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MARIAN TOMASEC

EXPLOSION PULPING FOR PAPERMAKING: EFFECT OF COOKING PARAMETERS ON MECHANICAL AND OPTICAL PROPERTIES

(MISE EN PÂTE D'EXPLOSION POUR LA PRODUCTION PAPETIÈRE: EFFET DES PARAMÈTRES DE LA CUISSON SUR LES PROPRIÉTÉS MÉCANIQUES ET OPTIQUES)

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SUMMARY

The purpose of this work is to study and scientifically explain the principles of high severity pulping process. The thesis has the following objectives: to establish a correlation between cooking conditions (temperature, time, pressure) and the physicochemical fiber changes due to vapor phase cooking, to establish a correlation between fiber changes and resulting mechanical and optical properties and to determine the optimum cooking conditions in order to obtain required paper properties. In the first experimental series, we have established the importance of chemical impregnation for good fiber development. We found that the $Na_2SO_3/NaHCO_3$ impregnation system yielded an excellent pulp quality without any negative side effect, such as yield or brightness loss. A comparison with conventional high-yield pulps (RMP, CTMP, CMP) at the same chemical charge, yield and ionic content, showed that the explosion pulps had better mechanical and similar optical properties at much lower refining energy (up to 50%). The superiority of the explosion pulps can be attributed to the chemical changes (higher crystallinity, better lignin softening) that occur as a result of the high-temperature-high-pressure cook as well as to the physical changes (better and easier fiber separation) that occur following high severity cook and explosive discharge from the digester. Increasing the digester pressure to 25 atm prior to the explosion also led to better fiber separation and hence lowered the refining energy consumption. Mechanical properties of such treated pulps showed (compared to RMP, CTMP and CMP) improved breaking length, burst and tear indexes. The second experimental series confirmed the superiority of a two-chemicals impregnation system compared to no or one chemical impregnation. We found that increasing the pressure prior to the explosion gave the best results at lower cooking severity or insufficient chemical treatment. In the third

experimental series, the X-ray diffractometry confirmed higher quantities of cellulose I and thicker micelles with increasing pulping temperature. Other spectroscopies (FTIR, Raman) showed lignin restructuring, higher cellulose quality and hemicellulose hydrolysis. Surface analysis (ESCA...) showed better fibrillation and better surface quality (more cellulose, better surface sulfonation) with increasing severity of treatment. Statistical analysis showed a good correlation between cooking parameters (time, temperature and pressure) and resulting pulp characteristics and properties (yield, refining energy, mechanical properties). We were able not only to predict pulp properties from the cooking parameters, but also to estimate the cooking conditions needed to reach required paper properties. The correlation coefficient was higher than 90% for all the important parameters.

RÉSUMÉ

L'objectif de ce travail est de comprendre et d'expliquer scientifiquement les bases du fonctionnement du procédé de mise en pâte d'explosion et ce qui le distingue des autres procédés à très haut rendement. Ce travail comprend l'établissement d'une corrélation entre les paramètres de cuisson (température, temps, pression) et les changements physico-chimiques qui se produisent sur les fibres pendant la cuisson en phase vapeur. Il comprend aussi l'établissement d'une corrélation entre des changements physico-chimiques des fibres et les propriétés mécaniques et optiques des pâtes résultantes. La détermination des paramètres de cuisson optimales pour obtenir les propriétés papetières requises a aussi été effectuée. Dans la première partie de ce travail, nous avons établi l'importance de l'imprégnation chimique pour un bon développement des fibres. Le système Na_2SO_3/$NaHCO_3$ a donné de meilleurs résultats et ce, sans aucun effet négatif. En utilisant le même système d'imprégnation, la même charge chimique, et en se basant sur le même rendement et le même contenu ionique, les pâtes d'explosion, en comparaision avec des procédés classiques (pâte mécanique de raffineur, pâte chimico-mécanique et chimico-thermomécanique) ont consommé moins d'énergie de raffinage (jusqu'à 50%) et exhibé de meilleures propriétés mécaniques. Les meilleures performances obtenues s'expliquent par une meilleure sulfonation, des fibres plus longues et plus flexibles dans les pâtes d'explosion et une plus grande quantité de cellulose I ordonnée. L'augmentation de la pression avant l'explosion a aussi permis de diminuer l'énergie de raffinage et d'améliorer les propriétés mécaniques. La deuxième série d'expériences a prouvé qu'une explosion à 25 atmosphères peut avoir des effets bénéfiques lorsque la sévérité du traitement est plus faible ou que le traitement chimique soit insuffisant (un seul agent d'imprégnation). La

troisième série d'essais a confirmé la supériorité des pâtes d'explosion par rapport des pâtes chimico-mécaniques et chimico-thermomécaniques. L'analyse de diffraction aux rayons X a confirmé la présence d'un taux plus élevé de cellulose ordonnée et de plus grands cristaux. Les spectroscopies (infrarouge, FTIR, Raman) ont montré une restructuration de la lignine, une meilleure qualité de cellulose et une hydrolyse des hémicelluloses. L'analyse de la surface (ESCA...) a montré une meilleure fibrillation des surfaces des fibres explosées. Aussi, la surface des pâtes d'explosion a été plus riche en cellulose et en ions sulfoniques, ce qui contribue grandement au développement des propriétés mécaniques. L'analyse statistique a montré une très bonne corrélation entre les paramètres de cuisson (température, temps, préssion) et les charactéristiques et les propriétés des pâtes résultantes (rendement, énergie du raffinage, propriétés mécaniques). On peut donc prédire non seulement les propriétés mécaniques et l'énergie de raffinage, mais aussi les conditions de cuisson nécessaires pour obtenir une qualité de papier donnée. Le coefficient de corrélation a été 90% ou plus pour tous les paramètres importants.

RÉSUMÉ SUBSTANTIEL

L'industrie forestière et papetière constitue la plus importante industrie du pays. L'industrie canadienne des pâtes et papiers compte environ 75 sociétés regroupant plus de 140 usines. Elle occupe le premier rang des producteurs mondiaux de papier journal.

La production des pâtes mécaniques et chimico-mécaniques a été développée pour économiser le bois et les produits chimiques. Les avantages de ces procédés comparativement avec les procédés kraft et sulfite sont: un rendement plus élevé, une meilleure blancheur et, généralement une utilisation moindre de produits chimiques pour la fabrication de la pâte. D'un autre côté, les propriétés mécaniques de ces pâtes sont généralement inférieures à celles des pâtes à bas rendement, ce qui empêche leur utilisation dans plusieurs domaines. Suite à ce constat, de nombreux chercheurs ont travaillé au développement et au rehaussement des propriétés des pâtes à haut et très haut rendement. Le but visé était de développer des pâtes compétitives avec les pâtes chimiques. Une des possibilités dans ce cheminement est la mise en pâte d'explosion.

La mise en pâte d'explosion pour la production papetière est un nouveau procédé proposé par Kokta et ses collaborateurs. Cette technique représente la poursuite des travaux effectués par d'autres chercheurs (Mason, Asplund, Mamers...), qui ont connu une certaine réussite avec diverses versions de la mise en pâte d'explosion. Malheureusement, les propriétés mécaniques des pâtes, ainsi obtenues, n'étaient pas suffisantes pour la production papetière.

Le procédé suggéré par Kokta augmente la résistance mécanique des pâtes d'explosion, aux niveaux égales ou supérieurs à ceux des procédés à haut rendement classiques (pâtes mécaniques de raffineur (PMR), pâtes chimico-mécaniques (PCM) et chimico-thermomécaniques (PCTM)). Dans certains cas, certaines des propriétés obtenues sont même comparables avec celles des procédés à bas rendement (kraft). De plus, les pâtes d'explosion exigent environ la moitié moins d'énergie du raffinage que celles produites par les procédés PCTM et PCM.

Le procédé de mise en pâte d'explosion consiste en une imprégnation chimique des copeaux (classiques ou déchiquetés), suivie d'une cuisson de courte durée (1 à 5 minutes) en phase vapeur à des températures variant entre 180 et 210°C. La cuisson est suivie d'un relâchement brusque de la pression (explosion) et d'un raffinage classique. La pâte produite peut être blanchie, au besoin.

Le traitement de haute sévérité peut être évalué de deux points de vue: premièrement, on peut examiner l'influence des paramètres de cuisson (haute température - haute pression - courte durée) sur les trois constituants du bois (lignine, cellulose, hemicelluloses) ou deuxièmement, on peut évaluer l'influence de chacune des étapes de cuisson (préchauffage, cuisson, explosion) sur la qualité et les propriétés de la pâte finale.

L'influence de la température élevée sur la production de la pâte, comparativement avec celle des procédés PCM et PCTM, est la suivante: La température étant au-dessus de la température de transition vitreuse de la lignine mène celle-ci à un ramollissement additionnel permanent. Les pâtes d'explosion sont bien ramollies et facilement raffinables (l'énergie de raffinage est jusqu'à 50 % plus faible en comparaison à l'énergie des PCM et PCTM). Les fibres sont aussi plus longues et plus flexibles, ce qui augmente la capacité de liaison et contribue à l'augmentation des propriétés mécaniques.

Cependant, à cause de la courte durée de la cuisson, la température élevée ne cause pas l'hydrolyse de la cellulose à grande échelle. Au contraire, cette haute température mène à l'augmentation du degré de cristallinité et augmente la longueur des micelles. Plusieurs travaux ont prouvé, que c'est l'influence de

la haute température et de la pression (et non l'explosion), qui augmente la cristallinité. Par les méthodes d'analyse physico-chimiques, on a trouvé, que la cellulose change aussi sa structure de cristallinité (Ib à la ou la').

L'explosion joue aussi un rôle important dans le procédé de mise en pâte d'explosion. La décharge explosive pendant les essais semi-industriels a permis de libérer 37% des fibres, tandis que les fibres restantes étaient facilement raffinables. En effet, la consommation d'énergie était de beaucoup inférieure à l'énergie de raffinage des PCM et des PCTM. Les effets de l'explosion ont été aussi étudiés par Tanahashi. Il a prouvé, que l'explosion ne libère pas seulement les fibres, mais que l'explosion était aussi trouvée dans les fibres mêmes. De plus, Kosik a montré (par la méthode de sorption d'azote), que la surface spécifique de la pâte d'explosion (autour de 8 m^2/g pour une pâte de tremble, indice d'égouttage 100 ml CSF, rendement 90%) a été deux fois supérieure à celle des pâtes commerciales. Si on fait la cuisson sous les conditions optimales, l'explosion diminue l'énergie de raffinage et augmente les propriétés papetières.

L'objectif de ce travail est de comprendre et d'expliquer scientifiquement la base sur laquelle la mise en pâte d'explosion fonctionne, ce qui la distingue des autres procédés à très haut rendement, et à partir de résultats expérimentaux, justifier les hypothèses posées.

Les recherches, constituant cette thèse doctorale, visent à:

1. L'établissement d'une corrélation entre les conditions de cuisson (température, temps, pression) et les changements physico-chimiques, qui se produisent sur les fibres pendant la cuisson en phase vapeur;

2. L'établissement d'une corrélation entre les changements physico-chimiques sur les fibres et les propriétés mécaniques et optiques résultantes;

3. L'établissement de la cinétique de création du contenu ionique et son influence sur les propriétés papetières;

4. La détermination des conditions de cuisson optimales pour obtenir les propriétés requises.

Mode d'approche.

Plusieures séries d'essai ont été entrepris:

Le but de la **première série d'essais** était de comparer la qualité des pâtes d'explosion avec des pâtes obtenues par des procédés classiques (PMM, PCTM, PCM). Les conditions de cuisson ont été fixées de façon à ce que le rendement et le contenu ionique soient les mêmes ou semblables. Les pâtes d'explosion ont été préparées aussi en pressurisant le réacteur avant l'explosion (sous azote) pour évaluer l'influence de la pression.

Les pâtes préparées avec 8% de Na_2SO_3 ont un rendement de 90%. La seule exception était la pâte PCTM dont le rendement a été de 93%. Pour fin de comparaison avec cette pâte nous avons aussi préparé une pâte d'explosion à ce même rendement. Même si le contenu ionique était le même pour toutes les pâtes, les pâtes d'explosion ont eu un taux de sulfonation plus élevé (une meilleure sulfonation diminue le caractère hydrophobe de la lignine ce qui peut mener à l'amélioration des propriétés mécaniques). Tel que nous l'avions remarqué par des recherches précédentes, nous avons enregistré la diminution d'énergie de raffinage avec la hausse de la sévérité du traitement. En comparaison avec les PCTM et PCM, les pâtes d'explosion ont demandé en moyenne la moitié moins d'énergie de raffinage. Dans le cas des pâtes d'explosion, l'augmentation de la température de 190 à 200°C a diminué l'énergie de raffinage de 10% (de 4 à 3.6 MJ/kg). L'analyse Bauer-McNett (la longueur moyenne des fibres) a demontré que les fibres des pâtes d'explosion sont plus longues (au moins 10%) que les fibres de PCTM et PCM. Cependant, grâce au ramollissement supplémentaire de la lignine, les fibres explosées sont plus flexibles telles que mesurées par la densité des pâtes d'explosion. Une plus grande densité et une meilleure sulfonation rendent le contact des fibres plus efficace. Le coefficient de diffusion de la lumière qui représente la surface non liée l'a aussi démontré. Ce coefficient a été plus

grand dans le cas de la pâte de raffineur et il a diminué avec l'augmentation de la sévérité de la cuisson: PMM > PCTM > PCM > pâtes d'explosion.

Les changements chimiques résultant des cuissons à haute température ont été évalués par spectroscopie infrarouge (FTIR). En utilisant le modèle cellulosique de Sukhov (quatre composants: cellulose I ordonnée, cellulose I désordonnée, cellulose II ordonnée et cellulose II désordonnée), nous avons trouvé que les échantillons des pâtes d'explosion ont une teneur en cellulose I plus élevée. La cellulose I est le matériel le plus bénéfique pour obtenir une bonne qualité de papier. En effet, le caractère et l'orientation des groupements hydroxyliques (OH) permet une très bonne création interfibrillaire des liens hydrogènes, ce qui contribue très fortement au développement des resistances mécaniques.

Le résultat de ces changements physiques et chimiques sur les pâtes d'explosion fut l'obtention de meilleurs paramètres mécaniques. Toutes les propriétés mesurées: la longueur de rupture, l'indice de déchirure, l'indice d'éclatement et d'allongement ont été nettement supérieurs dans le cas des pâtes d'explosion. En ce qui concerne les propriétés optiques, la plupart des pâtes ont démontré une blancheur de 60% MgO ou plus. La seule exception était la pâte d'explosion à l'eau (sans imprégnation chimique). Les fibres de cette pâte étaient couvertes par la lignine. La pâte ainsi obtenue était foncée et sa blancheur était d'environ 42% MgO. La réponse au blanchiment a été bonne pour toutes les pâtes et la hausse de la blancheur pour chaque pâte a été autour de 20%. L'opacité des pâtes d'explosion a été un peu inférieure aux autres pâtes, ce qui peut s'expliquer par sa meilleure densité et un meilleur coefficient de diffusion de la lumière.

Dans cette série d'essais, nous avons aussi évalué l'influence de la pression. Pour les trois pâtes d'explosion préparées (à 190°C/2 minutes, à 195°C/1.5 minute et à 200°C/1 minute), nous avons répété l'expérimentation, mais cette fois avec une explosion beaucoup plus forte (25 atmosphères au lieu de 11.5 à 15.5 atm). Pour les trois pâtes testées, nous avons amélioré les propriétés mécaniques et diminué l'énergie de raffinage.

Une autre importante partie de cette série d'essais était l'évaluation de plusieurs systèmes d'imprégnation. Les comparaisons entre les pâtes d'explosion et les pâtes classiques (PCTM, PCM) ont été effectuées en utilisant le système typique de l'industrie soit 8% Na_2SO_3. Nous avons aussi préparé des pâtes d'explosion sans aucune imprégnation chimique (explosion à l'eau) et avec un système à deux agents chimiques: Na_2SO_3/NaOH (pâte de soude) et Na_2SO_3/$NaHCO_3$ (pâte de bicarbonate). La pâte d'explosion à l'eau n'a pas démontré de bonnes qualités. En l'absence d'imprégnation chimique les fibres ont été couvertes par la lignine et les propriétés mécaniques ont été médiocres. Cependant, l'ajout d'un autre agent d'imprégnation a toujours apporté des changements importants. La soude est aussi populaire dans certains procédés industriels. La qualité des fibres a été excellente. Nous avons alors enregistré la meilleure longueur des fibres et les meilleurs paramètres mécaniques. Cette pâte (blanchie ou non) a même surpassé la qualité de la pâte kraft (à bas rendement) de tremble. La désavantage de l'utilisation de soude comme deuxième agent d'imprégnation est au niveau de la perte de rendement (de 90 à 83%) ainsi que de la perte de la blancheur.

Plusieurs chercheurs ont suggéré le bicarbonate de sodium comme agent de remplacement pour la soude. Notre expérimentation a confirmé cette hypothèse: la pâte avec le système Na_2SO_3/$NaHCO_3$ n'a pas perdu de rendement (on a resté autour de 90%) ni de blancheur (60%). Ainsi en comparant cette pâte avec celles préparées avec un seul agent d'imprégnation, ce système amélioré a diminué la consommation d'énergie de raffinage et a augmenté la sulfonation. Les résistances mécaniques ont aussi augmenté de façon très significative.

La **deuxième série d'essais** a été effectuée pour évaluer l'influence de la pression. Un système à deux agents d'imprégnation a été utilisé (on a montré auparavant que le système d'imprégnation Na_2SO_3/$NaHCO_3$ était plus efficace que le Na_2SO_3 seul et ce, sans baisse de rendement ou de blancheur). Cinq pressions différentes ont été utilisées pour couvrir l'intervalle entre la pression correspondante à la pression de la vapeur saturée pour la température de la cuisson et la pression de 25 atm.

Dans cette série, nous avons travaillé avec le système d'imprégnation amélioré. L'effet de l'ajout d'un autre agent d'imprégnation a causé une hausse du contenu sulfonique, des propriétés mécaniques, de la blancheur et a diminué la consommation de l'énergie de raffinage. Quant à l'influence de la pression, nous n'avons pas vu de changements aussi importantes que dans la première série d'essais. Pour la plupart des paramètres, la qualité était identique dans les deux cas: explosion ordinaire et explosion de 25 atm. L'effet de l'explosion pressurisée a été significatif seulement pour la longueur de la rupture et l'indice d'éclatement. Pour des conditions de 190°C/2 minutes, nous avons amélioré la longueur de la rupture de 8.6 à 9.5 km et pour 195°C/1.5 minute, ce paramètre a augmenté de 7.5 à 8.2 km. La similitude des valeurs obtenues pour les autres paramètres peut être expliquée par la présence du nouveau système d'imprégnation (deux agents chimiques). Dans la première série (un agent chimique) la plupart des qualités papetières n'ont pas été aussi bien développées qu'avec le système de deux agents chimiques. Il y avait donc beaucoup plus de possibilités d'amélioration des propriétés. Dans la deuxième série, l'effet de l'explosion pressurisé a été probablement diminué par l'ajout de bicarbonate. Le bicarbonate a tellement augmenté la valeur de certains paramètres, que l'influence de l'explosion a été négligeable. Cependant, la qualité de toutes les pâtes a été excellente.

Pour la **troisième série** d'essais, nous nous sommes concentrés sur les paramètres de la cuisson suivants: - la température, le temps et la pression. Pour bien évaluer l'influence de la sévérité, l'expérimentation a été planifiée sur trois niveaux complets pour deux variables (la température et le temps) et pour certains niveaux pour l'autre variable (pression). Ces expériences avec douze pâtes d'explosion ont couvert la majorité de l'intervalle de mise en pâte d'explosion, tel que définie dans les brevets. Le plan d'expérimentation comprenait aussi quatre pâtes de référence.

Le but de cette série était de travailler non pas seulement autour de l'optimum proposé dans la littérature mais aussi d'étudier les phénomènes présents dans les extrémités. En ce qui concerne les résultats, la qualité de toutes les pâtes obtenues a été un peu moins bonne que dans les séries précédentes. Nous pensons, que ceci a été causé par la moins bonne qualité des copeaux de tremble utilisé. Par contre, si on compare les pâtes d'explosion et les pâtes

classiques, nous sommes arrivés aux mêmes tendences que dans la première série. Les pâtes d'explosion ont eu une meilleure sulfonation, de meilleures propriétés des fibres (densité, LSC, porosité, longueur, facteur S...). Elles ont aussi demandé considérablement moins d'énergie de raffinage. Les propriétés mécaniques (longueur de rupture, indice d'éclatement et de déchirure, élongation...) ont aussi été supérieures en comparaison avec les pâtes chimico-thermomécaniques et chimicomécaniques.

Si on se concentre sur les pâtes d'explosion, on peut arriver aux conclusions suivantes:

- Le rendement des pâtes diminue proportionnellement avec la sévérité du traitement. Les conditions les moins sévères (180°C/1 minute) ont permis d'obtenir un rendement de plus de 90%, tandis que les conditions les plus sévères (200°C/4 minutes) ont diminué le rendement jusqu'à 83%.

- La chute de rendement a été causée majoritairement par l'hydrolyse des hémicelluloses. Les analyses ont prouvé que la teneur en lignine (méthode de Klason) fut la même dans la plupart des échantillons. Plusieurs autres analyses (diffractométrie des rayons X, spectroscopies diverses) ont montré que la quantité de cellulose est demeurée la même.

- L'hydrolyse des hémicelluloses a aussi été documentée concernant le contenu ionique. Les groupements COOH des hémicelluloses sont les constituants majeurs du contenu carboxylique. Leur diminution a confirmé la théorie que l'hydrolyse est la réaction la plus rapide dans les conditions de traitement de haute sévérité. D'autre part, la teneur en ions sulfoniques a augmenté pour la plupart de l'intervalle de l'expérience. C'est seulement dans les conditions extrêmes, que le contenu sulfonique a commencé à diminuer. Ceci s'explique par l'hydrolyse partielle des groupements sulfoniques ainsi que par les réactions de la lignine.

- Les propriétés des fibres ont été améliorées avec chaque hausse de sévérité du traitement. Ceci était un peu surprenant. On avait plutôt prévu que la qualité de la pâte augmenterait jusqu'à un certain optimum et qu'on assisterait à une chute des propriétés pour des conditions de traitement trop

fortes. Lors de nos essais, la meilleure qualité de la pâte a été obtenue pour des conditions de 200°C/4 minutes. Si on parle des propriétés des fibres, le coefficient de diffusion de la lumière était très près de ceux obtenues avec des pâtes chimiques dont le rendement est beaucoup plus bas (presque deux fois moindre). De plus, les résistances mécaniques étaient meilleurs pour les plus grandes sévérités de traitement.

- En ce qui concerne l'explosion pressurisée (à 25 atm), nous avons trouvé que son influence était plus grande pour les conditions de traitement les plus légères (180°C/1 minute). Dans plusieurs cas, l'augmentation de la pression avant l'explosion a eu le même effet que le temps de cuisson doublé. Pour ce qui est du point central (190°C/2 minutes), nous avons vu une légère amélioration de longueur de rupture et pour les conditions les plus sévères, l'explosion pressurisée n'a pas changé les propriétés papetières. Ceci confirme les conclusions des séries précédentes. L'explosion à 25 atmosphères peut avoir des effets bénéfiques à condition que la sévérité de traitement soit faible ou que le traitement chimique soit insuffisant.

Pour expliquer la meilleure performance des pâtes d'explosion, nous avons effectué plusieurs analyses supplémentaires. L'analyse de diffraction aux rayons X a confirmé l'augmentation de la cellulose, de sa cristallinité et de la grandeur des micelles. Comme nous l'avons expliqué dans la première série d'essais, la cellulose I ordonnée représente la meilleure qualité de cellulose pour la formation des liens entre les fibres. Les bonnes propriétés de la surface et la meilleure fibrillation ont été confirmées par de plus grandes valeurs de rétention d'eau. Ces valeurs ont augmenté avec la hausse de sévérité. L'explosion pressurisée a aussi amélioré ce paramètre de 15% (dans tous les cas). Ceci montre que l'explosion est bénéfique pour la fibrillation interne.

L'analyse ESCA a montré des différences très importantes de qualité de surface. En comparaison avec le bois ou les pâtes classiques, les pâtes d'explosion ont un plus grand pourcentage de cellulose sur la surface des fibres. La lignine a aussi été sulfonée plus fortement sur la surface des fibres explosées. Les effets principaux contribuant au développement des propriétés mécaniques sont une meilleure qualité et quantité de cellulose et une plus

grande quantité d'ions sulfoniques sur la surface. Cette analyse explique donc pourquoi un traitement plus sévère rend la pâte de meilleure qualité.

L'analyse statistique a montré une très bonne corrélation entre les paramètres de cuisson (température, temps, préssion) et les charactéristiques et les propriétés des pâtes résultantes (rendement, énergie du raffinage, propriétés mécaniques). On peut donc prédire non seulement les propriétés mécaniques et l'énergie de raffinage, mais aussi les conditions de cuisson nécessaires pour obtenir une qualité de la feuille donnée. Le coefficient de corrélation a été 90% ou plus entre les paramètres les plus importants.

En conclusion, ce travail a démontré que le procédé de mise en pâte d'explosion est une technologie vraiment prometteuse. La cuisson à une haute sévérité peut produire une pâte avec le même rendement que les procédés conventionnels (pâtes chimico-thermomécaniques et chimico-mécaniques). En utilisant le même traitement chimique, les pâtes d'explosion utilisent jusqu'à 50% moins d'énergie de raffinage. Avec un système d'imprégnation plus développé (Na_2SO_3/$NaHCO_3$), les pâtes d'explosion économisent davantage d'énergie de raffinage et améliorent les propriétés mécaniques. La meilleure qualité et les meilleures propriétés mécaniques des pâtes d'explosion sont expliqués par la meilleure qualité des fibres. En comparaison avec les fibres préparées par des procédés classiques, les fibres des pâtes d'explosion sont plus longues, plus flexibles et leur qualité de surface est aussi supérieure.

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LIST OF SYMBOLS AND ABBREVIATIONS

Å	Angström
AQ	Antraquinone
atm	Atmosphere
CMP	Chemimechanical pulp
CP	Cross polarization
CPPA	Canadian Pulp and Paper Association
Cr	Crystallinity
CSF	Canadian Standard freeness
CTMP	Chemi-thermomechanical pulp
d	Distance
Eb	Binding energy
Ek	Kinetic energy
ESCA	Electron spectroscopy for chemical analysis
eV	Electronvolt
EXP	Explosion, exploded
FTIR	Fourier transform infrared spectroscopy
g	Gram
GC	Gas chromatography
h	Hour
IR	Infrared
J	Joule
K	Kelvin
l	Litre
LC	Liquid chromatography
LSC	Light-scattering coefficient
L/W	Liquor to wood ratio

m	Meter
MAS	Magic angle spinning
min	Minute
MS	Mass spectroscopy
N	Newton
N-EXP	Nitrogen explosion
NMR	Nuclear magnetic resonance
Pa	Pascal
Paprican	Pulp and Paper Research Institute of Canada
ppm	part per million
PTLC	Preparative thin-layer chromatography
RMP	Refiner mechanical pulp
RSRE	Relative specific refining energy
SEM	Scanning electron microscopy
SEP	Steam explosion pulp (or pulping)
TAPPI	Technical Association of the Pulp and Paper Industry
TEM	Transmission electron microscopy
T_g	Glass transition temperature
TMP	Thermomechanical pulp
UHY	Ultra high yield
UM	Useful method (Recommended by TAPPI)
W-EXP	Water explosion (no chemicals added)
WRV	Water retention value
°C	Degree Celsius

1. INTRODUCTION

Ultra-high yield (UHY) pulping represents pulping processes with yield over 85% and serves the papermaking industry and our society basically by excellent wood mass valorization. These processes usually involve one or several of the following operations: wood or chip grinding, refining, thermal and/or chemical treatment. Commercially used processes for papermaking purposes produce different pulp types, known as the refiner mechanical pulp (RMP), thermomechanical pulp (TMP), chemi-thermomechanical pulp (CTMP) and chemimechanical pulp (CMP). Main outcome of these processes is an ultra-high yield pulp with reasonably good mechanical and optical properties accompanied by reduction in environmental pollution (water and air, compared to low yield processes). However, there are several drawbacks limiting the use of UHY pulps:

- limited mechanical properties. Ultra-high yield pulps conserve large majority of original wood components. As compared to chemical pulps which consist from highly delignified fibers with excellent bonding capacity, the fibers are usually less flexible and do not bond as well as in chemical pulps.

- color reversion. Most mechanical pulps can be bleached to excellent brightness levels, but their brightness decreases with time.

- very high refining energy consumption.

- preference for the softwoods. Conventional mechanical processes work best with softwood species because of the long fiber length, thin cell walls, high fiber uniformity and low amounts of non-fibrous material.

The research in the field of ultra-high yield pulping faces an uneasy task - finding solutions to the above mentioned deficiencies. One of the possible ways (other than improving existing processes) is to work at high severity pulping conditions (high cooking temperature and pressure) which, according to the literature review, can provide pulps with excellent mechanical and optical properties, consumes less refining energy and is adaptable to hardwood and softwood species.

1.1 PRESENTLY USED AND STUDIED HIGH SEVERITY PULPING PROCESS

In its essence, high severity pulping is not a new approach. In the past, there has been a number of pulping trials implementing high temperature, high pressure and/or explosive pulp release. Mostly known and still industrially employed are processes based on discoveries by Mason [1 to 7] and Asplund [8]. However, masonite process, working at temperatures up to 265°C diminishes fiber quality [9] and the use of masonite pulp is basically limited to insulating panels and boards. The Asplund's system (the Defibrator process) with its high temperature defibration does not have larger application scale, either. Neither of these processes is capable to produce pulp with acceptable papermaking quality. More recently, a series of projects carried out in Australia [10 to 18]. They showed more promising results using both annuals and wood. A feasibility study based on a 200 ton/day plant [11] showed good economy perspectives.

Present research in the high severity treatment can be divided into several areas:

- wood fibres separation, characterization of morphological and chemical changes and/or secondary chemical treatment of basic wood components
- ultra-high yield pulping that would produce an excellent quality pulp at a 90%+ yield
- pulp recycling and deinking

In any of the above areas, good progress was made in recent years. In our review, we shall focus on high severity pulping for papermaking i.e. the process development, the changes due to high temperature, high pressure and explosive discharge and the characterization of these changes and their influence on final pulp and paper quality.

Most of the publications came from The UQTR Pulp and Paper Research Center in Trois-Rivières, Canada. UQTR made a major contribution in this field and defined the high severity pulping (V-pulping, S-pulping, Steam explosion

pulping, Explosion pulping, SEP description names were also used in some references) as a process that can produce a papermaking ultra-high yield quality pulp [19 to 28]. Various wood species were used, such as the aspen [29 to 72], birch [29, 55 to 57, 66, 73, 74], eucalyptus [10, 11, 13, 17, 29, 36, 66, 75 to 79], maple [29, 36, 56, 61, 62, 66], pine [12, 54, 79, 80], spruce [31, 36, 54, 61, 62, 65, 66, 81 to 89], fir [31, 36, 61, 62, 66, 90], oak [56], beech [56], larch [91 to 93], cypress [93], hickory [56], kenaf [14, 18, 94, 95], rice straw [14, 96], wheat straw [14, 16], bagasse [14, 16, 95, 97, 98], flax [17, 95], bamboo [48, 99, 100] and their mixtures.

1.2 STEAM EXPLOSION PULPING PROCESS AS DEFINED AT THE UQTR

The process (as depicted on Figure 1.1) consists of the following steps:

- chip impregnation
- presteaming
- high temperature/high pressure/short time cooking
- sudden pressure release (explosion, but slow pressure release is also possible)
- pulp washing
- refining

If necessary, optional bleaching may be added to the process.

1.2.1 CHIP IMPREGNATION

As the cooking time at high temperatures is relatively short (0.5 to 5 minutes), deep and uniform impregnation is essential for good pulp quality. Generally, two different methods are used: soak impregnation for laboratory trials and press-impregnation for semi-industrial trials. The latter type has several advantages: at the compression ratio 4:1 (the chips are comprised to one fourth of their original volume), most of the air leaves the system making thus space for impregnation liquor absorption. Furthermore, at this pressure the chips undergo a certain degree of mechanical destruction as well [83]. Created cracks and openings (mostly between fibers in the middle lamella) do not cause any harm to fibers. On the contrary, they increase chip porosity and help the impregnation solution to penetrate more evenly. Not to waste any chemicals, Stake Tech system [59] has a second compression before the chips enter the digester. During this compression, about 50% of the impregnation solution can be recovered and reused without any additional treatment.

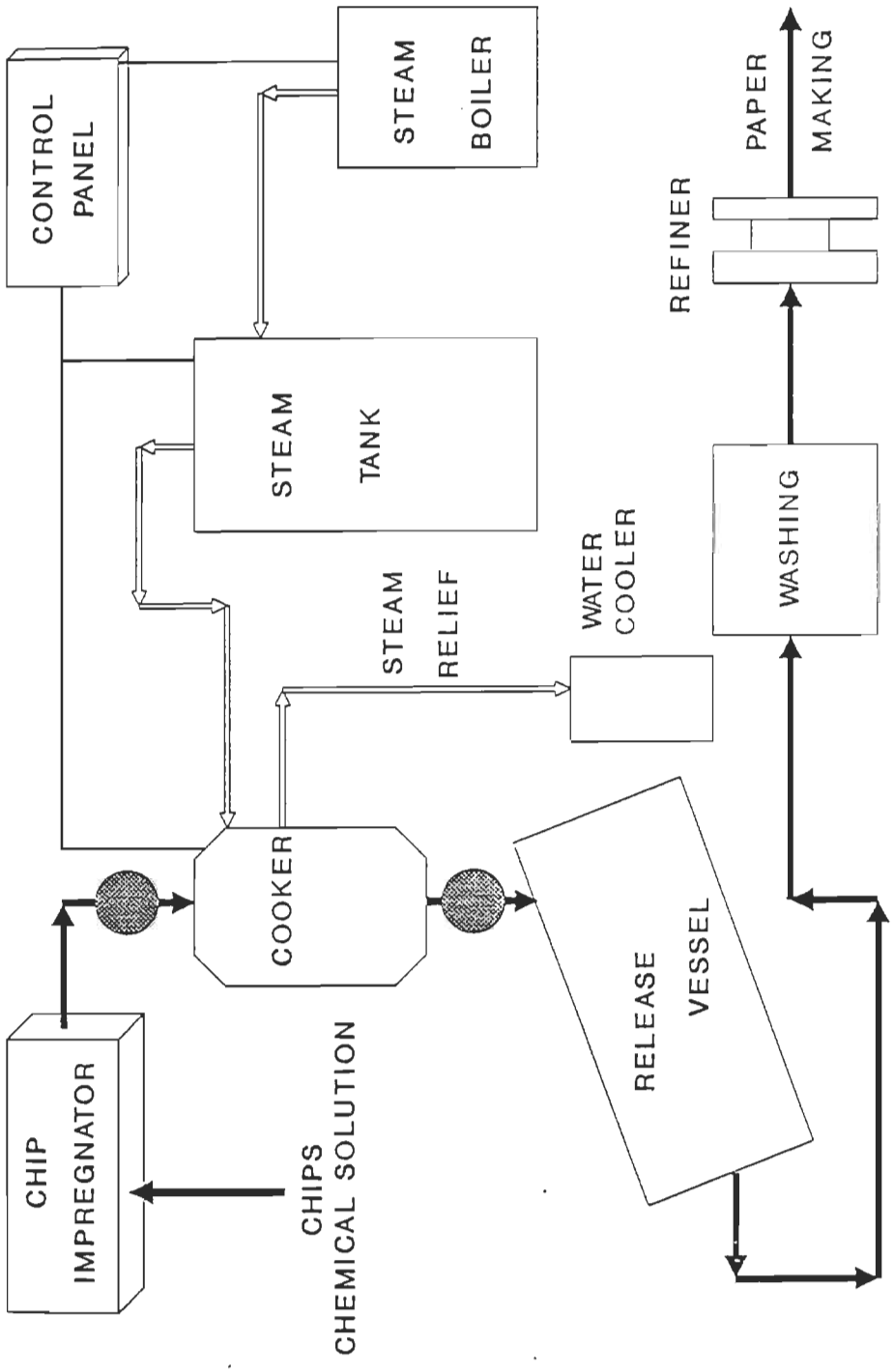


FIGURE 1.1 Schematic diagram of Steam explosion apparatus at the UQTR

Soak impregnation used in the laboratory trials is less effective and the impregnation time is also longer - about 24 hours.

1.2.2 IMPREGNATION CHEMICALS

The goal of impregnation is to introduce cooking chemicals into the fibers. In high yield pulping, high severity or regular, the most commonly used agent by far is sodium sulfite [13, 14, 31 to 49, 52 to 55, 59 to 70, 72, 76, 78, 79, 81 to 83, 85, 87 to 89, 94, 96 to 105]. It protects chips from oxidation reactions, sulfonates the lignin (increasing its hydrophylicity) and even protects pulp brightness (by eliminating the carbonyls from coniferylaldehydes) [105]. An addition of a second chemical agent can often have additional beneficial effect. Sodium hydroxide is the most favorite second cooking chemical [12 to 14, 16,17, 29, 30, 32, 34 to 40, 45, 47, 50, 51, 53 to 55, 58, 59, 62 to 66, 68 to 70, 76 to 79, 88, 89, 94, 96 to 104, 106 to 108]. It helps increasing the mechanical properties, and degree of sulfonation with a reduction in refining energy. On the other hand, it reduces pulp yield and often provokes darkening.

In cooking process (mostly high severity), much research has been done in order to replace NaOH with more suitable chemicals (with or without Na_2SO_3), such as: $NaHCO_3$ [12, 39, 42, 44, 53, 58, 64, 68, 88, 89, 96, 98, 106], Na_2CO_3 [39, 42, 44, 53, 64, 88, 89, 96, 98, 106], $MgCO_3$ [39, 43, 58, 68], $MgCl_2$ [39, 68, 106], $ZnCl_2$ [39], H_2O_2 [39, 68, 108], Na_2S [12, 39, 68], SO_2 [10, 11], CO_2 [12], NH_3 or NH_4OH [11, 14, 56, 57, 74], H_2SO_4 [75], AQ [65, 99, 109], percarbonate [110], metabisulphite [96, 98, 100], ammonium bisulphite [10], magnesium bisulphite [10], urea [10, 14] and others. Due to environmental protection, sulfur-free trials were also carried out and compared to conventional cooks [51, 106].

As a result, one of the best replacements for NaOH is sodium bicarbonate. It provides same benefits without sacrifying yield, properties or brightness. One of the reasons why $NaHCO_3$ works so well is its pH. Previous studies indicated [39] that if pH drops below 9.0, weaker sheets with lower brightness result, while a pH over 10.0 causes a drop in yield and pulp darkening. $NaHCO_3$ at most concentration levels fitted the balanced range between 9 and 10.

1.2.3 COOKING

1.2.3.1 PRESTEAMING

To increase chip temperature and to eliminate the air from the system, an atmospheric presteaming precedes the cook. In the laboratory, chips already placed in the reactor are flushed during 1 minute and in the semi-industrial trials the presteaming takes about 20 minutes.

1.2.3.2 COOK

The process developed at the UQTR is patented for temperatures from 180 to 210°C. The most often used conditions are usually between 190 and 200°C. Cooking pressure corresponds to cooking temperature and can be determined by the saturated steam pressure at given cooking temperature: 9.9 atm for 180°C, 11.9 atm for 190°C and 15.5 atm for 200°C. Cooking time is quite short and usually ranges between 1 and 4 minutes. The higher is the cooking temperature, the shorter is the cooking time, conforming with the Arhenius' kinetic laws. Wood species also influence cooking time. Softwoods, due to the different lignin content and different morphology, as well as species with high wood density require somewhat longer cooking time.

Some other authors [46, 47, 82, 86] tried cooking at these very high temperatures up to 9 minutes. As a result, they obtained lower yields and sometime, lower properties.

If the process is based on the use of chemicals other than Na_2SO_3, cooking conditions vary accordingly. For CO_2, SO_2 and NH_3, cooking temperatures ranged from 90 to well over 200°C, pressures went up to 138 atm and cooking times were between 3 and 60 minutes [10, 12, 14, 16, 17].

1.2.3.3 COOK TERMINATION AND PULP RELEASE

Even if high temperature - short cooking time at high pressure are the basis of high severity pulping, literature shows that the pulp release plays also an important role.

Provided the chips are well softened, a sudden pressure release can significantly contribute to fiber separation. Press impregnation can further enhance this benefit and as a result, in the semi-industrial trials, about 37% of the pulp was released as free fibers [36]. It is the explosion that causes fiber separation, since in the blowing system, there is no possibility for chips to have a direct impact against any wall or nozzle bars.

In laboratory trials, however, chip separation is not as evident. Visual inspection indicates that exploded chips (particularly resulting from higher severity cooks) are quite flexible and fairly easy to separate into fiber bundles. For laboratory trials, some other authors did not observe visible fiber separation [46 to 48, 82, 86].

For better explosion evaluation, the digester pressure can be increased prior to pulp release. For its inert nature, nitrogen is used for this purpose, and the pressure increase can go up to 25 atmospheres.

For pulp comparison purposes, it is also possible to release the pressure slowly and without explosion. From pressures about 10 to 15 atmospheres, depressurization can take from about 15 seconds to 4 minutes.

1.2.4 PULP REFINING

Pulp washing follows the cooking process and then the pulp can be refined. As there is no existent equipment able to duplicate industrial refining, domestic blender is often used for pulp refining. Compared to other methods, the blender was found to be the most suitable instrument, because [29, 36, 49, 55, 59, 88, 89, 111]:

- refining energies are very well comparable to industrial ones
- pulp quality and paper properties are very well comparable to industrial ones
- blender does not cut fibers to such damaging extent as the other refiners do
- blender does not require large pulp quantities

Based on these proven facts, in spite of different refining nature [111], blender scores better than other laboratory beaters, which are mostly designed for chemical pulps defibration and refining, such as the PFI mill, Valley Beater, etc. Blender values were quite well comparable to semi-industrial refiners, such as Sunds, Sprout and Bauer [36, 49, 59, 88, 89].

To get a representative pulp sample, a batch of 15 blenders for each pulp and each CSF value is usually used. Due to uneven blade wear and the effect of air agitation, the freeness values of every blender in a batch were not necessarily the same and there were also slight differences in the color of individual suspensions. Some objections concerning the differences in fiber surface development (in comparison to industrial refiners) were raised, but based on the results and literature references [111], a blender is judged as the best laboratory choice.

1.3 THEORETICAL CONSIDERATIONS

As far as high severity conditions are involved, we can look at them from two points of view: what happens to the individual wood components (lignin, cellulose, hemicelluloses) at high temperature/high pressure/short time cooking and what happens at the individual cooking stages (steaming, cook, explosion) to the chips and/or cooked pulp.

Even if there are several articles reporting on the progress and understanding of other ultra-high yield pulping processes [112 to 118], it would be difficult to use them as a basis for our purposes. The reason is very simple - other processes (TMP, CTMP, CMP and their modifications) work at conditions so different from the steam explosion process that their chemical outcome is hardly comparable.

Based on our knowledge of wood chemistry and literature review, it would appear that these reactions take place:

1.3.1 LIGNIN

With high temperatures used in steam explosion pulping, lignin undergoes an additional permanent softening. With rising temperature, lignin as a solid polymer absorbs more energy and its chains develop more violent motion until a temperature is reached at which intermolecular bonds are broken and the macromolecules become capable of large scale displacement with respect to each other. The mechanical properties of the polymer change rapidly in this temperature region and the solid undergoes what is known as a glass transition. Below this transition, polymer behaves as glassy solid and above, it becomes rubbery palstic [68]. Steam explosion cooking temperature is higher than the glass transition temperature (T_g) of aspen lignin and its model compounds (C9 oligomer units from which lignin is composed) [68]. For some model compounds of aspen lignin, the T_g is about 135°C. Wood lignin behaves somewhat differently from its model compounds and due to its higher complexity and molecular weight has higher T_g. On the other hand, the presence of steam during the cook decreases the T_g and with temperatures of 190°C+ there would

be a guarantee for a significant increase in lignin softening, when compared to CTMP/CMP lignins.

Some other sources [39, 73, 91 to 93, 119, 120] also confirmed rapid chemical degradation, if no preservative chemicals were added. In the water explosion process (steam explosion with no chemicals added), lignin in the secondary walls of fibers was degraded to low molecular fractions by cleavage of the ether linkages after only 4 minutes of steaming [119]. The middle lamella lignin was more resistant to steaming and has partially melted yielding small oily droplets. Differences in lignin reactivity can be ascribed to the differences in the chemical structure and the concentration of lignin between the secondary walls and middle lamellae. Similar results of lignin melting were reported by Kosik [121].

Products of lignin degradation by steam explosion are similar to an acidolysis reactions which includes cleavage of the α- and β-ether linkages followed by an increase of phenolic-hydroxyl groups. However, the analyses showed that the contents of carbonyl groups of exploded lignin were very much smaller than in the acidolysis of milled wood lignin [92, 120]. Therefore, the cleavage reactions of lignin by an explosion are different from those in acidolysis.

From exploded wood (Figure 1.2), fractions of vanillin (5), syringaldehyde (5'), coniferyl aldehyde (4), coniferyl alcohol (2), sinapyl alcohol (2'), sinapaldehyde (4'), d,l-syringaresinol (9'), d,l-episyringaresinol (10'), dehydrodiconiferyl alcohol (11), vanillic acid (7), syringic acid (7'), furfural (29) and 5-hydroxymethyl furfural (30) were isolated and identified by ^{1}H-NMR, ^{13}C-NMR and GC-MS [92].

In further investigation of lignin degradation, guaiacylglycerol-β-guaiacyl ether (1) after high severity treatment (230°C, 16 minutes) yielded (Figure 1.2) mostly coniferyl alcohol (2), its γ-methyl ether (13) and guaiacol (3). Coniferyl aldehyde (4), vanillin (5), vanillin alcohol (6), vanillic acid (7) dehydrodiconiferyl alcohol (11), d,l-pinoresinol (9) and d,l-epipinoresinol (10) were separated by PTLC and identified by NMR [92].

Steam explosion (230°C, 16 min) of guaiacylglycerol-β-guaiacyl ether formed mainly coniferyl alcohol and guaiacol, but products of 120°C/4 hour acidolysis of this compound (1) were mainly composed of β-oxyconiferyl alcohol (14), which

was separable into keto and enol types by acetylation, 1-propanone (16), 2-propanone (15), guaiacyl acetone (18), vanilloyl methyl ketone (17) and guaiacol (3), as it shows Figure 1.3. Coniferyl alcohol (2), dehydrodiconiferyl alcohol (11) and pinoresinol (9,10) which are the main products resulting from a steam explosion were hardly detected in the acidolysis of product (1). Thus, the mechanism of lignin degradation accompanying a steam explosion is entirely different from acidolysis. Tanahashi et al. [92] proposed that by steam explosion, lignin is cleaved mainly homolytically to produce cinnamylalcohol radicals which couple to give Cβ-Cβ or Cβ-C5 linkages. Disproportionation of the radical produces cinnamyl alcohol and cinnamyl aldehyde and cinnamyl-alcohol radicals also can be reduced by sugars to give cinnamyl alcohol.

Based on their further research, Tanahashi et al. [91, 92, 119] proposed a possible mechanism of lignin degradation by steam explosion, as shown in Figure 1.4. Even if they slightly misrepresented the ionization of water [122] under steaming conditions as of 10^{-7} (which is about 10^{7} times greater than under normal conditions), it is true that hydroxyl groups or ether linkage of the α-position of lignin side-chains could be easily protonated and converted to the quinone methide structures (21). Thus, a β-O-4 ether linkage can be homolytically degraded to produce coniferyl alcohol and sinapylalcohol radicals (22, 22'). These radicals then could react as described in Figure 1.4.

