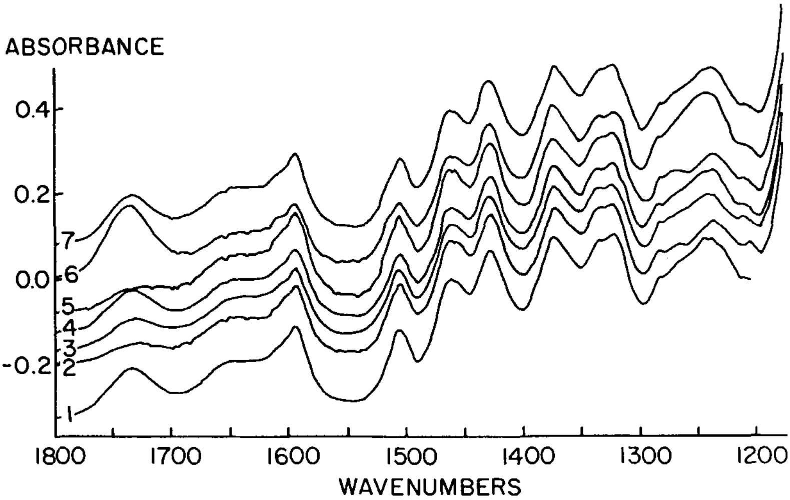

FIGURE 10. FTIR Spectra (in range from 1200 to 1800 cm$^{-1}$) of SEP Pulps with Various Impregnation Solutions: 1) 8% $Na_2SO_3$; 2) 8% $Na_2SO_3$ + 1% NaOH, after Mild Acid Wash; 3) $Na_2SO_3$ + 1% $NaHCO_3$; 4) 2% $H_2O_2$ -- 6% $Na_2SO_3$; 5) 3% NaOH + 1% $NaCl_2$, after Mild Acid Wash; 6) No Chemicals; 7) 8% $Na_2SO_3$ + 1% $MgCO_3$.

pulps. The decrease of these bands implies the partial elimination of the xylan by deacetylation and/or of the uronic acid groups during the steam explosion cooking process. This may be because the xylan is easily dissolved under alkaline conditions. However, loss of intensity at 1735 cm$^{-1}$ need not be attributed entirely to the removal of acetyl and uronic acid groups, since the absorption of the carbonyl group may shift from 1735 cm$^{-1}$ to 1600 cm$^{-1}$ by salt formation, where it could be obscured by bands raising from moisture (H-OH bending), or from lignin ($\alpha$-keto carbonyl or C=C vibration of benzene ring)[27,31]. To verify whether or not this is the case, the spectra of these two pulps were recorded following a mild acid wash. The absorption band at 1735 cm$^{-1}$ was still very week (see Fig. 10), which confirms the elimination of both the uronic acid group and xylan. The band at 1235 cm$^{-1}$ due to C-O stretching vibration of acetyl and carboxyl in xylan slightly diminished with a drop in intensity of the band at 1735cm$^{-1}$. These results are in agreement with those observed in the spectra of microtomed sections of wood submitted to a neutral sulfite semichemical treatment[27]. Therefore, the diminution in the intensity of bands at 1735 and 1235 cm$^{-1}$ implies the partial elimination of xylan. This explains that pulps using 8% $Na_2SO_3$ + 1% NaOH and 3% NaOH + 1% $MgCl_2$ as an impregnation solution had a lower yield and higher lignin content compared to other pulps.

The bands at 1593 and 1504 cm$^{-1}$ ascribed to C=C stretching vibration in the benzene ring[26,27,31] showed little significant variation, but the bands at 1593 and 1504 cm$^{-1}$ showed some for pulps using 8% $Na_2SO_3$ + 1% NaOH and 3% NaOH + 1% $MgCl_2$ as an impregnation solution, which implied they had a slightly higher lignin content. These are in good agreement with the chemical analysis results.

## CONCLUSION

The impregnation agent should be chosen to provide an initial pH of 9-10 for the impregnation solution which normally leads to high-yield of SEP pulps. The presence of $MgCO_3$ can protect carboxylate against hydrolysis, oxidation and degradation during the steam cooking process when compared to $Na_2SO_3$ alone or other chemical systems which were studied, therefore resulting in a higher brightness and yield.

The presence of NaOH, $NaHCO_3$ or $MgCO_3$ compared to $Na_2SO_3$ alone or other chemical pretreatment examined in the present study led to a higher sulfonate and carboxylate content, although the bulk lignin content of SEP pulps showed little change. The physical strength and brightness of paper improved when the pulp exhibited a higher hydrophilic group content. On the other hand, a surface analysis showed that the presence of NaOH, $NaHCO_3$ or $MgCO_3$, when compared to $Na_2SO_3$ alone or other chemical systems which were studied, led to more carbohydrates and less lignin and extractives exposed on the fiber surface as well as to a higher degree of lignin sulfonation. This increased the exposure of hydrophilic groups on the fiber surface and facilitates hydrogen bonding during paper formation, which increased the bonding properties among fibers.