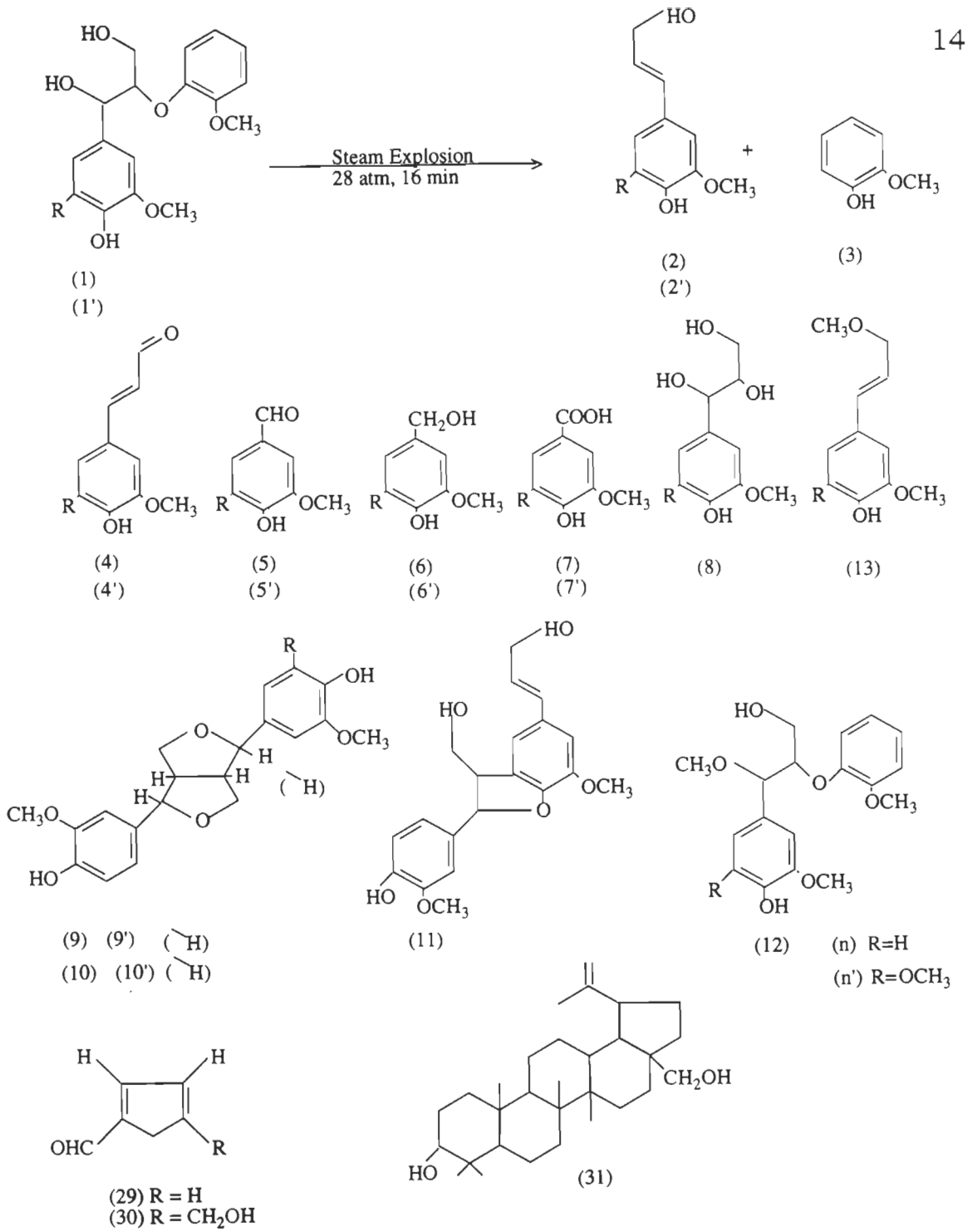


FIGURE 1.2: Degradation products of guaiacylglycerol- and syringylglycerol-β-guaiacyl ethers resulting from a steam explosion [92]

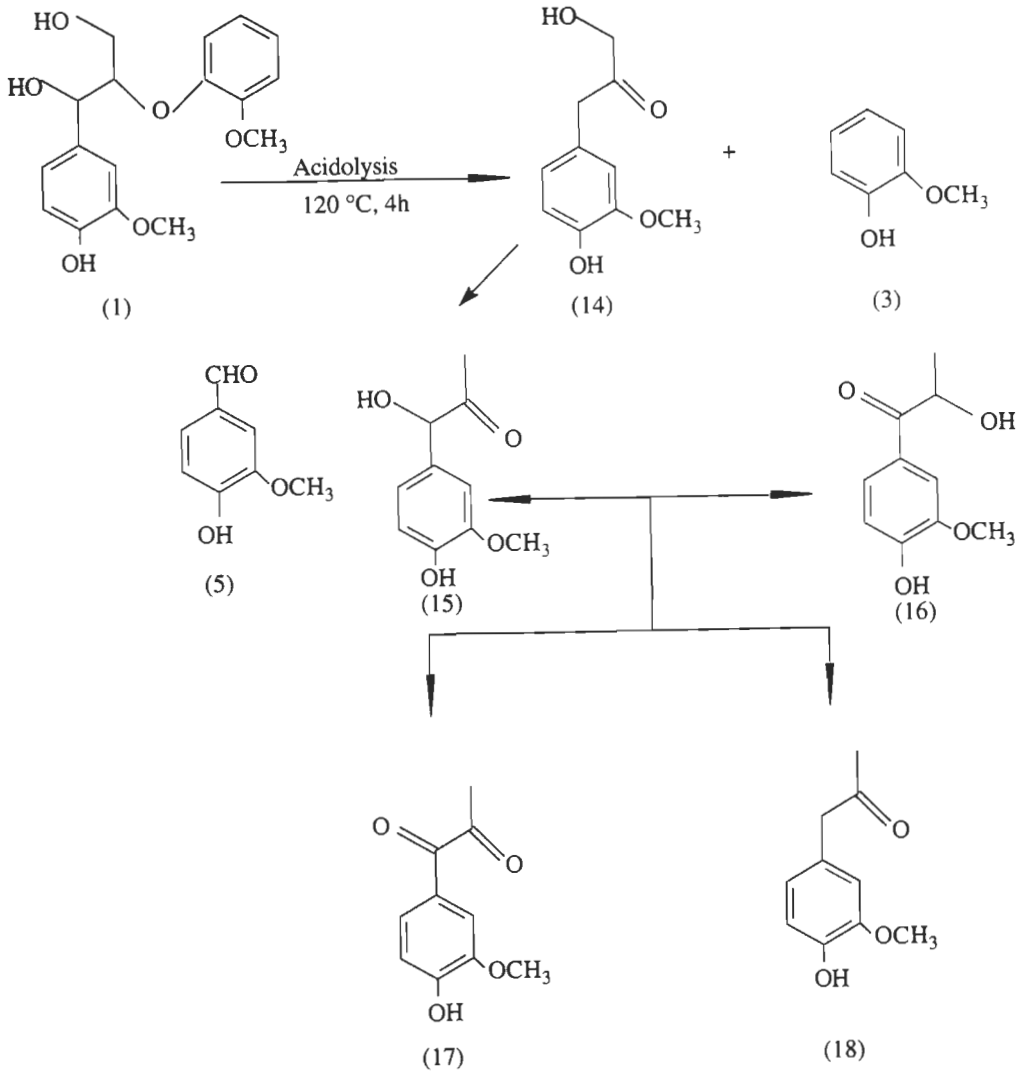


FIGURE 1.3: Acidolysis products of guaiacylglycerol-β-guaiacyl ether [92]

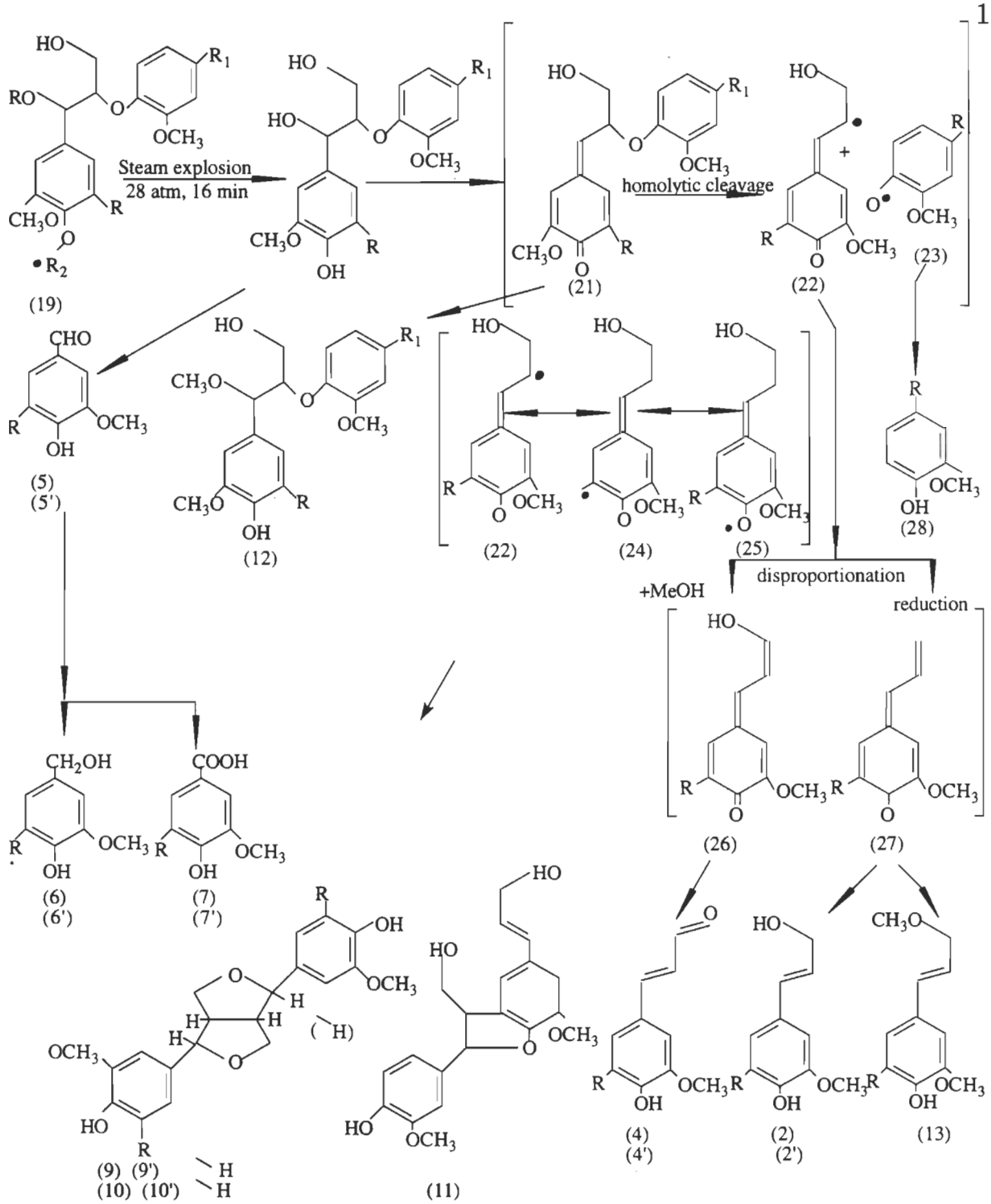


FIGURE 1.4: Possible degradation mechanism of lignin resulting from a steam explosion [92]

1.3.1 CELLULOSE AND HEMICELLULOSES

Several studies [93, 120, 123 to 128] revealed what happens to cellulose, its derivatives and to hemicelluloses at elevated temperatures. Similarly, to the case of lignin, the temperatures up to 200°C are below the glass transition temperature of dry cellulose. However, Atalla and Ellis [124] states that in the presence of polar media, T_g is depressed and molecular mobility is sufficient to allow structural reorganization.

In recent Japanese studies of explosion pulping [91, 93, 120] it has been shown that the fastest reaction by far is the hemicellulose hydrolysis. This is not surprising, since hemicelluloses are the most reactive wood component. In the case of white birch, hemicelluloses in wood were easily hydrolyzed (mostly into oligosaccharides) and converted into almost soluble materials by only 1 minute steam treatment at 20 atm. By increasing the severity to 28 atm (about 230°C) and 8 minutes, more than a half of hemicelluloses can be converted into monosaccharides. As Table 2.1 shows, in a 2 minute steaming at 28 atm, the cellulose in the exploded wood was hardly degraded to glucose (only 4.9% of all monosaccharides) [91].

TABLE 1.1 Composition of monosacharides in water soluble fraction of steam-exploded white birch wood [91]

Sample [atm/min]	Unknown	Arabinose	Xylose	Mannose	Galactose	Glucose	Total
20-1	-	0.8	1.1	-	-	-	1.9
24-1	-	1.0	3.4	-	-	-	4.4
28-1	-	1.5	3.9	-	-	-	5.4
28-2	1.0	2.6	8.8	0.6	0.7	0.7	14.4
(%)	(6.9)	(18.1)	(61.1)	(4.2)	(4.9)	(4.9)	(100)
28-4	1.6	0.3	28.8	1.9	2.5	5.7	40.8
(%)	(3.9)	(0.7)	(70.6)	(4.7)	(6.1)	(14.0)	(100)
28-8	2.1	2.6	37.5	2.5	3.0	6.0	53.7
(%)	(3.9)	(4.8)	(69.8)	(4.6)	(5.6)	(11.2)	(100)

Nuclear magnetic resonance (NMR), X-ray diffractometry and Transmission electron microscopy (TEM) studies revealed other interesting physical and chemical changes in exploded wood cellulose composition:

- firstly, the micelle width (micelles are microcrystalline regions in the cellulose which are perfectly ordered in all three directions in space) of exploded wood was more than twice that of original material (increase from 25 to 52 Å) [93]. These findings (Tab 2.2) correspond well with those of Taylor et al. [129] discussing the influence of high severity cooking on aspen, spruce and straw. Similar increase was also found in preceding research at the UQTR (Ahmed at al.) [65]. Very comparable micelle width can be observed and confirmed by TEM [93].

- secondly, exploded wood has a significant increase in cellulose crystallinity (Table 2.2). For both hardwoods and softwoods, the NMR crystallinity can be calculated by measuring each crystalline and non-crystalline area of carbons C4 and C6. In addition, this method can discern two different crystalline forms of native cellulose: a cotton-ramie type (cellulose Ia) and a bacteria-valonia type (cellulose Ib) [128]. Even if wood cellulose cannot be assigned to type Ia or Ib, from a comparison of the peak width of C1, C4 and C6 peaks in the crystalline component spectra of the wood with those of valonia and cotton cellulose, the crystalline form of intact wood cellulose would be identical with cellulose Ib rather than Ia. However, the spectra of the crystalline component showed that the crystalline form clearly changed after the explosion. Horii et al. [128] showed the transformation of the cellulose crystalline form by a high-pressure-saturated-steam treatment at a high temperature by NMR. The crystalline form, type Ib of valonia and bacteria cellulose, was transformed by increasing the steam temperature to cellulose Ia' which is almost identical to cellulose Ia. 4 minutes of steaming is enough for complete transformation of the crystalline form of wood cellulose to cellulose Ia. Thus the crystalline form of original wood cellulose was considered to be of a less-ordered orientation and was transformed to cellulose Ia' by increasing the order of orientation and crystallinity by the steam explosion.

TABLE 1.2 Crystallinity evaluation of various lignocellulosic steam-exploded samples [93]

SAMPLE	Crystallinity [%]			Microfibril			
	X-ray	^{13}C-NMR		Width [Å]		Length [Å]	Crystalline form
	Cr.-I	C-4	C-6	X-ray (002)	TEM	SEM	
White birch:							
original	51	43	58	25	32	∞	?(Ib)
28 atm / 1 min	64	-	-	42	53	-	-
2 min	67	-	-	44	59	-	-
4 min	70	66	69	51	58	1900	Ia`
8 min	70	-	-	54	48	2000	-
16 min	67	68	64	52	50	2000	-
Japanese larch:							
original	50	-	-	24	-	-	-
28 atm / 1 min	65	-	-	42	-	-	-
2 min	68	-	-	41	-	-	-
4 min	69	-	-	45	-	-	-
8 min	69	-	-	44	-	-	-
16 min	65	-	-	43	-	-	-
Japanese cypress:							
original	48	51	46	-	-	-	?(Ib)
28 kg/cm^2 4 min	63	62	59	-	-	-	Ia`
Filter paper:							
original	88	75	67	60	-	∞	Ia
28 kg/cm^2 16 min	89	83**	74**	67	80	1000	Ia`
Cotton*:							
original	77	72	70	47	-	∞	Ia
49 kg/cm^2 30 min	88**	70**	61**	62	76	1200	Ia`
Valonia*:							
original	90	87	90	143	-	-	Ib
28 kg/cm^2 30 min*	90**	89**	-	-	-	-	Ia+Ib
49 kg/cm^2 30 min*	95**	90**	99**	108	140	1400	Ia`

* : These data were taken partially from [128] and the reaction conditions were only steaming without explosion

** : These data were observed on the sample after washing it with water

Micelle width and crystallinity values [91, 93] were compared to samples prepared with a slow release of steam pressure. Results indicate that the increases of micelle width and cellulose crystallinity were caused only by the high temperature and steam pressure independently of the explosion.

The increase of microfibril (microfibril is an agglomerate of cellulose molecules in a fiber) or micelle width could be explained as follows:

- rearrangement or reorientation of cellulose molecules inside and near the crystalline region of microfibrils by relaxation caused by high temperature and pressure, and/or by

- removal of other components such as hemicelluloses and lignin, and

- crystalline fusion with adjacent microfibrils by removal of hemicelluloses and lignin

Steam ionization (into H_3O^+ and OH^- ions) increases at high temperatures and pressures helps well this process. Ionized steam reacts with polysaccharides and hydrolyses them to smaller molecular-weight sugars. In addition, acetic acid formed from the acetyl groups of hemicelluloses, and levulinic and formic acids partially formed by degradation of the hemicelluloses, catalyze the hydrolysis of carbohydrates [91, 93, 120]. Lignin degradation (mainly through homolytic cleavage) gives dimers, cinnamyl alcohol and aldehydes [73, 92, 119, 120]. By these reactions the wood constituents can be partly degraded and become mobile. The inner stress in the crystalline region of cellulose is loosened and in such a condition, the crystallinity of wood cellulose could be increased by rearrangement and reorientation of the cellulose molecules of the paracrystalline regions during steaming.

On the other hand, in relatively pure cellulose materials such as bleached kraft pulp or filter paper, almost constant crystallinity was observed before and after steam explosions [93, 120]. This is ascribed to the fact that original materials do not contain hemicelluloses which affect the rearrangement of paracrystalline regions. The fusion of microfibrils to become greater fibrils observed by TEM can be ascribed to the fact that lignin in inter-fibril spaces becomes soluble or

mobile by heating and is removed. The microfibril width has a maximum peak at certain steaming time (different for every temperature) and further steaming causes a decrease of the crystalline width of microfibrils by a gradual hydrolysis of the cellulose at the surface of the crystallite.

These considerations suggest three stages in the reaction of cellulose during steam explosion:

- In the first stage of steaming, hemicelluloses and paracrystalline cellulose are partially hydrolyzed and the inner stress in the crystalline regions of the cellulose is loosened. Then paracrystalline cellulose is relocated to the crystalline region and the width of cellulose microfibrils increases.

- In the second stage, microfibrils are cut at some nodes of the cellulose crystallite to give microcrystalline cellulose and the length of the microfibrils decreases to 1000 - 2000Å.

- In the third stage, the surfaces of cellulose crystallite are gradually hydrolyzed Then the microfibril width and cellulose crystallinity decrease.

In addition to these reactions of cellulose during steaming, transformation from cellulose Ib or Ia to Ia' of cellulose crystalline form is accomplished.

The changes in cellulose structure and its importance to mechanical and chemical behavior were further examined and mathematically quantified by Sukhov et al. [130]. In his research, they used recently developed non-destructive analytical methods, such as advanced laser techniques facilitated by computers. Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy revealed twice as many bands as before. FTIR spectroscopy of acetone-substituted samples and Raman spectroscopy of deuterium-substituted samples enabled not only to discern the structural differences between both native cellulose (C-I) and mercerized cellulose (C-II), but also their ordered and disordered forms.

In the case of high severity pulping, there are no conditions for mercerized cellulose formation (in most cases, work was carried out without NaOH which is

necessary for the mercerisation process) and C-II has not been confirmed by any other analysis (X-ray diffractometry, for example would show a clear C-II peak different from other cellulose forms). However, the hemicelluloses give similar FTIR/Raman spectra as cellulose C-II and it would be very helpful to use this approach in high severity pulps evaluation.

Valov et al. [131] developed an algorithm for a quantitative evaluation of the contents of these four components: C-I ordered,C-I disordered, C-II ordered and C-II disordered. A special computer program was developed for automatic interpretation of IR spectra. Investigation of the differences between cellulose types C-I and C-II [130] showed fundamentally different characters of intermolecular interaction. The chain packing energy in an elementary cell of cellulose C-II is represented by Van der Waals interactions [126]. Therefore C-II hydroxyls are considered to be involved mostly in intramolecular hydrogen bonds, and interchain interactions are likely to be limited by weaker bonds of Van der Waals type. On the other hand, the hydroxyl spectra of cellulose C-I are intensive in both inter and intremolecular orientations. This fact shows that there is a developed system of intermolecular and intramolecular hydrogen bonds which is responsible for the strong interchain interactions in native celluloses. When the C-II type is obtained, the intermolecular hydrogen bonds are destroyed, macromolecule units are separated and their configuration is defined by intramolecular forces.

The differences in the character of interchain interactions in C-I and C-II are apparent at macromolecule and fibril levels. Naturally, the different ways by which the microfibrils and fibrils are formed in C-I and C-II should affect the properties of individual cellulose fibers. To prove this hypothesis, Sukhov et al. [130] compared paper formation properties of purified fibers of cotton, native and mercerized celluloses. Conventionally prepared handsheets made of cellulose C-II appeared to be heterogeneous compared to those made of C-I. In the comparison of maximum sample break forces, the tensile strength of handsheets made of native cellulose was found to be more than twice as large as that of handsheets made of mercerized cellulose. For the purpose of high severity pulping, we should thus try to preserve the native form of cellulose I, which more resembles a kraft pulp cellulose and shows better bonding potential and physical strength compared to mercerized cellulose.

Infrared, Fourier transform infrared and Raman spectroscopies, especially after recent laser technology and computer implementation were improved and successfully applied in lignocellulosic research by several other authors [39, 40, 52, 58, 64, 67, 132 to 143, 151]

Among other methods helping to understand the influence of high severity cooking conditions on the properties of resulting pulps, a mention should be made of the nuclear magnetic resonance spectroscopy [58, 91, 93, 120, 128, 129, 143 to 149]. Since wood and pulp are not normally soluble (in water or NMR solvents) and the main components have very different solvents and their partial or total dissolution is accompanied by drastic chemical modifications, only progress in solid state NMR enabled research in this area. High resolution solid state 13C NMR can, for example, differentiate the signals from ordered (crystalline) and disordered (amorphous) cellulose regions [144]. It has been shown that the intensity of 89 ppm line increases while that of a 84 ppm line considerably decreases as a result of an increase in cellulose crystallinity. As a result, the NMR factor of crystallinity can be determined as the portion of 89 ppm line to the total intensity of C-4 carbon signals (at 89 and 84 ppm) in the simulated spectra.

Hua et al. [145] and Focher et al. [67] offered more detail characterization. From their ^{13}C NMR spectra comparison of aspen wood, industrially prepared high severity and conventional pulps in the Figure 1.5, they reached these conclusions:

Wood spectrum is dominated by cellulose and hemicellulose resonance signals. The peak at 106 ppm is the resonance of C-1 in polysaccharides. Peaks at 84 and 89 ppm are the resonances of C-4. The apparent doublet in the 70-80 ppm region is assigned to the C-2, C-3 and C-5 carbons of cellulose. The signal at 65 ppm is due to C-6 cellulose. The signal at 21 ppm is due to acetyl groups in hemicellulose. The presence of hemicellulose is also shown by a background of 50 to 90 ppm (C-2, C-3, C-4, C-5 and C-6). The signals from lignin are located between 160 and 110 ppm. The signals are due to the aromatic ring carbons of lignin. The intensity between 160 and 143 ppm is specifically due to oxygen-

substituted aromatic ring carbons (C-3, C-4 and C-5). The peak at 56 ppm corresponds to the methoxyl groups of lignin.

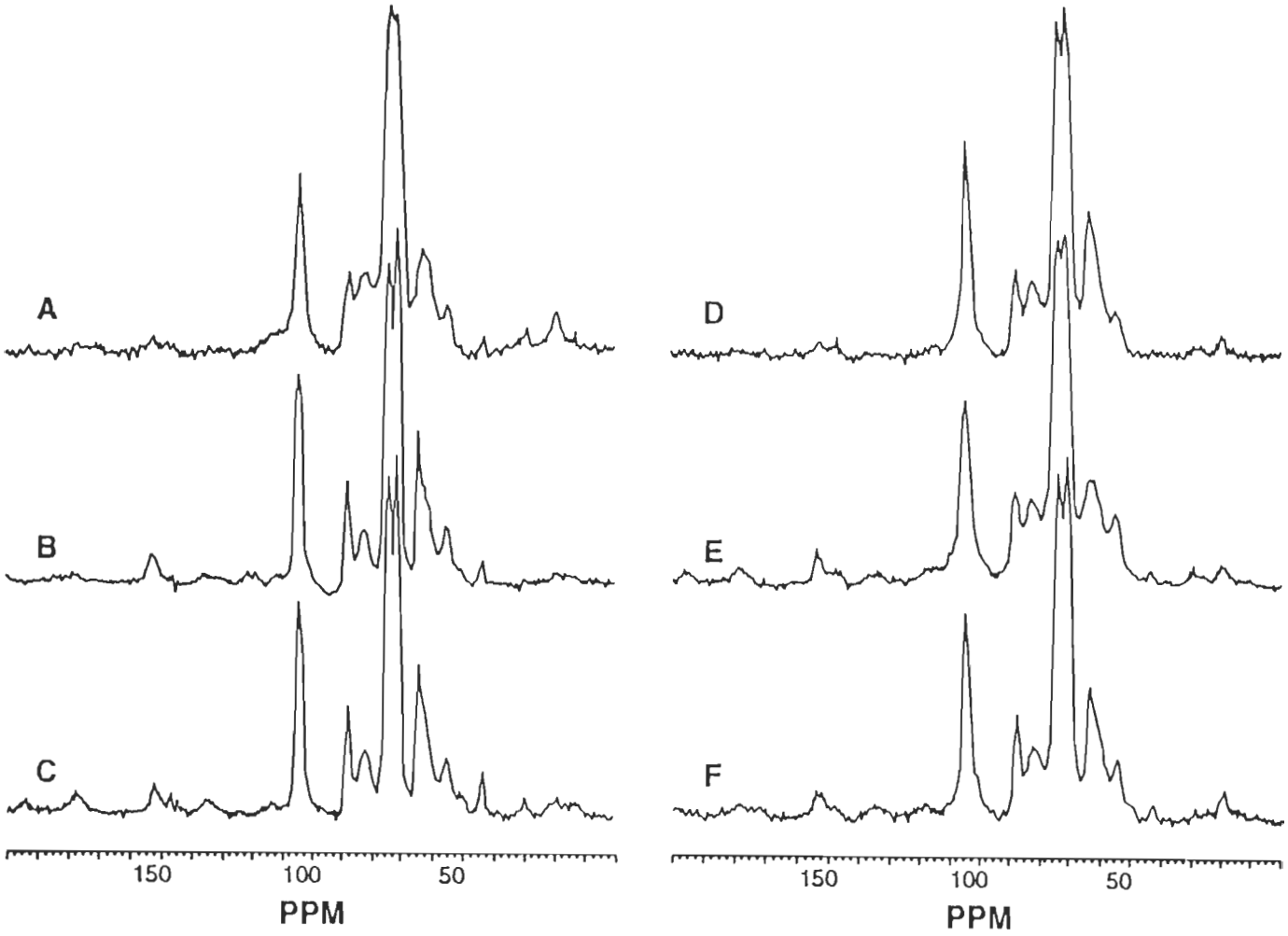


FIGURE 1.5: CP-MAS ^{13}C NMR spectra for: (A) untreated wood; (B) Explosion pulp 8% Na_2SO_3; (C) Explosion pulp 8% Na_2SO_3 + 0.5% NaOH; (D) CMP 8% Na_2SO_3 + 1% NaOH; (E) CTMP 8% Na_2SO_3 + 0.5% NaOH and (F) CTMP 5% Na_2SO_3 + 5% NaOH [150]

Explosion pulp has a less intensive signal at 21 ppm, which indicates a removal of acetyl groups from xylan. This observation suggests that these groups were dissolved in the cooking solution under high temperature. A small reduction of peak intensity at 56 ppm may imply some structural changes in lignin. Another proof that the lignin was modified rather than removed is in the shift of the 150 ppm line to 154 ppm. These considerations may explain why explosion pulp could have high yield. Lignin modifications suggested by Hua et al. [145] are in the conversion of aromatic lignin units into aliphatic chains due to aromatic ring opening, in partial breaking of the lignol network structures, in the formation of sidechain structures of the ketone type and other reactions. A considerable drop of the 84/89-ppm signal ratio after a steam explosion treatment indicates a dissolution of hemicellulose (C-4 of 4-OMe glucuronic residue) and an increase in cellulose crystallinity. The loss of hemicellulose and the increase in cellulose crystallinity are confirmed by the decrease of the high-shielding shoulder on the peak at 65 ppm, since this shoulder is due to C-6 amorphous cellulose and C-5 of xylan for aspen wood.

In comparison with conventional processes [67, 145], the CMP pulp showed lower lignin content, corresponding to its lower yield. Also, a higher 84/89 ppm ratio suggests higher hemicellulose content and lower crystallinity in the CMP case. As for CTMP, their spectra show the least changes when compared to the untreated wood sample. This is quite understandable, since the CTMP process is carried out under the lowest temperature and generally milder conditions.

Electron microscopy (both SEM and TEM) is also very helpful. Hua [150] found that exploded fibers exhibited higher fiber conformability than CMP or CTMP. There was more contact between SEP fibers, consequently leaving less void in the pulp pad. Exploded fibers were well separated, long and flexible. Fiber cutting was not common. These properties in combination with higher average fiber length should provide SEP paper sheet with higher density and physical strength, low porosity and smooth surface. Fiber cells were flattened, collapsed and somewhat shrunk and wrinkled. CMP and CTMP micrographs showed more stiffness and inflexibility in the network with more shives, broken fibers and more cell fragments from the fiber wall destruction.

After high severity treatment, Focher et al. [67] observed well separated fibers exposing some areas of the outer cell wall portions (middle lamella), as well as inner layers (S-1, S-2). This could indicate that the separation occurs at the level of compound middle lamella. No fibrillation was observed. The presence of NaOH during high severity treatment increased the exposure of inner layers, probably through higher fibre swelling. As lignin in fines was lower, it was suggested that the middle lamella peeling occurred with the outer layer of the secondary wall. This could lead to higher polysaccharide surface concentration which is very important for fiber bonding and for sheet strength improvement.

1.4 OBJECTIVES OF THIS WORK

Summarizing the theoretical cosiderations, it can be concluded that the high severity cooking conditions provoked certain distinct physical and chemical changes in wood material. In the present work, investigating efforts will be devoted to improve current knowledge and understanding of the influence of high temperature and high pressure on wood and fibers, hopefully leading to mill exploitation by the papermaking industry.

The main objectives of this work are:

A: establish a correlation between cooking conditions (temperature, time, pressure) and the physicochemical fiber changes due to vapor phase cooking

Justification: It is believed that the most important process variables are the cooking parameters. High severity cooking conditions lead to physical physicochemical and chemical changes such as additional permanent lignin softening, increase in the ordered cellulose I content, easier defibration, preservation of higher fiber length, higher quality fiber surface, etc. Confirmation of this hypothesis could explain superior performance of explosion pulps. As far as the bibliographical research is concerned, lot of these influences were not studied well enough or have not been quantified.

B: establish a correlation between fiber changes and resulting mechanical and optical properties

Justification: Statistical methods for the correlation evaluation were planned to be used as confirmed by earlier research. The experimental design and resulting data should help understanding what happens (at various levels) with the fibers not only around process optimum parameters, but on a much larger scale. Based on this analysis, the most important parameters and their influence on the final product could be determined and evaluated.

C: establish the kinetics of ionic content creation and its influence on paper properties

Justification: For mechanical pulps, a review of the literature showed the importance of ionic content (sulphonic and carboxylic) up to 150°C. At temperatures around 200°C, the influence of the ionic content might become even more important to explain from chemical and mathematical points of view.

D: determine the optimum cooking conditions in order to obtain required paper properties

Justification: Process optimization is a logical outcome of the preceding points.

In the time of project preparation, lot of preliminary work has already been done: i.e. the basics of the process, parameters such as chemical requirements, optimum cooking conditions were estimated and various wood species were used as well. However, none of these studies had shown clearly what actually happens to the fibers, and how are their surfaces and bonding ability altered, and which are the most critical parameters to be further studied. To answer these questions, different analytical methods were used: surface analysis by the electron spectroscopy for chemical analysis (ESCA) and Fourier transform infrared spectroscopy (FTIR), hydrophility by the water retention value (WRV) and light-scattering coefficient (LSC), ionic evaluations and their differences on the surface and in bulk (ESCA/conductometric titrations) and on chemical changes on the cellulose and lignin (X-ray diffraction and FTIR/Raman spectroscopy) due to cooking conditions.

The process optimization carried out at the UQTR resulted in successful laboratory trials leading to superior pulp in comparison to conventional ultra-high yield pulping methods. The questions were: can we reach further improvement and how can we mathematically and statistically evaluate the process? What are the optimum pulping conditions, can they be mathematically evaluated and can cooking conditions for required paper properties be calculated?

According with the objectives previously stated, the purpose of my work is to understand and scientifically explain the principles of high severity pulping, clarify the differences between this and other ultra-high yield processes and to justify the original hypotheses. The experimental design covers whole region of high severity pulping and the analyses should be sufficient for a complete and objective fundamental process characterization.

The work will be presented as follows: in the chapter 2, there will be a description of the experimental plan and all the experimental procedures including pulp preparation, quality evaluation and physicochemical methods to evaluate various pulp and paper properties. Chapter 3 will present obtained results and the discussion of our findings. Chapter 4 will deal with the mathematical treatment of the results and the chapter 5 will bring the general conclusion.

2. EXPERIMENTAL

2.1 EXPERIMENTAL CONSIDERATIONS

In comparison to conventional ultra-high yield pulping processes, the main benefits of high severity pulping seems to be in property improvement (higher mechanical parameters) and in refining energy reduction. Kokta (inventor of the process that will be used in this work) as well as several other authors (in cooperation or independently) from around the world claim that explosion pulping can lead to pulp and/or paper with higher mechanical strength [29, 31, 32, 34, 35, 37, 40 to 44, 49, 50, 52, 54, 55, 57 to 59, 61, 62, 64, 65, 85, 87 to 89], lower refining energy [29, 31, 32, 34, 35, 37, 40 to 44, 49, 50, 52, 54, 55, 57 to 59, 61, 62, 64, 65, 85, 87, 89, 104], longer average fiber length [31, 32, 34, 35, 37, 40, 42, 43, 50, 54, 55, 58, 61, 62, 65, 85, 89, 104] and higher wet web properties [35]. These experiments were carried out either in laboratory conditions [12, 29, 31, 34, 36 to 38, 58, 61, 66, 81, 87] or in semi-industrial or industrial conditions [11, 14, 16, 31, 32, 36 to 38, 40, 58, 61, 66, 81, 87]. Explosion pulp release at the end of the cooking process was compared to slow pulp release [31, 81, 88] and several other analyses were carried out in order to characterize explosion pulps and to explain their superior behaviour.

On the other hand, other authors claimed that they did not observe any fiber separation [46, 47, 82, 86], that the explosion pulps cannot be prepared at ultra-high yield [47, 82, 86], that the properties of explosion pulps were worse or equal to conventional processes [47, 70, 82, 87] and that the refining energy was higher for explosion pulps [46, 47, 82, 86].

An independent research study by the Pulp and Paper research Institute of Canada (Paprican) [33, 45] was undertaken to clear these controversies. According to this pilot plant study results, high severity pulping can produce a good quality pulp, even if the results did not show refining energy savings or superior paper properties compared to CMP and CTMP. It has been stated that explosion pulping produced more uniform pulp with less rejects and shives and would require smaller investment capital.

Taylor et al. [59] explained that some the Paprican study conclusions [45] might have been based on incorrectly considered chemical charge. He states that the dewatering zone of the Stake Tech. equipment for high severity pulping squeezes about 50% of the impregnation liquor out of the system prior to steaming and cooking which was not considered in Paprican evaluation [45]. Thus the chemical charges considered by Paprican were in fact 200% of chemicals actually used in explosion pulping, which was confirmed by detail chemical analyses of the chips and the pressates [59]. Based on the recalculation of Paprican results, Kokta et al. showed [44] that the explosion pulping process does save refining energy and does produce mechanically stronger pulp.

2.2 EXPERIMENTAL CONDITIONS

Having considered the above mentioned information it was decided to undertake process evaluation and optimization using the following approach:

2.2.1 WOOD SPECIES

As described in the introduction (chapter 1.1), the steam explosion pulping process was successfully applied to both softwoods and hardwoods. In our work, trembling aspen wood (Populus tremuloides, Michx.) was selected. This choice was based on several reasons: firstly, aspen is one of the most widely distributed hardwood species in North America. In Quebec only, Deilgat [153] estimated 50 million cubic meters of aspen. Secondly, aspen in the beginning of our study was a very underused species in high yield pulping. Lower mechanical properties resulting from the TMP, CTMP and CMP processes prevent aspen from a larger scale industrial use. This is due mainly to its short fibers. Kraft pulping is thus the most common way of chemical treatment of aspen wood.

From the morphological point of view, aspen is an excellent species for processes with chemical charges. It has low density, lots of large vessels (3 times more in comparison with white birch) and thin fiber walls which much helps the impregnation process. Fibers are very flexible, pliable and easy to flatten. From the chemical point of view, over 80% of the wood mass is represented by holocellulose [154]. Aspen contains more than 50% of cellulose and only about 18% of lignin, which facilitates swelling and chemical treatment in pulping process.

Other advantages of selecting aspen are the high initial wood brightness and opacity enabling the production of UHY pulp with little or no bleaching.

In the present trials, freshly cut aspen trees from Quebec region were debarked and chipped at la Station Forestière Duchesnay (Quebec). The chips were screened at the Pulp and Paper Research Center at the Université du Québec à Trois-Rivières. The average chip size corresponded to the industrial conditions and the mean chip dimensions were 31 x 15 x 5 mm.

2.2.2 IMPREGNATION

Several works concerning chip impregnation were carried out at the UQTR. Based on their summarization in [36], we have chosen these conditions:

In the early stages of this work, an 8% Na_2SO_3 impregnation solution was mainly used. This has been reported [36] as the effective amnount for the laboratory trials. As the process evolved, gained experience from other researchers' results [39] led to the selection of $Na_2SO_3/NaHCO_3$ system as the basis for further process enhancement. As a reference, no chemical impregnation (water explosion pulps, refiner mechanical pulps) and a Na_2SO_3/NaOH system (in the very early stages) were used.

Impregnation for every cooking batch (75g calculated to oven dry wood) was carried out individually. Chip humidity prior to the impregnation was about 86 to 93%. Chips were placed in plastic bags and blended with the impregnation solution. Usual liquor-to-wood ratio was 6:1. Impregnation time was 24 hours and impregnation temperature was 60°C. Exact impregnation concentrations will be described in detail with every pulping condition.

2.2.3 COOKING

All pulps were produced at the UQTR in the laboratory steam explosion reactor (Figure 1.1). For every pulping condition, a series of 15 cooks was performed. This produced about 1 kg of pulp for every pulping condition, which was sufficient for all planned analyses.

2.2.3.1 FIRST EXPERIMENTAL SERIES

According to the objectives, in the first series of experiments, efforts were devoted to answer some important questions concerning the new approach of high severity pulping for papermaking. Some of the most significant ones were: is it possible to prepare both conventional and high severity pulps at the same chemical charge and same yield levels? If so, what would be the difference in

specific refining energy requirements, in pulp and paper properties, in the ionic content development, in chemical composition, in surface characteristics...? It was considered important that to keep the two very important parameters (chemical charge and yield) constant, to be able to have a good basis of comparison between these otherwise very different processes.

From this point of view, a series of explosion pulps (Table 2.1) at usual conditions (190°C/2 min; 195°C/1.5 min; 200°C/1 min) were prepared. The resulting pulps showed a yield very close to 90%. In order to have the same CMP cooking yield, it was necessary to cook somewhat longer than in usual industrial conditions. In the CTMP case, the treatment being much milder, a 90% yield was not obtained even after a one hour cooking. That's why another explosion pulp, cooked for only 80 seconds at 190°C with a yield comparable to that of CTMP was prepared.

To find out the influence of the explosion alone, three additional explosion pulps were subjected to higher pressure of 25 atm (under nitrogen) immediately after the cook and then discharged from the digester. Nitrogen was chosen as the pressurizing agent because of its inert character.

As a chemical basis, an 8% Na_2SO_3 solution at the liquor-to-wood ratio 6:1 was used. Because of same chemical charge during the impregnation, the chemical uptake was the same for all pulps. Two pulps - water explosion and refiner mechanical pulp - were processed without any added chemicals.

To compare with industrial processes using Na_2SO_3/NaOH impregnation, two pulps using this impregnation system (Table 2.2) were also prepared . As an alternative to the NaOH [39], one pulp sample was prepared with the Na_2SO_3/$NaHCO_3$ impregnation.

To determine effects of bleaching response, all the above pulps were bleached in one stage peroxide system with bleaching conditions [156] shown in the Table 2.3.

TABLE 2.1 Pulping conditions in the first experimental series

Pulp	Impregnation	Cook			Liquor-to-wood ratio
	Na_2SO_3 [%]	Temperature [°C]	Time [min]	Pressure [atm]	
RMP	0	-	-	-	-
CTMP	8	128	10	1.8	6:1
CTMP	8	128	60	1.8	6:1
CMP	8	150	55	4.0	6:1
CMP	8	160	30	5.2	6:1
WATER EXPLOSION	0	190	2.5	11.9	6:1
EXP	8	190	1.3	11.9	6:1
EXP	8	190	2	11.9	6:1
EXP	8	195	1.5	13.5	6:1
EXP	8	200	1	15.5	6:1
N-EXP	8	190	2	11.9/25	6:1
N-EXP	8	195	1.5	13.5/25	6:1
N-EXP	8	200	1	15.5/25	6:1

TABLE 2.2: Pulping conditions in the additional experiment

TRIAL	Impregnation			Cook		Liquor-to-wood ratio
	Na_2SO_3 [%]	NaOH [%]	$NaHCO_3$ [%]	Temperature [°C]	Time [min]	
1	8	0.5	0	190	4	6:1
2	16	1	0	190	4	3:1
3	8	0	1	190	2	6:1

TABLE 2.3: Bleaching conditions in the first experimental series

H_2O_2	4%
NaOH	2%
Na_2SiO_3	4%
$MgSO_4$	0.05%
DTPA	0.5%
Consistency	20%
Temperature	80°C
Time	180 min

2.2.3.2 SECOND EXPERIMENTAL SERIES

Encouraged by the results from the first experimental series and to answer other objectives questions, more in depth research was undertaken to better understand the action of explosion on the fibres.

In the second series of experiments, the work was carried out with a new impregnation solution system of $Na_2SO_3/NaHCO_3$. For all cases, the Na_2SO_3 concentration was kept at 8% and the $NaHCO_3$ addition was 1%. For all conditions, the liquor-to-wood ratio was 6:1. Two temperature levels of 190 and 195°C were chosen. In the case of nitrogen explosion, pressures prior to the explosion increased from 11.9/13.3 atm (corresponding to saturated steam pressure at 190/195°C) to 25 atm (Table 2.4).

TABLE 2.4: Pulping conditions in the second experimental series

TRIAL	Cook		
	Temperature [°C]	Time [min]	Pressure [atm]
1	190	2	11.9
2	190	2	11.9/17.5
3	190	2	11.9/20
4	190	2	11.9/22.5
5	190	2	11.9/25
6	195	1.5	13.5
7	195	1.5	13.5/17.5
8	195	1.5	13.5/20
9	195	1.5	13.5/22.5
10	195	1.5	13.5/25

2.2.3.3 THIRD EXPERIMENTAL SERIES

The conditions of the third trial series are listed in Table 2.5. The goal of this series was not only to work around the suggested optimum [36] (190°C/2 minutes), but also to stretch severity of treatment in both directions - to underdo and to exaggerate cooking conditions, keeping in mind that these extreme conditions might not lead to excellent quality pulps, but to generate valuable information about chemical changes during high severity cooking as well as good reference points for mathematical processing and process optimization.

The impregnation system was the same as in the second series - 8% Na_2SO_3 + 1% $NaHCO_3$ with the liquor-to-wood ratio 6:1. As the purpose of this work was not to enhance the impregnation, the best system known at that time was used. Three reference pulps (CMP, CTMP and one explosion pulp) were prepared with Na_2SO_3 only and one explosion pulp (water explosion) was prepared chemically free.

TABLE 2.5: Pulping conditions in the third experimental series

TRIAL	PULP	Impregnation		Cook		
		Na_2SO_3 [%]	$NaHCO_3$ [%]	Temperature [°C]	Time [min]	Pressure [atm]
1	EXP	8	1	180	1	9.9
2	EXP	8	1	180	2	9.9
3	EXP	8	1	180	4	9.9
4	EXP	8	1	190	1	11.9
5	EXP	8	1	190	2	11.9
6	EXP	8	1	190	4	11.9
7	EXP	8	1	200	1	15.5
8	EXP	8	1	200	2	15.5
9	EXP	8	1	200	4	15.5
10	N-EXP	8	1	180	1	9.9/25
11	N-EXP	8	1	190	2	11.9/25
12	N-EXP	8	1	200	4	15.5/25
13	EXP	8	0	190	2	11.9
14	W-EXP	0	0	190	2	11.9
15	CTMP	8	0	128	10	1.8
16	CMP	8	0	150	30	4.0

For cooking conditions, the temperature, time and pressure were the parameters to be studied. For good cooking severity evaluation, the experiment was planned at three complete levels for two variables (temperature and time) and for several levels for third variable (pressure). Three temperatures at levels of 180°C, 190°C and 200°C were chosen. Cooking times were of 1, 2 and 4 minutes. These conditions were selected to see the changes at doubling the reaction effect, which can be achieved not only by doubling the reaction time but also by increasing the reaction temperature by 10°C (Arhenius' law). This series involves 12 high severity pulps which should cover the majority of the explosion pulping interval. Together with four reference pulps, the experimental design is charted in Figure 2.1.

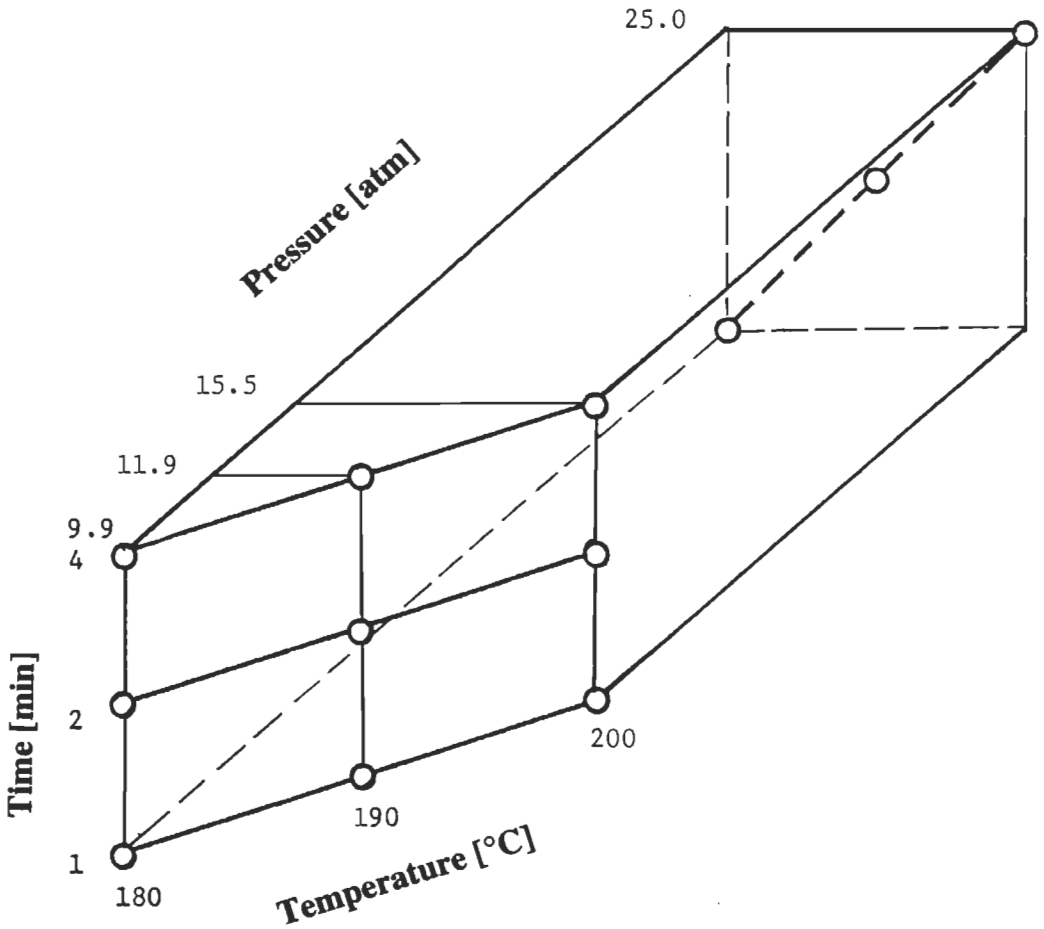


FIGURE 2.1: Experimental design in the third pulping series

2.3 PULP EVALUATION AND TESTING

2.3.1 PULP YIELD

Cooked pulp was washed with 1l of water, refined during 90 seconds in a laboratory blender, washed again with 1l of water and dried at 105°C. Yield was calculated as the oven dry pulp weight compared to oven dry chip weight.

2.3.2 REFINING AND REFINING ENERGY

Based on the information presented in chapter 1.2.4, refining was done using a domestic blender Osterizer B-9614 at a 2% consistency level. The resulting pulp was then washed and kept at 5°C for further evaluations. The refining energy was measured using a EW-604 wattmeter. Relative specific refining energy was calculated by substracting the blending energy of fully beaten pulp from the total energy needed to refine and blend the fiber suspension to given freeness level.

Each pulp was refined to at least three different freeness levels. The target values were 100, 300 and 500 ml CSF. If the lowest freeness value was between 101 and 110 ml CSF, we extrapolated the result to the 100 ml CSF level. If the lowest freeness value was over 110 ml CSF, we carried out another refining to get to 100 ml CSF or lower.

Most of the evaluations were carried out at 100 and at 200 ml CSF. The tendencies were very similar and since the most usual range of UHY pulp utilization is between 50 and 200 ml CSF, 100 ml CSF has been chosen to be presented in this work.

2.3.3 LATENCY REMOVAL AND PULP DISINTEGRATION

As a result of refining and subsequent pulp cooling, pulp fibers can be curled and twisted. This effect is called pulp latency and may cause inconsistencies in the freeness and paper properties. Therefore the pulp latency was removed

prior to freeness tests, sheet forming and any other analysis. Latency removal was carried out on never dried pulp by disintegration in hot water according to the CPPA standard C.10P.

2.3.4 FREENESS

The Canadian standard freeness (CSF) is a measure of the drainage rate at which a dilute suspension of pulp may be dewatered. It is a useful index of the amount of mechanical treatment given to the pulp and may correlate with the drainage behaviour of pulp material on a commercial paper machine. The CSF values were determined according to the CPPA standard C.1.

2.3.5 FIBER CLASSIFICATION AND S FACTOR

The pulps were fractionated into R14, 14/28, 28/48, 48/100, 100/200 and P200 using a Bauer-McNett fiber clasifier according to the TAPPI standard T233 cm-82. The abbreviation R14 means retained on a 14 mesh sieve, 14/28 (or the latter number alone) means fraction that passed through a 14 mesh sieve and retained on a 28 mesh sieve and P200 means passed through a 200 mesh sieve. S factor is defined as the CSF of the 48/100 fraction.

2.3.6 WATER RETENTION VALUE

Even if water retention value evaluation is not a specific fiber surface test method, it can lead to significant conclusions. WRV values reflect the surface accessibility of cellulose and its ability to swell, which is another important fiber parameter. Sakai [166] directly associated swelling to external fibrillation (which can be measured as specific surface) and Garceau [167] successfully used WRV measurement as an indirect measurement of specific surface. Other authors [67, 71, 137] also used WRV in pulp evaluation. In our trials, we used Lebel's description [168] of the WRV technique.

From the practical point of view, water retention value is a percentile amount of water held in the pulp sample after a 12-minute long centrifuging at 2500 rpm.

2.3.7 IONIC GROUP CONTENT

Ionic groups (both sulfonic and carboxylic) were determined by means of conductometric titration [181]

2.4 PAPER SHEET FORMING

Paper sheets were prepared according to the CPPA standard C.4. At least 7 sheets were prepared for each pulp sample at each freeness value. Paper sheets were prepared at two different weights: 1.2g (60 g/m^2) for physical testing and 3g (150 g/m^2) for physical and optical testing.

2.5 PHYSICAL AND OPTICAL PAPER TESTING

Physical and optical tests were performed on prepared handsheets according to the CPPA standards. These are the tests carried out:

Density: The density is the weight per unit volume or the apparent specific gravity and is usually reported as grams per cubic cemtimeter. Bulk is a reciprocal of paper density and represents the volume in cubic centimeters, occupied by 1 gram of paper. Both values are calculated from the oven dry basis weight and paper thickness (CPPA standard D.4).

Breaking lenght: The tensile breaking lenght is the maximum load or weight that the paper specimen will support before pullinf apart. Breaking length expresses length of paper that will cause its own rupture (CPPA standard D.6H).

Stretch: Stretch of paper is defined as the leongation per unit length at tensile failure (CPPA standard D.7H).

Burst: Bursting strength is defined as the hydrostatic pressure, required to produce paper rupture, when the force to the paper sheet is applied in perpendicular direction (CPPA standard D.8).

Tear: Internal tearing resistance of paper is defined as the work to tear a paper sheet where part of the work is represented by rupturing the paper and partly in bending the sample as it is being torn (CPPA standard D.9).

Porosity: Since paper sheet has a porous nature, porosity is a ratio of pores volume to the total sheet volume. Sheet porosity is evaluated by measuring its air permeability which is dependent on the number of pores and their distribution in siza, shape and orientation (TAPPI standard T547 pm-88).

Light-scattering coefficient (LSC): LSC is a measurement of the ability of the interior of the test sheet to scatter light. It depends on the unbonded fiber surface area (TAPPI standard T220 om-83).

Brightness: Absolute brightness is defined as the reflectance of blue light with a specified spectral distribution peaking at 457 nm compared to that of perfectly reflecting, perfectly diffusing surface (CPPA standard E.1).

Opacity: Opacity is described by means of the ratio of two values of reflectance. This ratio is derived by dividing the reflectance of a single sheet over black by that of a pad of the sample, or alternatively that of a single sheet over white (CPPA standard E.2).

Brightness reversion: This test provide an accelerated procedure for determining the brightness loss by an exposure to a combination of high humidity and high temperature (CPPA standard E.4P).

2.6 OTHER INSTRUMENTAL ANALYSES

In this section, some of the more recent evaluation methods will be mentioned. As these procedures are not as common as those above mentioned, more detail description will be given.

2.6.1 X-RAY DIFFRACTOMETRY

Based on the literature review of [41, 52, 58, 65, 67, 71, 93, 120, 123 to 129, 137, 139, 143, 144, 148, 162], the X-ray diffractometry was selected as one of the analysis approaches. This method should result in information about cellulose crystallinity and crystal size.

X-ray diffractometry is one of the three basic uses of X rays in instrumental analysis (the other two are the fluorescent and absorption analyses) [163]. X-ray diffractometry depends upon the wave character of X rays and the regular spacing of planes in a crystal. Although diffraction methods can be used for quantitative analysis, they are also widely used for qualitative identification of crystalline phases.

In analyzing a crystal, virtually monochromatic radiation is obtained by reflecting X rays from crystal planes. The relationship between the wavelength of the X-ray beam, and the angle of diffraction θ, and the distance between each set of atomic planes of the crystal lattice, d, is given by the Bragg condition [164]:

$$m\lambda = 2d.\sin\theta$$

where m represents the order of the diffraction and λ is the wavelength of the X-ray. The geometric relations are shown in Figure 2.2.

For the ray diffracted by the second plane of the crystal, the distance CBD represents the additional distance of travel in comparison to a ray reflected from the surface. Angles CAB and BAD are both equal to θ. Therefore,

$$CB = BD = AB.\sin\theta$$

and

$$CBD = 2AB.\sin\theta$$

where AB is the interplanar spacing d. In order to observe a beam in the direction of the diffracted rays, CBD must be some multiple of the wavelength of the X rays, so the diffracted waves will be on phase. The range of wavelengths usable is governed by the d-spacings of the crystal planes and by the geometric limits of the rotation.

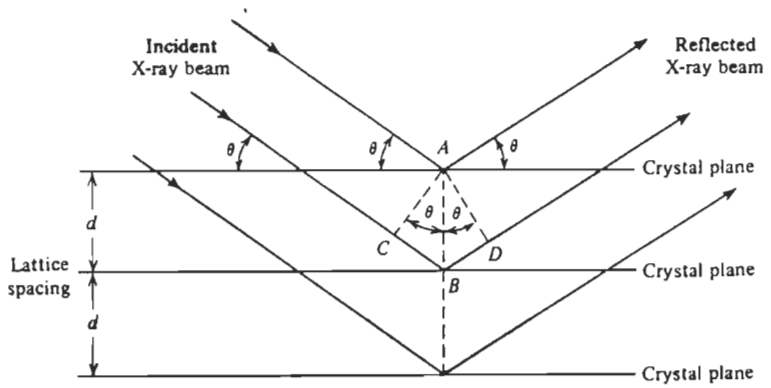


FIGURE 2.2: Diffraction of X-rays from a set of crystal planes.

Every atom in the crystal scatters an X-ray beam incident upon it in all directions. Because even the smallest crystal contains a very large number of atoms, the chance that these scattered waves would constructively interfere would be almost zero except for the fact that the atoms in crystals are arranged in a regular, repetitive manner. Atoms located exactly on the crystal planes

contribute maximally to the intensity of the diffracted beam. The scattering power of an atom for X-rays depends upon the number of electrons it possesses. Thus the position of the diffraction beams from a crystal depends only upon the size and shape of the repetitive unit of a crystal and the wavelength of the incident X-ray beam, whereas the intensities of the diffracted beams depend also upon the type of atoms in the crystal and the location of the atoms in the fundamental repetitive unit, the unit cell. From these considerations, calculation of the width of the crystal, as well as the number of levels participating at the diffraction can be made.

Another important information concerns the crystallinity index was given by Browning who showed [165] that the crystallinity index can be determined from the ratio of the intensity of diffraction to that of scattered radiation:

$$\text{Crystallinity index} = (L002\text{-}Lam)/L002$$

where L002 is the intensity of the diffraction from the (002) plane at $2\theta = 22.5°$ and Lam is the intensity of the background scatter measured at $2\theta = 18.0°$.

2.6.2 ESCA

ESCA (Electron Spectroscopy for Chemical Analysis) is a technique for surface chemical analysis. The method is concerned with the measurement of core-electron binding energies. A molecule or atom is bombarded with a source of high-energy X-rays which cause the emission from sample atoms of inner-shell electrons. All electrons whose binding energies are less than the energy of the exciting X-rays are ejected. The kinetic energies, E_k, of these photoelectrons are then measured by an energy analyser. The core-electron binding energies, E_b, can be then computed via the relationship

$$E_b = h\nu - E_k - \phi$$

where $h\nu$ is the energy of the exciting radiation and ϕ is the spectrometer work function, a constant for a given analyzer.

Although the X-ray photon may penetrate and excite photoelectrons to a depth of several hundred nanometers, only the photoelectrons from the outermost layers have any chance to escape from the material environment and to be eventually measured. Most of ESCA measurements of solids generate useful information from only the outer 2.0 nm of the surface layer.

CHEMICAL SHIFT

The utility of ESCA for the chemist is the result of chemical shifts that are observed in electron binding energies. The binding energies of core electrons are influenced by the valence electrons and therefore by the chemical environment of the atom. When the atomic arrangement surrounding the atom ejecting a photoelectron is changed, it alters the local (quantum) charge environment at the atomic site. This change, in turn, reflects itself as a variation in the binding energy of all the electrons of that atom. thus, not only the valence electrons, but also the binding energies of the core electrons experience a characteristic shift. Such a shift is inherent to the chemical species producing the results and thus provides the capability of chemical analysis. In a simple sense, the shifts of the photoelectron lines in an ESCA spectrum reflect an increase in binding energy as the oxidation state of the atom becomes more positive. In general, any parameter, such as oxidation state, ligand electronegativity, or coordination, that effects the electron density about the atom is expected to result in a chemical shift in electron binding energy.

A major portion of the strength of ESCA as an analytical tool lies in the fact that chemical shifts can be observed for every element in the periodic chart (except for hydrogen and helium). Magnitudes of chemical shifts will vary from element to element, and in general they lie in the range 0 to 1500 eV.

Even if the absolute quantification has not been accomplished so far, a relative quantification of one species to another can be made. This is based on peak area sensitivity factors. The number of photoelectrons per second in a specific spectral peak, I, can be given by:

$$I = K n \sigma \lambda T$$

Where:

K is a proportionality constant,
n is the number of atoms of the element per cm^3 of sample,
σ is the photoelectric cross-section for the atomic orbital of interest,
λ is the inelastic mean free path of the electron,
T is the detection efficiency for electrons emitted from the sample.

This can be rewritten as:

$$n = I / K \sigma \lambda T$$

The denominator in this equation can be assigned the symbol S, defined as the atomic sensitivity factor. If we take another element R as reference, the mean atomic ratio of the element X we are interested in, to the element R is:

$$n_x / n_r = (I_x / S_x) / (I_r / S_r)$$

From this equation, we are able to quantify the element of interest.

For peak synthesis, which is a curve fitting technique for resolving the complex spectra, we used a VGS 1000 computer software. The atomic ratio on the surface can be estimated from corresponding peak and from the above equation. Using Scoffield's cross sections [171] for oxygen O_{1s}, carbon C_{1s} and sulfur S_{2p} peaks, corrected for angular asymmetry, electron attenuation length and instrument transmission [172], the following equations can be obtained:

$$O/C = I_O / (2.851\ I_C)$$

$$S/O = 1.497\ I_S / I_O$$

Thus:

$$S/C = (S/O) / (O/C) = 0.525\ I_S / I_C$$

Where:

O/C is the atomic ratio of oxygen to carbon
S/O is the atomic ratio of sulfur to oxygen
S/C is the atomic ratio of sulfur to carbon
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_{2p} peak

Based on these equations, the various atomic ratios can be calculated from corresponding normalized peak areas.

2.6.3 FTIR AND RAMAN SPECTROSCOPY

Infrared spectroscopy is one of the most commonly used instrumental techniques for identification and characterization of chemical structures. It is a technique investigating the vibrational energy levels of a molecule that are mostly in the range of infrared radiation. The conventional IR approach uses a dispersive technique in which the IR radiation passes through a narrow slit and grating system to limit the frequency range of the radiation reaching the detector to one resolution width. Thus, the disatvantage of this approach is its low sensitivity, limiting its use to sampling techniques in which a substantial proportion of the incident energy reached the reactor, and to slow events. This could be overcome by the combined application of interferometry and Fourier transform techniques with digital computers. Thendetected signal intensity is improved by using the Michelson type of interferometer (instead of the grating one). The detected signal intensity is dependent on the readiation frequency and the displacement of the moving mirror in the interferometer. The resulting interferogram contains thus information of the intensity of each frequency in the spectrum. This interferogram is then calculated by Fourier transformation to yoeld the IR spectrum. Because the FTIR process uses a laser to monitor the position of the moving mirror, the frequency of the measured spectrum is very accurate, and the risk of drift during multiple scanning is absent. Moreover, the computation ability is improved since the data are in digital form. This allows the spectrum to be mathematically treated and the most commonly used techniques

helping to spectra interpretation are spectral substraction, derivatization and deconvolution [142].

Raman spectra (although related to infrared absorption spectra) arise in a quite different manner and thus provide complementary information. Vibration spectra that are active in Raman may be inactive in the infrared and vice versa.

The Raman effect arises when a beam of intense monochromatic light passes through a sample that contains molecules that can undergo a change in molecular polarizability as they vibrate [161]. The electric field produced by the polarized molecule oscillates at the same frequency as the passing electromagnetic wave, so that the molecule acts as a source sending out radiation of that frequency in all directions. As the electromagnetic wave passes, the polarized molecule ceases to oscillate and returns to its original ground level in a very short time (approximately 10-12 sec).

3. RESULTS AND DISCUSSION

3.1 FIRST EXPERIMENTAL SERIES

3.1.1 PULP PREPARATION AND PULPING RESULTS

High yield pulps and even ultra-high yield pulps (85%+) can be prepared over a wide range of process conditions. Based on results of previous research as well as on theoretical considerations, the high temperature and pressure are probably the most influential factors contributing to better performance of explosion pulps.

Pulping conditions, pulp and paper properties resulted from this experimental series are presented in Table 3.1 to 3.3. In most of the figures in this chapter, pulping temperature has been chosen as an independent variable - as a simple manner for better visualization of our results. In reality, pulp response is a complex function of multiple influences (we would need at least two or three parameters to explain satisfactorily different effects on individual pulp properties) and the mathematical treatment will be presented more in detail in the next chapter.

In this part, particular attention was focused on the influence of temperature and pressure. Pulping conditions were adapted to eliminate some of the process variables. First, pulps were produced at the same yield. Table 3.1 and Figure 3.1 show that pulp yield for the two CMPs and most of the explosion pulps (SEP) was 90%. Explosion pulps were cooked under usual conditions while the CMP cooking times were extended somewhat to obtain a yield of

90%. In the case of CTMP, conventional cooking gave a yield of 95% (Pulp 2). However, we managed to prepare a CTMP and an explosion pulp at comparable yield (about 93%) by extending the CTMP cook and shortening the SEP cook.

Second, all pulps received the same amount of chemical added, except for the RMP, where no chemicals were used. The chemical charge during the impregnation as well as the resulting uptake was the same for all chemically treated pulps.

We do realize that the cooking conditions for the CMP and CTMP are somewhat different from the industrially used ones, but as we explained in the project description, we wanted to compare the outcome of different processes based on the same chemical charge and same yield.

Figure 3.2 shows that the total ionic content was similar for most of chemically treated pulps. However, Figure 3.3 shows that the degree of sulfonation was higher in explosion pulps.

Ionic content is one of the most important factors contributing to the pulp's mechanical properties [82, 182]. As shown previously [36], mechanical properties of explosion pulps are superior to those of other high yield pulps at the same ionic (sulfonic) content. Similarly, explosion pulps provide comparable mechanical properties at lower ionic content. This was confirmed in our study and is discussed later in this chapter.

TABLE 3.1 Pulping conditions and some of the characteristics of resulted pulps in the first experimental series

#	Pulp type	Cooking					Ionic content [mmol/kg]				Symbol used in figures
		Time [min]	Temp. [°C]	Pressure [atm]	Yield [%]		Sulfonic	Carboxylic	Total		
					Value	Error			Value	Error [%]	
1	RMP	-	-	-	98.8	0.7	0.0	77	77	3.2	▫
2	CTMP	10	128	1.8	95.3	0.8	35	143	178	3.3	▫
3	CTMP	60	128	1.8	93.1	1.0	39	141	180	2.9	▫
4	CMP	55	150	4.0	89.6	0.6	37	128	165	3.0	○
5	CMP	30	160	5.2	89.9	0.6	38	141	179	4.1	○
6	WATER EXPLO-SION	2.5	190	11.9	91.3	0.6	0.0	94	94	3.6	▲
7	EXP	1.3	190	11.9	92.6	0.4	46	134	180	2.2	●
8	EXP	2.0	190	11.9	90.4	0.7	43	137	180	3.4	●
9	EXP	1.5	195	13.6	90.1	0.3	46	134	180	3.4	●
10	EXP	1.0	200	15.5	89.9	0.6	45	121	166	5.0	●
11	N-EXP	2.0	190	11.9/25	90.0	0.5	40	140	180	4.5	■
12	N-EXP	1.5	195	13.6/25	89.7	0.7	51	132	183	3.8	■
13	N-EXP	1.0	200	15.5/25	90.0	0.4	42	137	179	4.1	■

TABLE 3.2 Mechanical paper properties obtained in the first experimental series

Pulp			Parameter values and experimental error in [%]											
#	Type	CSF [ml]	Density [kg/m^3]		Porosity [ml/min]		Breaking length [km]		Stretch [%]		Tear [mNm^2/g]		Burst [kPam^2/g]	
			Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	RMP	95	211	2.3	600	3.3	1.6	2.8	1.1	4.2	3.3	2.0	0.6	6.3
		305	234	3.3	2480	3.2	0.8	2.6	1.0	3.6	2.3	6.3	0.3	2.3
		513	It was not possible to prepare handsheets at this freeness											
2	CTMP	104	378	2.9	360	3.9	3.4	2.9	1.3	4.3	4.1	3.2	1.3	3.2
		280	339	2.6	1150	4.0	2.7	2.6	1.2	3.6	4.0	4.4	0.9	1.9
		440	294	2.3	2490	2.3	1.8	3.0	0.9	3.8	4.5	5.0	0.6	2.6
3	CTMP	110	415	2.4	242	2.6	4.1	2.4	1.6	4.0	5.1	6.4	1.8	3.0
		295	452	3.6	1160	3.6	3.0	2.9	1.1	4.3	4.5	5.9	1.1	2.4
		55	284	2.2	3600	5.0	1.7	3.2	0.8	3.2	3.4	6.2	0.6	2.6
4	CMP	85	435	1.9	90	2.9	4.9	4.1	1.5	2.9	6.3	4.4	2.2	2.3
		240	395	2.0	500	3.1	4.1	3.6	1.4	3.5	5.7	5.8	1.6	3.5
		520	314	1.8	2500	4.6	2.6	2.9	1.0	3.6	5.1	6.0	0.9	4.3
5	CMP	106	475	2.6	90	4.4	5.9	3.5	1.9	3.6	7.1	3.9	2.2	2.3
		275	417	2.2	400	4.4	4.6	3.6	1.5	4.0	6.4	1.0	1.6	2.0
		500	370	2.2	2045	2.6	3.4	3.4	1.2	4.3	5.9	5.8	0.9	2.1
6	W-EXP	75	413	2.3	80	2.4	4.6	2.0	1.7	4.6	6.2	6.3	2.0	2.9
		195	381	2.5	300	2.5	3.6	3.6	1.3	2.1	5.4	4.5	1.5	2.6
		420	335	2.0	1415	2.9	2.4	2.9	1.0	3.9	4.7	7.6	0.9	3.0
7	EXP	100	510	2.9	50	3.6	5.9	2.1	1.8	3.1	8.2	3.6	3.0	3.5
		325	433	3.4	630	2.5	4.5	3.6	1.3	2.6	6.2	5.6	2.0	2.0
		545	381	4.0	1945	2.6	3.5	3.4	1.1	3.0	6.4	6.4	1.3	2.6
8	EXP	98	530	2.6	30	2.4	6.4	4.3	1.9	3.3	7.5	5.7	3.1	2.7
		270	480	2.7	345	2.8	5.2	4.3	1.7	4.6	7.1	7.3	2.3	2.7
		500	422	2.9	1490	2.9	4.5	1.9	1.4	4.2	7.4	6.8	1.9	2.7
9	EXP	95	516	2.0	40	2.9	6.7	1.6	2.0	4.3	7.7	6.6	3.2	2.5
		180	487	1.8	175	2.0	5.7	2.9	1.8	4.1	7.2	5.3	2.5	2.1
		476	395	3.9	1770	2.6	3.9	4.3	1.2	4.1	7.2	4.6	1.7	2.6
10	EXP	103	520	1.6	75	4.0	6.5	3.5	2.0	3.5	7.4	6.4	3.1	3.2
		210	473	3.0	210	3.6	5.2	2.8	1.7	3.6	7.3	5.8	2.3	3.3
		330	438	2.5	685	2.5	4.6	3.1	1.5	3.5	7.0	5.4	1.9	1.6
11	N-EXP	108	554	2.6	60	2.6	6.9	2.6	1.9	3.0	7.4	5.0	3.2	2.6
		245	460	2.1	200	3.2	5.6	3.0	1.7	3.4	7.6	6.3	2.6	3.3
		496	404	3.5	1920	2.8	4.0	3.0	1.3	1.3	7.4	4.4	1.6	3.4
12	N-EXP	100	533	2.9	50	3.9	6.4	3.0	2.0	3.6	8.0	5.7	3.2	4.2
		217	494	3.6	235	4.0	5.6	2.4	1.7	2.6	7.5	6.1	2.4	4.1
		520	404	2.0	2190	2.4	4.1	4.2	1.3	3.5	8.1	5.6	1.6	3.2
13	N-EXP	98	540	1.6	15	2.6	6.6	3.9	1.8	4.3	8.1	5.9	3.8	3.6
		210	460	3.1	200	3.5	5.8	3.4	1.5	4.4	8.1	7.1	2.8	3.4
		520	431	2.4	2130	4.0	4.0	4.0	3.2	4.9	6.9	3.2	1.5	2.1

TABLE 3.3 Refining energy and optical paper properties obtained in the first experimental series

Pulp			Parameter values and experimental error in [%]											
#	Type	CSF [ml]	Relative specific refining energy [MJ/kg]		Brightness 1.2 g sheet (60 g/m^2) [%MgO]		Brightness 3.0 g sheet (150 g/m^2) [%MgO]		Brightness loss [%]		Opacity [%]		Light-scattering coefficient [cm^2/g]	
			Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	RMP	95	12.0	4.2	64.1	1.2	65.2	1.3	0.2	-	95.2	1.3	639	2.6
		305	9.6	3.6	63.9	2.3	64.1	1.5	0.2	-	92.7	1.5	519	2.5
		513	6.3	5.6	It was not possible to prepare handsheets at this freeness									
2	CTMP	104	13.6	3.1	65.8	1.5	69.3	1.6	0.4	-	93.5	1.2	579	2.6
		280	11.4	2.6	65.9	1.6	68.6	1.4	0.3	-	92.9	1.2	522	2.6
		440	9.4	3.5	66.9	1.4	68.9	1.5	0.3	-	92.6	0.3	493	2.5
3	CTMP	110	9.7	6.3	65.7	1.4	67.6	1.8	0.3	-	92.9	0.4	563	3.2
		295	7.2	2.9	65.6	1.6	67.9	1.7	0.4	-	91.3	1.9	503.	3.4
		55	4.4	1.8	64.2	1.8	67.1	1.8	0.6	-	90.0	1.5	443	2.6
4	CMP	85	9.0	3.2	57.4	1.7	58.5	1.9	0.1	-	94.8	1.2	490	2.8
		240	8.0	3.6	60.5	0.6	62.4	1.4	0.1	-	92.4	1.0	477	2.9
		520	5.5	6.2	58.5	0.5	60.9	1.5	0.2	-	92.1	1.0	428	2.7
5	CMP	106	7.9	4.4	59.3	1.1	60.7	1.4	0.1	-	92.8	1.6	447	2.1
		275	5.5	5.0	60.5	1.0	62.4	1.5	0.2	-	91.7	1.5	437	2.6
		500	3.0	1.6	57.9	1.0	59.6	1.7	0.2	-	91.7	0.2	421	3.2
6	W-EXP	75	11.0	3.5	41.6	1.3	42.9	1.6	0.1	-	99.6	0.5	668	1.0
		195	9.9	3.6	42.3	1.2	42.9	1.6	0.1	-	99.1	1.3	615	5.2
		420	7.6	3.4	41.8	1.6	42.8	1.2	0.1	-	98.9	1.2	580	3.6
7	EXP	100	4.5	3.5	61.5	1.1	63.3	1.4	0.4	-	92.5	1.2	440	3.4
		325	2.6	3.6	60.0	1.9	63.0	1.2	0.4	-	90.0	1.0	427	2.6
		545	1.7	5.9	61.4	1.8	63.8	1.6	0.3	-	89.6	1.1	418	2.8
8	EXP	98	4.0	2.9	62.0	1.7	64.0	1.5	0.5	-	89.6	1.1	400	3.2
		270	3.3	2.6	59.7	1.8	62.2	1.2	0.7	-	89.4	0.6	410	3.1
		500	2.0	3.5	62.3	1.9	64.2	1.0	0.4	–	87.2	0.8	391	3.6
9	EXP	95	3.7	4.6	60.2	1.7	65.1	1.3	1.0	-	88.6	2.3	399	3.2
		180	3.2	2.6	60.0	1.7	64.2	1.0	1.2	-	89.0	2.1	396	3.5
		476	1.5	2.4	60.2	1.9	64.9	1.2	1.6	-	88.3	0.5	388	2.6
10	EXP	103	3.5	2.5	61.6	1.6	63.5	1.6	0.6	-	89.0	0.6	425	2.5
		210	3.0	2.9	60.9	1.4	63.7	1.5	0.7	-	90.3	1.6	423	3.5
		330	2.5	6.2	60.5	1.5	63.5	0.3	0.9	-	89.0	1.4	414	1.8
11	N-EXP	108	3.2	3.5	57.6	1.1	58.3	0.5	0.4	-	90.8	1.8	400	4.3
		245	2.8	3.3	60.6	1.8	65.1	1.6	1.3	-	88.5	1.4	390	2.9
		496	1.4	6.8	57.6	1.7	61.4	1.4	1.4	-	89.9	1.4	390	3.7
12	N-EXP	100	3.1	1.9	61.3	1.9	65.8	1.1	1.0	-	87.8	1.4	382	5.1
		217	2.7	3.5	59.1	1.8	63.9	1.6	0.8	-	88.1	1.4	368	2.6
		520	1.2	4.6	59.0	1.7	64.4	2.1	1.1	-	88.1	1.4	384	3.5
13	N-EXP	98	2.9	6.5	61.0	1.8	65.4	0.6	1.0	-	88.7	1.6	375	3.4
		210	2.4	3.9	61.4	1.6	65.7	2.3	1.0	-	86.0	1.6	369	3.6
		520	1.0	4.7	60.9	1.0	65.7	2.0	0.6	-	88.7	1.2	383	1.2

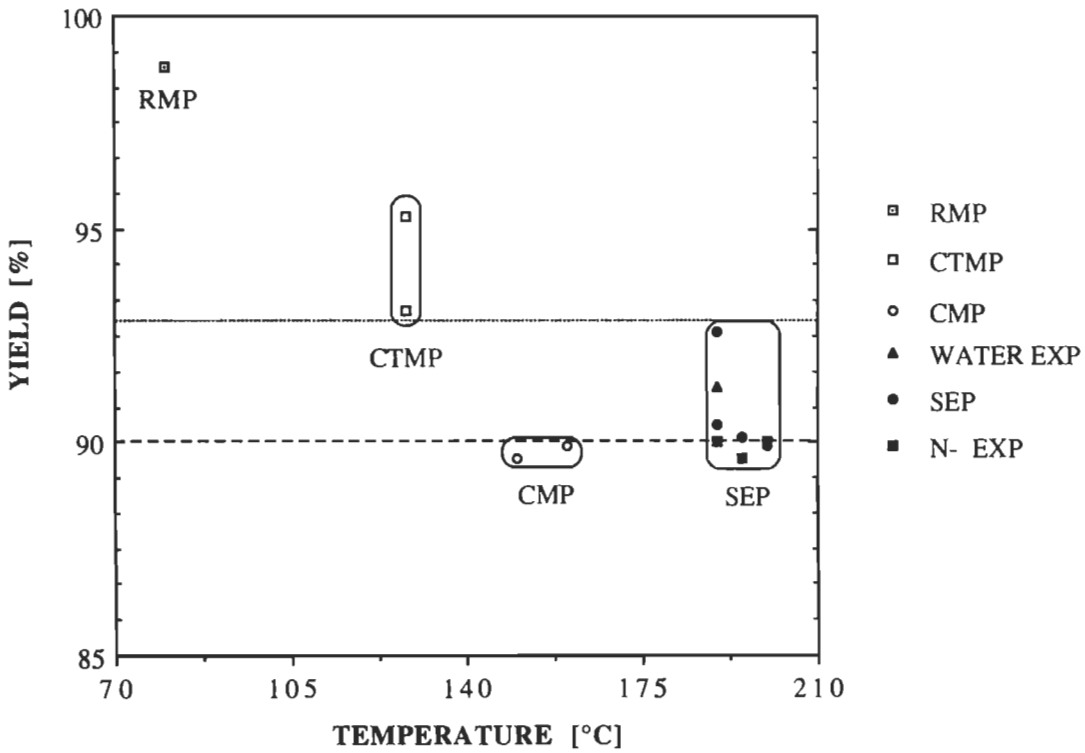


FIGURE 3.1 Yield as a function of temperature

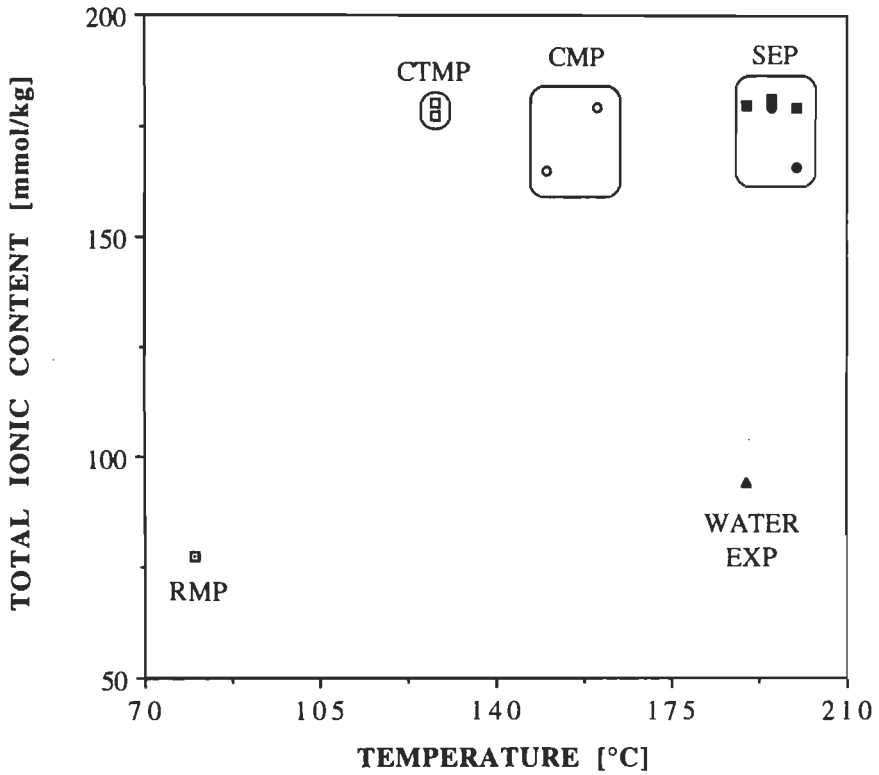


FIGURE 3.2 Ionic content as a function of temperature

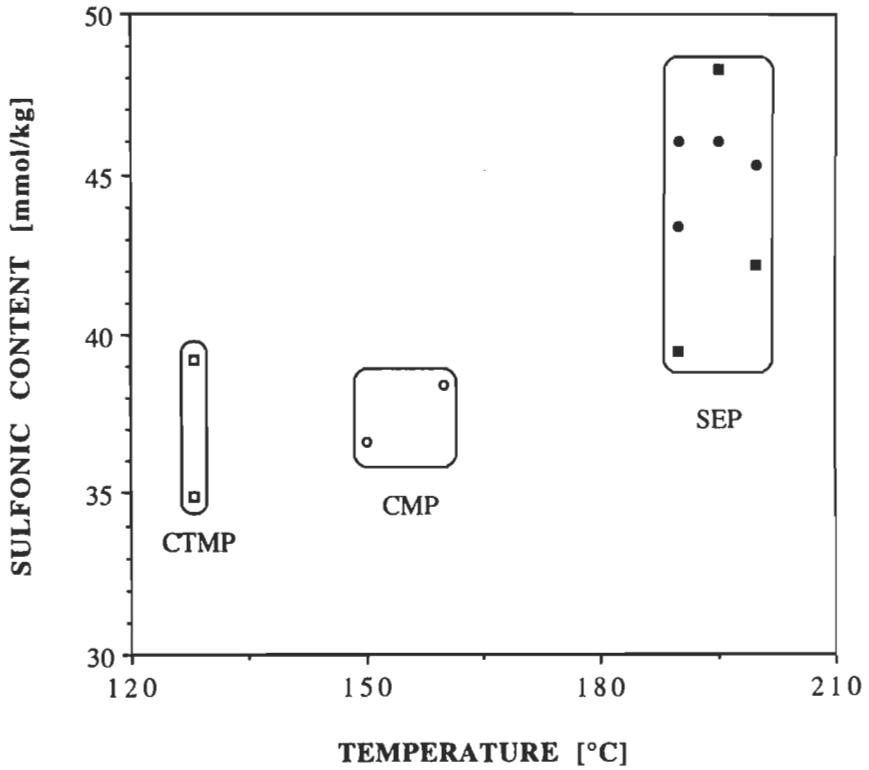


FIGURE 3.3 Sulfonic content as a function of temperature

3.1.2 REFINING ENERGY

As we stated in the chapter 1, the blender may not be the ideal method for refining pulp, but it has been reported as the best method for refining in a small scale [111]. Pulp properties and refining energies obtained with the blender compared well with the semi-industrial results [36, 50].

Figure 3.4 shows the relative specific refining energies for chemically treated pulps at a freeness of 100 ml CSF. The decrease in refining energy in the case of SEP can be attributed to the influence of temperature and explosive discharge from the digester. The cooking temperature in the SEP process is above the glass-transition temperature for lignin, which leads to additional permanent softening of the chips. The explosive discharge helps to separate the softened chips into individual fibers as well as fibrillating the individual fibers themselves [120]. Even if we didn't achieve the extent of defibration as in the semi-industrial trials (up to 37% of fibers), it was evident, that exploded chips were on touch much more flexible than CMP or CTMP and could be easily separated into fibers and refined. The shorter refining time (diminished energy requirements) also helps preserve fiber length.

If we concentrate more specifically on the high severity area (Figure 3.5), we can see a drop in the relative specific refining energy with an increase of either cooking time and cooking temperature. This suggests that cooking severity does have a significant influence on the pulp quality. If we compare the two pulps cooked at 190°C - a 40 second increase in cooking time (from 80 seconds to 2 minutes) was sufficient to cause a 0.5 MJ/kg drop in refining energy requirement (from 4.5 to 4.0 MJ/kg). Working at the same yield, a 10°C temperature increase caused another drop from 4.0 to 3.5 MJ/kg. If the reactor was pressurized to 25 atmospheres prior to the explosion, the pulp was even easier to refine and the refining energies were in the neighborhood of 3.0 MJ/kg. The highest drop caused by the nitrogen explosion was in the case of 190°C/2 min (at the highest pressure difference). However, the lowest refining energy was measured for pulp #13 (200°C/1 min).

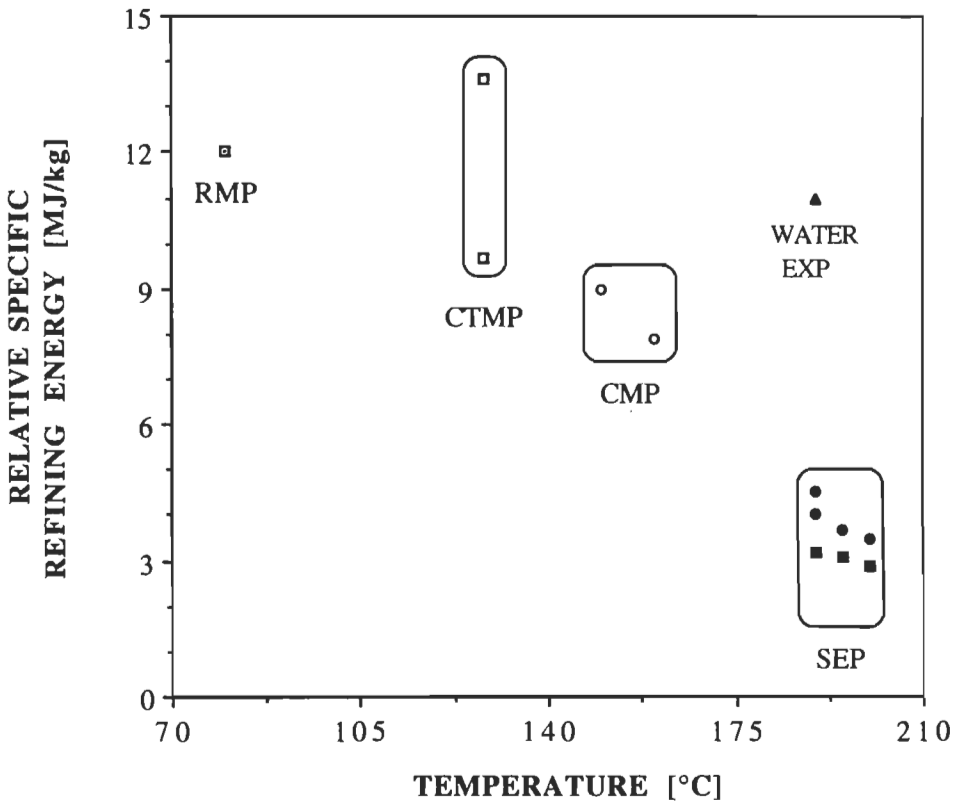


FIGURE 3.4 Relative specific refining energy as a function of temperature (at 100 ml CSF)

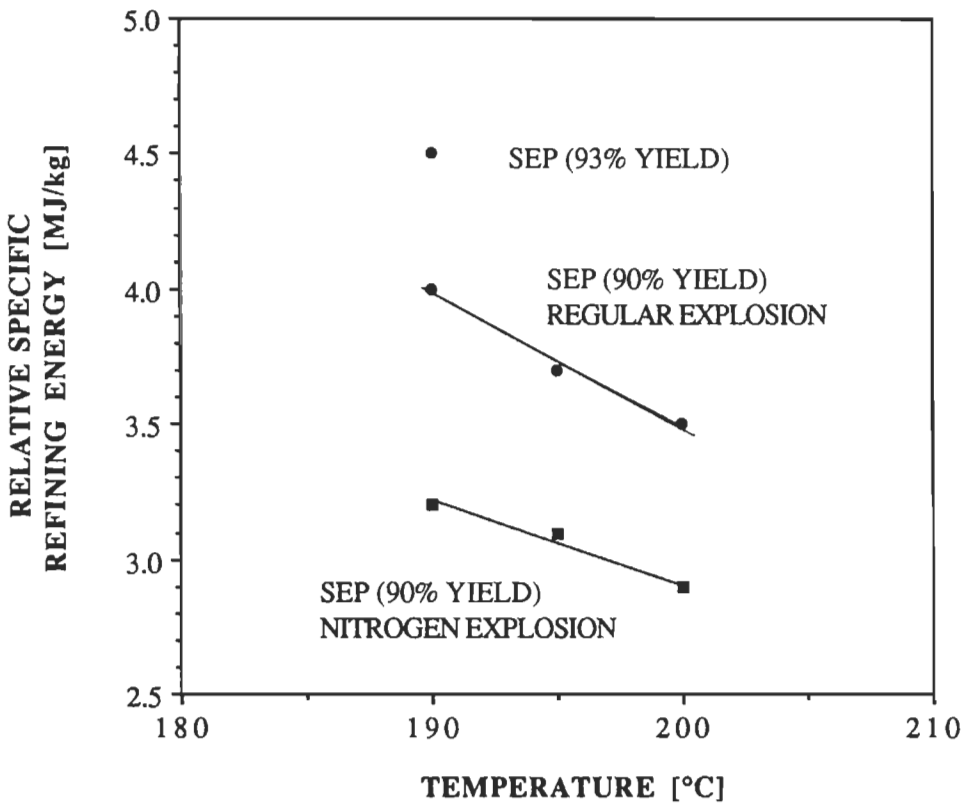


FIGURE 3.5 Relative specific refining energy as a function of temperature for high severity pulps (at 100 ml CSF)

3.1.3 FIBER PROPERTIES

Because of the permanent lignin softening and the explosive discharge, explosion pulps need substantially less energy for fiber separation. It is supposed that most of the energy is thus applied to fiber development. The higher average fiber length of explosion pulps (which will be discussed later in this section) can be explained by the shorter refining time and by fiber separation. (The blade does not cut into the shives or fiber particles, treating separated fibers instead). The fiber length distribution for some pulps is shown later in this chapter in Figure 3.25. It is clear that high severity cooking conditions resulted in longer fibers. The microscopic study of our explosion pulps samples also showed that even in the coarser fractions (R-14 and R-28) we did have very few fiber bundles and shives. This count seemed to be several times higher in the case of RMP, CTMP and CMP. Explosion pulps had the overwhelming majority of fibers well separated with more or less developed surface fibrillation. Scanning electron microscopy (SEM) revealed that the surface fibrillation was mostly dependent on freeness level and on the fraction size. Unfortunately, due to low photoprint quality, we were unable to include them as a confirmation of our observation.

The surface development of fibers can be evaluated using the S-factor. (S-factor is a measure of the freeness of the fraction that has passed through a 48-mesh wire but has been retained on a 100-mesh wire on the Bauer-McNett fiber classifier). Figure 3.6 shows that the SEPs had a lower S-factor than the CMPs, indicating higher specific surface, possibly as a result of good fiber development. Most of the SEPs also had a lower S-factor than CTMP and RMP. S-factor of CTMP and RMP is lowered by higher amount of debris and fines, both of which significantly retard pulp drainage.

Because of the lignin softening that occurs at high temperature, we expected the longer fibers in the SEPs to be also more flexible. Figure 3.7 depicts pulp density as a function of cooking temperature for pulps at 100 ml CSF. High density is a sign of fiber flexibility (since the explosion pulps have higher amount of long fibers, as it is shown in the Figure 3.24), and it is clear that pulp density increased with the severity of the cooking process. Even the water explosion pulp (no chemicals) had a density comparable with that of CTMP.

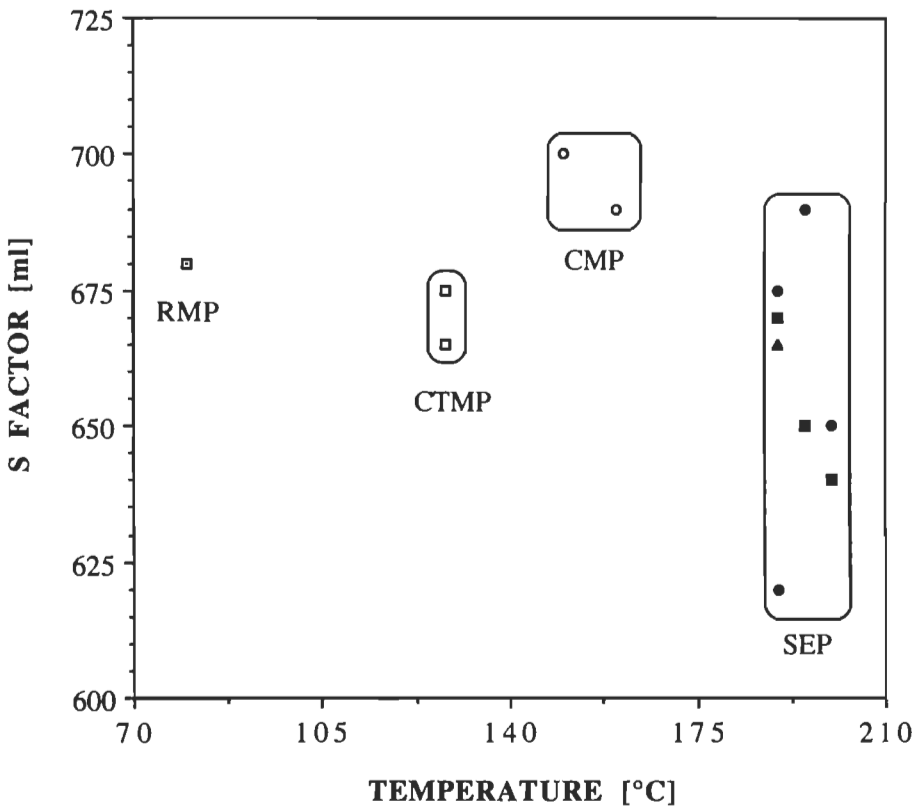


FIGURE 3.6 S factor as a function of temperature (at 100 ml CSF)

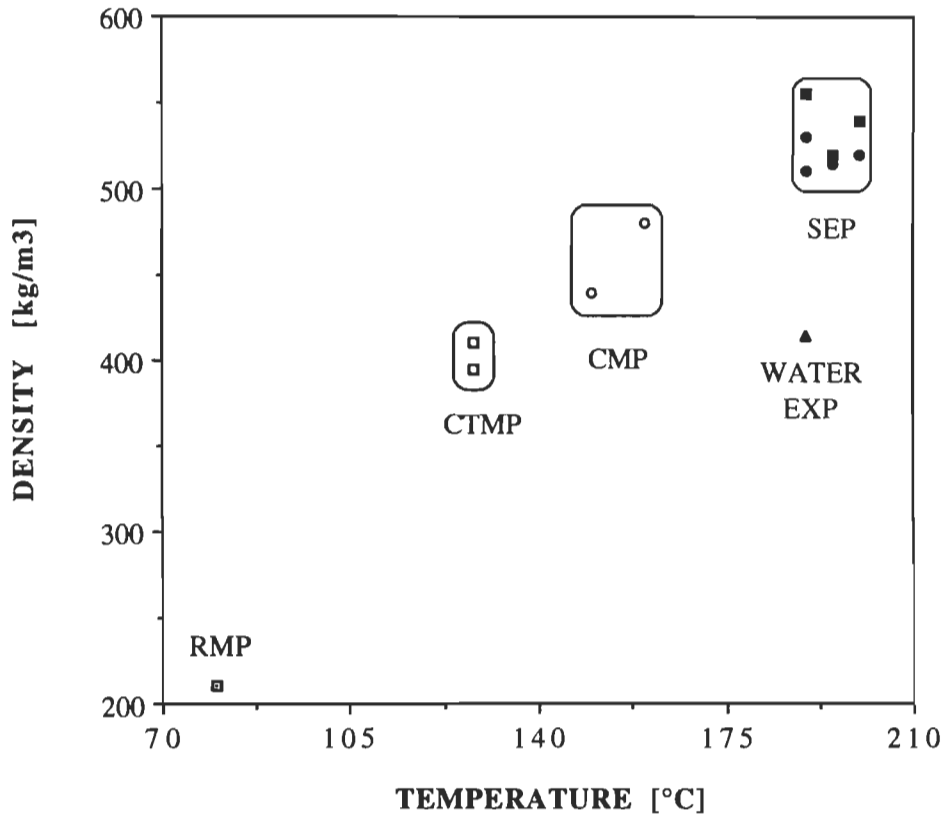


FIGURE 3.7 Density as a function of temperature (at 100 ml CSF)

Presumed higher flexibility of the longer SEP fibers should improve the fiber to fiber contact possibilities. This should contribute to better bonding capacity, and subsequently to better mechanical properties of explosion pulps. Light-scattering coefficient (LSC) is another way of measuring bonding capacity. The LSC refers to the unbound surface in the pulp sample which is a parameter that can relate to at least two important facts. In optical properties, the lower LSC shows to the lower capacity to reflect and scatter light beams which results in lower opacity. On the other hand, lower LSC means that there is more bonded surface in pulp or paper sample which should logically suggest higher mechanical parameters, such as the breaking length and tear. Generally, the LSC factor is higher for mechanical pulps and decreases with the degree of chemical treatment. The lowest LSC factors are in the case of chemical pulps (kraft and sulfite). Figure 3.8 shows LSC as a function of pulping temperature. The low LSC for the SEPs suggests better contact between the fibers and hence their better bonding capacity. As in Figure 3.7, pulp density (bonding potential) increases with increasing severity of the cooking process (represented by the temperature), favoring the explosion pulps over the conventional CMP and CTMP.