When using 8% $Na_2SO_3$ + 1% NaOH and 3% NaOH + 1% $MgCl_2$ as an impregnation solution, xylan was partially dissolved by deacetylation and/or removal of the uronic acid groups during the steam explosion cooking process. This is why these two pulps had a lower yield and higher lignin content compared to other pulps.

The bulk lignin content of SEP pulps was little affected by pulp pretreatment. A slightly higher lignin content was observed for the pulp prepared using 8% $Na_2SO_3$ + 1% NaOH or 3% NaOH + 1% $MgCl_2$ as impregnation solution.

## ACKNOWLEDGEMENT

We wish to thank the NSERC, Mechanical pulping Network of Center of Excellence, FCAR, Stake Technology Limited and Centre Spécialisé en pâte et papier of the CEGEP de Trois-Rivières for their financial support and/or cooperation.

## REFERENCES

1. Y. Ben, B. V. Kokta and J. Doucet, Cellulose '91, 408, New Orleans, Dec. 1991.
2. X. Hua, B. V. Kokta and S. Kaliaguine, Cellulose '91, 340, New Orleans, Dec. 1991.
3. C. Heitner, D. Atack, Pulp and Paper of Canada, 84(11), T252 (1983).
4. D.N.S. Hon, J. Appl. polym. Sci., 29,2777 (1984).
5. P. J. Mjöberg, Cell. Chem. Technol., 15, 481 (1981).
6. S. Takyama and D.G. Gray, Cell. Chem. Technol., 16, 133 (1982).
7. G. M. Dorris, D. G. Gray, Cell. Chem. Technol., 12, 9 (1978).
8. G. M. Dorris, D. G. Gray, Cell. Chem. Technol., 12, 721 (1978).
9. D. G. Gray, Cell. Chem. Technol., 12, 735 (1978).
10. A. Ahmed, A. Adnot and S. Kaliaguine, J. Appl. Polym. Sci., 34, 359 (1987).

11. A. Ahmed, A. Adnot, J. I. Grandmaison, S. Kaliaguine and J. Doucet, Cell. Chem. Technol., 21, 483 (1987).

12. A. Ahmed, H. Pakdel, C. Roy, and S. Kaliaguine, J. Anal. Appl. Pyrolysis, 14, 281 (1989).

13. A. O. Barry, Z. Koran and S. Kaliaguine, J. Appl. Polym. Sci., 39, 31 (1990).

14. D. P. Kamdem, B. Riedl, A. Adnot and S. Kaliaguine, J. Appl. Polym. Sci., 43, 1901 (1991).

15. S. Katz, R. p. Beatson and A. M. Scallan, Sven. Papperstidn., 87(6), R48 (1984).

16. S. Katz, R. and D. G. Gray, Sven. Papperstidn., 83(8), 226 (1980).

17. R. A. Young, R. M. Rammon, S. S. Kelley and R. H. Gillespie, Wood Sci., 3(14), 110 (1980).

18. A. Ahmed, A. Adnot and S. Kaliaguine, J. Appl. Polym. Sci., 35, 1909 (1988).

19. X. Hua, S. Kaliaguine, B. V. Kokta and A. Adnot, Accepted by Wood chemistry and Technology.

20. A. J. Michell, Cell. Chem. Technol., 22, 105 (1988).

21. S. M. Saad, R. M. Issa and M. S. Fahmy, Holzforschung, 34, 218 (1980).

22. R. H. Marchessault, S. Coulombe, H. Morikawa and D. Robert, Can. J. Chem., 60, 2372 (1982).

23. K. S. Kalasinsky, G. R. Lightsey, P. H. Short and J. R. Durig, Appl. Spectrosc., 44(3), 404 (1990).

24. Y. Ben, X. Hua, B. V. Kokta, S. Kaliaguine and J. Doucet, Accepted by China Pulp and Paper.

25. Standard CPPA testing methods, TAPPI, Atlanta, (1988).

26. TAPPI test methods, Technical section, Canadian Pulp and Paper Association, Montreal, (1991).

27. B. A. Lindberg, K. Harmin, U. Gelius, A. Fahlman, C. Nordling and K. Siegbahn, Physica Scripta, 1, 286 (1970).

28. C. Y. Liang, K. H. Bassette, E. A. McGinnes and R. H. Marchesseault, Tappi, 43(12), 1017 (1960).

29. A. J. Michell, A. J. Waston and H. G. Higgins, Tappi, 48 (9), 520 (1965).

30. N. M. Bikales, Cellulose and cellulose Derivatives, Part IV, Chapter 8, 1971.

31. J. L. Grandmaison, J. Thibault and S. Kaliaguine, Anal. Chem., 59(17), 2153 (1987).

32. H. G. Higgins, A. J. Michell and A. J. Waston, Appita, 20 (6), 126 (1967).