Pulp porosity is another analysis that confirms that the structure of explosion pulps is more dense and more bonded. For the majority of explosion pulps, the porosity was several times lower than in the case of CMP and CTMP (Figure 3.9).

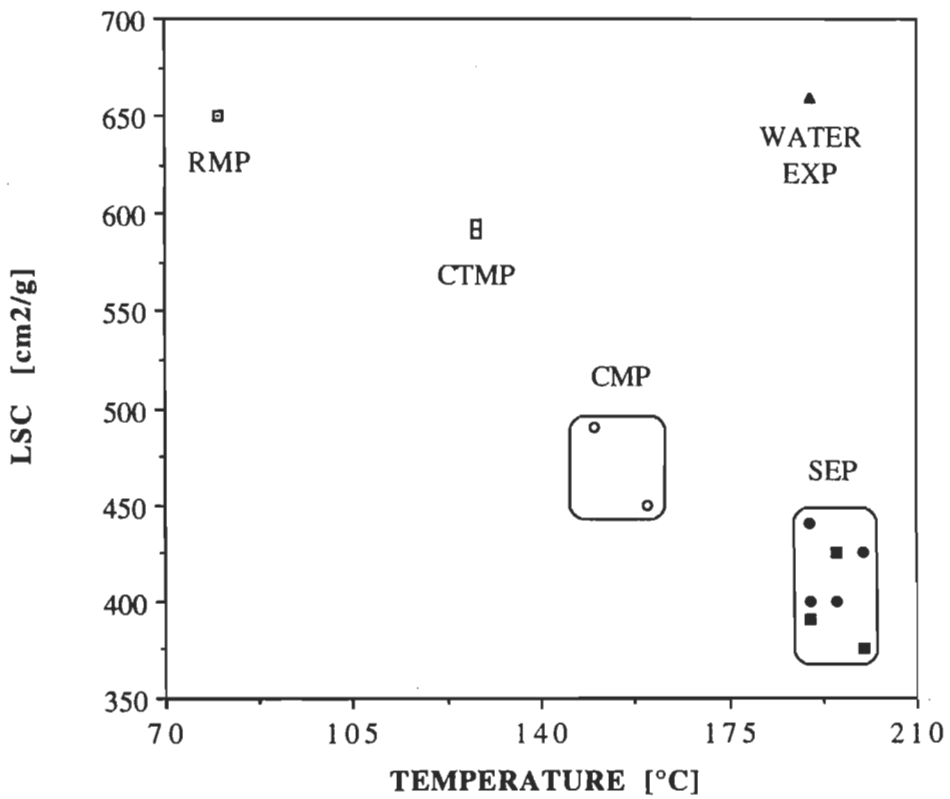


FIGURE 3.8 LSC as a function of temperature (at 100 ml CSF)

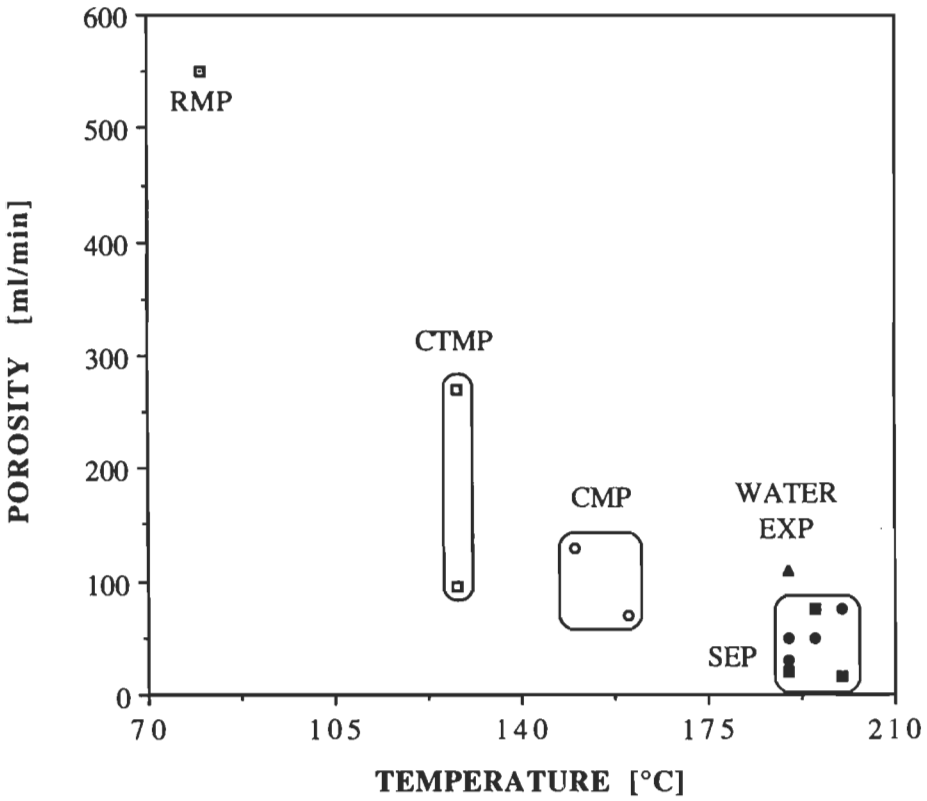


FIGURE 3.9 Porosity as a function of temperature (at 100 ml CSF)

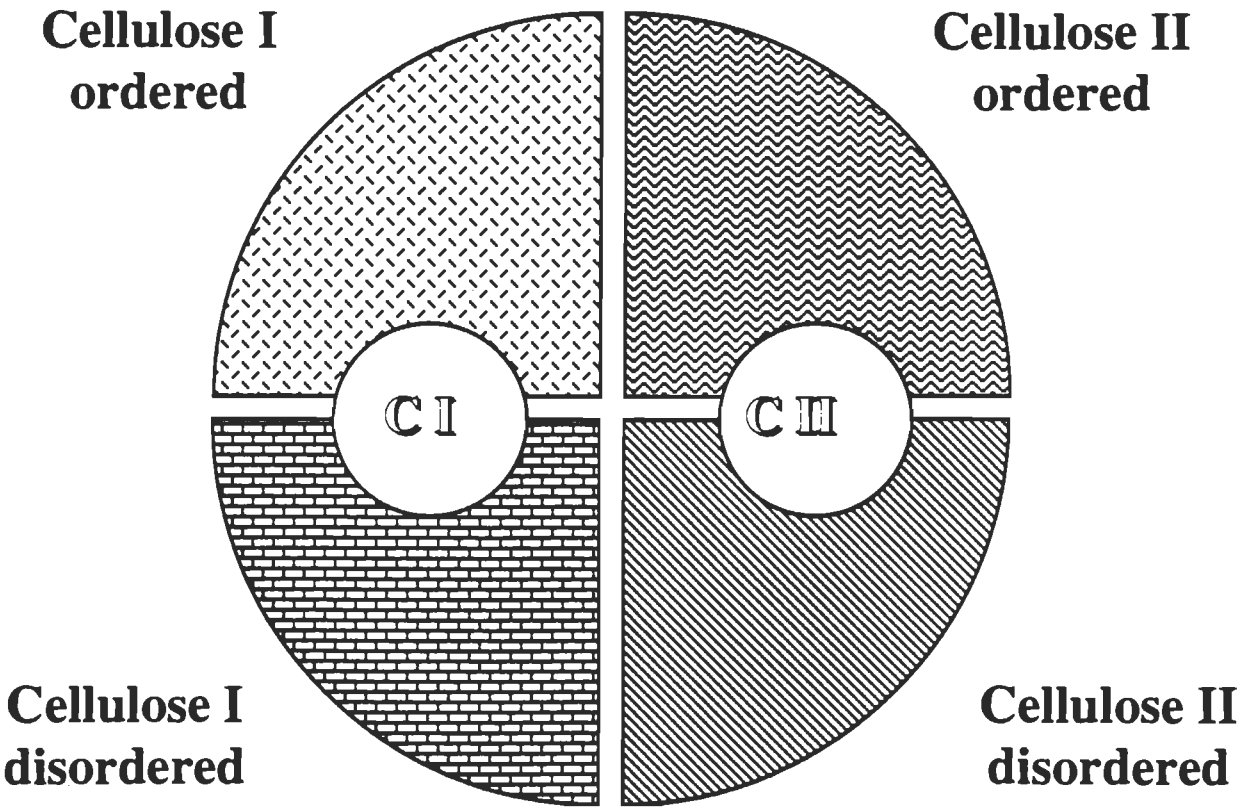
The chemical changes that take place during the cook are another important consideration. Tanahashi et al. [91, 93, 120] have recently reported an increase in the crystallinity of cellulose following steam treatment at high temperature and pressure. For our considerations, we worked with Sukhov's modification phase model of cellulose structure [130], as it shows Figure 3.10. Using Sukhov's qualitative methods for evaluating cellulosic materials via FTIR (Fourier-transform infrared reflectance) and Raman spectroscopy [130, 131], we found that explosion pulps have the highest content of ordered Cellulose I (C-I). The results in Figure 3.11 (with one impregnation chemical) show that crystallinity of C-I increased in order milled wood > CTMP > CMP > explosion pulps. Ordered C-I is the highest quality cellulose (highest bonding capacity) and contributes significantly to pulp mechanical properties [126, 130].

Disordered cellulose II (C-II), on the other hand, is a lesser quality material composed of a mercerized-type of cellulose and hemicelluloses. Figure 3.12 shows the distribution of C-I ordered and C-II disordered cellulose in the samples of SEP, CMP, CTMP, RMP and in milled aspen wood. It is apparent from Figure 3.11 and Figure 3.12, that the cellulose structure, represented by an increase of C-I ordered and the C-I/C-II ratio has improved with increasing temperature and pressure of cooking. From this point of view, the best C-I/C-II ratio was found in the water explosion pulp. These results are in excellent agreement with other study by Kokta et al. [58]. It has been shown that at various impregnation conditions, there was a sharp increase of cellulose I and sharp decrease of cellulose II occurring at the cooking temperature of 190°C and cooking time at least two minutes.

The high C-I/C-II ratio in the water explosion pulp (no chemicals), as it is shown in Figure 3.12, can probably be explained by the fact that these chips were not chemically protected by an antioxidant. In this case, the predominant reaction is hydrolysis of the unprotected hemicelluloses, which produces a higher proportion of C-I compared with C-II in the resultant pulp.

According to another analysis [68], the concentration of cellulose and sulfur on the fiber surface is higher for explosion pulps than for conventional pulps. The fibers in explosion pulps also were reported to have less lignin on their surface

than the fibers in conventional pulps, even though the concentration in the bulk was the same for both types of pulp.



$$C = C\,I + C\,II = (C\,I\,ord + C\,I\,disord) + (C\,II\,ord + C\,II\,disord)$$

FIGURE 3.10 Model of modification phases for the cellulose structure

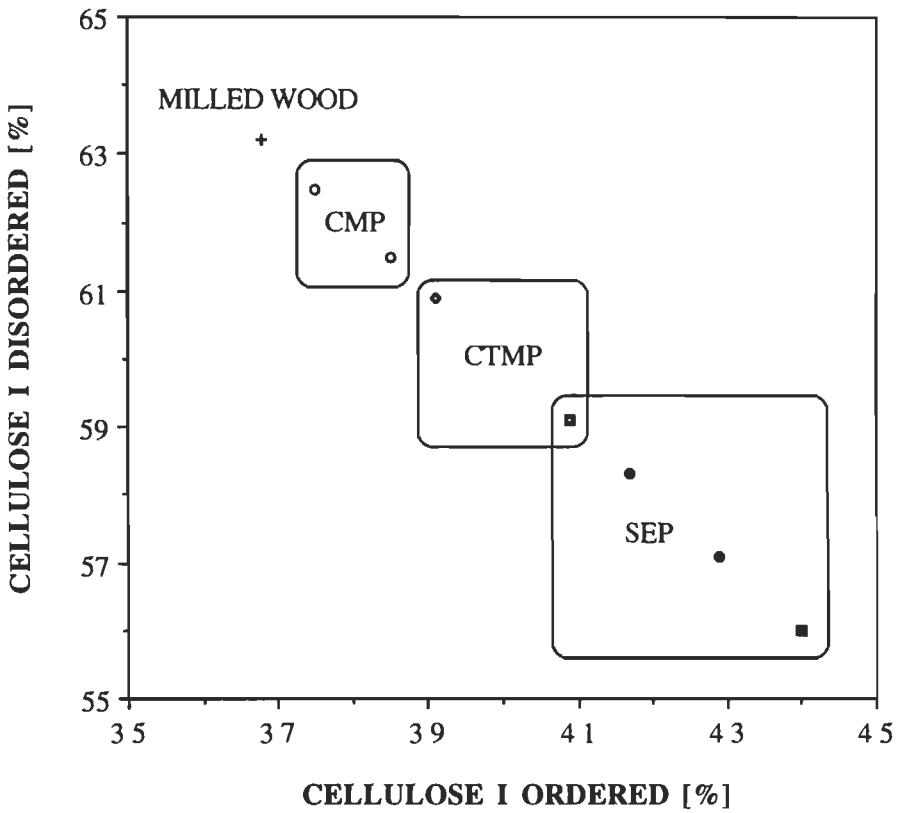


FIGURE 3.11 Distribution of cellulose I in aspen milled wood and in resulting pulps

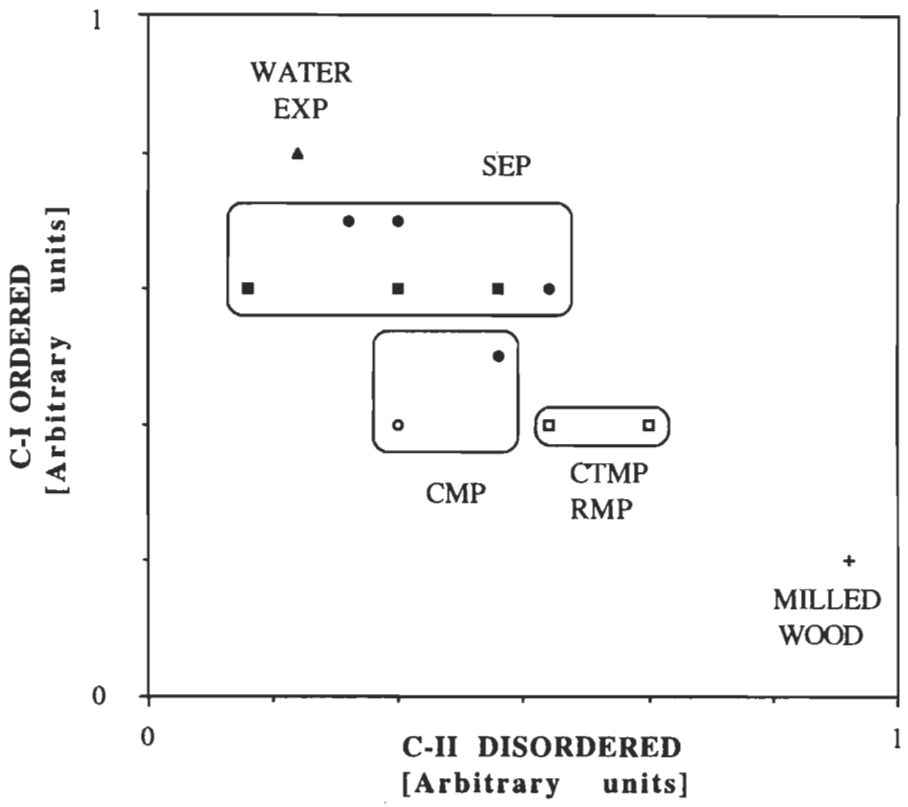


FIGURE 3.12 Relative distribution of cellulosic material in aspen wood and high yield pulps

3.1.4 MECHANICAL PROPERTIES

The results presented so far show that the physical and chemical changes that take place during the high-temperature-and-pressure cook and subsequent explosive discharge are beneficial and should provide a pulp with superior mechanical properties. This was experimentally confirmed and results for breaking length, stretch, burst index and tear index are presented in Figures. 3.13 to 3.16, respectively.

If we compare CTMP and SEP, the explosion pulps have: higher mechanical properties (breaking length, tear and burst), higher density and C-I crystallinity at lower LSC, and lower refining energy. This was accomplished either at conventional CTMP conditions (Pulp 2) or at similar yield (Pulp 3) and at the same chemical treatment and similar ionic content. The only difference between the CTMP and SEP pulps were the cooking conditions (temperature, pressure and time), which emphasizes the influence of these parameters on pulp quality.

While the differences between CMP and SEP were not as pronounced as between CTMP and SEP, Figures 3.13 to 3.16 show that the mechanical properties of SEP were superior. This is also apparent in Figure 3.17, which relates tear index and breaking length. This relationship is most useful in evaluating the mechanical strength of pulp [112], and we can see that strength increases in the direction RMP < CTMP < CMP < SEP, correspondingly with increasing severity of the cooking process. The only exception in this order is the water explosion pulp, which is placed between CTMP and CMP, because of the lack of chemical treatment.

The CMP and SEP pulps were prepared at the same yield using the same chemical treatment during impregnation and cooking. The total ionic content was almost identical for CMP Pulp 4 (150°C, 55 min) and SEP Pulp 10 (200°C, 1 min). This is also true of CMP Pulp 5 (160°C, 30 min) and SEP Pulp 8 (190°C, 2 min) and SEP Pulp 9 (195°C, 1.5 min). The results in Figure 3.17 thus confirm previous research [36] showing that explosion pulping provides comparable strength at lower ionic (sulfonic) content, or higher strength at the same ionic content compared with conventional high-yield pulping processes.

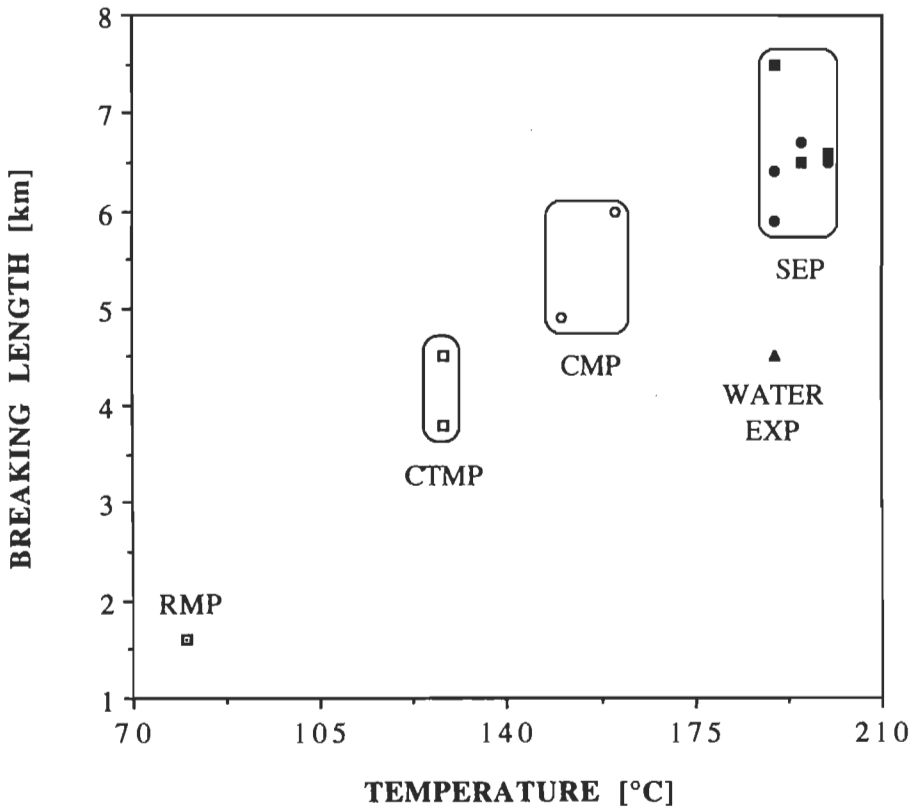


FIGURE 3.13 Breaking length as a function of temperature (at 100 ml CSF)

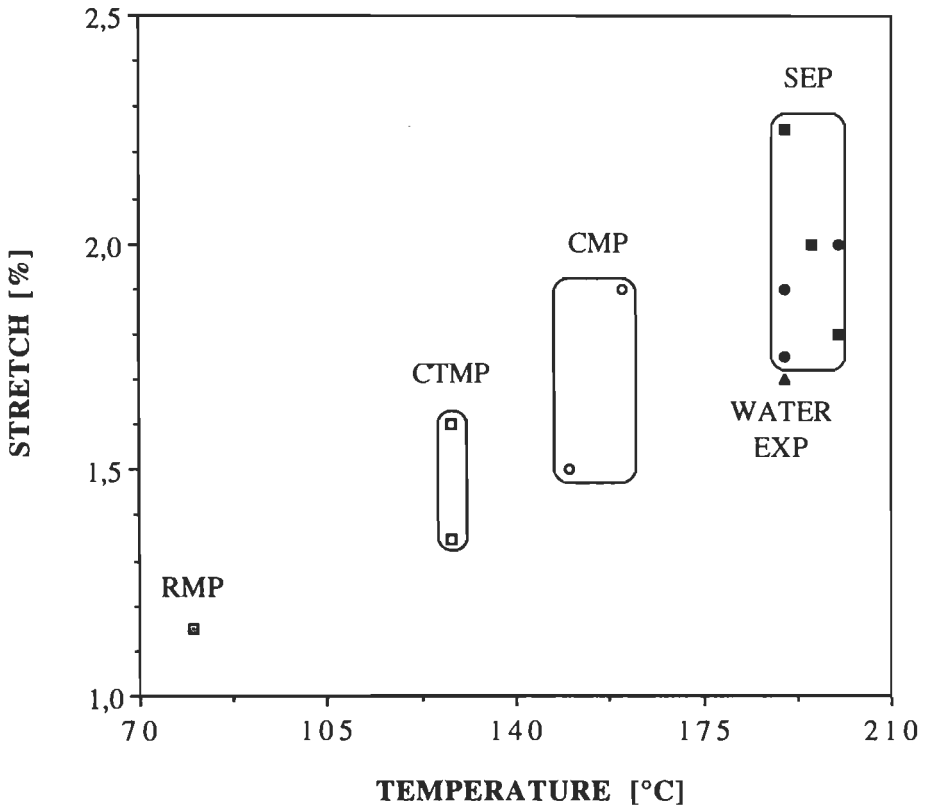


FIGURE 3.14 Stretch as a function of temperature (at 100 ml CSF)

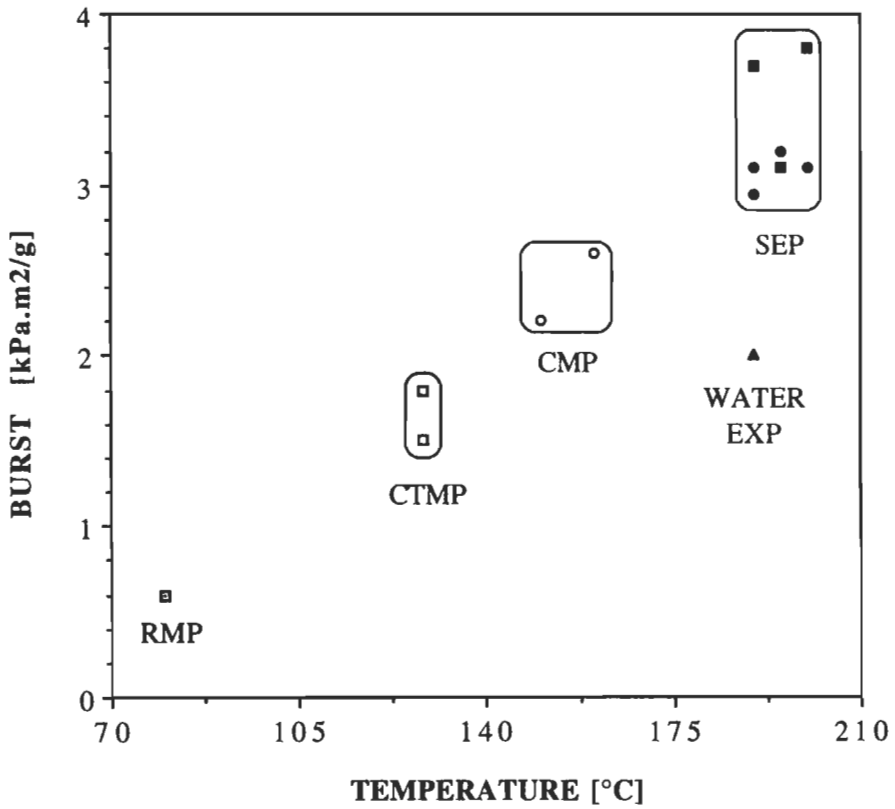


FIGURE 3.15 Burst as a function of temperature (at 100 ml CSF)

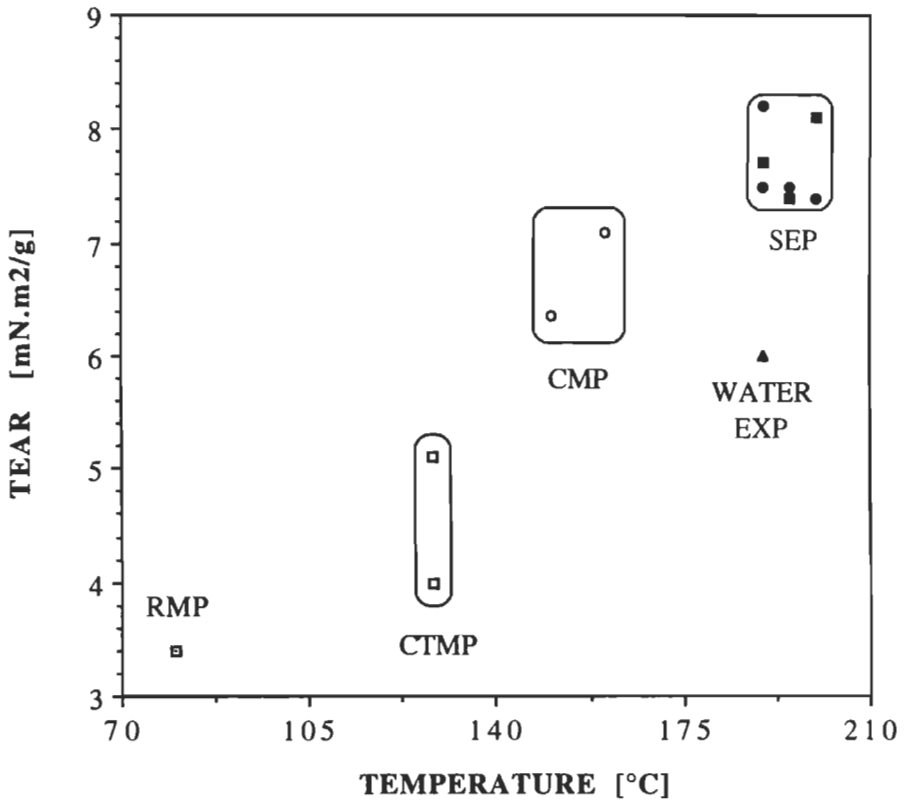


FIGURE 3.16 Tear as a function of temperature (at 100 ml CSF)

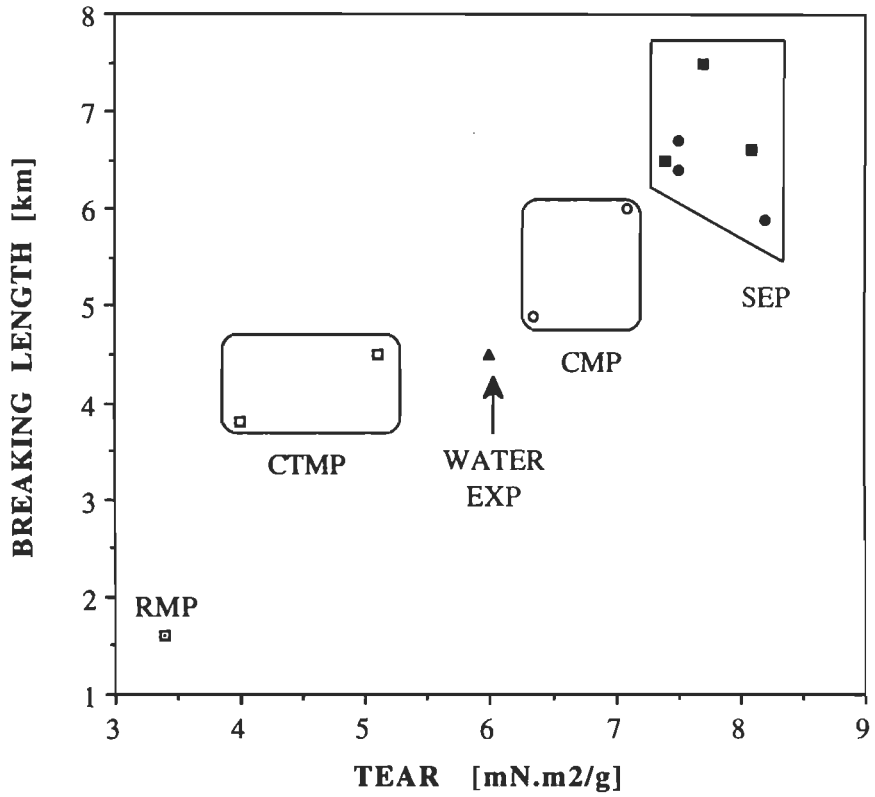


FIGURE 3.17 Mechanical resistance of aspen high yield pulps: The tear vs. breaking length relation (at 100 ml CSF)

3.1.5 OPTICAL PROPERTIES

Brightness exceeding 60% can be obtained if the chip quality is satisfactory (Figure 3.18). Water explosion (no chemicals) was the only process where brightness dropped significantly (to about 42%) because of the condensation reactions. Otherwise, brightness values ranged from 60% to 66% MgO for the unbleached and from 79% to 84% MgO for bleached pulps (Figure 3.19). These results are in agreement with those reported previously [36]. For both unbleached and bleached pulps, the CTMP had the highest brightness level, closely followed by other pulp types. Explosion pulps showed slightly higher brightness stability.

As far as opacity is concerned (Figure 3.20), the highest level was found for the water explosion pulp. This was quite expected since this pulp had the lowest brightness (around 42%). Also, compared to other pulps, its fiber surface is much more rich in lignin rather than in cellulose. For other pulps, the order of opacity was inversely following density, porosity and LSC with the highest value in the RMP case and lower values in order CTMP > CMP > explosion pulps.

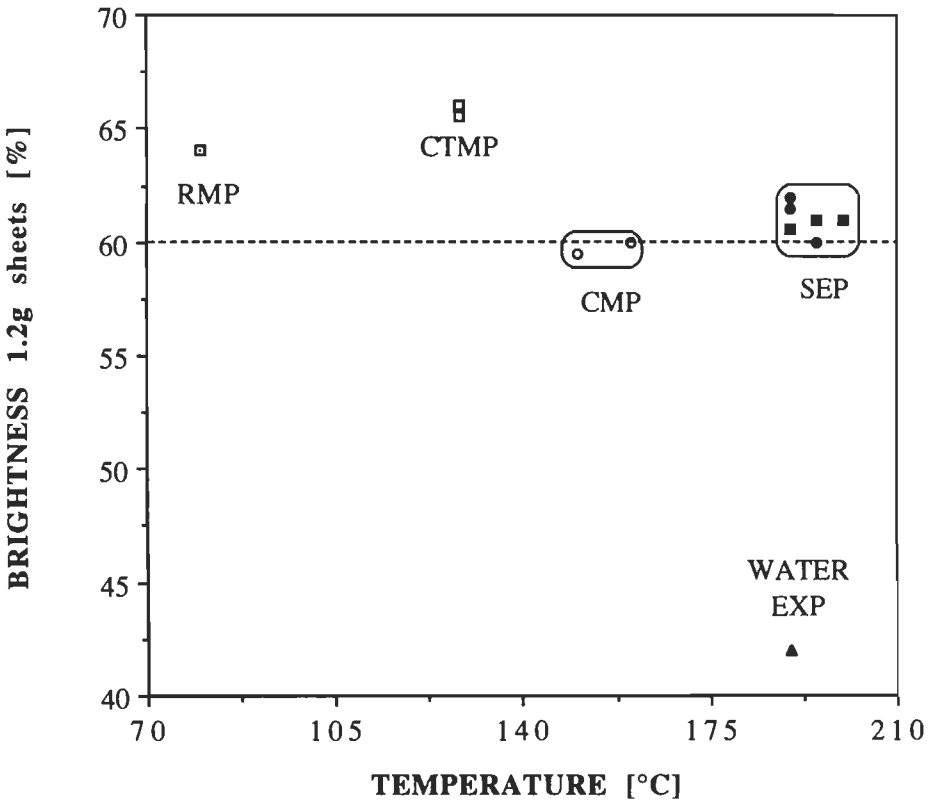


FIGURE 3.18 Brightness as a function of temperature

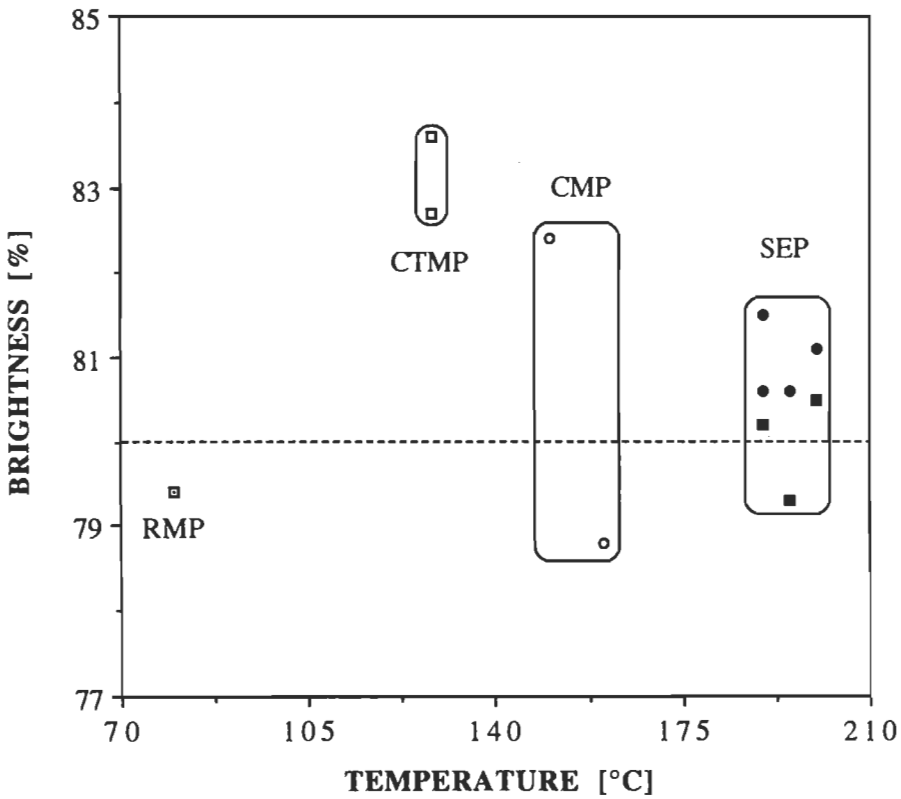


FIGURE 3.19 Bleached pulps brightness as a function of temperature

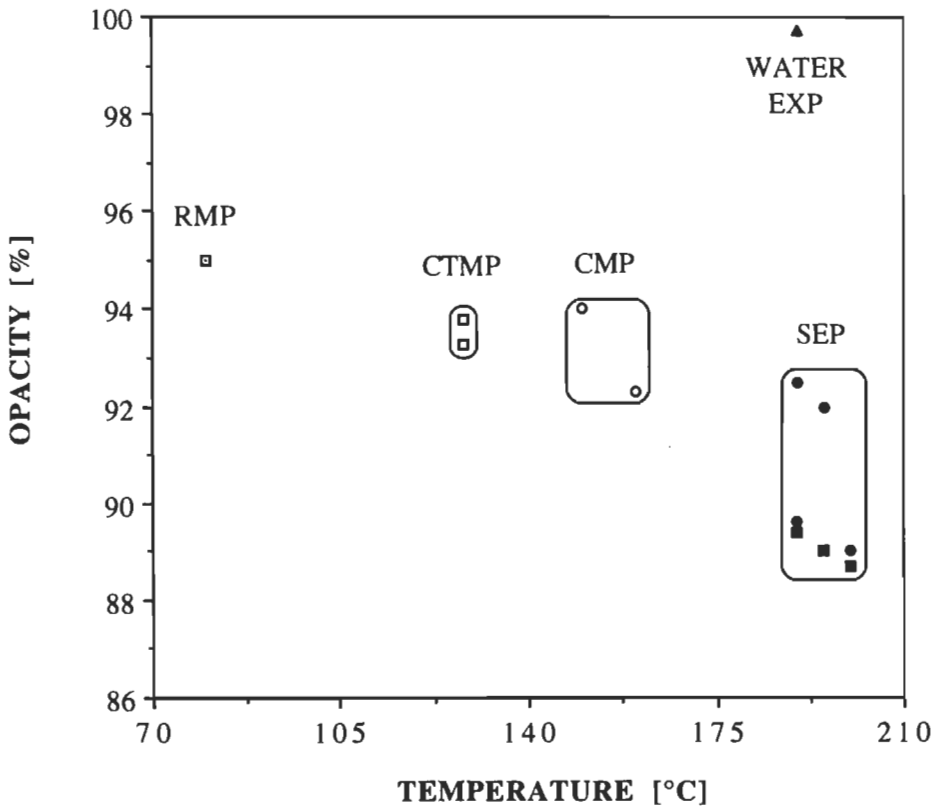


FIGURE 3.20 Opacity as a function of temperature

3.1.6 INFLUENCE OF PRESSURE

The cooking conditions used to produce the SEP Pulps 8 to 10 were replicated for Pulps 11 to 13. These latter pulps were subjected to a pressure of 25 atm under nitrogen immediately after the cook and then discharged explosively. The high-pressure explosion increased the mechanical properties, as seen in Figure 3.21, which shows the results for SEP Pulps 10 and 13, both cooked at 200°C for 1 minute at 15.5 atm. These pulps showed the greatest difference in mechanical properties, with the pulp discharged at high pressure showing an increase in tear index at constant breaking length. Overall mechanical strength improvement is shown in the Figure 3.22. Increasing the pressure prior to the explosion also leads to better fiber separation and hence lowers refining energy consumption (Figure 3.5). The time to increase the digester pressure is very short and has no negative influence on pulp yield or any other parameter. The effect of pressure on explosion pulps over a wider pressure range was the subject of second experimental trial and will be discussed later on. Pulps 8/11 and 9/12 did show similar tendencies.

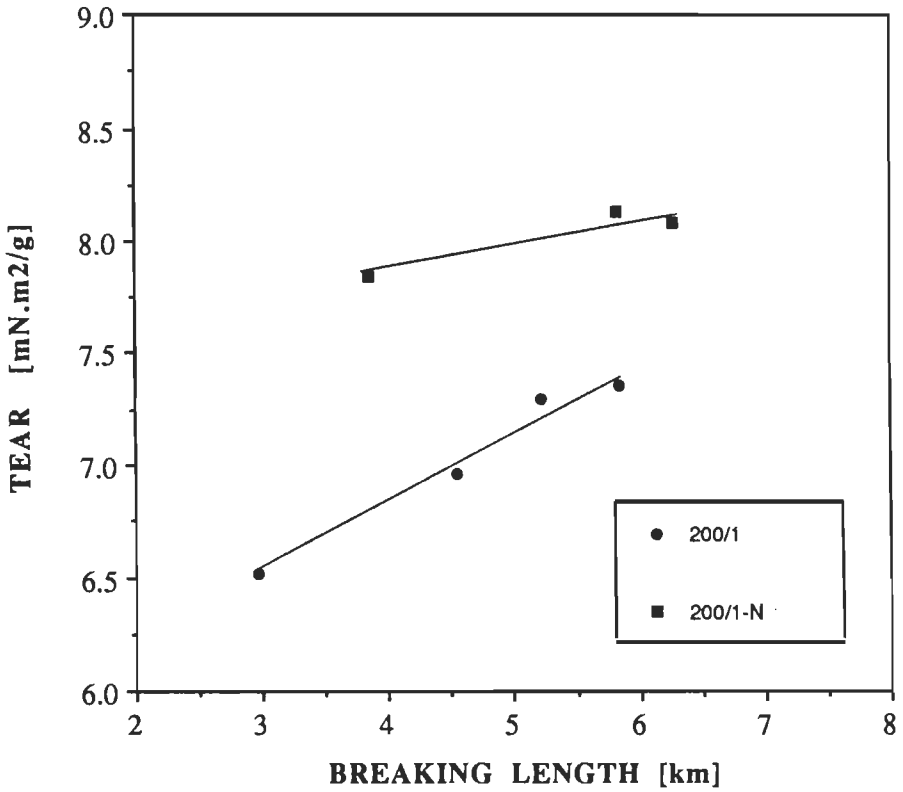


FIGURE 3.21 Mechanical strength of explosion pulps prepared at 200°C and 1 minute

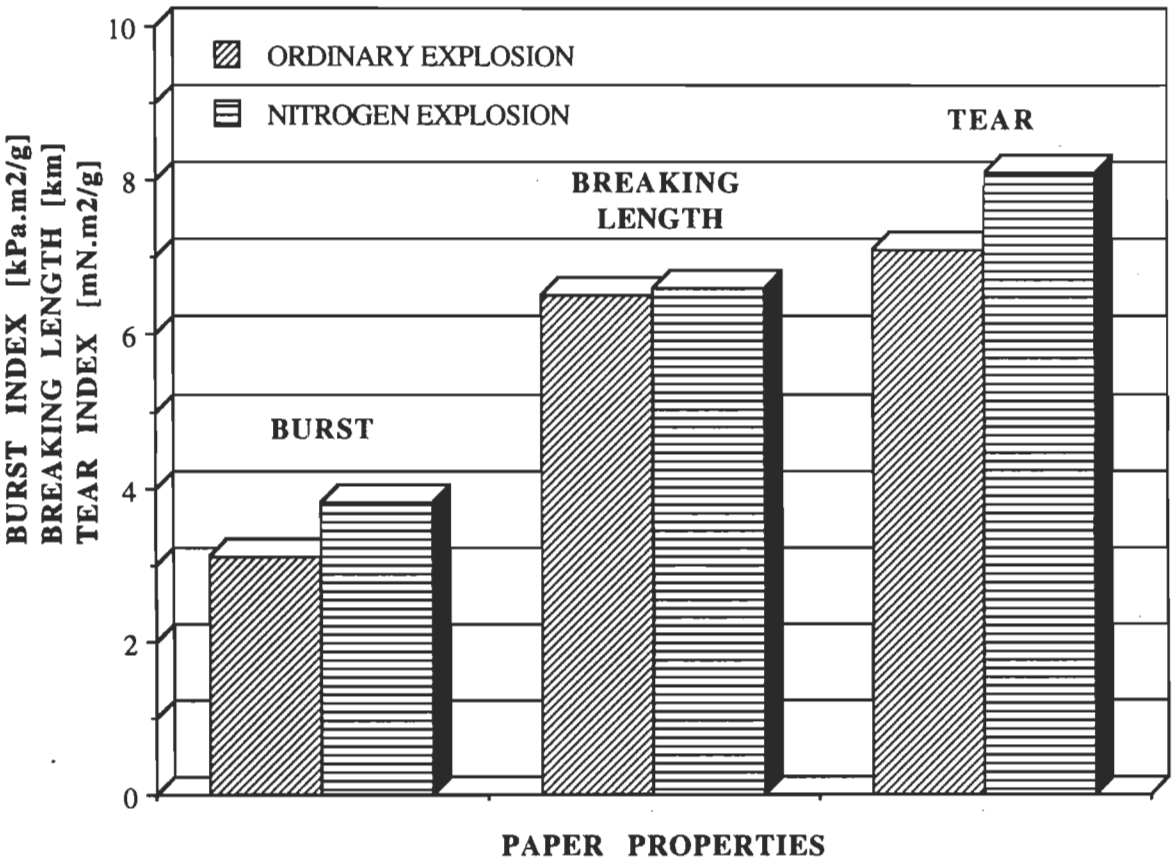


FIGURE 3.22 Paper strength improvement as a result of explosion pressure increase at 200°C/1 minute cooking conditions

3.1.7 THE IMPORTANCE OF A CHEMICAL AGENT

Good chemical impregnation is essential for the development of papermaking qualities. If we take the two pulps without chemical impregnation (RMP and water explosion), we can see from the results presented in this chapter that both of them are weaker in strength parameters. In the case of refiner mechanical pulp, the unsoftened fibers (quite fragile due to their thin cell wall) were broken (often several times), did not develop good bonding capacity and as a result it was almost impossible to prepare paper sheets if the freeness level was over 250 ml.

In the case of the water explosion pulp, we have obtained quite dark pulp. Even if it was fairly easy to separate the individual fibers, they remained enveloped with a lignin layer. This goes very well with the theory of refining which says that the higher is the process temperature, the higher is the lignin amount on fiber surface [183]. Lignin softens more at higher temperatures and the following refining goes more towards the middle lamella, where the resistance against fiber separation becomes lower at increased temperatures.

A chemical impregnation agent helps to soften whole fiber, contributes to the ionic content development, protects the pulp against the brightness loss and hence helps to develop mechanical strength. Based on several research works in the area of impregnation [34, 36, 39, 63, 65, 68, 70, 72, 83, 89, 157, 158], we cooked several more pulps with a second impregnation agent (the cooking conditions are presented in the Table 2.2). We used the sodium hydroxide and sodium bicarbonate along with sodium sulfite. Cooking results and the pulp and paper properties are listed in the table 3.4. As these pulps were cooked mostly as a reference, we only present values at 100 ml CSF, which id the reference freeness with the pulps cooked in this series.

As a result of an additional chemical impregnation (second chemical), the pulps were more easy to refine and the Figure 3.23 shows the refining energies for no-chemical, 1-chemical and 2-chemicals impregnation system. In our case, the biggest savings were observed with Na_2SO_3/NaOH solution. Also, this impregnation substantially improved the ionic content. Figure 3.24 shows that the sulphonic content has significantly increased with a 2-chemicals

impregnation (in comparison with 1-chemical impregnation in the case of SEP or conventional pulps).

TABLE 3.4 Pulping conditions, pulp and paper properties in the additional experiment. For the parameters, where freeness is important, the value is 100 ml CSF

Pulp	1 8% Na_2SO_3 0.5% NaOH L/W 6:1 190°C/4 min		2 16% Na_2SO_3 1% NaOH L/W 3:1 190°C/4 min		3 8% Na_2SO_3 1% $NaHCO_3$ L/W 6:1 190°C/2 min	
Parameter	Value	Error	Value	Error	Value	Error
Yield [%]	83.7	1.2	82.7	1.4	90.8	0.6
Sulf. content [mmol/kg]	72.3	-	61.6	-	52.7	-
Carb. content [mmol/kg]	146	-	142	-	151	-
Total ion. cont. [mmol/kg]	218	5.3	204	4.6	204	3.6
RSRE [MJ/kg]	2.2	5.0	2.4	3.2	2.6	1.6
Density [kg/m^3]	590	2.3	625	4.6	585	3.5
Porosity [ml/min]	12	1.9	10	2.6	9	4.6
Breaking length [km]	9.8	3.0	9.1	3.1	8.6	3.9
Stretch [%]	2.5	1.2	2.7	5.9	2.0	5.0
Tear [mNm^2/g]	8.4	4.8	6.7	4.3	6.8	1.7
Burst [kPam^2/g]	5.8	4.1	6.1	1.9	4.5	3.5
Brightness 1.2 g sheet [%MgO]	56.0	0.6	56.5	3.8	65.0	3.6
Brightness 3.0 g sheet [%MgO]	60.3	3.1	60.7	4.0	68.2	1.1
Brightness loss [%]	0.4	-	0.4	-	1.1	-
Opacity [%]	84.7	1.6	83.4	2.2	83.2	3.6
LSC [cm^2/g]	280	3.7	245	3.1	340	4.3

Another important improvement was found in the fiber fractionation (Figure 3.25). In the case of $NaOH/Na_2SO_3$, we have obtained the highest fraction of long fibers (R14 + R28 + R48). These longer fibers are very important for paper strength development (tear index). The difference in pulps with the highest percentage of R14 fraction (RMP, nitrogen explosion and soda pulp) was also obvious. It was clear that under a microscope, in the RMP case, the fraction retained on a 14 mesh sieve was mostly represented by fiber bundles and shives. High severity pulping resulted in single fibers, even in the longest fractions. Less rejects were also confirmed by Sommerville analysis. In the case of the RMP, we found the highest reject amount (4.3%) The reject amount for high severity pulps was hardly measurable. Similar results were confirmed in [33].

It can be concluded that the addition of a second impregnation chemical strongly helps in the development of mechanical parameters. These pulps reach in general higher ionic content, higher average fiber length, higher density, lower S-factor and lower refining energy. All these parameters suggest higher strength. As seen from Figure 3.26, the breaking length increased by 2 km for $NaHCO_3$ and even more with NaOH, when compared to the average value of breaking length for a SEP with only one impregnation agent. Similar tendency could be observed for the burst index (Figure 3.27) when $NaHCO_3$ addition caused an increase to about 3.5 $kPa.m^2/g$ and NaOH to 6 $kPa.m^2/g$ (compared to about 3.5 $kPa.m^2/g$ for a simple impregnation). Tear index of these pulps could be slightly lower, which may be as a result of higher density [159] and lower fines amount. In the case of bleached pulps, the breaking length went over 10 km (Figure 3.26), which is even higher than in the case of low yield kraft aspen pulp [160].

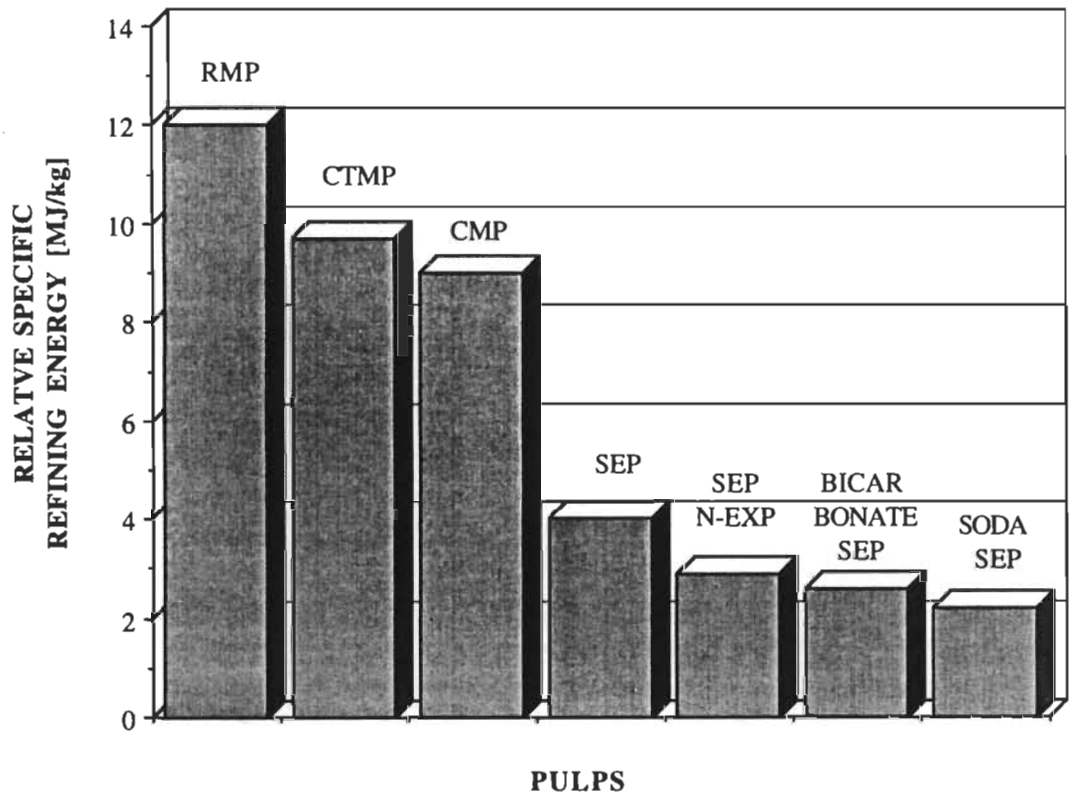


Figure 3.23 Refining energy requirements for pulps prepared at various impregnation conditions

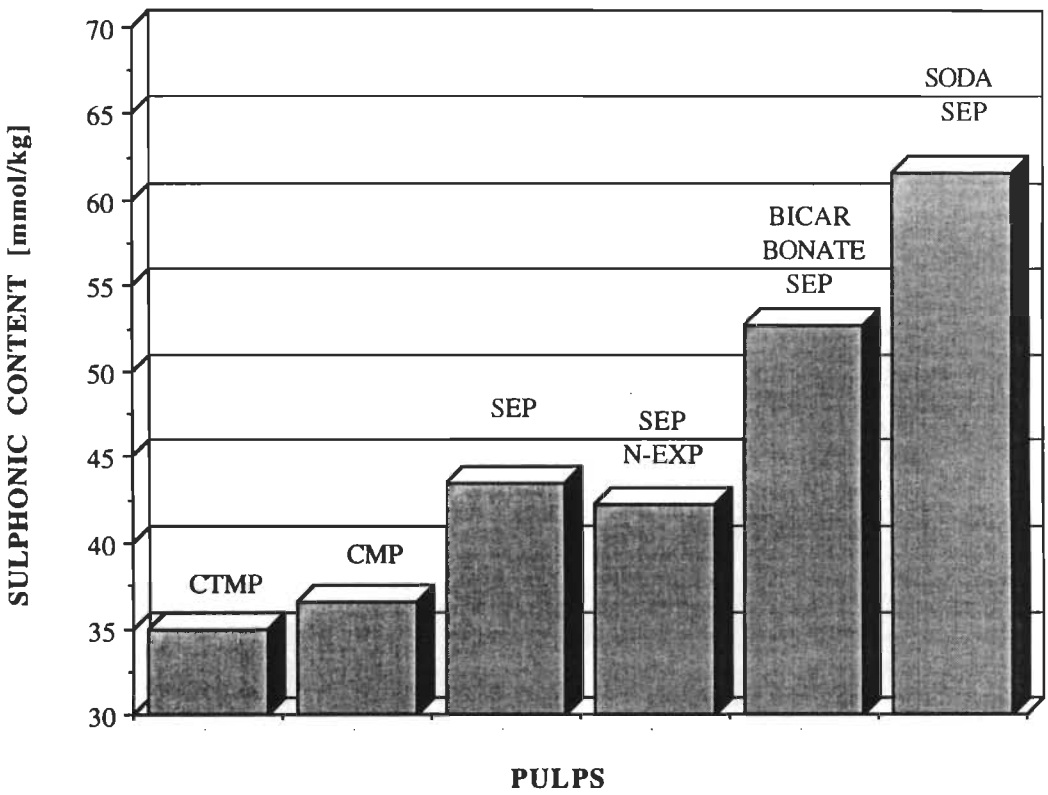


Figure 3.24 Sulfonation of pulps prepared at various impregnation conditions

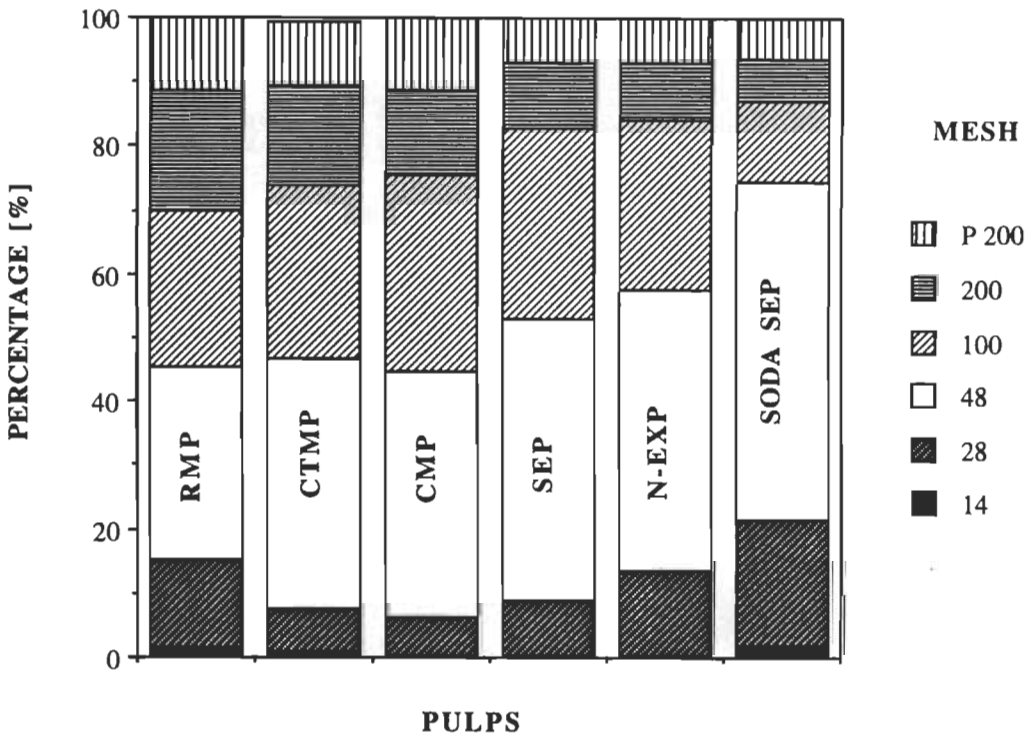


Figure 3.25 Bauer-McNett fiber classification of pulps prepared at various impregnation conditions

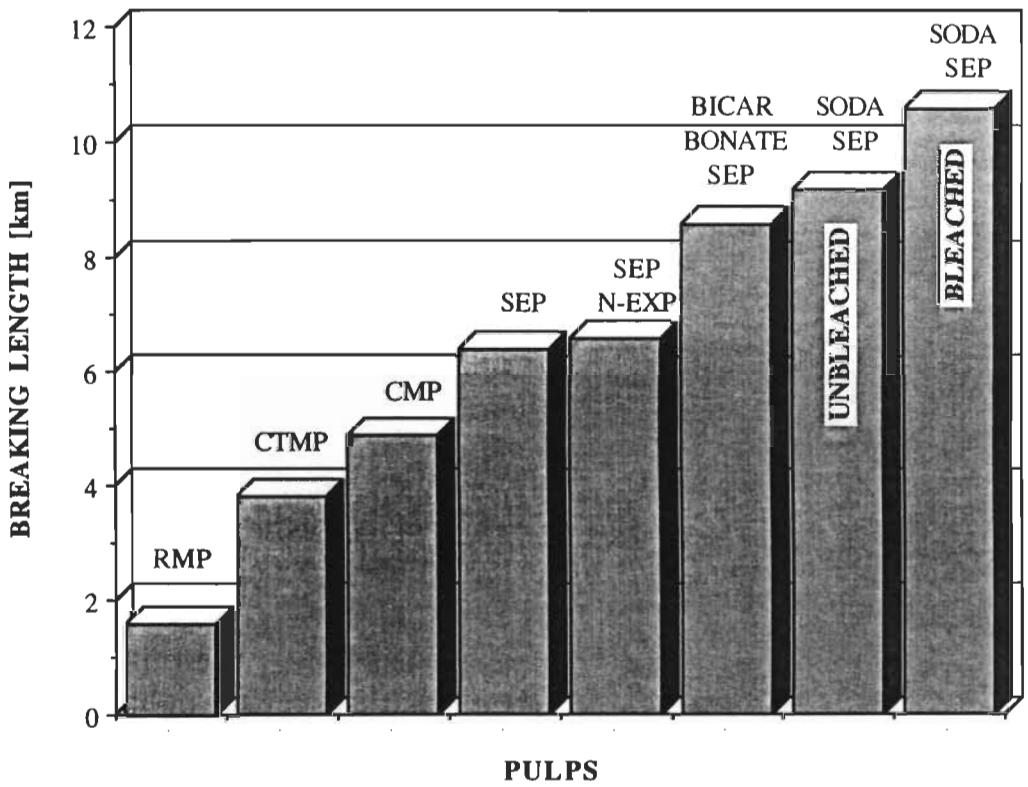


Figure 3.26 Breaking length for pulps prepared at various impregnation conditions

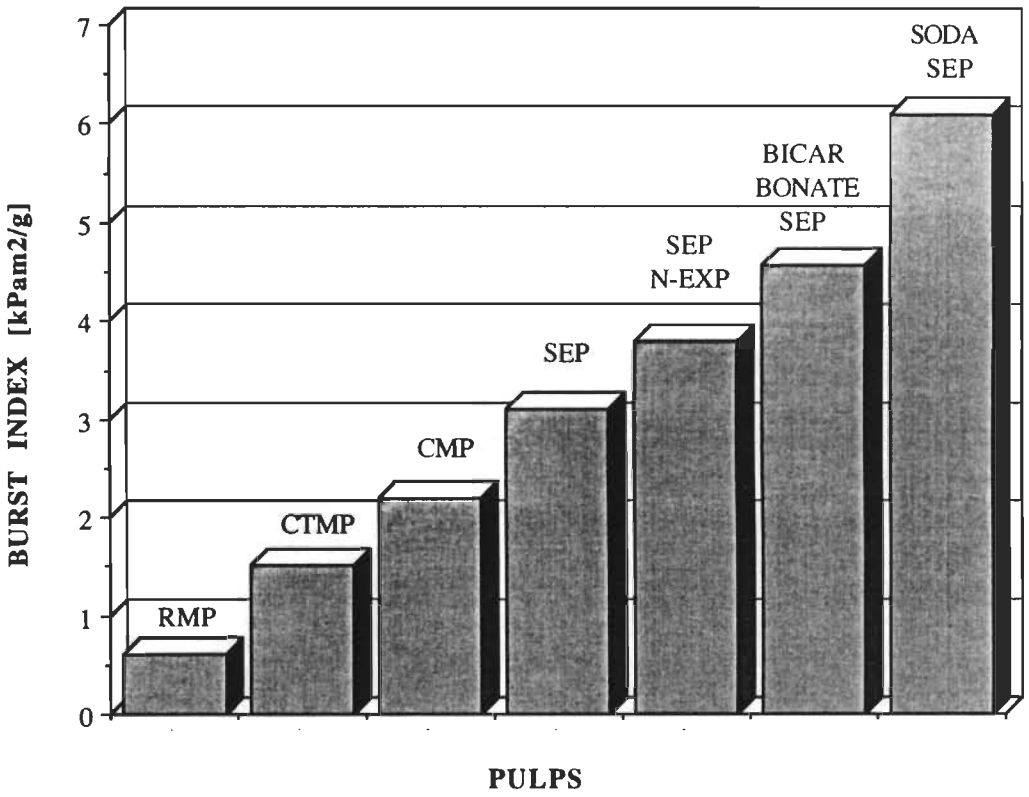


Figure 3.27 Burst index for pulps prepared at various impregnation conditions

The biggest paper strength were found in the case of NaOH. Unfortunately, in the case of NaOH, the price to pay for the property increase is the yield loss (about 7%) and lower brightness. The addition of $NaHCO_3$, on the other hand, enhances the mechanical properties and reduces the refining energy without decreasing the yield or brightness. From this point of view, the impregnation system $Na_2SO_3/NaHCO_3$ seems to be the most promising, as far as it provides high mechanical properties with a very low refining energy and good brightness at a 90% or possibly higher yield.

3.1.8 CONCLUSIONS FROM THE FIRST TRIAL RESULTS

Comparison of high-yield pulps at the same chemical charge, yield and ionic content showed that the explosion pulps had better mechanical properties and much lower refining energy than the conventionally cooked CMP and CTMP pulps. Explosion pulps had optical properties similar as the CMP pulps and the CTMP pulps were slightly better than those of SEP and CMP.

Explosive pulp release also seemed to help in some aspects. It decreased the refining energy (Figure 3.5) and improved the paper strength. Pressurizing the reactor prior to the explosion helped in further refining energy reducing also improved the breaking length and burst index. Figure 3.22 shows the breaking length, burst and tear index comparison for pulps prepared at 200°C and 1 minute, where the improvement was most evident.

In this work, we showed the results obtained at 100 ml CSF. Since the same tendencies were found at the 200 ml CSF evaluation, we did not include them in this work.

The addition of a second impregnation agent enhances the process and resulted in significantly higher mechanical properties and lowers refining energies (at increased ionic content). With $NaHCO_3$ as second impregnation chemical, the pulp yield is preserved, while NaOH addition leads to a yield drop (about 7% in our case). However the property gain was the highest with NaOH.

Better properties of the explosion pulps can be attributed to the chemical changes (higher crystallinity, better lignin softening) that occur following the high-temperature-high-pressure cook as well as the physical changes (better and easier fiber separation) that occur following high severity cook and explosive discharge from the digester and consequently better fiber surface and flexibility during refining.

The first experimental series confirmed most of our theoretical considerations and results showed that the high severity pulps can be prepared at ultra-high yield comparable to conventional UHY pulping processes. At the same chemical charge, yield and ionic content, the explosion pulps showed much lower refining

energy and higher paper strength. This occurred as a result of high severity pulping conditions: high temperature, high pressure and short cooking time.

As a result, we can conclude that the explosion pulping shows promise as a viable ultra-high yield pulping process. In addition to the discussed comparison with the conventional methods of chemimechanical and chemi-thermo-mechanical pulping, explosion pulping is also very fast (usually 2 min or less) and requires little chemicals. As a result, it was suggested [33] that the industrial application would require smaller size equipment and therefore lower capital investment.

3.2 SECOND EXPERIMENTAL SERIES

3.2.1 PULP PREPARATION AND PULPING RESULTS

In the second series, five different explosion pressures were chosen. As an impregnation medium, Na_2SO_3/$NaHCO_3$ system was selected (this combination provides excellent results without sacrifying yield or brightness), with two cooking temperatures of 190 and 195°C. With this new impregnation system, the level of 200°C was considered too high requiring very short cooking time which might lead to insufficient cooking deeper inside the wood chip. The five pressures levels used were 11.9 and 13.6 atmospheres (saturated steam pressure at 190/195°C), 17.5 atm, 20.0 atm, 22.5 atm and 25.0 atm. This was about the maximum achievable with our laboratory cooking system. Pulping conditions, pulp and paper properties resulted from this experimental series are presented in Table 3.5 to 3.7.

TABLE 3.5 Pulping conditions and some of the characteristics of resulted pulps in the second experimental series

	Cooking					Ionic content [mmol/kg]			
#	Time	Temp.	Pressure	Yield [%]		Sulfonic	Carboxylic	Total	
	[min]	[°C]	[atm]	Value	Error			Value	Error [%]
1	2	190	11.9	90.8	0.3	42.7	152	194	2.9
2	2	190	11.9/17.5	91.6	0.6	42.3	155	197	3.4
3	2	190	11.9/20	90.3	1.0	43.6	158	202	4.4
4	2	190	11.9/22.5	90.3	0.6	51.7	153	205	1.3
5	2	190	11.9/25	89.3	0.8	46.9	153	200	2.9
6	1.5	195	13.5	90.6	0.9	42.7	150	193	5.0
7	1.5	195	13.5/17.5	90.0	1.1	48.9	146	195	4.3
8	1.5	195	13.5/20	90.5	0.4	51.1	147	198	3.6
9	1.5	195	13.5/22.5	89.8	0.7	50.7	147	198	3.8
10	1.5	195	13.5/25	90.3	0.7	48.7	147	196	4.0

TABLE 3.6 Mechanical paper properties obtained in the second experimental series (at 100 ml CSF)

Pulp		Parameter values and experimental error in [%]											
#	Final pressure [atm]	Density [kg/m^3]		Porosity [ml/min]		Breaking length [km]		Stretch [%]		Tear [mNm^2/g]		Burst [kPam^2/g]	
		Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	11.9	585	3.3	9	2.2	8.6	2.6	2.0	2.6	6.8	6.4	4.5	0.5
2	17.5	593	2.5	17	2.9	9.1	3.5	1.9	2.4	6.9	5.3	4.1	3.2
3	20	570	3.4	18	3.1	8.9	3.4	2.0	2.5	6.8	2.6	4.4	1.6
4	22.5	602	2.6	17	2.0	9.4	3.6	1.8	2.5	6.7	0.1	4.1	2.5
5	25	557	3.4	20	3.4	8.1	3.2	1.7	2.5	6.8	6.7	3.9	2.3
6	13.5	571	4.0	16	2.9	8.6	1.2	1.9	2.3	7.0	6.8	4.7	2.9
7	17.5	526	1.3	21	2.7	7.4	0.5	1.7	2.3	6.6	5.1	3.6	3.4
8	20	543	1.5	20	2.8	7.8	2.9	1.7	1.9	6.7	5.3	3.6	0.9
9	22.5	556	3.3	17	3.1	7.8	3.1	2.0	3.3	6.8	3.4	4.0	1.4
10	25	542	2.4	21	4.2	8.0	2.3	1.9	3.7	6.7	3.9	3.9	2.9

TABLE 3.7 Refining energy and optical paper properties obtained in the second experimental series (at 100 ml CSF)

Pulp		Parameter values and experimental error in [%]											
#	Final pressure [atm]	Relative specific refining energy [MJ/kg]		Brightness 1.2 g sheet (60 g/m^2) [%MgO]		Brightness 3.0 g sheet (150 g/m^2) [%MgO]		Brightness loss [%]		Opacity [%]		Light-scattering coefficient [cm^2/g]	
		Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	11.9	2.6	3.4	65.0	1.5	68.2	1.2	1.1	-	83.2	1.1	340	2.6
2	17.5	2.7	6.5	61.9	1.3	63.6	1.3	0.3	-	84.4	3.0	323	2.3
3	20	2.6	5.6	61.0	1.6	62.7	1.1	0.5	-	84.5	1.4	331	2.5
4	22.5	2.9	5.7	61.4	1.4	63.0	1.1	0.2	-	84.7	1.8	316	2.4
5	25	3.6	4.9	62.5	1.8	63.8	1.0	0.4	-	85.0	1.9	360	4.1
6	13.5	3.7	3.6	63.4	2.0	65.3	1.5	1.3	-	83.1	1.6	320	1.0
7	17.5	3.1	3.5	64.1	1.6	64.2	3.0	0.2	-	87.3	1.1	365	1.1
8	20	3.2	4.8	63.3	1.3	65.2	0.5	0.3	-	86.8	1.1	370	3.5
9	22.5	2.0	2.9	63.2	1.0	64.6	1.6	0.4	-	86.0	1.4	360	3.4
10	25	2.8	6.1	62.1	0.8	64.3	1.1	0.6	-	85.9	1.0	350	4.4

3.2.2 PULP EVALUATION

Similarly to the first series, the explosion pressure did not seem to influence pulp yield. Most of the pulps were prepared at or very close to 90% yield. This was not a surprise, because the cooking conditions for all the pulps were the same. The only difference was in the pressure increase at the end and the pressurizing time was very short, so there was no obvious reason for additional chemical changes. We did not find higher degree of fiber separation with the "higher pressures". The chips were usually very flexible and it was very easy to separate them into smaller units. As the explosion pressure increased, the chips were more crushed and with the highest pressure of 25 atmospheres, the visually observed separation degree was the highest and almost every chip showed some sort of defibration. We believe that this is due to two reasons. Firstly, the difference between internal pressure in the chip and the pressure in the release vessel helps to tear the chip apart. This was shown by Tanahashi [120], where the explosive discharge from 28 atmospheres did cause not only the fiber separation, but also an explosion of the chip per se. Secondly, the impact against the release vessel wall is much stronger with increasing pressure which also contributes to the breakdown of softened chips.

As far as ionic content is concerned (Table 3.5), again, the pressure increase did not cause any significant changes. For most of the pulps, the total ionic content was around 200 mmol/kg.

Refining times were very similar for each pulping condition and a 100 ml CSF freeness was reached after about 43 minute blending for 190°C/2 min pulps and after about 50 minutes for 195°C/1.5 min pulps. In this case, we did not find any significant difference in refining energy requirements. The relative specific refining energies were mostly between 2.5 and 3.0 MJ/kg, which corresponds to our previous findings. Refining energy measurement using a blender is influenced with higher possibility of experimental error than most of our other analyses and making conclusions based on the differences in such a short span could be erroneous. What we did confirm was that all the pulps had low refining energies placed between 2.5 and 3.0 MJ/kg.

Concerning the fiber properties, not much differences were found either. Compared to the first experimental series, lower light-scattering coefficient values were obtained. These values were between 320 and 340 cm^2/g for both pulping conditions. Density was around 580 kg/m^3 for 190°C/2 minutes and 550 kg/m^3 for 195°C/1.5 min. For both conditions, the porosity factor at 100 ml CSF was around 15 to 20 ml, which was lower than in the first experimental series. This is a result of higher density and the higher ionic content (compared to the first experimental series) also contributes to better bonding and interfiber connections, which leaves less open space in the handsheet.

When comparing the mechanical strength parameters with the first series, pulps in this series showed real improvement. In the case of breaking length, for 190°C/2 minutes, the pulps reached values of 9 km or even more (Figure 3.28). For 195°C/1.5 min, the values were somewhat lower and approached 8 km. Again, these are excellent results for non-bleached, 90% yield aspen pulps. As far as pressure influence is concerned, we can see a slight increase in breaking length for both pulping temperatures. It can be seen that the pressure-caused improvement was almost one kilometer for 190°C/2 minutes and about 0.5 km for 195°C/1.5 min.

Stretch values were very similar (around 1.8%) and did not seem to be influenced by pressure increase.

Burst indexes also reached excellent values - over 4.0 $kPa.m^2/g$ for most pulps. When the burst indexes are plotted against pressure or other parameters, unfortunately, no clear pattern becomes discernible.

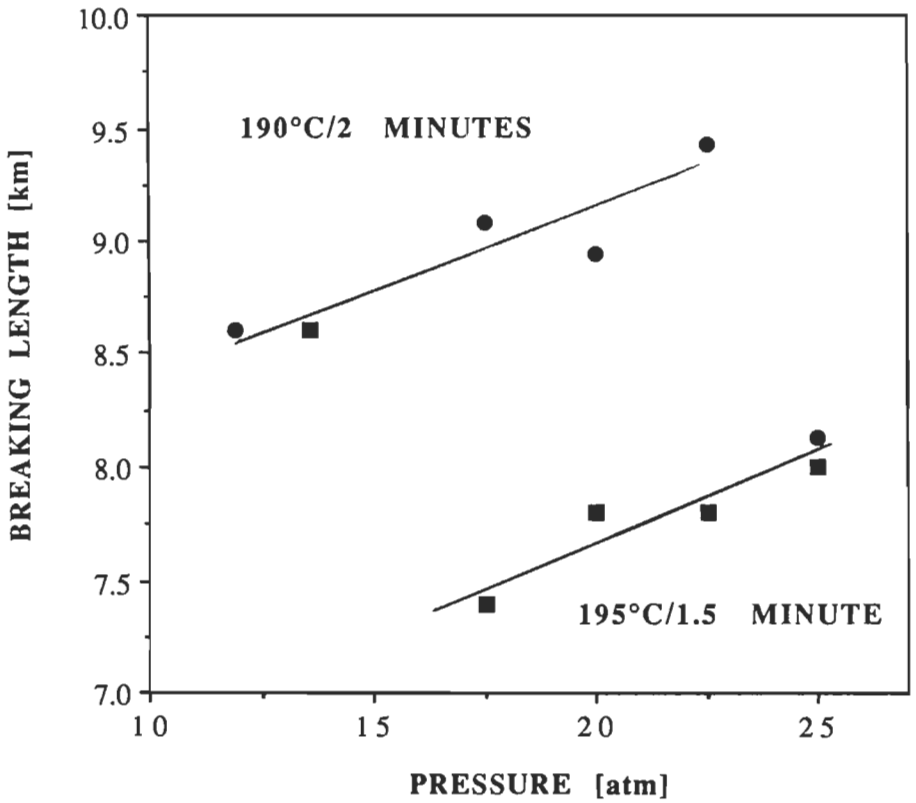


FIGURE 3.28 Breaking length improvement as a result of increasing explosion pressure

Tear values were the only parameter that were lower in comparison with the first experimental series. For the tear index values, we did not find any tendency as a function of either - freeness, cooking temperature or pressure. All the values were within the 6.6 - 7.0 $mN.m^2/g$ range with most points scattered around 6.8 mN.m2/g. If tear indexes are plotted against breaking length, burst, density or relative specific refining energy, no conclusive result could be reached. Most often, pressure did not seem to influence these parameters in a clear manner and the values were too close to each other to make any reasonable conclusion.

Aspen wood is known for its high initial wood brightness and in all cases, the pulp brightness was also excellent and remained higher than 60% MgO. For 1.2 g sheets (60 g/m^2), most of the values were around 62 to 63% and were slightly higher for 195°C/1.5 min. Brightness measured on 3.0 g sheets (150 g/m^2) averaged 2% MgO higher brightness. Opacity values were higher for 195°C (86 to 87%) as compared to 190°C with an 85% average opacity. Again, the pressure did not seem to influence the optical parameters.

3.2.3 CONCLUSIONS FROM THE SECOND TRIAL RESULTS

A two-chemical-based impregnation system confirmed its superiority compared to no or one chemical impregnation from the first series. The Na_2SO_3/$NaHCO_3$ impregnation appears to be a much better choice than Na_2SO_3/NaOH that we used as an alternative in the first series. The quality improvement is almost the same, without noticeable drop in yield or brightness which is usually caused by NaOH addition. It was possible to prepare ten pulps with a yield of 90% (or very close to 90%) with very low refining energies (about 2.5 to 3.0 MJ/kg) and with excellent papermaking properties. The breaking lengths reached up to 9 km, burst was over 4.0 kPa.m^2/g and the tear was at about 7 mN.m^2/g. Also, the brightness level exceeded 60% MgO in every case with an average value of 63% for unbleached pulps.

As to the pressure influence, no major changes were obtained as it was the case in the first experimental series. The only parameter where a pressure-related changes were noticed, was the breaking length. Pressure increase improved this parameter by one kilometer at 190°C/2 minutes conditions and by almost 0.5 km at 195°C/1.5 min. The reason why no significant changes in other areas were observed was due probably to the impregnation approach. In the first series, we used one-chemical impregnation (Na_2SO_3) and most of the papermaking qualities were lower compared to this two-chemical impregnation series. If the parameters in the first series were lower, there was much more space for further improvement and the changes caused by the pressure increase prior to the explosion were measured in all three cases: 190°C/2 min; 195°C/1.5 min and 200°C/1 minute. In this second series, much of the improvement was reached by the addition of the second impregnation chemical. Resulting quality leap was probably so high that it overlapped the smaller partial improvement caused by the pressure increase.

Despite the fact that the influence of pressure increase on pulp quality could not be demonstrated, this series was not a failure, since it was possible to produce ten high severity pulps with excellent properties and the feedback from this series had helped in the designing of the third series of experiments.

3.3 THIRD EXPERIMENTAL SERIES

The first experimental series compared high severity pulping process to conventional chemimechanical and chemi-thermomechanical pulping. We used the same chemical charge and have cooked these pulps to the same yield. It was demonstrated that, at these comparable conditions, high severity pulping necessitated much lower amounts of refining energy. Compared to CTMP, the mechanical properties were much better and compared to CMP pulps, high severity pulping resulted in slightly higher properties. This has been reached at the same chemical charge (with one impregnation chemical), same yield and same total ionic content. Reactor pressurization prior to the explosion increased some mechanical properties and somewhat reduced the refining energy. Optical properties were very good for each pulp (with the exception of the water explosion pulp) with brightness of 60% MgO or more. One step peroxide bleaching resulted in about 20% MgO brightness increase.

The addition of a second impregnation chemical provoked another significant refining energy reduction and property increase (most evident in the case of breaking length and burst index). With a suitable choice of the second impregnation agent ($NaHCO_3$ rather than NaOH), this overall improvement is not accompanied by any negative side effect, such as the brightness or yield loss. In the case of the $Na_2SO_3/NaHCO_3$ impregnation system, the pressure increase did not cause any notable property increase.

The second experimental series confirmed the importance of a second impregnation chemical for paper property development. The only case, where the second impregnation agent did not help, was the tear index. As a result of the 2-chemicals impregnation, the only parameter that was found to be increased with pressurized explosion (up to 25 atm) was the breaking length.

In the first two experimental series, SEP pulping conditions were determined to reach certain product parameters, i.e. same yield at same chemical charge... at around the presumed optimum, such as it was suggested for hardwoods and softwoods in the literature [36, 38, 64, 79, 88, 89]. These conditions (for aspen) were 190°C/2 minutes, 195°C/1.5 minute and 200°C/1 minute. Up to this point, little information could be generated about what could happen if conditions went

beyond the suggested optimum. It was speculated that an insufficient level of treatment would lead to higher refining energy consumption and probably to shorter fibers with reduced papermaking properties.

In the case of softwoods, Kokta et al. found [36] that too high values in some pulping parameters (chemical charge, cooking time or cooking temperature) would lead to pulp deterioration resulting in loss in yield, brightness and properties (Figure 3.29). If the high severity pulping goes over the suggested optimum, the resultant pulp may have worse quality in comparison to a CMP or CTMP prepared at the same conditions, as it shows the Figure 3.30.

Similar results were showed by Law [99]. McLeod et al. reported about the same problems in the case of kraft pulp [104]. After a high degree of chemical treatment, the explosion effect and the impact of kraft fibers against the blow tank wall caused a significant decrease in pulp properties. This is also why it is believed that the high severity pulping is only possible in rather narrow area of process conditions. Good example of what happens at exaggerated treatment is the Masonite process resulting in pulp (high yield, though) with a very limited use.

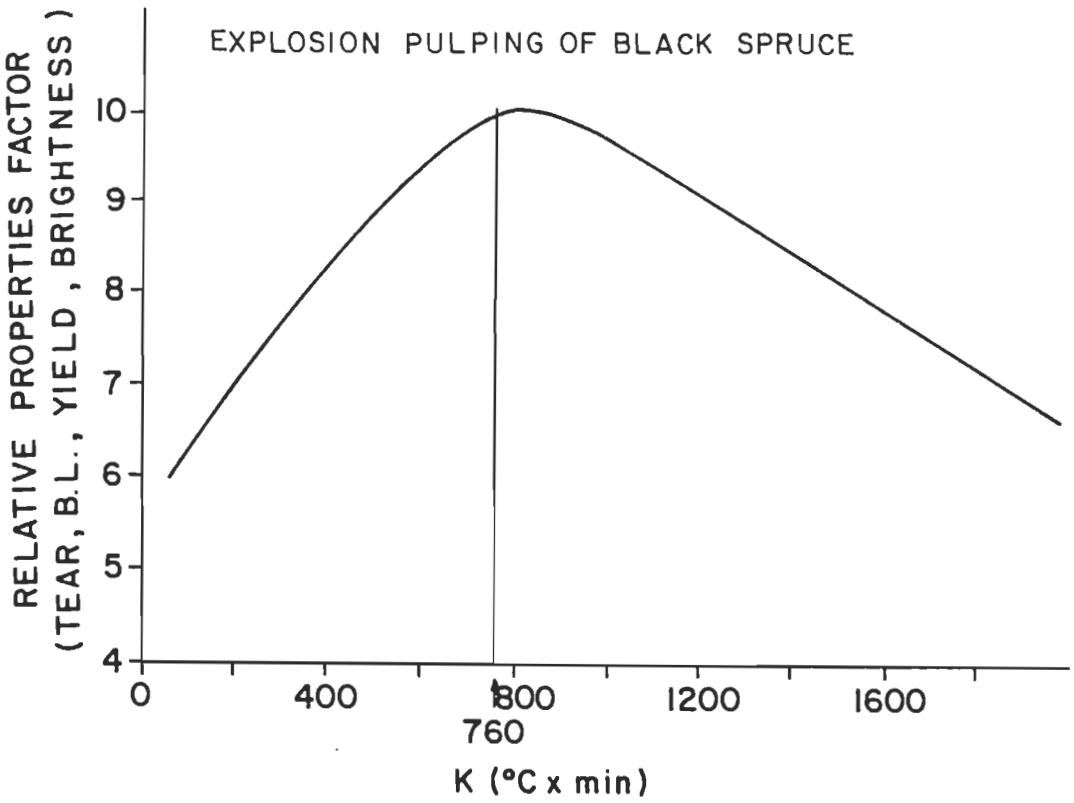


FIGURE 3.29: Explosion pulp properties as a function of chemical charge [36]

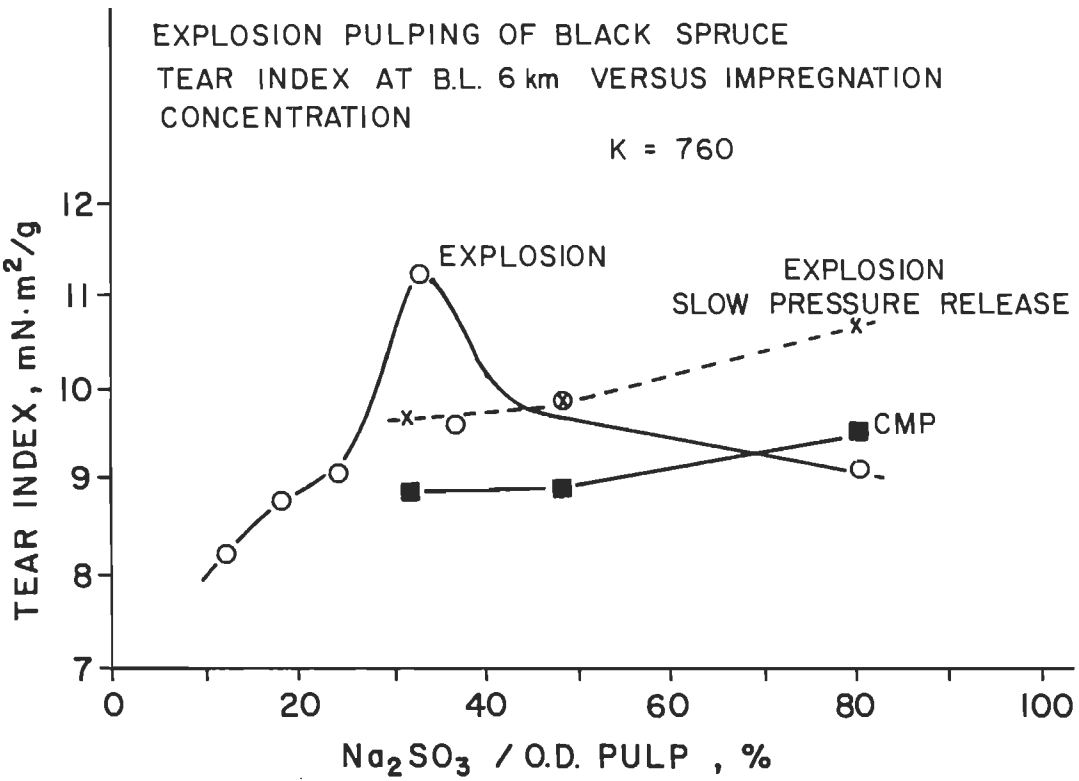


FIGURE 3.30: Comparison of high severity and conventional treatment at normal and extreme pulping conditions [36]

The objectives in the third trial were to plan the experiment to reach beyond the conditions considered as optimum earlier. The purpose was not only to optimize the process and to find the cooking conditions to reach suggested pulp properties, but also to see what kind of changes (chemical, physicochemical and physical) occur under very mild and very severe pulping conditions. For high severity pulps, cooking started at 180°C and one minute. A pulp with very high yield, higher level of refining energy and probably not too well developed mechanical properties was expected. For explosion pulps, the most severe conditions were 200°C and 4 minutes. Here, lower yield (estimated of somewhere between 80 and 85%) was anticipated with very low refining energy and probably lower properties due to fiber damage.

In spite of the previous findings (second series) that there was no evident effect of the high pressure on resulting pulps, it was decided to pressurize the reactor in three cases: the mildest conditions (180°C/1 minute), central point (190°C/2 minutes) and the highest severity point (200°C/4 minutes) to ascertain effects of pressure. As in the second trial, not much influence for the central point could be expected. However, the effect may be much more visible at 180°C and 1 minute, where the degree of cooking related changes is much lower. In the 200°C/4 minutes case, the nitrogen explosion may also lead to some additional changes.

For a reference, two other explosion pulps at the central point were prepared: a water explosion pulp with no added chemicals and a "base" explosion pulp prepared with Na_2SO_3 impregnation. CMP and CTMP were also prepared at these impregnation conditions. The experimental plan is shown in Chapter 2, Figure 2.1.

In this chapter, discussion of the cooking results, characterization of the pulps and paper sheets and the changes due to cooking process (such as the crystallinity and surface parameters) will be made. In the next chapter, mathematical evaluation to quantify the cooking variables will be given together with a study of the correlations between cooking parameters and the pulp and paper properties.

3.3.1 PULP EVALUATION

Pulping conditions, pulp and paper properties resulted from this experimental series are presented in Table 3.8 to 3.10.

Based on our previous experience, yields over 90% for the CTMP, CMP water explosion pulp, base explosion pulp (Na_2SO_3 only) and for the explosion pulps with lower severity of treatment (180°C/1, 2, 4 minutes, 190°C/1, 2 minutes and 200°C/1 minute) were expected. With the increased severity, a gradual shift below 90% yield limit was anticipated. Expectations came true for CTMP, CMP and for some explosion pulps (Figure 3.31). If yields for pulps cooked in this series are compared with the first and second trial (one impregnation chemical and the $Na_2SO_3/NaHCO_3$ impregnation system), it can be noticed that all the yields are about 1 to 1.5% lower. This could be due to lower chip quality. Indeed, chips used in this series were stored for several months and were slightly darker on the surface with occasional decay signs on few chips on the top in the storage bag (every chip was visually examined prior to impregnation and cooking and no unacceptable quality material was allowed to enter the process). Some of the wood degradation products are more soluble and are lost in the cooking, washing and refining process stages. This might have caused slight yield drop, as well as influence some of the pulp and paper parameters that we will discus later on.

TABLE 3.8 Pulping conditions and some of the characteristics of resulted pulps in the third experimental series

#	Pulp type	Impregnation		Cooking					Ionic content [mmol/kg]				Symbol used in figures
		Na_2SO_3 [%]	$NaHCO_3$ [%]	Temp [°C]	Time [min]	Pres. [atm]	Yield [%] Value	Yield [%] Error	Sulfonic	Carboxy	Total Value	Total Error [%]	
1	EXP	8	1	180	1	9.9	91.4	0.6	47.7	146	194	4.2	●
2	EXP	8	1	180	2	9.9	90.5	0.4	51.3	148	199	3.6	■
3	EXP	8	1	180	4	9.9	88.6	0.8	50.1	151	201	5.0	▲
4	EXP	8	1	190	1	11.9	89.1	0.6	50.1	141	191	3.9	●
5	EXP	8	1	190	2	11.9	88.3	0.5	52.1	143	195	4.8	■
6	EXP	8	1	190	4	11.9	85.2	0.5	55.3	139	194	6.1	▲
7	EXP	8	1	200	1	15.5	87.9	0.9	51.6	144	196	5.1	●
8	EXP	8	1	200	2	15.5	85.4	0.8	53.4	139	192	4.3	■
9	EXP	8	1	200	4	15.5	83.4	1.0	54.1	130	184	4.8	▲
10	N-EXP	8	1	180	1	9.9/25	91.0	0.4	48.1	148	196	4.1	◆
11	N-EXP	8	1	190	2	11.9/25	88.2	0.5	52.3	146	198	5.0	◆
12	N-EXP	8	1	200	4	15.5/25	82.4	0.4	51.3	130	181	3.8	◆
13	BASE EXP	8	0	190	2	11.9	90.0	0.8	34.6	131	166	3.9	◇
14	WATER EXP	0	0	190	2	11.9	91.9	0.6	0.0	96	96	1.4	△
15	CTMP	8	0	128	10	1.8	92.8	0.7	29.6	132	162	4.8	○
16	CMP	8	0	150	30	4.0	90.6	0.7	32.5	135	168	1.8	□

TABLE 3.9 Mechanical paper properties obtained in the third experimental series

Pulp			Parameter values and experimental error in [%]											
#	Type	CSF [ml]	Density [kg/m^3]		Porosity [ml/min]		Breaking length [km]		Stretch [%]		Tear [mNm^2/g]		Burst [kPam^2/g]	
			Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	EXP	100	490	2.3	110	4.3	5.5	3.5	1.7	1.6	5.0	6.3	2.6	2.6
		230	428	2.1	420	3.9	4.8	3.6	1.3	3.2	4.9	4.5	2.1	3.2
		370	392	3.6	574	5.0	3.9	2.1	1.1	5.3	5.1	3.8	1.6	3.2
2	EXP	107	499	3.1	82	4.6	6.4	3.2	1.7	0.6	5.6	5.6	3.2	3.5
		190	437	3.4	177	4.8	5.8	3.6	1.4	0.5	5.8	6.4	2.8	3.5
		350	394	2.0	467	4.9	4.7	2.5	1.2	2.6	5.6	5.6	2.1	.1.5
3	EXP	100	538	1.6	41	4.7	7.3	2.9	1.8	3.4	6.9	5.4	3.7	2.2
		140	478	2.3	69	4.4	6.2	2.4	1.4	3.2	6.3	5.9	3.2	2.5
		375	410	2.5	424	4.4	5.5	2.0	1.4	3.6	6.8	6.5	2.3	2.9
4	EXP	105	488	2.9	121	4.6	6.1	1.6	1.5	2.5	6.2	3.4	3.1	3.4
		195	467	0.6	233	5.2	5.6	1.8	1.4	1.9	5.8	5.9	2.7	4.1
		420	428	5.0	636	6.2	4.1	2.4	1.1	4.0	5.4	5.7	2.2	4.0
5	EXP	100	553	2.4	47	3.1	7.0	3.5	1.6	1.6	7.2	6.4	4.0	2.6
		190	485	4.2	154	5.2	6.3	2.9	1.5	3.2	6.6	8.1	3.1	2.0
		420	409	1.6	562	1.0	5.0	2.1	1.2	3.8	6.3	3.4	2.4	2.0
6	EXP	85	557	3.5	23	3.9	8.2	2.0	1.9	3.7	6.9	6.5	4.5	2.0
		117	504	3.4	35	3.6	7.5	2.9	1.7	3.3	6.5	6.7	4.0	2.6
		290	436	3.7	262	5.0	6.2	3.0	1.5	1.0	7.0	4.5	3.2	3.1
7	EXP	105	565	3.4	45	4.6	7.0	3.1	1.9	0.6	6.4	6.3	4.0	3.1
		210	468	5.0	152	5.8	6.3	3.1	1.5	0.5	6.3	6.4	2.9	0.5
		395	448	5.0	610	6.0	5.5	3.0	1.3	2.9	5.5	5.5	2.5	0.2
8	EXP	70	586	5.1	17	3.2	8.0	1.0	1.9	3.1	6.8	5.3	4.6	4.3
		170	546	3.4	74	6.2	7.4	6.4	1.7	3.2	6.7	2.6	3.7	3.2
		385	462	2.8	410	3.4	6.2	2.0	1.5	3.5	5.1	5.9	2.9	3.4
9	EXP	75	587	2.9	14	1.9	8.7	6.5	2.0	3.9	7.9	6.4	4.7	1.5
		180	519	2.4	63	3.4	7.8	4.1	1.7	3.4	7.2	4.2	4.0	3.2
		325	480	2.3	224	6.3	6.8	3.2	1.5	6.5	6.8	3.5	3.6	2.2
10	N-EXP	108	475	2.3	136	5.2	6.5	1.8	1.6	1.6	6.0	6.3	3.0	2.0
		230	432	1.6	362	1.6	5.5	4.4	1.3	2.3	5.8	6.1	2.1	1.6
		380	395	3.2	666	3.5	5.0	3.2	1.2	5.9	5.4	0.4	1.5	3.5
11	N-EXP	110	537	3.5	57	3.9	7.2	5.0	1.7	2.5	6.4	3.9	3.8	3.2
		145	467	2.9	110	6.8	6.1	5.6	1.4	6.3	7.1	7.8	3.2	1.6
		325	442	2.8	380	1.7	5.4	3.1	1.3	1.3	6.4	3.1	2.5	2.8
12	N-EXP	110	594	2.4	28	1.6	8.4	1.0	2.0	2.8	7.3	6.6	4.5	2.9
		183	511	2.6	76	4.5	7.8	2.6	1.8	2.9	7.9	6.4	4.0	6.2
		330	477	1.3	268	2.3	6.7	2.8	1.6	2.2	7.5	6.9	3.6	4.5
13	BASE EXP	110	445	1.9	442	2.9	4.8	3.7	1.3	2.3	4.1	5.9	3.0	3.5
		300	400	3.5	680	2.8	3.2	2.1	1.0	3.4	4.5	3.9	1.6	3.1
		450	379	4.6	870	5.1	2.6	2.9	0.8	4.1	3.4	5.4	1.0	3.5
14	WATER EXP	105	380	3.2	292	3.8	3.1	3.4	1.3	4.5	4.3	1.6	1.3	1.5
		200	332	3.8	618	2.6	2.5	2.6	1.1	2.6	3.2	2.1	0.9	4.1
		390	294	2.9	888	6.2	1.7	3.4	0.9	3.8	3.3	2.1	0.6	4.9
15	CTMP	102	375	6.0	450	4.6	3.0	5.0	1.2	2.0	2.8	5.6	1.2	2.6
		155	348	4.2	598	5.3	2.6	1.9	1.1	1.8	2.9	5.8	0.9	3.4
		295	303	3.8	833	2.9	1.8	3.6	0.9	3.9	2.7	5.4	0.6	1.5
16	CMP	96	425	3.5	200	4.6	4.7	3.4	1.4	3.4	3.7	6.1	2.1	3.6
		275	382	1.9	758	3.0	3.1	2.8	1.0	4.6	3.7	6.3	1.1	2.5
		380	351	3.7	977	3.2	2.4	1.5	0.8	1.7	3.3	1.3	0.8	3.5

TABLE 3.10 Refining energy and optical paper properties obtained in the third experimental series

Pulp			Parameter values and experimental error in [%]											
#	Type	CSF [ml]	Relative specific refining energy [MJ/kg]		Brightness 1.2 g sheet (60 g/m^2) [%MgO]		Brightness 3.0 g sheet (150 g/m^2) [%MgO]		Brightness loss [%]		Opacity [%]		Light-scattering coefficient [cm^2/g]	
			Value	Error	Value	Error	Value	Error	Value	Error	Value	Error	Value	Error
1	EXP	100	5.2	2.6	65.2	1.2	68.0	1.6	1.0	-	88.8	2.6	450	3.6
		230	4.7	3.5	65.3	1.6	68.1	1.3	0.7	-	88.5	2.3	428	2.5
		370	4.1	6.3	65.0	3.5	67.5	1.5	1.1	-	87.4	2.5	416	2.7
2	EXP	107	3.9	4.5	64.0	1.6	68.0	1.5	0.6	-	87.5	2.4	400	4.1
		190	3.5	6.8	62.8	1.4	66.1	1.4	1.4	-	87.9	3.2	397	3.6
		350	2.6	8.6	63.3	1.8	66.8	1.1	1.7	-	87.5	3.8	388	5.2
3	EXP	100	2.6	9.5	62.7	1.6	66.4	3.2	0.6	-	85.5	1.6	353	4.3
		140	2.4	6.4	61.4	1.4	64.6	1.5	1.7	-	86.8	1.5	363	1.6
		375	2.0	5.6	61.6	1.5	65.0	1.6	1.2	-	85.8	4.2	352	5.3
4	EXP	105	4.2	3.9	62.2	1.6	68.7	1.4	0.8	-	89.7	1.9	411	2.9
		195	4.1	5.7	63.3	1.4	65.9	1.1	0.7	-	88.1	2.6	399	4.0
		420	3.6	5.6	64.1	1.1	67.7	1.1	0.8	-	86.5	2.5	389	4.8
5	EXP	100	3.5	4.8	63.0	1.1	67.1	1.1	0.4	-	86.0	3.2	364	5.1
		190	3.3	6.4	63.3	1.0	67.2	1.2	0.6	-	86.8	3.6	377	2.6
		420	2.6	4.6	65.3	1.1	67.0	1.7	1.0	-	84.5	2.5	365	2.0
6	EXP	85	2.5	3.5	62.4	1.2	65.3	1.6	0.8	-	84.7	4.5	342	4.3
		117	2.4	5.5	63.0	1.1	65.1	1.4	0.3	-	85.3	4.6	351	2.9
		290	2.2	4.6	61.0	1.0	64.2	1.0	0.6	-	85.8	6.5	345	2.8
7	EXP	105	3.9	5.9	62.1	1.6	67.0	1.9	0.3	-	85.6	3.1	357	2.7
		210	3.7	3.8	62.8	1.8	66.6	1.6	0.2	-	86.7	2.0	363	2.5
		395	3.1	4.7	62.7	1.4	66.7	1.5	0.2	-	86.2	1.2	359	2.6
8	EXP	70	3.2	7.6	58.4	1.6	64.9	1.5	0.9	-	87.6	1.9	329	2.5
		170	3.1	9.5	61.5	1.1	65.0	1.4	1.3	-	85.2	6.5	339	2.4
		385	2.4	6.8	60.8	1.3	64.7	1.0	0.8	-	86.0	3.4	336	2.3
9	EXP	75	1.6	4.5	60.0	1.3	63.3	1.3	0.7	-	83.6	1.6	313	2.8
		180	1.5	4.1	59.7	1.2	63.3	1.6	1.1	-	85.0	3.7	325	2.9
		325	1.4	3.2	59.5	2.6	63.0	1.5	1.1	-	84.9	5.0	324	2.5
10	N-EXP	108	4.3	4.6	64.8	1.3	67.5	1.8	0.6	-	88.0	4.6	426	4.6
		230	4.1	4.9	65.2	1.8	68.5	1.9	1.1	-	88.2	4.3	420	3.5
		380	3.4	6.7	65.5	1.4	68.5	1.9	1.6	-	87.9	4.1	411	3.9
11	N-EXP	110	2.6	8.1	63.8	1.1	67.1	1.9	0.7	-	85.8	2.5	368	2.8
		145	2.5	2.0	61.1	1.0	65.0	3.2	1.1	-	87.7	4.3	378	2.4
		325	2.4	1.6	61.1	1.2	65.8	3.6	1.3	-	86.9	2.9	365	5.0
12	N-EXP	110	1.5	1.5	57.5	1.7	62.5	3.1	0.9	-	88.3	2.7	315	1.5
		183	1.4	6.8	58.3	1.4	62.1	2.6	0.7	-	86.2	2.6	328	2.6
		330	1.3	3.4	59.1	1.1	62.9	2.4	1.1	-	86.3	1.6	331	2.7
13	BASE EXP	110	5.6	6.6	63.9	3.5	69.3	1.5	0.6	-	89.4	2.6	477	2.7
		300	4.9	6.5	64.0	2.3	69.0	1.6	0.9	-	90.2	3.8	456	2.9
		450	4.2	6.9	64.3	1.6	69.5	2.6	1.0	-	88.9	3.	436	3.5
14	WATER EXP	105	6.2	6.8	45.7	1.8	47.2	2.4	0.1	-	98.3	4.1	510	3.1
		200	5.9	4.5	44.6	1.0	45.6	2.4	0.1	-	97.8	4.6	502	2.9
		390	5.1	5.5	43.7	1.7	44.8	1.2	0.1	-	97.3	2.9	463	3.8
15	CTMP	102	9.2	5.5	71.5	1.5	71.5	1.5	0.9	-	90.4	5.1	564	5.4
		155	8.8	5.8	71.6	1.6	73.8	1.6	0.7	-	90.0	3.7	561	2.1
		295	7.1	4.8	69.5	1.4	71.1	1.3	1.1	-	89.8	5.0	502	4.6
16	CMP	96	7.0	6.7	67.0	1.1	68.5	1.1	1.0	-	90.1	5.9	508	6.4
		275	5.6	6.9	65.0	1.1	67.1	1.0	0.7	-	90.7	2.4	487	5.5
		380	5.2	3.5	65.0	1.0	67.6	1.5	0.9	-	90.5	1.6	463	4.7

Concerning explosion pulps and their yields (Figure 3.32), almost equal drop for each cooking temperature can be observed. The highest yields were found at the lowest temperature (180°C) and with each pulping temperature increase the yield also dropped. When the three pulps cooked at similar severity (as it follows from the Arhenius' law): 180°C/4 minutes, 190°C/2 minutes and 200°C/1 minute are compared - we see that all the yields were at about 88.5% level. The yields for ordinary and nitrogen explosion pulping were very similar for 180 and 190°C. At 200°C, the difference was almost 1% which might have been caused by the effect of highly softened fibers blown against the release vessel wall. However, such small difference can be also represented as an experimental error.

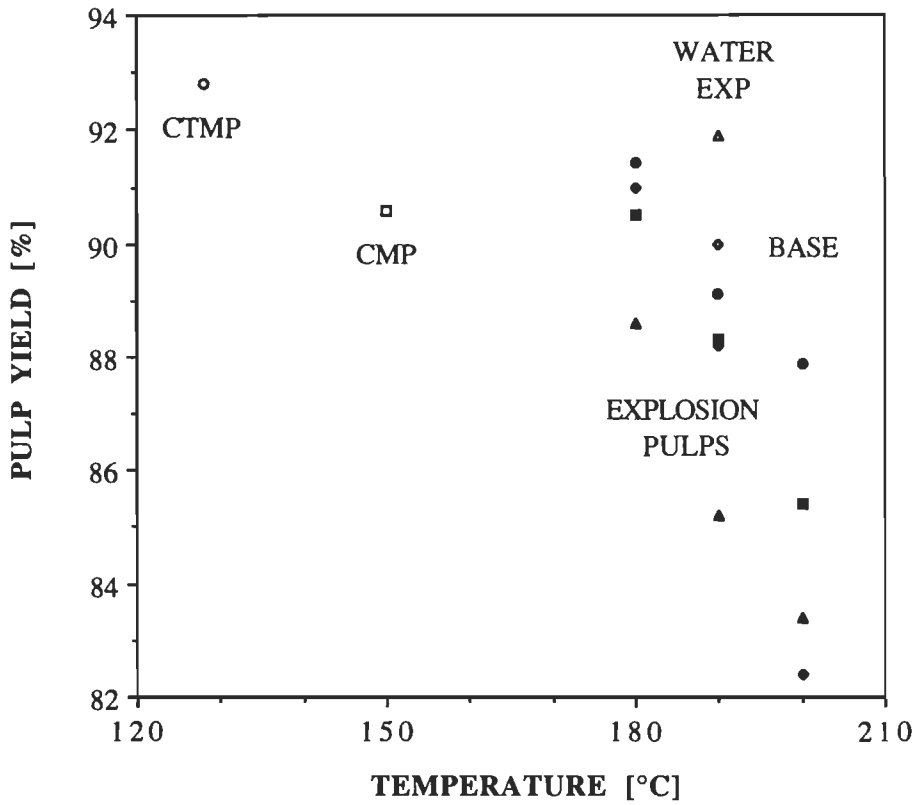


FIGURE 3.31 Pulp yield as a function of temperature for all the pulps in the third experimental series

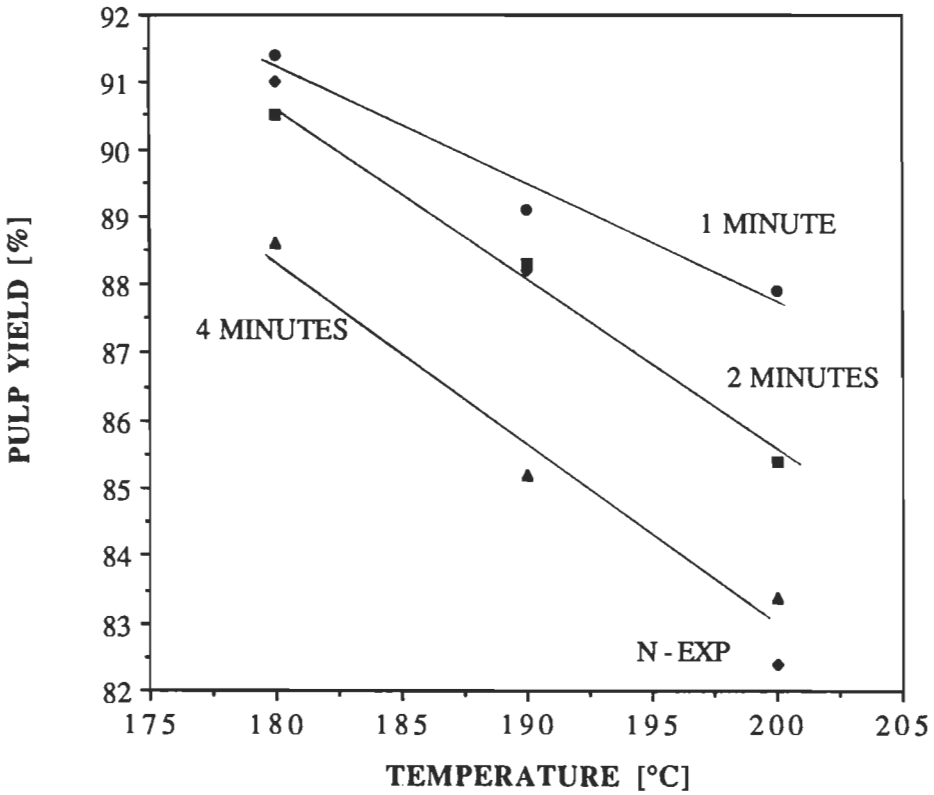


FIGURE 3.32 Pulp yield as a function of temperature for explosion pulps in the third experimental series

The ionic contents for the CTMP, CMP and base explosion pulps were similar - around 165 mmol/kg (Figure 3.33). The addition of a second impregnation chemical ($NaHCO_3$) raised the total ionic content by approximately 20%. However, the total ionic content had a dropping tendency with increasing temperature/time combination. In order to find out what happens, it should be realized that there are two important reactions that contribute to the ionic content development. Firstly, the hemicellulose hydrolysis, which is by far the fastest reaction. It reduces the yield as well as the carboxylic content. Carboxylic acids present in hemicelluloses are the units that contribute to carboxylic content, and their removal is mostly responsible for the total ionic content drop. Lignin sulphonation, on the other hand, is a reaction that increases the ionic content. From Figure 3.34 it can be seen, that the sulphonic content increased not only with rising temperature (CTMP < CMP < Base), but also with increased process severity (in the case of explosion pulps). This reaction also has certain maximum, where lignin changes and their influence can decrease the sulphonic content. Sulphonic groups can be lost either with sulphonated soluble fractions of lignin or by the hydrolysis from the insoluble lignin, as it was suggested by Ahmed et al. [60]. He reported several bell-shaped curves for the sulphonic content at high severity cooking treatment. An examination of pulps in Figures 3.33 and 3.34, (with the exception of the highest severity cook at 200°C/4 minutes) shows that the sulphonic content was rising. The total ionic content decrease was thus mainly caused by hemicellulose solvolysis, which is also confirmed by lower pulp yield at higher severity treatment. Previous research (first experimental series) showed that the sulphonic content is the more important part of the total ionic content. Results showed that if several pulps with similar total ionic content were produced, those ones with higher sulphonation had higher papermaking quality. Influence of higher sulphonation on paper quality will be demonstrated later in this chapter and will be also considered in the mathematical treatment.

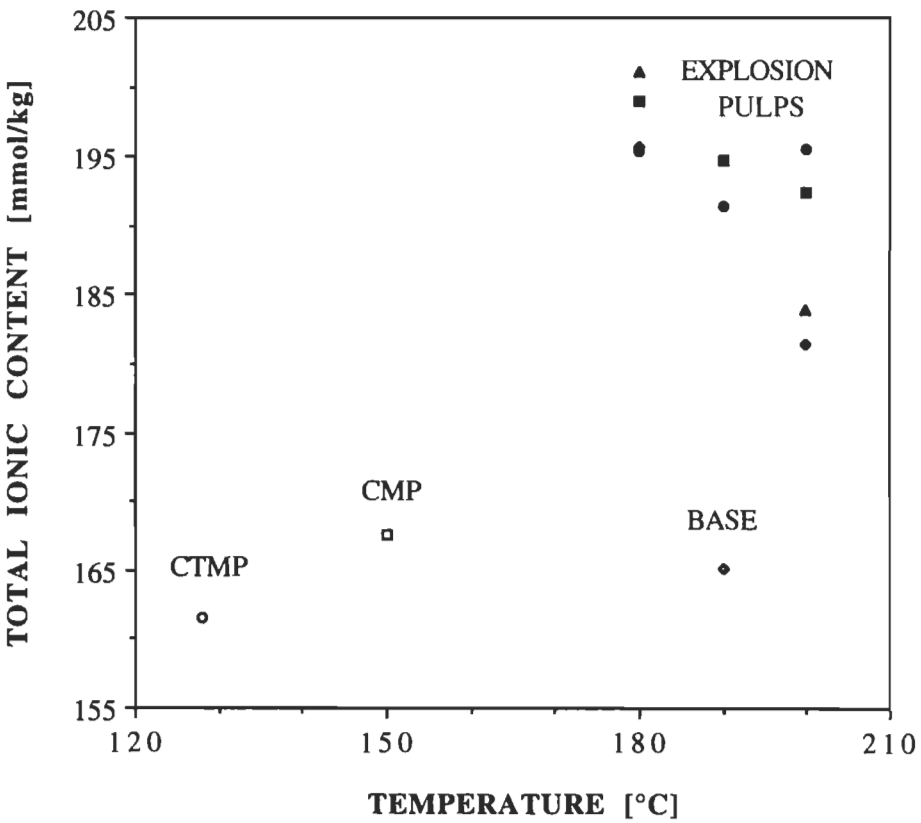


FIGURE 3.33 Total ionic content as a function of temperature for all the pulps in the third experimental series

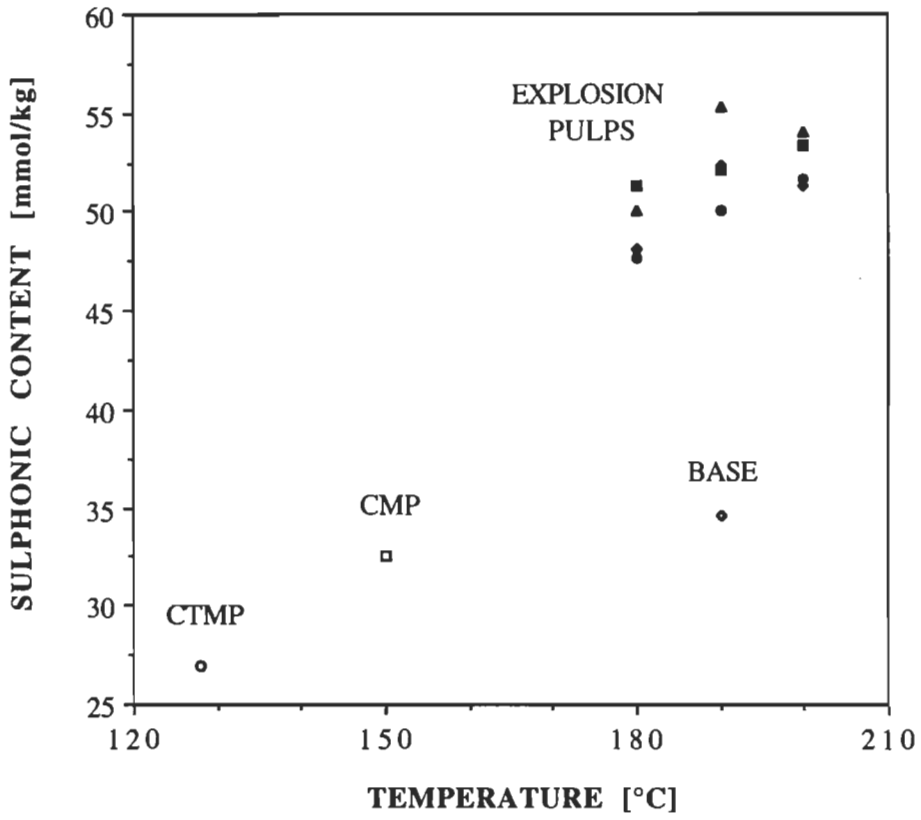


FIGURE 3.34 Sulphonic content as a function of temperature for all the pulps in the third experimental series

As mentioned earlier, the higher cooking severity and higher blowing pressures yielded cooked chips that were much more flexible and easier to separate. This is well reflected in the refining time and energy consumption figures (Figures 3.35 to 3.37). Since the relaxation times after the glass transition are in order 10^4 times higher [68] than the transition times, chips cooked at temperatures above the glass transition temperature remain flexible for substantially longer time than those cooked at lower temperatures. High severity cooking treatment thus significantly contributed to a more permanent lignin softening. The chips stayed flexible after cooling down and this characteristics remained even during pulp storage at 3°C. Softer lignin and reduced chip hardness (on touch) substantially decreased both refining time (Figure 3.35) and refining energy (Figure 3.36).

Refining times were about the same for CTMP, CMP and base explosion pulp (Na_2SO_3 impregnation in all cases). Refining energy, though, decreased with rising temperature. It was about 9 MJ/kg for CTMP, 7 MJ/kg for CMP and 6 MJ/kg for base explosion pulp. Water explosion pulp had the refining energy slightly higher than the base pulp.

If high severity 2-chemical cooks are examined, it can be concluded that refining time decreases with either temperature and cooking time. Comparing refining times at similar severity, slight increases can be observed with rising temperature: 180°C/4 minutes < 190°C/2 minutes < 200°C/1 minute (Figure 3.35). Similar effects were observed in the second experimental series, where the refining time for 190°C/2 minutes was slightly lower than at the 195°C/1.5 minute conditions. Refining energy shows the same tendency (Figure 3.37). The lowest severity treatment pulp (180°C/1 minute) had the relative specific refining energy around 5 MJ/kg and the lowest energy was found in the case of 200°C/4 minutes for pulps with ordinary and nitrogen explosion. Nitrogen addition seems to have the biggest influence at lower severity: at 180°C/1 minute and 190°C/2 minutes. conditions. At 200°C/4 minutes, the values for ordinary and nitrogen explosion were very similar.

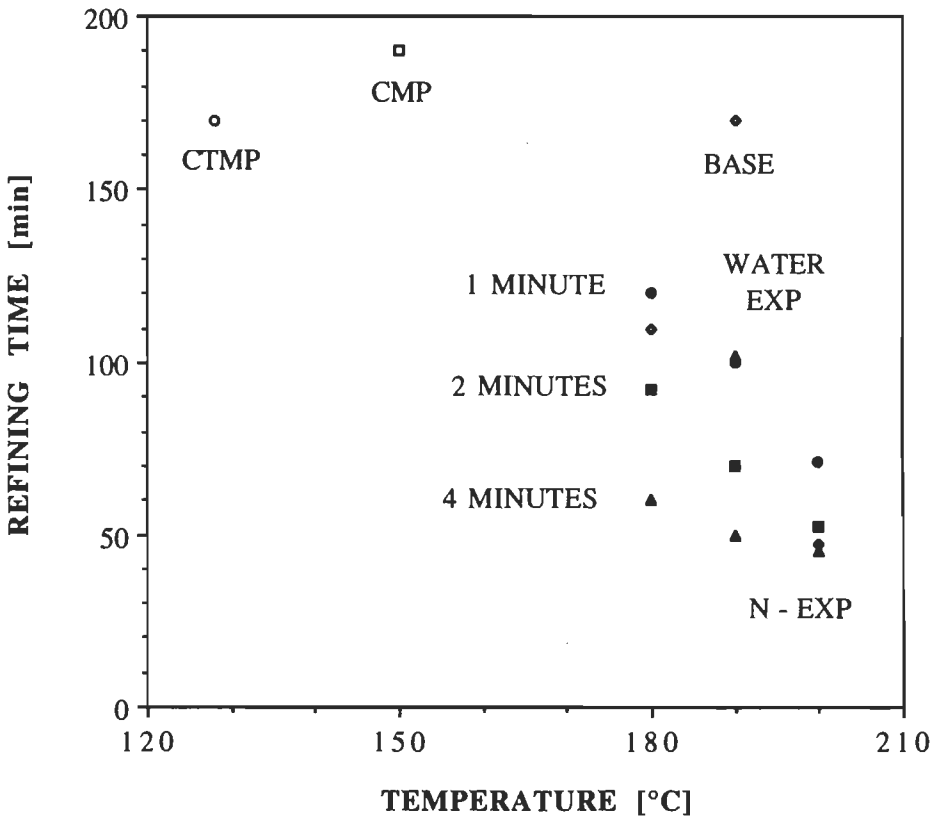


FIGURE 3.35 Refining time for a 100 ml CSF as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

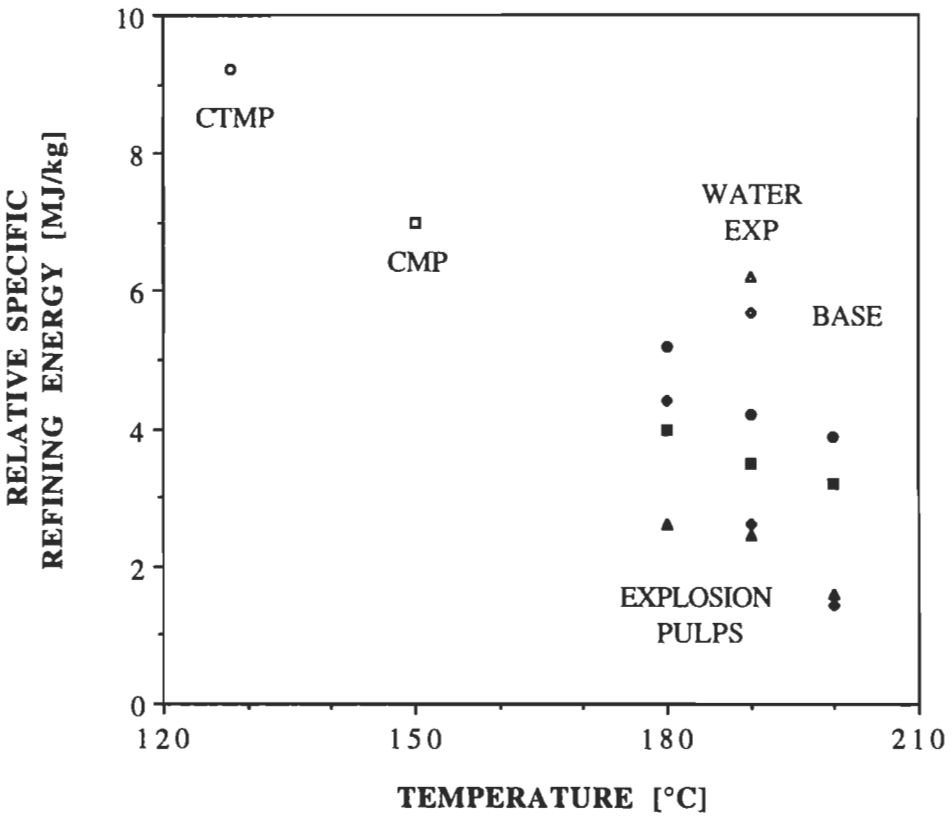


FIGURE 3.36 Relative specific refining energy as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

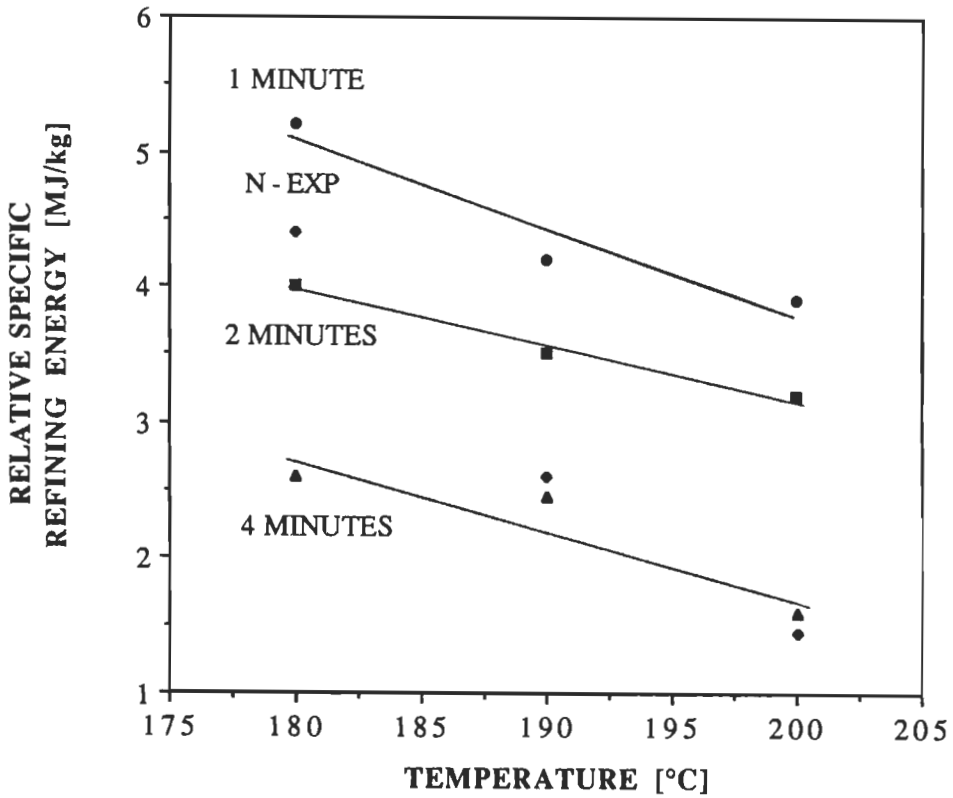


FIGURE 3.37 Relative specific refining energy as a function of temperature for explosion pulps in the third experimental series (at 100 ml CSF)

The results so far show a very good accord between the three experimental series. When several fiber/sheet parameters - density, light-scattering coefficient and porosity are considered (Figures 3.38 to 3.42), similar conclusions can be reached. The average fiber length also increased with the treatment severity. If the rising temperature is considered as a reference, the average fiber length increased in the order CTMP < CMP < explosion pulps. If we take the 6 pulps prepared at the central point temperature (190°C), we found that the fiber length increased in order water explosion < base explosion < 190°C/1 minute < 190°C/2 minutes = 190°C/2 minutes nitrogen explosion < 190°C/4 minutes. Even if the differences (especially for the 4 latter pulps) were not very large, they showed a tendency that has been repeated for all three cooking temperatures (180, 190 and 200°C). The increase in fiber length with increasing cooking severity can be explained by the shorter refining time and lesser amount of energy attributed to each fiber during the refining stage. If there is less energy and less contact with refining plates/blades, the fibers are cut to a lesser extent compared to less flexible, less softened and more stiff CTMP and CMP.

In spite of the longer average fiber length, the higher severity cooking conditions resulted in higher pulp density. Figure 3.38 shows the density increase as a function of treatment. The CTMP and the water explosion pulp are at similar level, CMP pulp has density slightly lower than the base explosion (Na_2SO_3 only), and the explosion pulps' density rises with increasing severity of both time and temperature. This fact resulted in a better fiber softening and therefore an improved space filling by fibers treated with increased severity. From this point of view, it is not surprising to see that the explosion pulps had also lower light-scattering coefficient values. Figure 3.39 shows this tendency for all pulps and Figure 3.40 concentrates on the 2-chemical explosion pulps. If a comparison is made at similar severity, the values are very close for 180°C/4 minutes, 190°C/2 minutes and 200°C/1 minute and are slightly rising with increasing temperature. The influence of nitrogen pressurization confirms earlier reported results - it diminishes the LSC in the case of 180°C/1 minute and does not cause significant differences at higher temperatures. As a matter of fact, the LSC values at 190°C/2 minutes and 200°C/4 minutes were identical for ordinary and nitrogen explosion. Higher density and larger fiber contact (represented by lower scattering capacity) naturally lead to lower porosity values. Figure 3.41 shows

this tendency for all pulps. The porosity drops in the order CTMP > CMP > water explosion > explosion pulps. The only exception is the base explosion (one chemical) pulp with porosity matching that of CTMP. This is quite unexpected and was not found in the first experimental series. Higher density, lower LSC and better surface characteristics should definitely put this explosion pulp's porosity below the water explosion value. It is interesting to note that if the other (2-chemical) explosion pulps (Figure 3.42) are examined, it can be seen that regardless of the starting point, pulping condition or the digester pressurization, the porosity values seem to converge into one value (about 10 ml). In order to investigate this particularity, several sheets with the freeness level below 100 ml were prepared. From the "meeting point" at 10 ml, the porosity curves were very similar, and at all pulping times at 200°C, they reached virtually zero porosity at about 65 to 70 ml CSF.

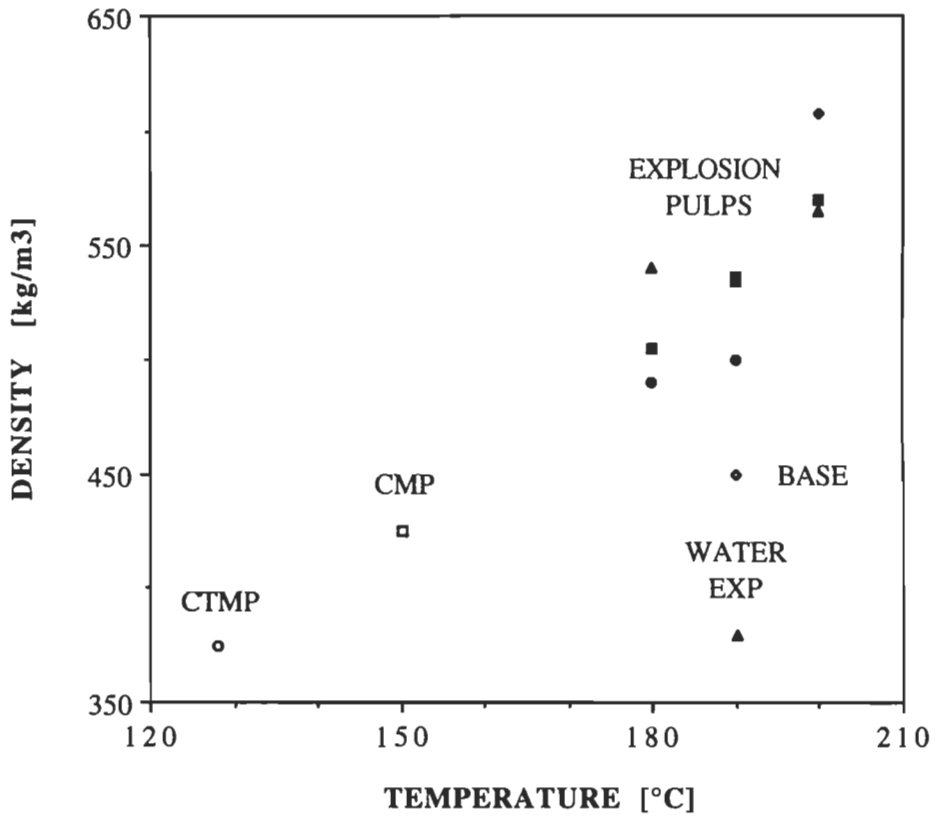


FIGURE 3.38 Pulp density as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

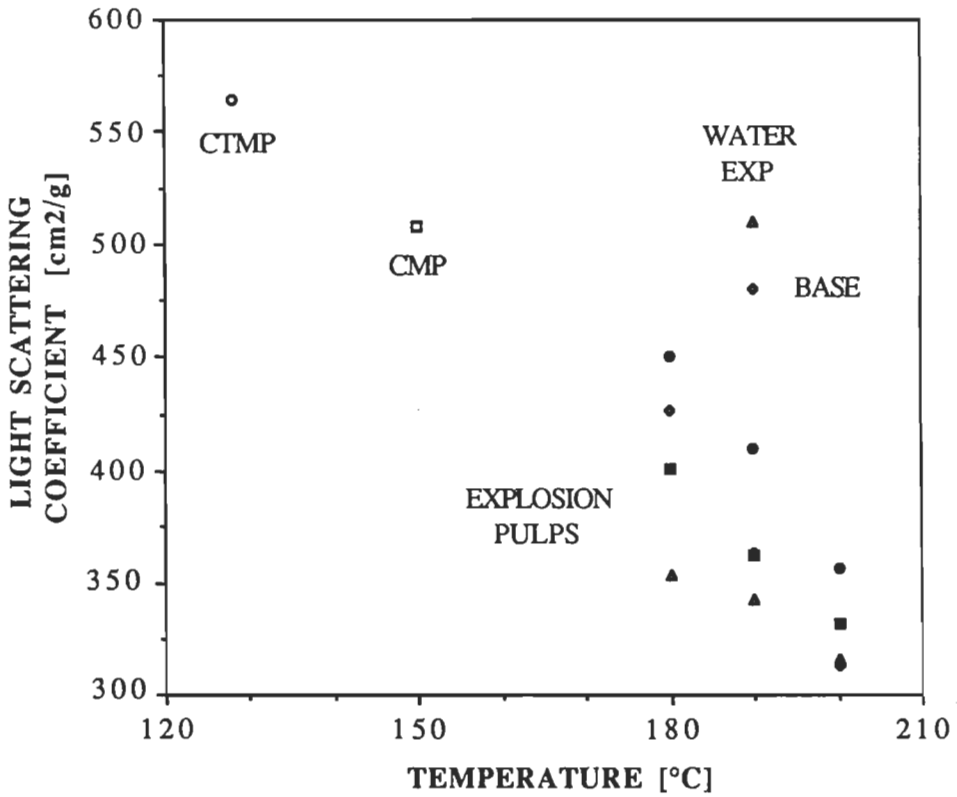


FIGURE 3.39 Light-scattering coefficient as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

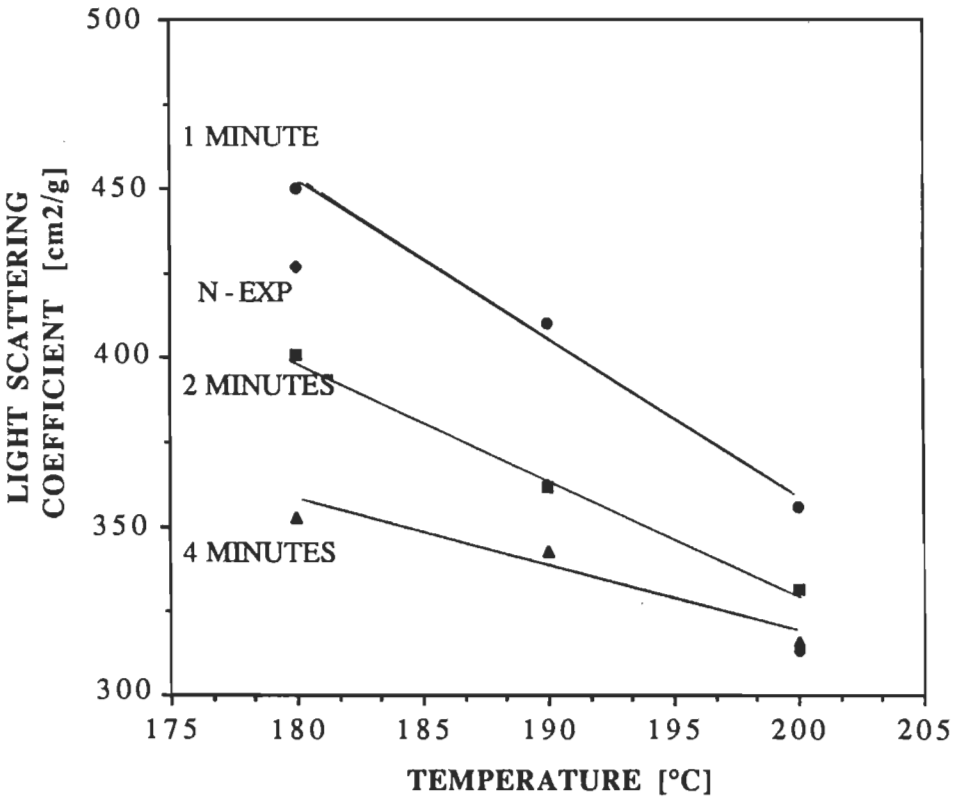


FIGURE 3.40 Light-scattering coefficient as a function of temperature for explosion pulps in the third experimental series (at 100 ml CSF)

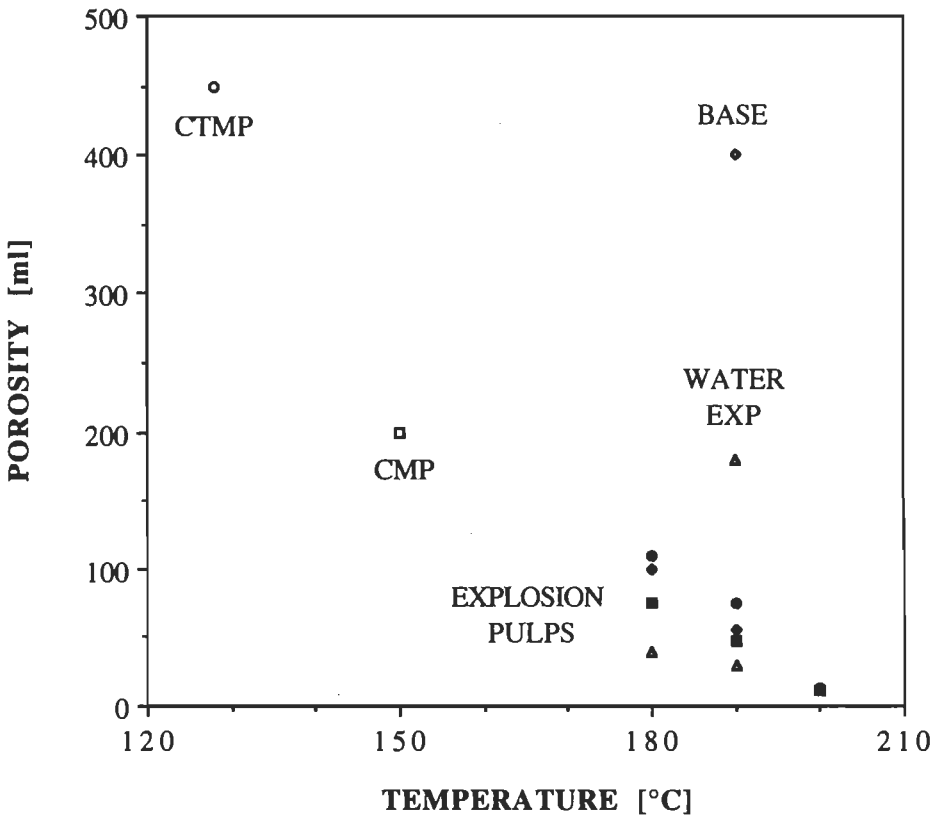


FIGURE 3.41 Porosity as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

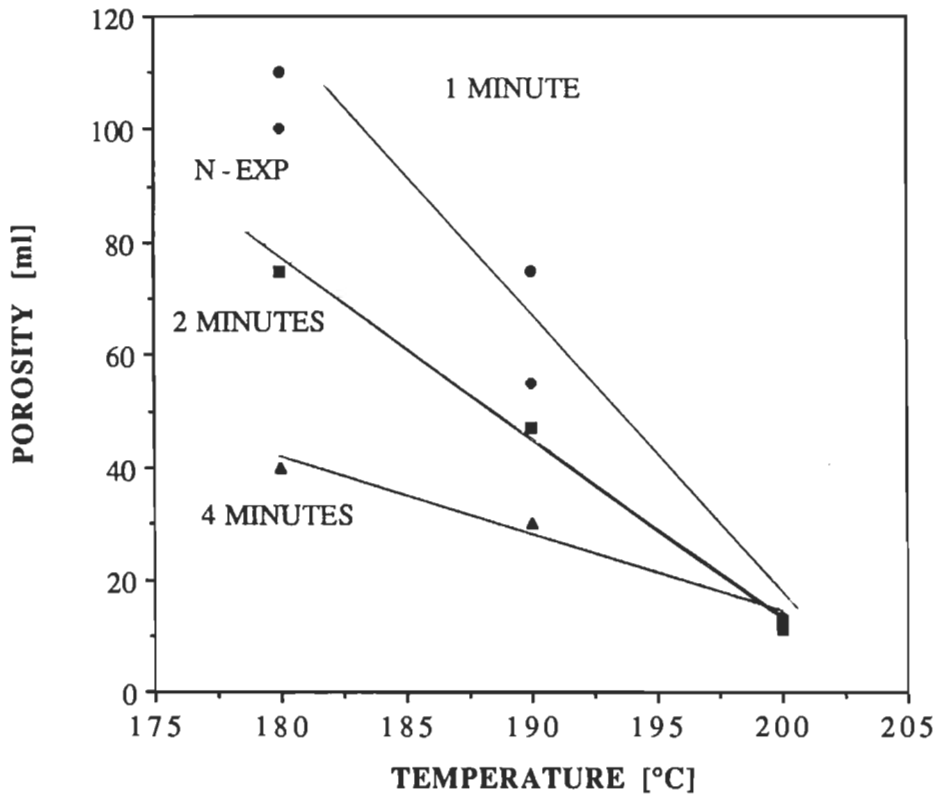


FIGURE 3.42 Porosity as a function of temperature for explosion pulps in the third experimental series (at 100 ml CSF)

Better physical fiber characteristics as well as higher sulfonic content suggest higher mechanical properties for the explosion pulps. Figures 3.43 to 3.49 fully confirm these suggestions. Breaking length values (Figure 3.43) nicely rise with increasing temperature in order CTMP < CMP < base pulp < explosion pulps. Water explosion pulp has its breaking length similar to the CTMP and the one-chemical base explosion pulp is slightly stronger than the CMP. Explosion pulps (Figure 3.44) show improvement with either cooking time and cooking temperature increase. Nitrogen explosion again confirmed its beneficial influence on breaking length development. This seems to be the most improved mechanical parameter in all three experimental series. In the case of 180°C/1 minute, the pressure increase (over 15 atmospheres) caused an increase in breaking length so significant that this pulp was almost equal to the double-length time cooking conditions at 180°C/2 minutes. At 190°C/2 minutes, the increase was less pronounced and the 200°C/4 minutes conditions produced equal breaking length values for both ordinary and nitrogen explosion.

Stretch values (Figure 3.45) improved accordingly with the breaking length - beginning at 1.2% for the CTMP and reaching to about 2% for the 200°C/4 minute cook.

Burst indexes (Figure 3.46) showed very similar behavior increasing linearly with increasing cooking severity (temperature). Water explosion pulp reached about the same strength than the CTMP and the base explosion pulp has its burst index about 30% higher when compared to the CMP. In the explosion pulps case (Figure 3.47), the biggest improvement was found when the cooking time was increased from one to two minutes. Further increase to four minutes added hardly half of the former improvement. Similarly to the breaking length, the nitrogen explosion was mostly pronounced at 180°C/1 minute - almost matching the burst of the 180°C/2 minute cook. The difference at 190°C/2 minutes and 200°C/4 minutes were much lower. In fact, the pressurized explosion pulps ended up with burst values slightly lower compared to ordinary explosions.

Tear values (Figure 3.48) followed the tendencies described for the breaking length, stretch and burst indexes.

A comparison of breaking length and the tear index, (Figure 3.49) shows the mechanical strength improvement in the following order: CTMP < water explosion < CMP < base explosion < explosion pulps. If we draw a line through these 16 pulps, the relationship tear = f(breaking length) is almost linear with none of these pulps being much "off limits". This was the order found in the first experimental series and it was again confirmed that the explosion pulping process working at high severity cooking conditions does produce pulps with higher mechanical strength quality. From this point of view, expected results were obtained.

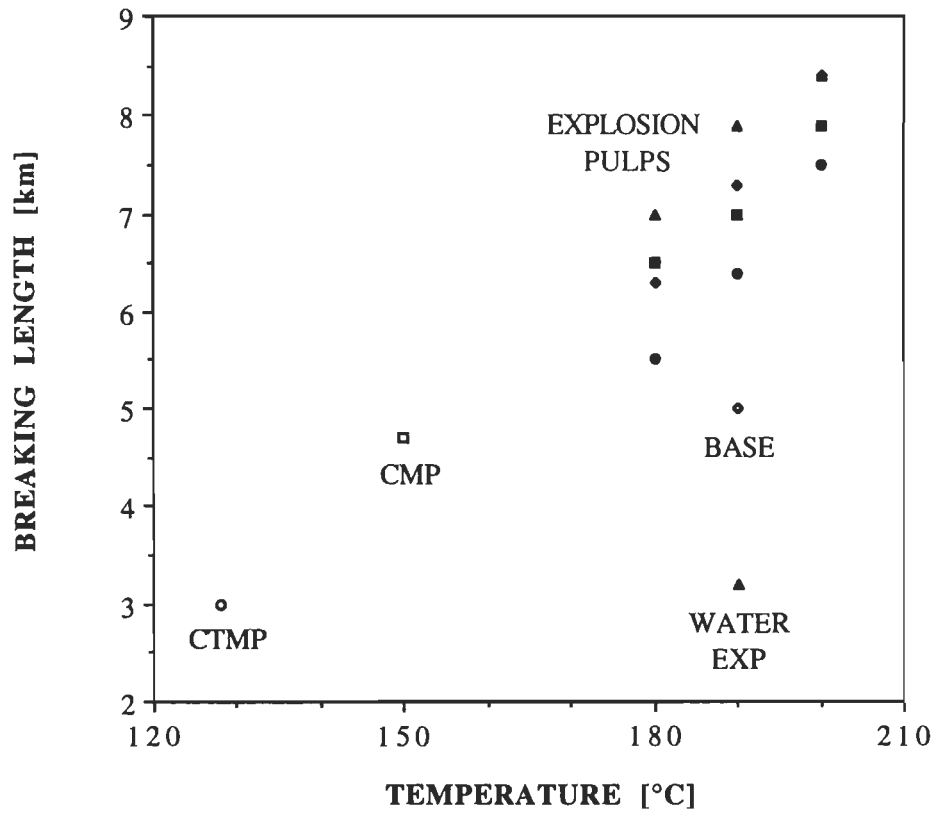


FIGURE 3.43 Breaking length as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

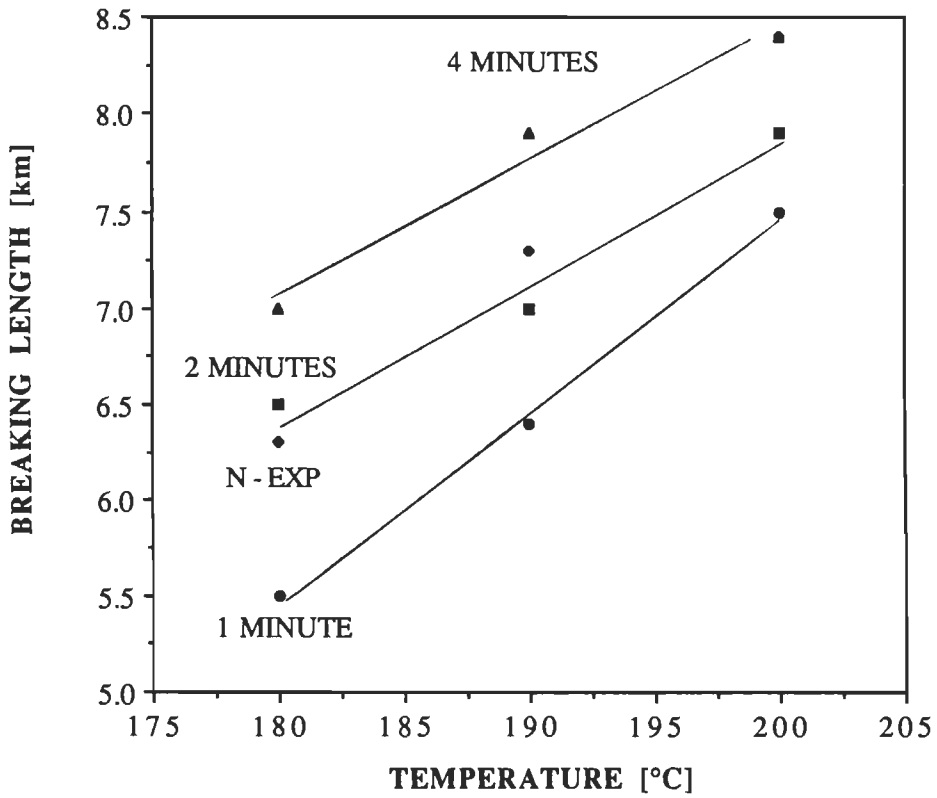


FIGURE 3.44 Breaking length as a function of temperature for explosion pulps in the third experimental series (at 100 ml CSF)

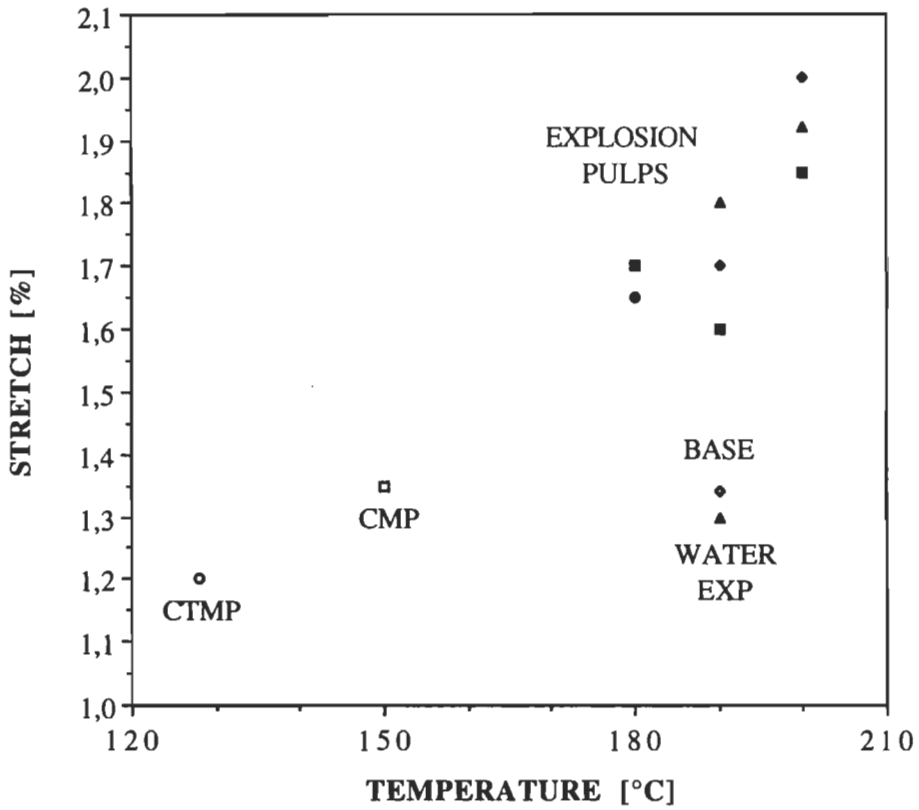


FIGURE 3.45 Stretch as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

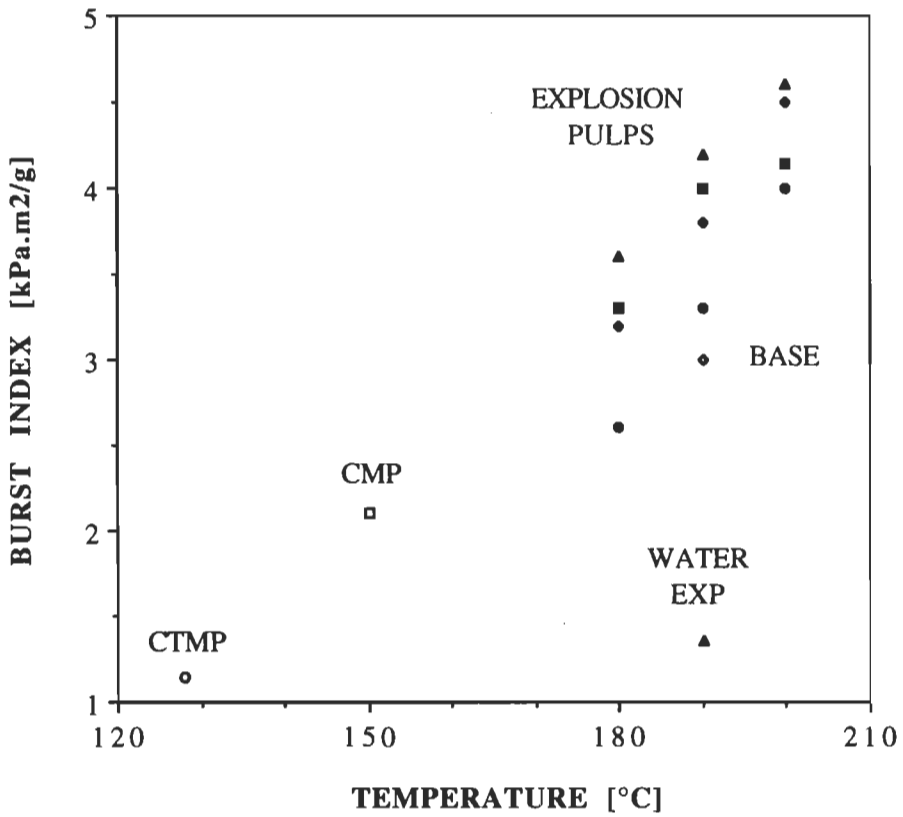


FIGURE 3.46 Burst index as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

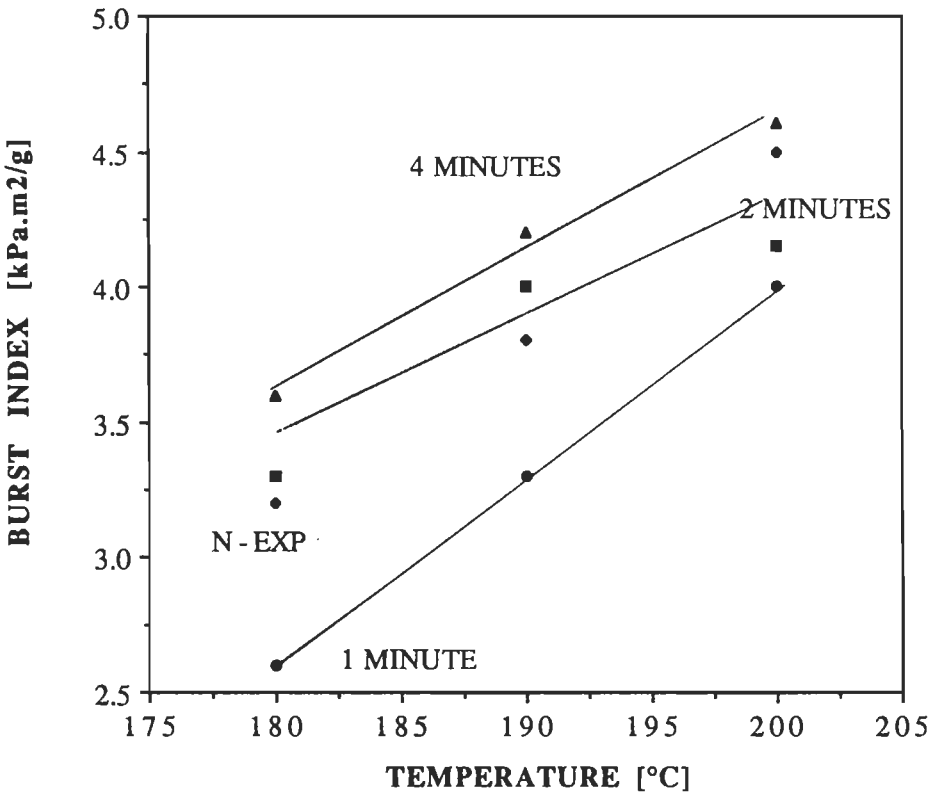


FIGURE 3.47 Burst index as a function of temperature for explosion pulps in the third experimental series (at 100 ml CSF)

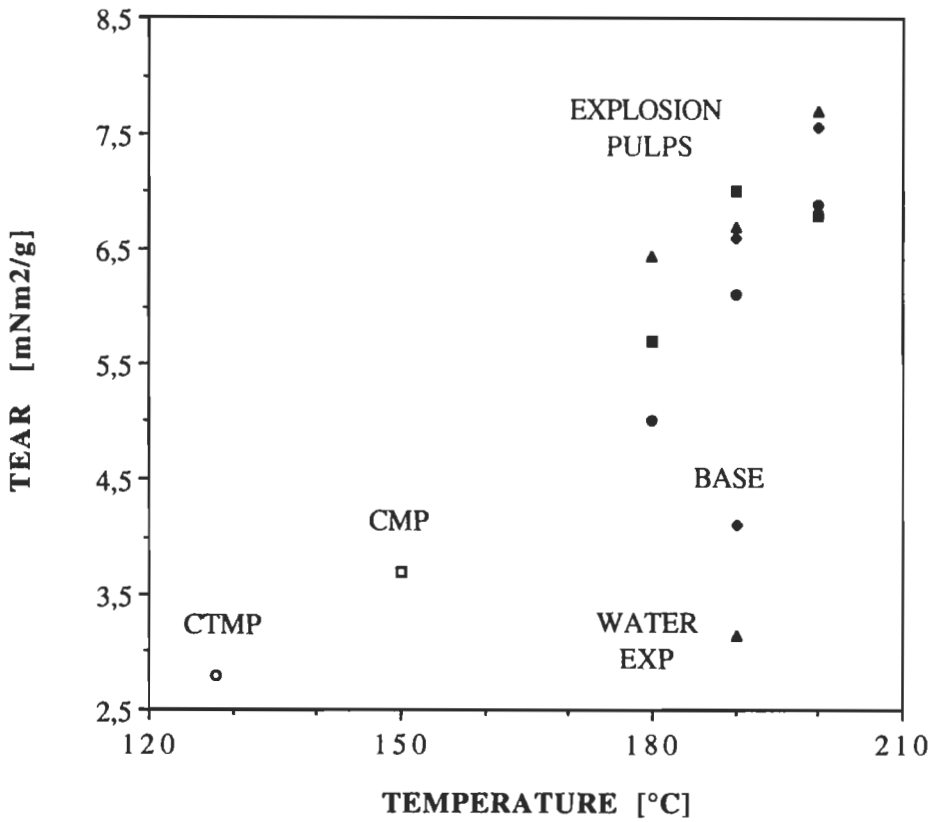


FIGURE 3.48 Tear index as a function of temperature for all the pulps in the third experimental series (at 100 ml CSF)

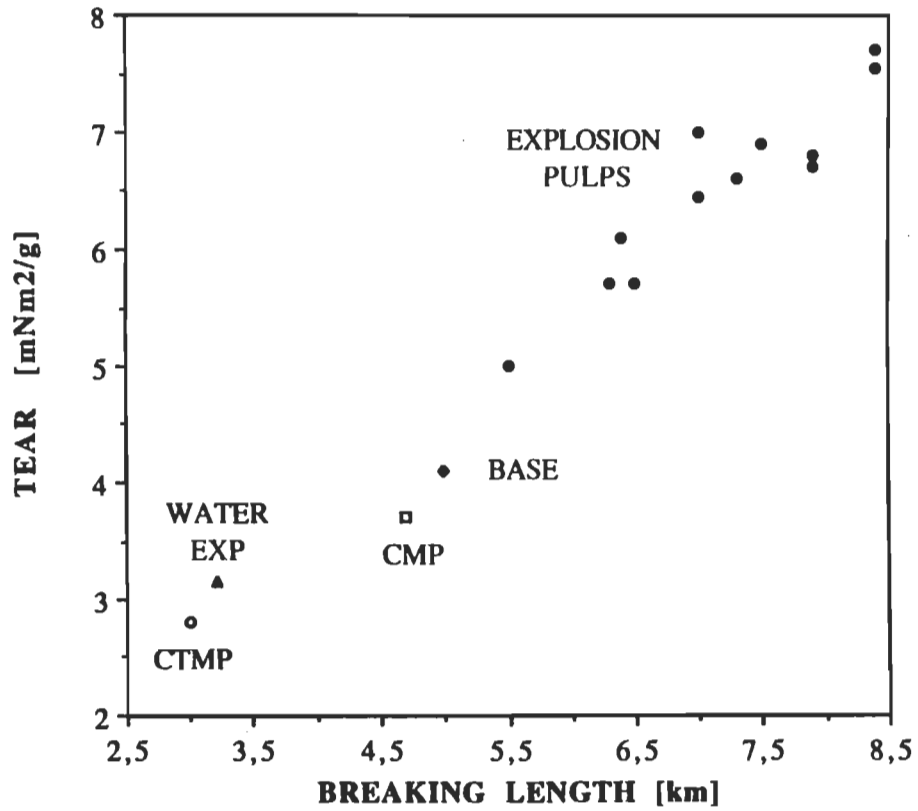


FIGURE 3.49 Mechanical resistance for all the pulps in the third experimental series (at 100 ml CSF)

This series, however, did result in some surprising results:

First of all, most of the mechanical parameters were lower than previous experiments suggested. These lower values are not caused by an experimental error. Every pulp was refined to four or five CSF levels and all the values at 100 ml CSF were interpolated rather than extrapolated. Also, it is worth mentioning that the statistical design for testing the reproducibility of this experiment was sufficiently good - a series of randomly prepared pulps at several cooking conditions showed only a 3 to 5% variation in properties with the exception of the tear index, where the variation was about 7% (we will describe this test more in detail with the mathematical treatment). The reason for lower pulp quality probably lies in the chip quality. The same causes that decreased all pulps' yield could be applied as well on the mechanical parameters.

Secondly, the curve shapes were also surprising. What was confirmed - it was lower properties for lower severity explosion pulps (180°C/1 minute). Quite surprisingly, even this pulp surpassed in all cases both CTMP and CMP, often with 50 to 100% quality improvement. What was not expected was the superior quality improvement at the highest severity pulping conditions (200°C/4 minutes, 200°C/4 minutes - nitrogen explosion). Lower yield, carboxylic content, refining energy. LSC, porosity and higher density can be explained quite logically - they just follow out as a result of all the changes underwent during the high severity treatment. What was expected as the result of the above mentioned changes, was much more profound fiber damage resulting in shorter fibers with lower mechanical properties. This did not happen and the probable explanation of this fact is that the cooking conditions were not severe enough so that the damaging effects of high severity did not overlap the positive ones. In this case - in order to lower the properties we would have to go to either or a combination of:

- much heavier chemical impregnation;
- press-impregnation (for the pre-cook chip destruction);
- increasing the cooking severity by using longer cooking time, higher cooking temperature and/or pressure.

Thirdly, the influence of pressure. The results at 190°C/2 minutes did not come as a surprise and correlated quite well with the second experimental series.

However, the improvement for the 180°C/1 minute was bigger than expected. This confirms the results from the first and second experimental series that if the cooking severity does not reach certain degree and does not develop fiber and paper properties, there is a room for further improvement that can be obtained by a pressure increase. Also, the pressure increase at 180°C was the highest one (over 15 atmospheres, compared to 13 atm for 190°C and 9.5 atm for 200°C) and it is quite logical that the property improvement was the most pronounced in this case. In several occasions, the nitrogen-exploded pulp at 180°C/1 minute showed similar properties as the following one in the line: 180°C/2 minutes, meaning that digester pressurization prior to the explosion can have almost the same effect as doubling the cooking time from 1 to 2 minutes. The most severe conditions, on the other hand, did not have either good or bad influence. With the exception of pulp yield, where the difference was about 1% (which is insignificant if we consider the experimental error), all other parameters were almost identical for the ordinary and nitrogen explosion. This was not expected at the beginning. As explained earlier in the theoretical considerations and in the experimental planning section, it was thought that this pulp should be really "overcooked" and the pressurization could cause certain damage to very soft fibers. The explanation why this did not happen would be the same as for the mechanical parameters i.e. the cooking conditions were not severe enough to cause damages sufficient to decrease fiber and paper quality.

When examining the optical properties, it can be seen that excellent brightness values for all pulps with the exception (again) for the water explosion pulp are obtained (Figure 3.50). Water explosion pulp (no chemical protection) comes out of the reactor very brown, the fibers are covered by lignin and the resulting brightness was (as in other series) around 45% MgO. Highest severity (200°C/4 minutes and 200°C/4 minutes - nitrogen explosion) was the only case where the brightness dropped below 60%. The highest value (close to 72%) was found at the CTMP pulping conditions. Brightness was little lower for the CMP and the explosion pulps followed closely behind. The highest explosion pulp brightness was found at the least severe conditions (180°C/1 minute): around 65% MgO. At 190°C, the highest value was found for the base pulp prepared with only one impregnation chemical. Anyhow, the addition of the second impregnation agent did not cause a significant decrease and all five pulps were within a 2% brightness span from 61 to 63% MgO.

Opacity was again highest in the water explosion pulp case (Figure 3.51). Very similar opacity (around 90%) was found for CTMP and CMP pulps. Explosion pulps, once again showed lower opacity. The reason for lower opacity is not only in pulp brightness: the explosion pulps (in the first and third experimental series) did have significantly higher pulp density and lower light-scattering coefficients. These factors also contributed to a slightly less opaque sheets.

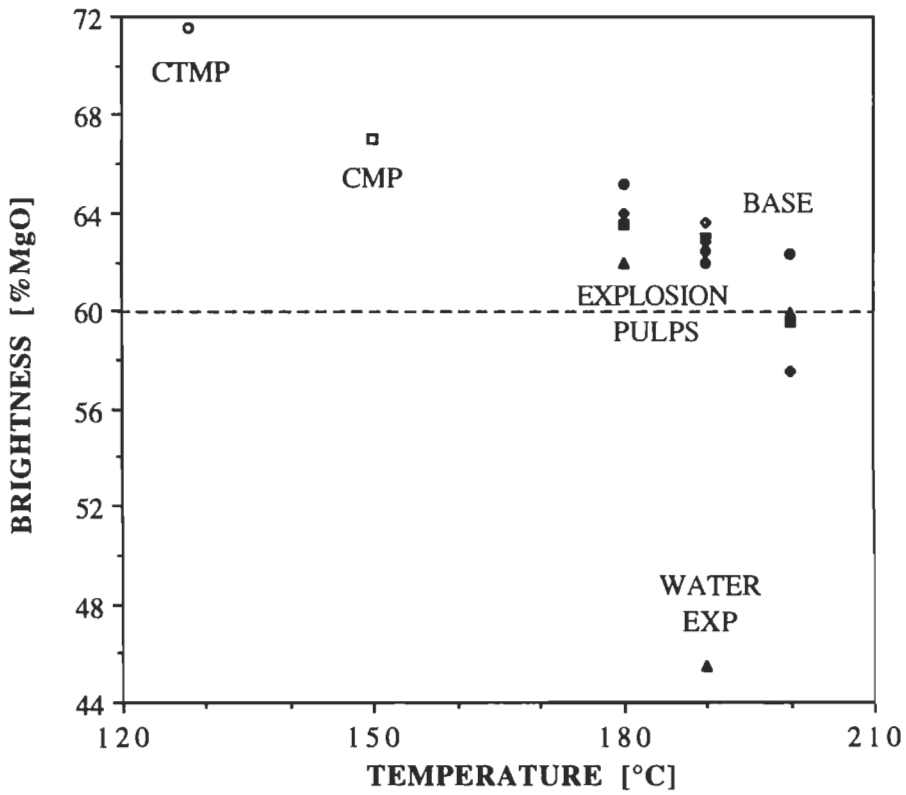


FIGURE 3.50 Brightness in 60 g/m^2 sheets as a function of temperature for all the pulps in the third experimental series

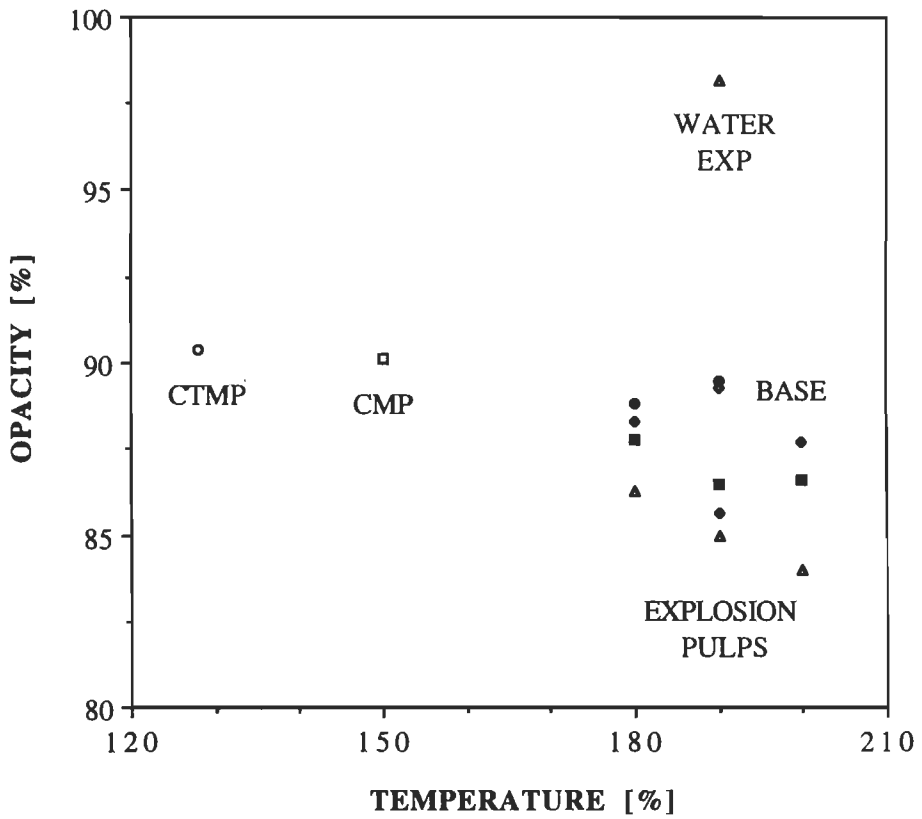


FIGURE 3.51 Opacity in 60 g/m^2 sheets as a function of temperature for all the pulps in the third experimental series

3.3.2 EXPLANATORY ANALYSES

All three experimental series showed that the high severity cooks can produce ultra-high yield pulps at very low refining energy with excellent papermaking properties. In this part, efforts will be focused on the physical, physicochemical and chemical changes that happen during the cook. By planning these analyses it is believed that the results would bring new insight into this topic and would contribute to a better understanding on what is going on at the high severity treatment.

3.3.2.1 LIGNIN

As we stated previously, lignin undergoes an additional softening. From the lignin loss point of view, there were no major changes, as revealed by the Klason lignin analysis (varying between 18 and 21% of acid insoluble lignin in all samples). Figure 3.52 shows that there was about 21% of lignin in original wood and this value did not change for the CTMP, CMP, water explosion pulp (no chemicals added) and for the base explosion (one impregnation chemical). If explosion pulps resulting from a two-chemical impregnation were examined, a certain drop in the lignin content could be observed. The only exception was at the mildest condition (180°C/1 minute) where the lignin content was almost unchanged. For other pulps, the percentage of lignin was usually found between 18 and 19%.

If the pulp yield and the lignin content are examined, it can be seen (Figure 3.52) that both variables change at similar rate. In our considerations, not much variation in the lignin content was expected. Indeed, in the high yield pulping (particularly in the ultra-high yield pulping), one of the objectives is to preserve as much wood material as possible and that is why pulping conditions and chemicals that are not very harmful to any of the wood components were chosen. Other research [39] also confirmed very small changes in the lignin content during high severity wood treatment (with several chemical impregnation systems).

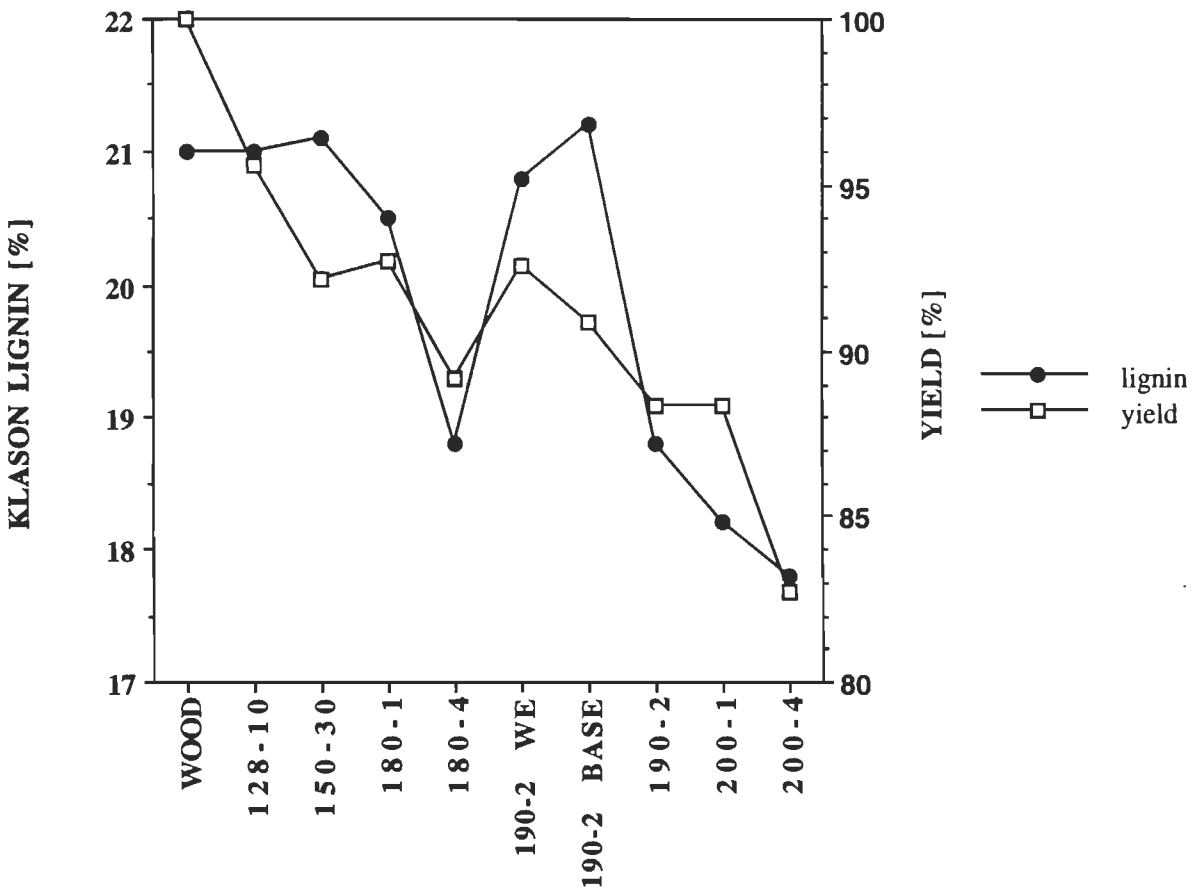


FIGURE 3.52: Klason lignin and pulp yield comparison for increasing pulping severity.

Various methods have already been used in order to investigate the influence of high severity cooking conditions on lignin changes. In our experimentation, the FTIR and mostly Raman spectroscopy have effectively been used.

RAMAN AND FTIR SPECTROSCOPY

A significant part of the Raman spectra for wood and explosion pulps prepared at 180°C/4 minutes and 200°C/4 minutes is plotted in Figures 3.53 to 3.55. The most valuable Raman information is obtained from the 1600 cm^{-1} and 1650 cm^{-1} peaks and from the peaks at 1500, 1600 and 1650 cm^{-1} from the FTIR spectra. Peaks at 1600 and 1500 cm^{-1} relate to different modes of lignin aromatic ring vibrations and the 1650 cm^{-1} peak relates to C=O and C=C bonds in lignin. As the cooking temperature rises, we found less lignin in pulp samples. This is true for both comparisons: conventional processes (CTMP and CMP) and the explosion pulps, as well as for the explosion pulps prepared at different degree of severity. FTIR revealed narrowing tendency for the half-peak width at 1500 cm^{-1} with the temperature increase (which was not visible in the Raman spectra). This fact (Figure 3.56) shows that a quiet significant lignin restructuring leading to a certain degree of coalescence is taking place, particularly at high severity cooking conditions.

Raman and FTIR spectroscopy analyses showed distinct differences in lignin quality. Compared to the CTMP and CMP, there is a lesser lignin quantity in the explosion pulps lignin samples and the remaining lignin is more structurally organized. These spectra even suggest a unique phase, which was probably caused by the coalescence effect [68, 121].

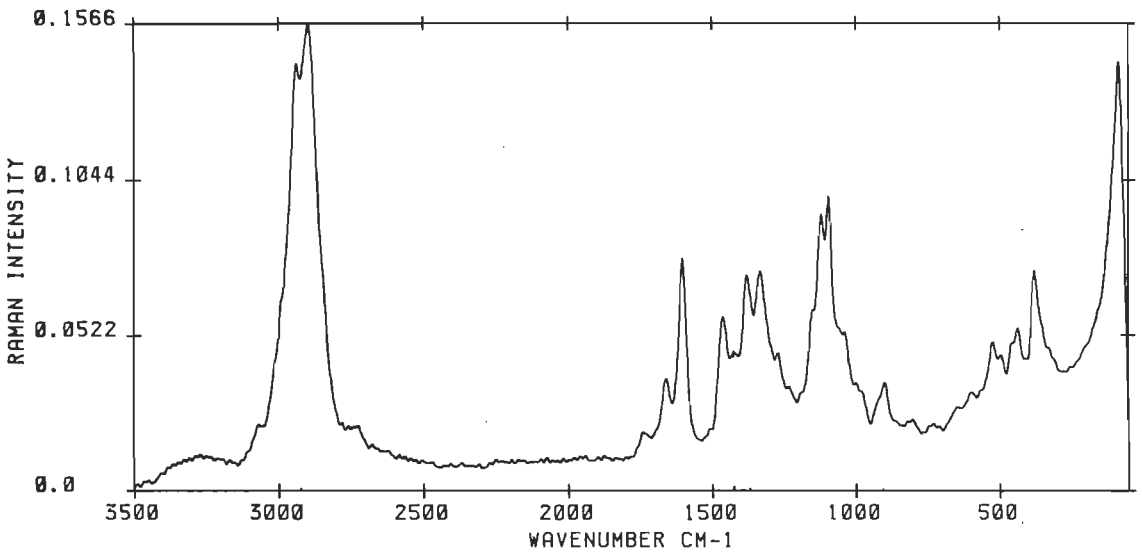


FIGURE 3.53 Raman spectrum of the aspen wood

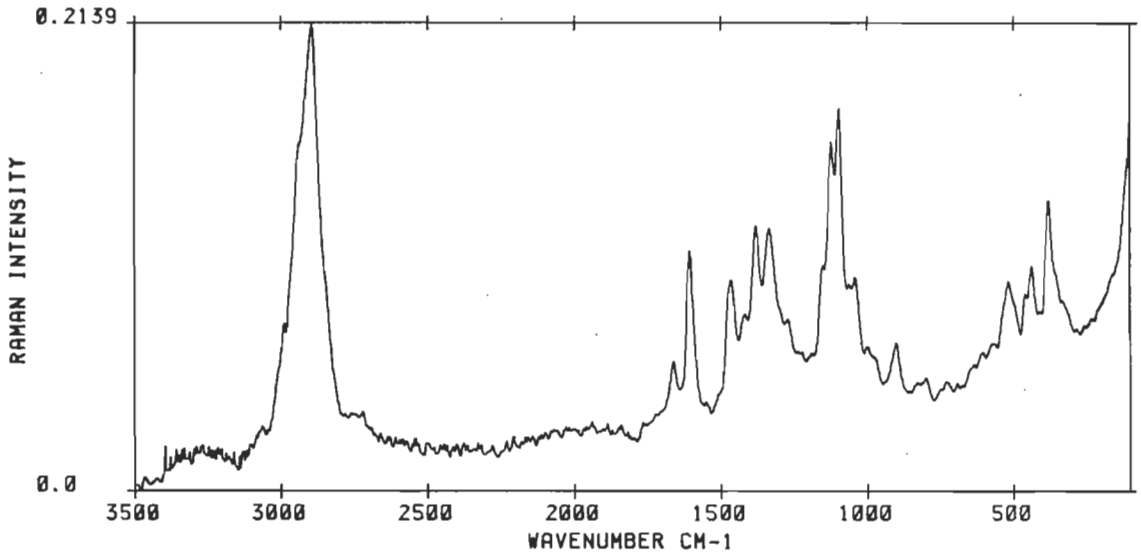


FIGURE 3.54 Raman spectrum of the explosion pulp prepared at 180°C/4 minutes conditions

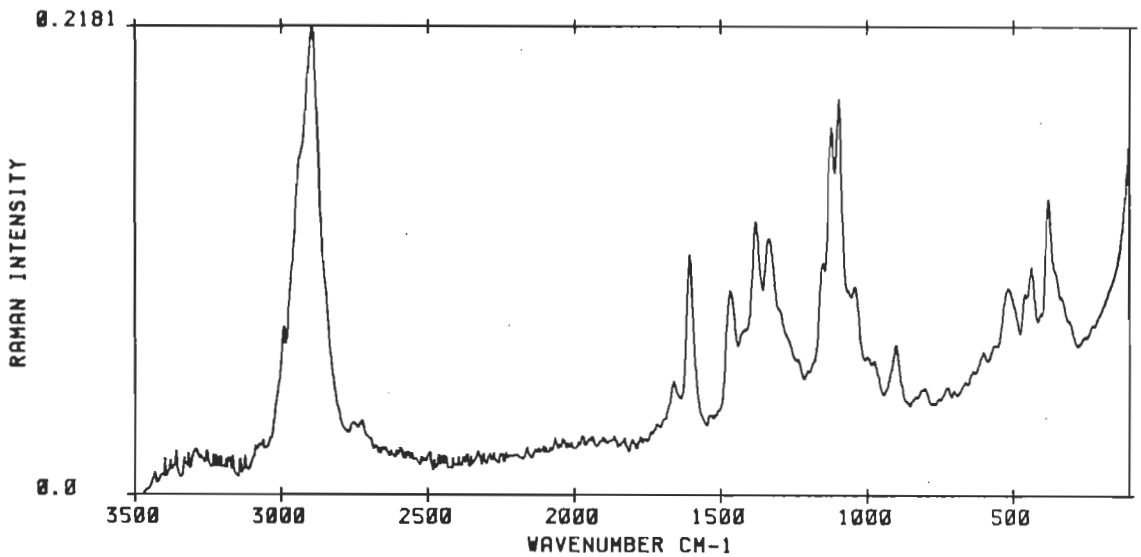


FIGURE 3.55 Raman spectrum of the explosion pulp prepared at 200°C/4 minutes conditions

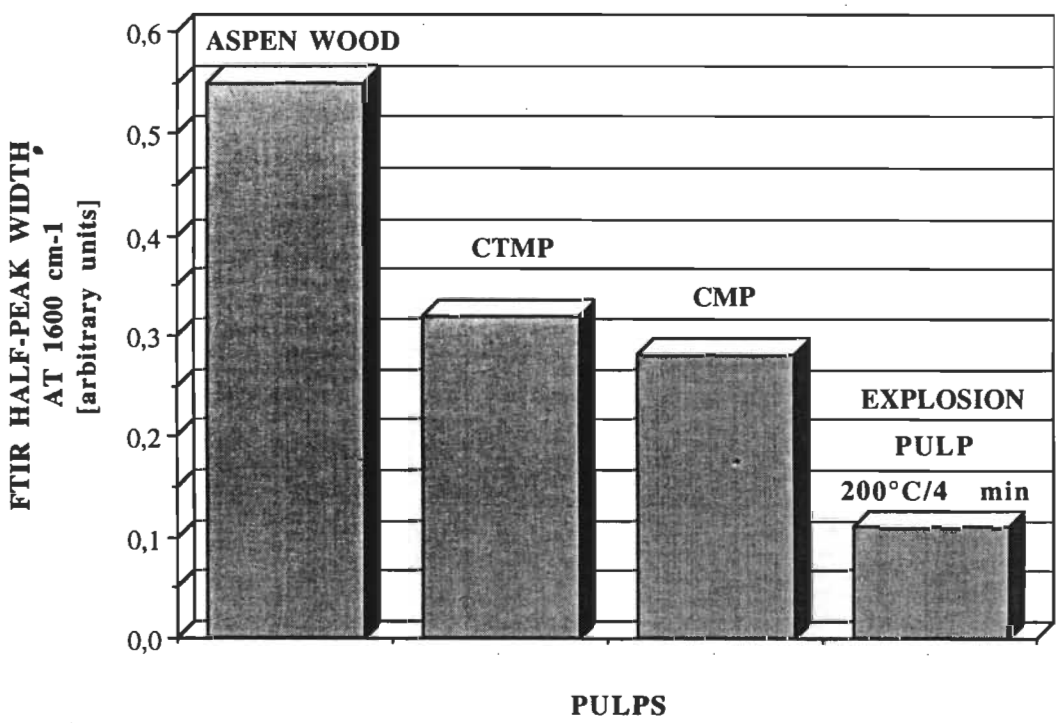


FIGURE 3.56 Comparison of the half peak width at 1600 cm^{-1} in the FTIR spectra of pulps prepared at different pulping methods

Lignin sulfonation of high severity treated wood was higher in comparison to the CTMP and CMP. This fact was observed in the first and in the third experimental series and we believe that lesser hydrophobic character of lignin also helped to improve the mechanical properties (this aspect will be further investigated in the mathematical treatment). The importance of lignin sulfonation is not only in the quantity, but also in the distribution. This topic (lignin sulfonation in bulk and on fiber surface) will be discussed later in this chapter. However, there was one slight difference. In another reference [60], it was mentioned that the lignin sulfonation curve is a bell-shaped one. The explanation of this fact was that at the earlier stages of the cooking process, the lignin sulfonation reaction is quite fast and according to Arhenius' law, the kinetic constant increases twofold to threefold with a 10°C increase of the reaction temperature. When the cook begins, the lignin sulfonation is the dominant reaction. At the later stage, lignin changes and the hydrolytic reactions do cause a decrease in the sulfonic content. The sulfonic groups can be hydrolyzed from the lignin and lignin may also produce (even if in smaller quantities) soluble products of homolytic cleavage [92, 120] that can be sulfonized, too. In our case, the lignin sulfonation curves were steadily rising with the increase of cooking temperature and cooking time. Only at the highest severity conditions (200°C/4 minutes and 200°C/4 minutes with nitrogen explosion), the sulfonic content seemed to level off or slightly dropped (Table 3.8, Figure 3.34). Otherwise, we did not see any dramatic drop in lignin sulfonation. This characteristic may vary with different wood species, different impregnation chemicals or methods and with other factors. In all our experimental series, in spite of relatively high possible experimental error in the sulfonic content measurement, the results were reproducible and comparable within each series as well as between individual series.

3.3.2.2 CELLULOSE AND HEMICELLULOSES

As we stated before, the hemicellulose degradation (hydrolysis) is the predominant reaction in the vapour-phase cooking at high temperatures. This is extremely well documented by the yield loss with increasing cooking severity. With almost constant cellulose and lignin content, the yield loss can be attributed to the hemicellulose loss. Another proof of this theory is the carboxylic

content decrease. With the increasing pulping severity, an increase in the pulp sulfonation, even if the total ionic content values were dropping, was found. This means that the carboxylic content was significantly decreased at higher cooking times and temperatures. The carboxylic content is mostly created by the carboxylic groups in hemicelluloses, since there are no such groups in the cellulose chain and the carboxylation of lignin is very low (usually less than 1 or 2 COOH groups per 100 C_9 lignin units), then it can be concluded that the loss in the carboxylates can be indeed interpreted as a result of hemicellulose hydrolysis.

The cellulose itself undergoes some changes, too. In the first series, an increase in the ordered portion of cellulose I and a decrease in the disordered portion of cellulose II-type (hemicelluloses in our case) was found. Results of the FTIR analysis were very similar for the third series. Furthermore, a Raman spectroscopy and the X-ray diffractometry were carried out to confirm the results from the FTIR. Another series of analyses were meant to bring more information about the surface characteristics. Higher light-scattering coefficient at high severity treatment showed to better bonding and an attempt to prove this suggestion by the surface quality investigation by ESCA and WRV was undertaken.

3.3.2.2.1 RAMAN SPECTROSCOPY

Raman spectroscopy unfortunately did not provide much information. A distinct decrease in the hemicelluloses' content (acetyl groups peak decrease at 2937 cm^{-1}) was observed but if these spectra were compared with the FTIR, no worthwhile information could be obtained. Despite excellent equipment, the background noises and weak signals did not allow a more profound study.

3.3.2.2.2 X-RAY DIFFRACTOMETRY

The results from the FTIR and Raman spectroscopy suggested an increase in cellulose content with rising cooking severity. By using Valov's et al. mathematical model [131], a higher portion of ordered cellulose I and

decreasing amounts of cellulose II-type (hemicelluloses) with rising temperature were found. However, this analysis did not result in any specific number. The values obtained led only to a relative comparison between several samples. From this point of view, it was decided to use another method to confirm findings from the infrared spectra and their interpretation. Based on the literature review of [41, 52, 58, 65, 67, 71, 93, 120, 123 to 129, 137, 139, 143, 144, 148, 162], the X-ray diffractometry was selected as one of the analysis approaches. This method results in information about cellulose crystallinity and crystal size.

For our analyses, an X-ray diffractometry was performed on most of the pulp samples. An example of a X-ray diffractogram is on the Figure 3.57. It was clear from all the diffractograms that the difference between the crystalline peak and the amorphous part was getting bigger with an increasing temperature. Also, the crystalline peak width (at the half-height) was narrowing which means that the degree of crystallinity order was increasing with cooking severity.

Figure 3.58 shows a comparison of the crystallinity index for six samples (aspen wood, CTMP, CMP, 180°C/1 minute, base explosion pulp and 200°C/4 minutes). It can be seen that the crystallinity increase is evident with rising temperature. The overall increase between wood and 200°C/4 minutes is 10% which represents a very significant improvement. On the other hand, it should be considered that the original wood sample and all the other pulps are fairly different, because of the differences in pulp yield. Figure 3.59 reveals that the crystallinity increase is very proportional to the yield loss. This could be explained in the fact that the yield decrease is mostly due to hemicellulose hydrolysis and that from this point of view the crystallinity increase is natural even without anything happening to the cellulose per se. When the crystallinity values were recalculated according to the pulp yield (Figure 3.60), a certain increase in the crystallinity in all cases emerges, with the exception of the most severe pulping conditions (200°C/4 minutes). It is important to say that the crystallinity indexes must not be taken as absolute values. Since it is only a very small part that actually participates at the diffraction (in the test pellet, the crystals are randomly oriented), the crystallinity indexes serve more like units of comparison between individual samples, rather than as absolute values in comparison with other analyses.

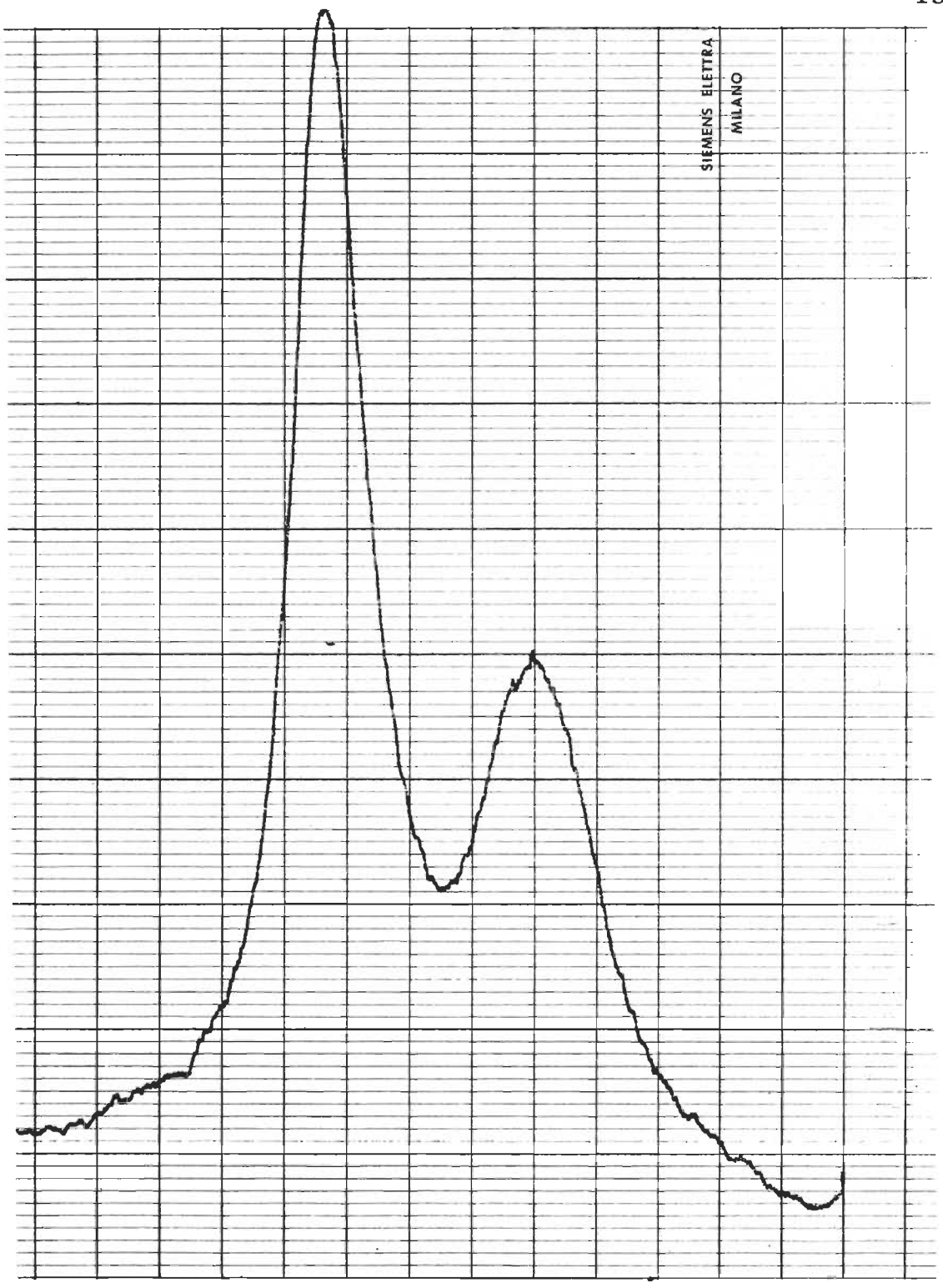


FIGURE 3.57 X-ray diffractogram of the explosion pulp prepared at 190°C/2 minutes

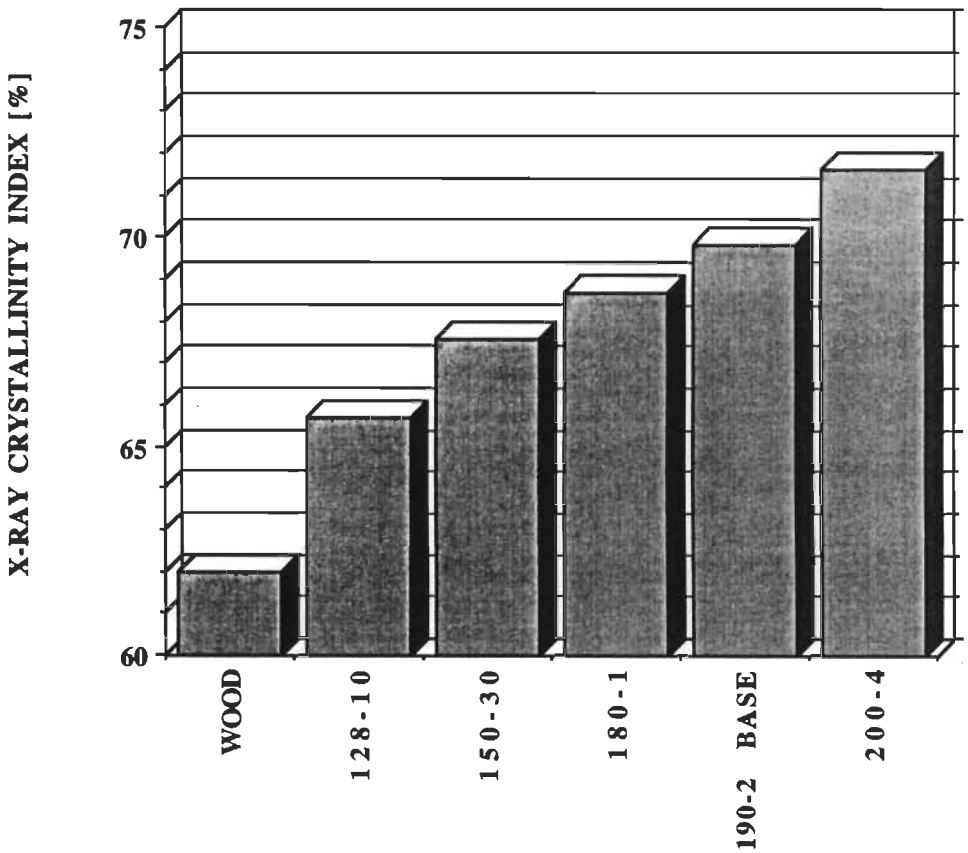


FIGURE 3.58 Comparison of the X-ray crystallinity indexes for six pulps prepared at increasing treatment severity

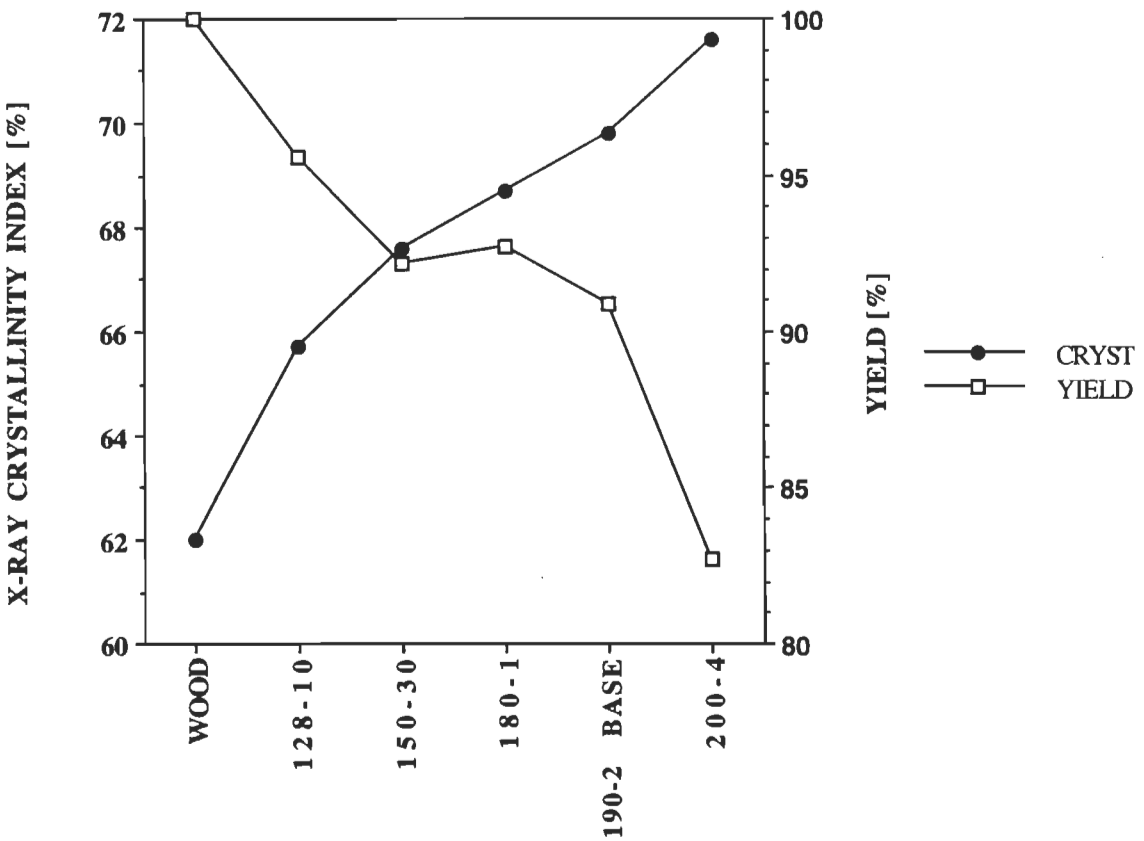


FIGURE 3.59 Comparison of the X-ray crystallinity indexes and pulp yield for six pulps prepared at increasing treatment severity

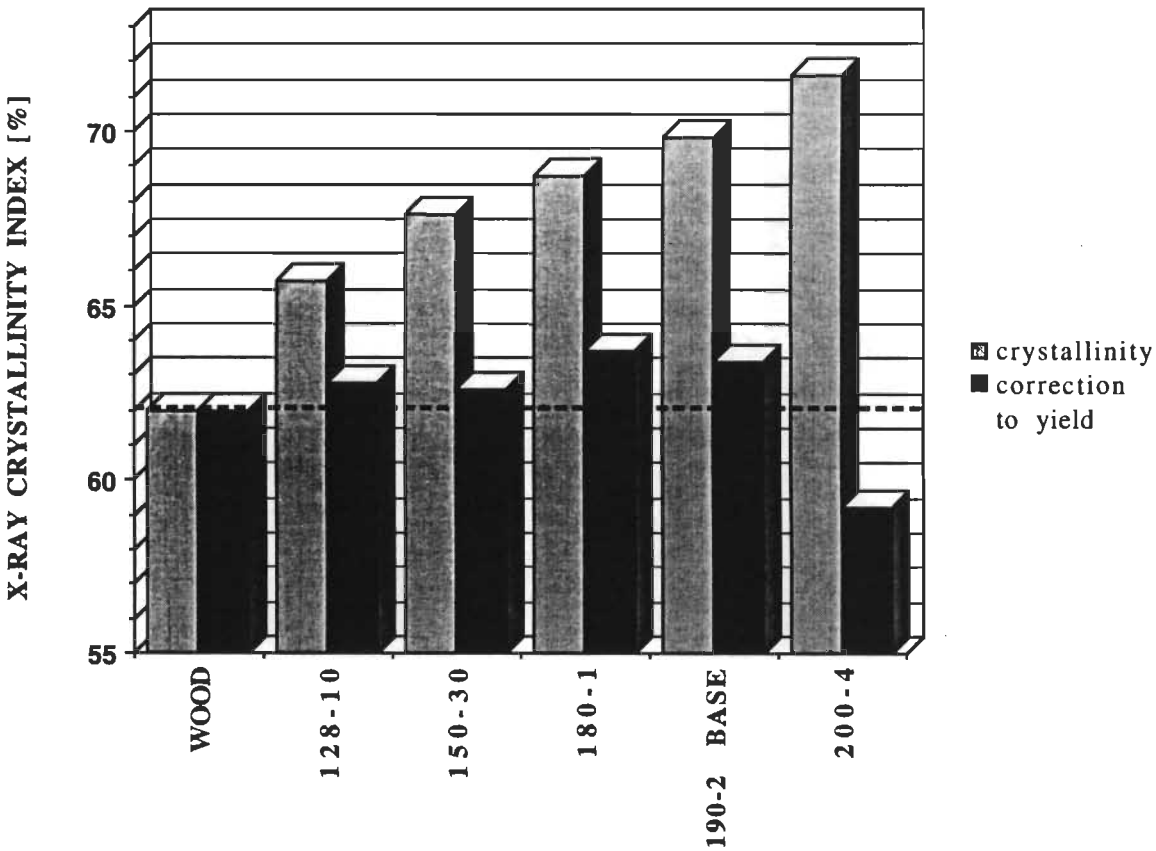


FIGURE 3.60 Comparison of the X-ray crystallinity indexes and their recalculated values with pulp yield consideration for six pulps prepared at increasing treatment severity

However, the crystal size is an absolute value. From Figure 3.61 one can see that the crystal size was rising with increased cooking severity. Considering that the calculated thickness of one crystalline layer of cellulose I is about 4 Å, these values were increasing in order wood (11.5 layers) < CTMP (12.5 layers) < CMP (12.75 layers) < explosion pulps (14 to 15 layers).

In our comparison of 6 pulps (Figures 3.58 to 3.60) we can see that the crystallinity increase was not much dependent on the cooking chemicals. In this case, one sample with no chemicals, three pulps with one impregnation chemical and two pulps with two impregnation chemicals were used. The crystallinity sequence was however rising with increasing pulping severity. Similar effect can be seen in the crystal thickness case (Figure 3.61). The leaps are clearly a function of pulping conditions. In the central point, for example -water explosion pulp (no chemicals), base explosion pulp (Na_2SO_3 only) and explosion pulp (Na_2SO_3 + $NaHCO_3$) had the very same number of crystalline levels participating at the diffraction. The only further increase was found at the highest severity conditions (200°C/4 minutes), where the crystal thickness rose from 56 to 60 Å as there was one more layer in the cellulose crystal.

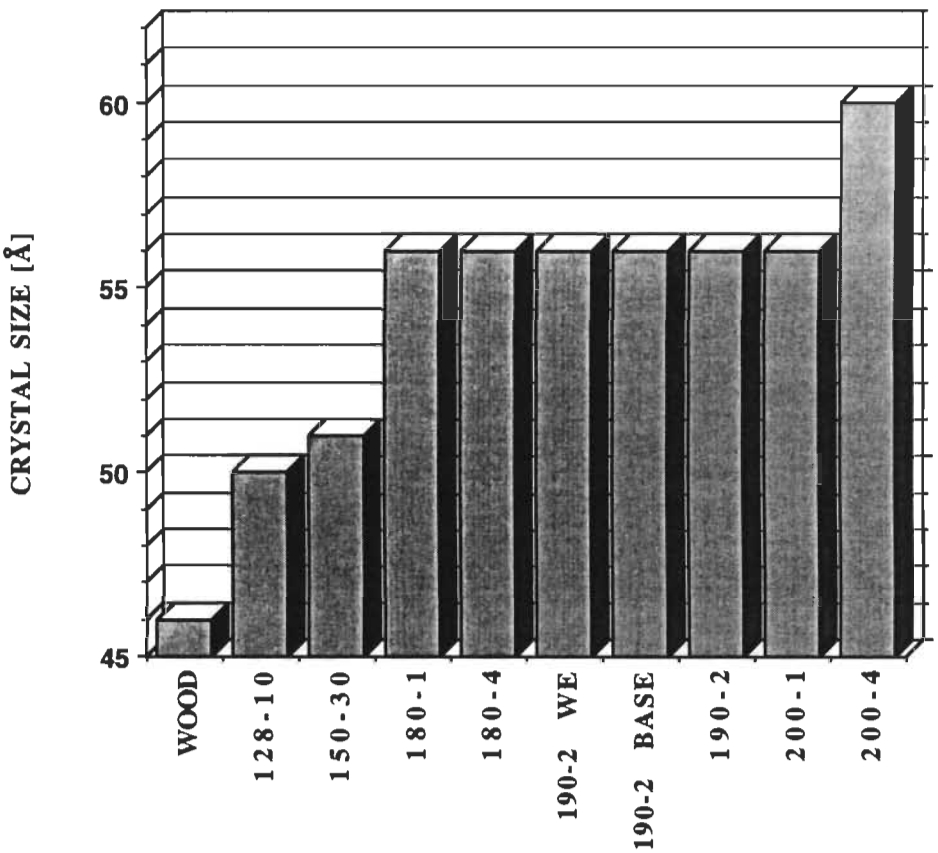


FIGURE 3.61 X-ray crystal size measurement for aspen wood, CTMP, CMP and explosion pulps prepared at different conditions

3.3.2.3 SURFACE ANALYSES

In previous paragraphs, we have shown and explained some important changes that occur during or as a result of the high severity cooking. We have found chemical differences in the lignin structure, and more cellulose I and higher degree of cellulose order in explosion pulps. Some of these changes, such as the sulfonic content, are caused by both: the chemistry of impregnation and high severity. Other changes, such as cellulose crystallinity are caused mainly by the high temperature and high pressure during the cooking process. In general, high severity pulp fibers needed much lesser amounts of refining energy. As a result, pulp fibers were longer, more flexible and the lignin was less hydrophobic in nature compared to conventional ultra-high yield pulps.

From the papermaker's point of view, there is one more important aspect to evaluate. All previous analyses dealt with physical and chemical parameters in bulk mass. The question is: What are the surface characteristics of fibers treated at high severity? Are there some differences in comparison to the RMP, CTMP and CMP and if so, how the paper quality is affected.

In this approach, we can basically use two types of methods: first type are the methods that would indirectly demonstrate fiber surface quality and the second type are direct methods.
An example of an indirect method is the light-scattering coefficient. In the first and third experimental series, much lower values of LSC in the case of high severity pulps (Figures 3.8, 3.39 and 3.40) was found. Even if Kosik showed [121] almost twice as large specific surface area for aspen explosion pulps, the LSC coefficients presumes to a lower area of unbound surfaces (meaning higher degree of fiber bonding). Lower values of CSF can be explained by two factors. Primarily, higher flexibility (higher density with longer fibers) of softer explosion pulps allows more fiber contact. Secondly, higher surface quality does lead to better interfiber bonding. Higher surface quality can be explained by both higher surface sulfonation (which decreases the hydrophobic lignin character) and mainly by more cellulose exposure on the surface of fibers. These are very important reasons how lower LSC values in the case of higher severity treatment could be interpreted. To prove these assumptions, it was decided to use two more methods of surface evaluation.

3.3.2.3.1 WATER RETENTION VALUE

Even if water retention value evaluation is not a specific fiber surface test method, it can lead to significant conclusions. WRV values reflect the surface accessibility of cellulose and its ability to swell, which is another important fiber parameter. Sakai et al. [166] directly associated swelling to external fibrillation (which can be measured as specific surface) and Garceau [167] successfully used WRV measurement as an indirect measurement of specific surface. Other authors [67, 71, 137] also used WRV in pulp evaluation. In our trials, we used Lebel's et al. description [168] of the WRV technique.

From the practical point of view, water retention value is a percentile amount of water held in the pulp sample after a 12-minute long centrifuging at 2500 rpm. If we look at the Figure 3.62, we can see the WRV values for most of reference and high severity pulps. The capacity to absorb water rises in order CTMP < CMP < water explosion < base explosion < 180°C/1 minute < 190°C/2 minutes < 200°C/4 minutes. This classification is quite logical if the WRV value is considered to reflect the degree of chemical changes. In the CTMP case, the chemical modification is less pronounced as compared to CMP pulp and when the explosion pulps are examined, the order is also self-explanatory: water explosion pulp with no chemicals was the darkest pulp with presumably lot of lignin on the fiber surface, what barriers the entry channels against higher water intake. One impregnation chemical (base explosion pulp) helped the swelling and exposed more cellulose on the fiber surface. With the two-chemical impregnation, the highest values of WRV are obtained. All values rose with increasing severity and the big difference between two-chemical impregnation and any other pulp can be attributed to better fibrillation, higher cellulose exposure on the fiber surface as well as to higher sulfonation of these fibers (which reduces the hydrophobe character of lignin).

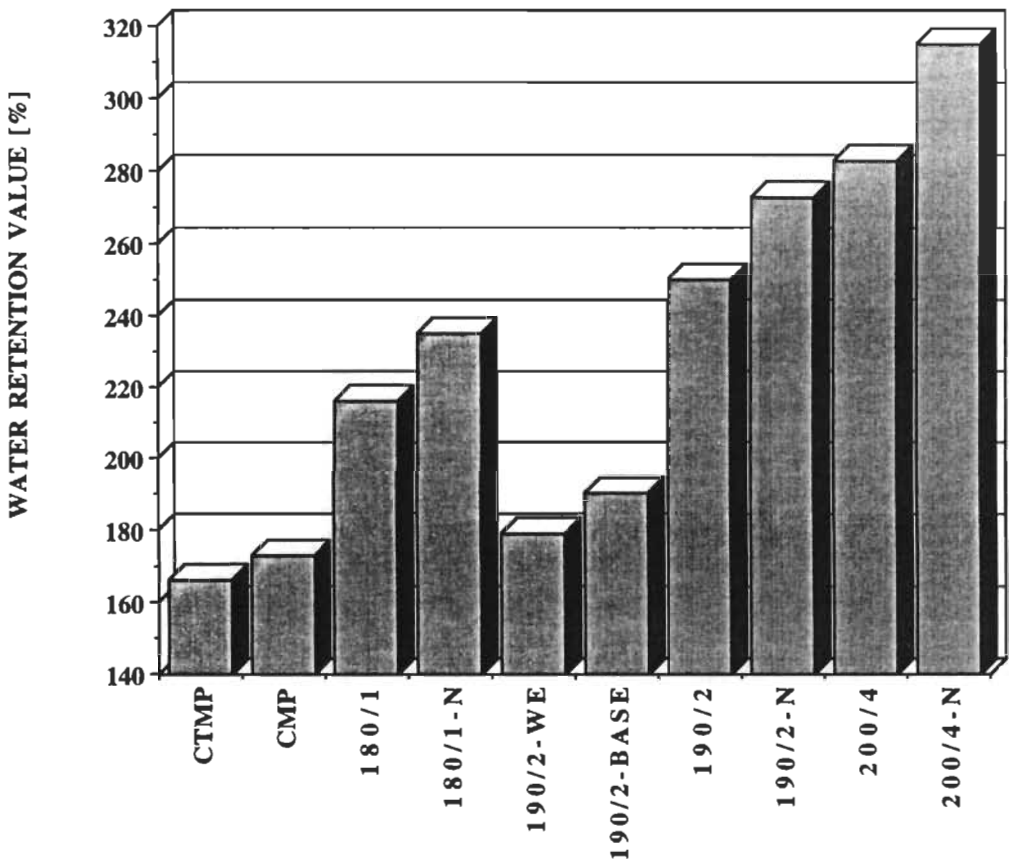


FIGURE 3.62 Water retention values of CTMP, CMP and explosion pulps prepared at different conditions

Other very important conclusion can be drawn from the regular explosion and nitrogen explosion water retention values. In all three cases, the WRV improvement caused by a pressure increase to 25 atmospheres was around 15%. This confirms that the explosion from higher pressures does not only help to separate chips into fibers or fiber bundles but also helps in internal fibrillation which is a very important parameter for paper strength development.

If the best high severity pulps (200°C/4 minutes and 200°C/4 minutes - nitrogen explosion) are compared with CMP and CTMP, a dramatic improvement (almost 100%) in the water retention value results. This indicates that a better fibrillation takes place with higher surface quality in the case of exploded fibers i.e. more surface cellulose and higher surface sulfonation.

3.3.2.3.2 ESCA

In the biomass and pulp/paper research, ESCA studies were used by several authors [39, 58, 65, 67 to 69, 71, 136,169 to 180]. For our analyses, we used the ESCALAB MKII equipment at the Université Laval. During our experiment, we recorded the C_{1s}, O_{1s} and S_{2p} spectra for several pulp samples. Since our samples were electric insulators, a charge built up on the sample surface due to X-ray bombardment and acted as an additional retarding potential, which reduced the kinetic energy of photoelectrons. To get true binding energies, we corrected our results with a suggested reference point [169, 170] - O_{1s} peak of cellulose, whose binding energy is 553.2 eV. All our samples were very close to this value and the peak shifts were usually less than 2 eV. A spectrum recorded for the 190°C/2 minutes explosion pulp is on Figure 3.63.

The binding energy of C_{1s} and its peak deconvolution have been well documented. There is a general agreement on the assignment of components C1, C2, C3 and C4 of C1s peak for wood derivated materials [169, 170, 173 to 176]. C1 corresponds to carbon atoms linked only to hydrogen or carbon atoms (C-H or C-C), C2 has a single bond link to one oxygen atom (C-O) and C3 carbon has a single bond link to two oxygen atoms (O-C-O) or one carbonyl bond (C=O). C4 represents carbon atoms linked to one carbonyl and one non-carbonyl oxygen (O-C=O). Due to low concentration of carboxylic groups, we were not able to discern C4 atoms on our sample surfaces.

Figure 3.64 shows the C1s peak for the explosion pulp prepared at 190°C/2 minutes along with the deconvolution into C1, C2 and C3 peaks. This type of information is important for cellulosic/non-cellulosic material assignment for the fiber surfaces. It is believed that C1 mainly comes from lignin and extractives, because the carbohydrates only contribute to C2 and C3 peak [177, 178]. Theoretically, there are 83% C2, 17% C3 and no C1 in pure cellulose (which corresponds to five C-O and one O-C-O atoms in a C6 cellulose unit). Hemicelluloses have similar carbon bond structure as cellulose, that is, all the carbons in hemicelluloses are linked to at least one oxygen. According to Freudenberg's spruce lignin empirical model [169], lignin has higher C1 components. Its C1, C2 and C3 contents are 49.2, 48.8 and 2%. As for the extractives, they should have the highest C1 percentage, since they are mainly

hydrocarbons. However, we expected to have insignificant extractive content: we suppose that almost all these chemicals got extracted during impregnation, cook, washing and refining process stages, similarly as shown previously [32].

Figure 3.65 shows the C2/C1 ratio for wood and three explosion pulps prepared at 190°C/2 minutes. Since the C3 portion in each of these pulps is very low, the C2/C1 ratio is good enough to compare the saccharidic and lignin presence on the surface of untreated and treated fibers.

For wood, the ratio is only slightly above 1.0 which indicates to higher lignin percentage on the fiber surface. If we look at the water explosion pulp, we can see that the C2/C1 ratio is even lower. This confirms the theory that if we do not protect chips chemically, high severity pulping conditions, leading to higher permanent lignin softening will also lead to fiber separation mostly in the middle lamella. Visually, water exploded chips were much darker (about 20 brightness points compared to any other pulp) and we presume that this dark colour is caused by lignin and its condensation products. Higher percentage of lignin on fiber surface (in this case, even non-sulfonated lignin) prevents the creation of hydrogen bonding sites and thus largely reduces paper strength. Considering this lignin encrust on water exploded fibers, it is not surprising that the mechanical parameters of this paper were lower than in any other explosion pulp. Some property similarity with some other pulps (CTMP, CMP) can be explained by higher fiber length, higher fiber flexibility (due to higher degree of permanent lignin softening) and similar paper density.

If we look at the water explosion, base explosion pulp and the 190°C/2 minutes explosion pulp, we can see that the C2 portion has a significant increase with each chemical added. Na_2SO_3 improved the C2 content by approximately 30% and in the case of $Na_2SO_3/NaHCO_3$ impregnation, the C2 portion was almost 70% higher than the C1 component. From our previous considerations, it follows that higher C2 content proves higher surface exposure of the cellulose and hemicelluloses.

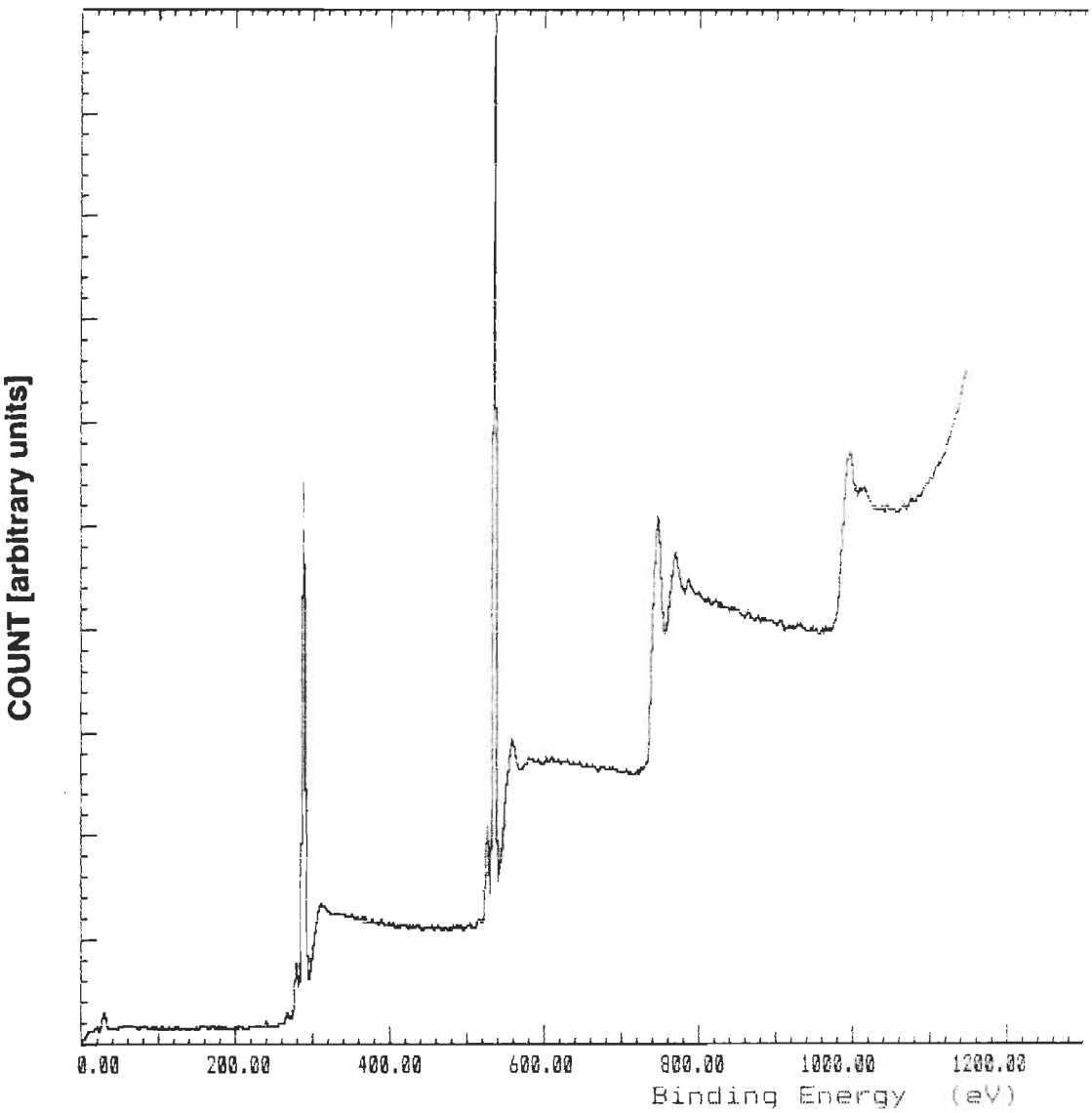


FIGURE 3.63 Survey ESCA spectrum for the explosion pulp prepared at 190°C/2 minutes

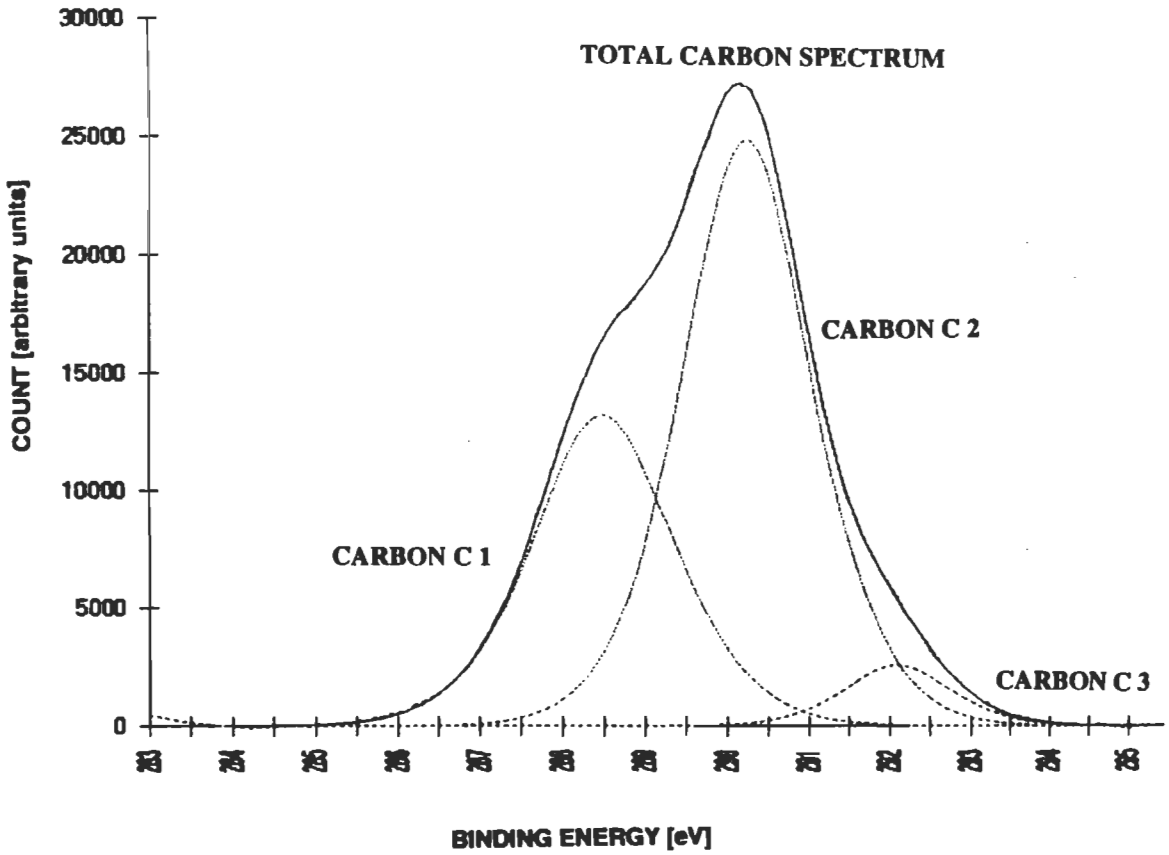


FIGURE 3.64 Carbon C_{1s} spectrum with C1, C2 and C3 peak deconvolution for the 190°C/2 minutes explosion pulp

Another confirmation of this theory is in the oxygen peak evaluation. An example of an O_{1s} peak (190°C/2 minutes) is in Figure 3.66. Figure 3.67 shows the oxygen/carbon ratio for aspen wood, CMP, and the three explosion pulps prepared at 190°C/2 minutes. The clear tendency in the O/C ratio is the very same as in the C2/C1 analysis. We have a reference value for aspen wood, in the case of water explosion pulp the O/C value is lower due to higher lignin (less oxygen) surface exposure and for other pulps, the O/C ratio is rising in sequence CMP < base explosion < steam explosion. From this picture, it is obvious that the explosion pulps have more carbohydrate and less lignin on the fiber surface compared to the CMP or wood. A rise in exposure for carbohydrates means more exposure for hydrophilic groups on the fiber surface, which facilitates the formation of hydrogen bonding between fibers during paper making. This is one of the partial explanations why explosion pulps show greater strength compared to conventional CTMP and CMP.

Peak synthesis technique revealed that there was only one peak present in the S_{2p} spectra. In our case, the binding energies indicate the sulfonate state. Therefore, it may be concluded that the sulfur in our samples is completely in the form of sulfonate. Consequently, the S/C ratio will reflect the amount of the sulfonate group on the fiber surface. An example of a sulfur peak is on Figure 3.68. Figure 3.69 shows that explosion pulps higher S/C ratios than the CMP. In this case, we have no reference point, since neither aspen wood, nor water explosion pulp contain detectable (or comparable) amount of sulfur. For explosion pulps we see that the S/C ratio has increased with the addition of a second impregnation chemical.

As the formation of the sulfonate group in lignin improves its hydrophilicity, more sulfonate may help fiber bonding and consequently, lead to a greater paper strength. In addition, an introduction of sulfonate groups into lignin reduces its glass transition temperature and makes it softer, which leads to lower refining energy and an increase in long fiber fraction, fiber specific surface and conformability [159]. Therefore, it might be suggested that lower refining energy and more long fibers of steam explosion pulps may result from their greater sulfonation.

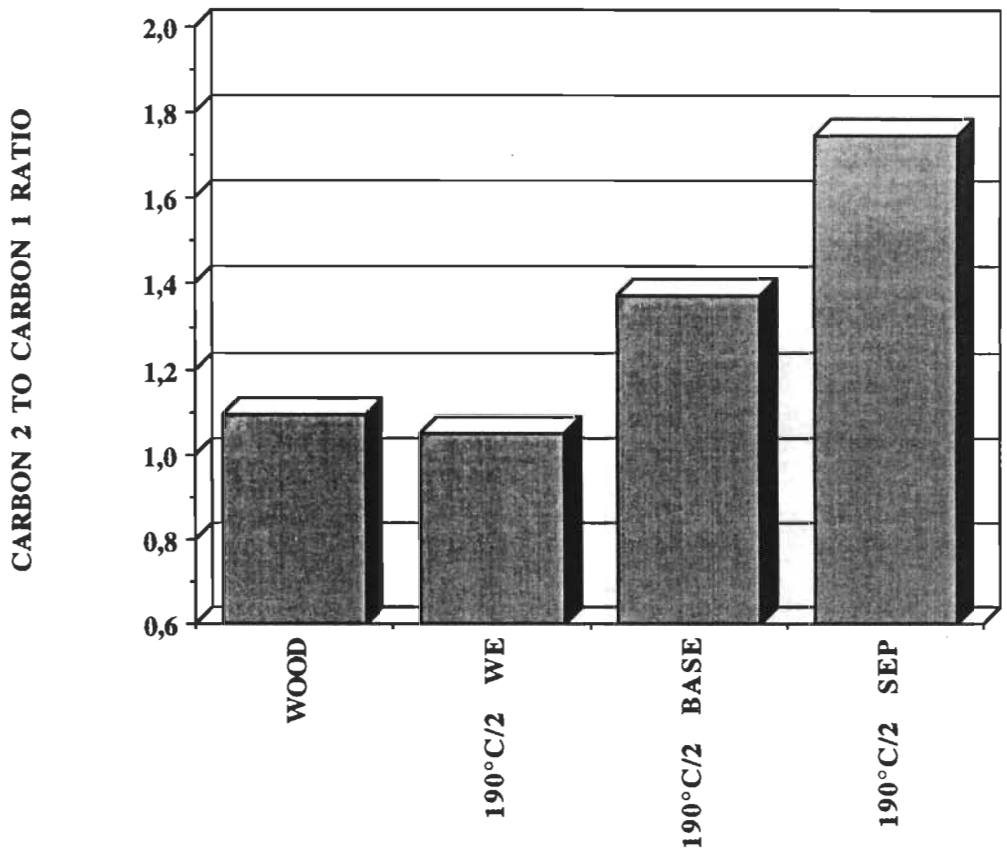


FIGURE 3.65 C1/C2 evaluation for aspen wood and three explosion pulps prepared at 190°C/2 minutes

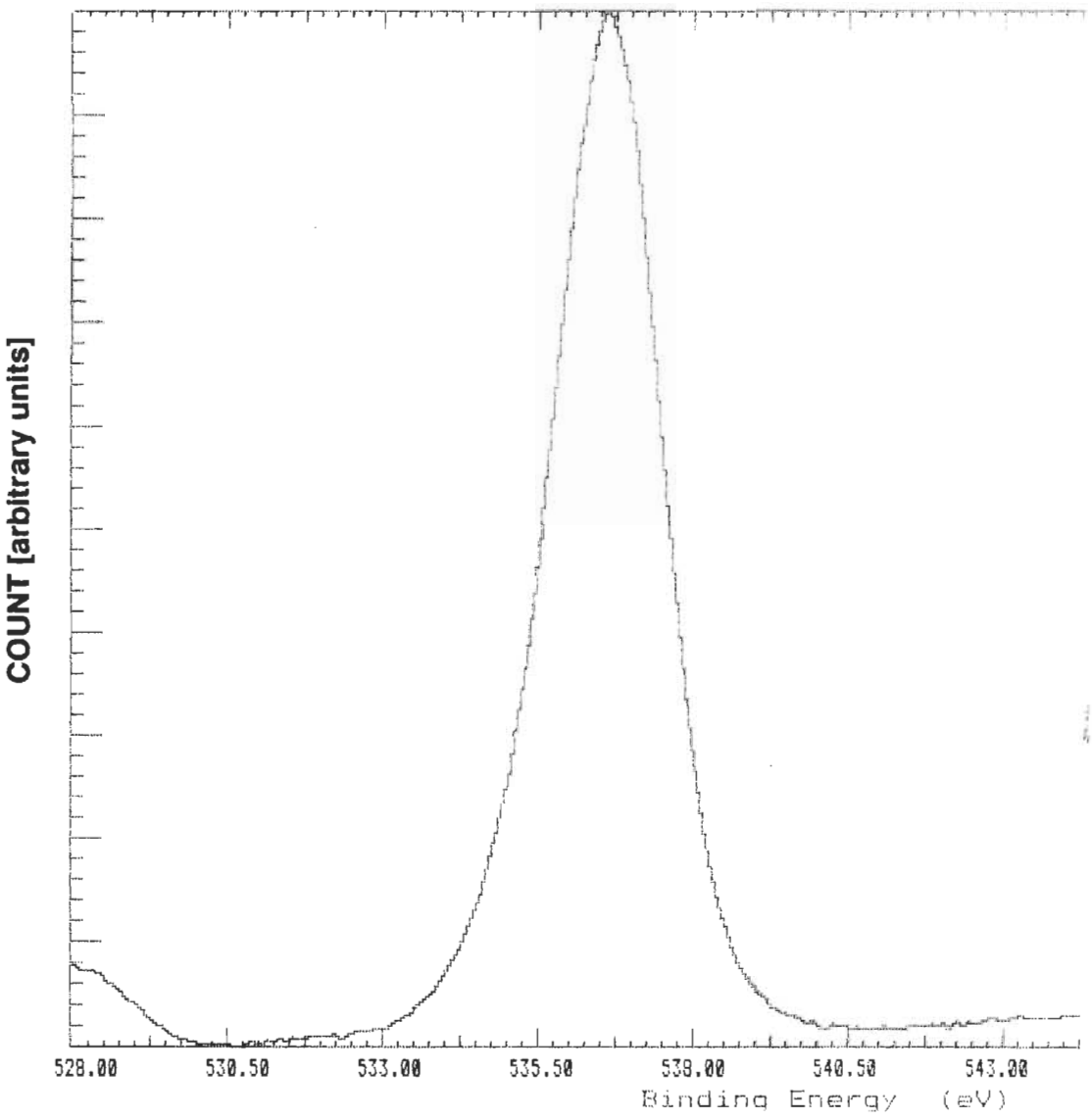


FIGURE 3.66 Oxygen O_{1s} peak for the 190°C/2 minutes explosion pulp

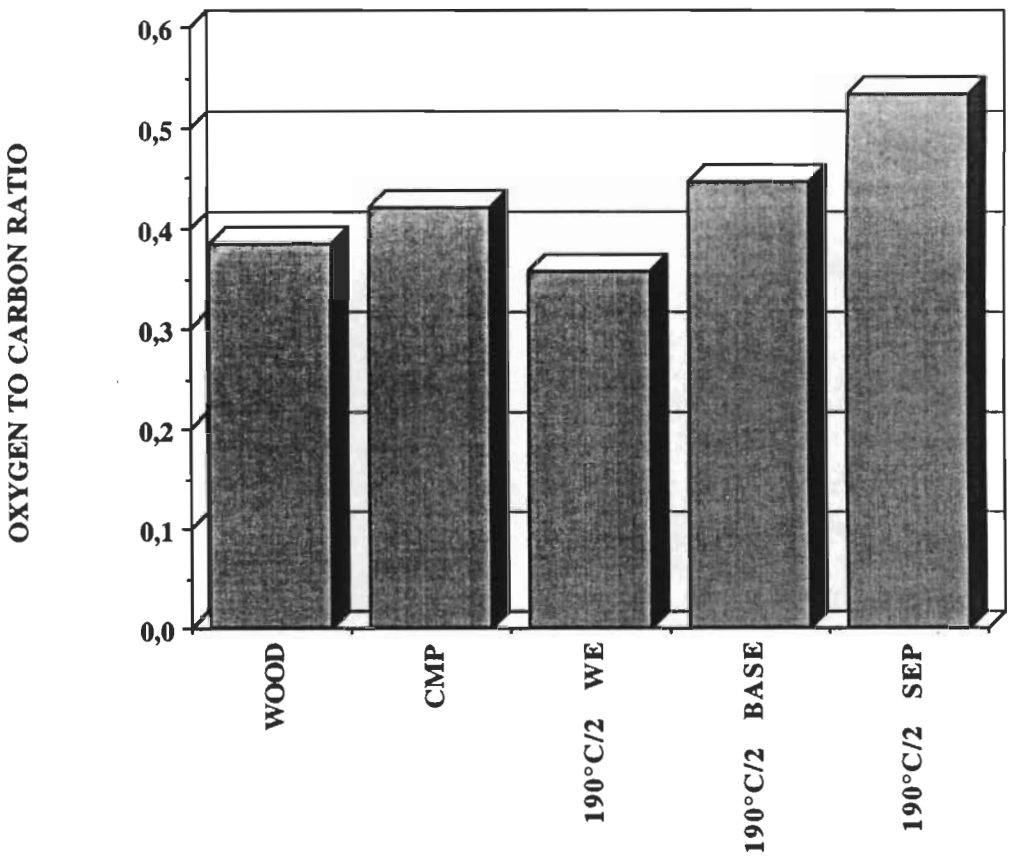


FIGURE 3.67 Oxygen-to-carbon evaluation for aspen wood, CMP and three explosion pulps prepared at 190°C/2 minutes

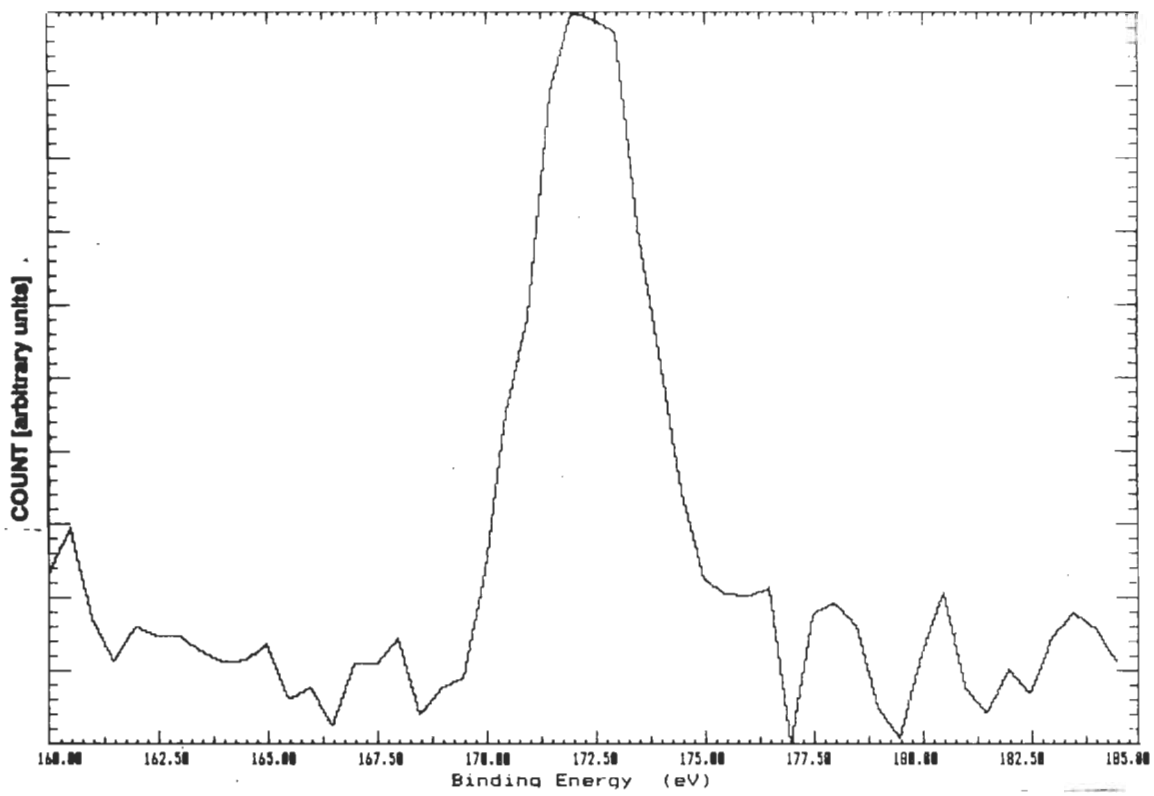


FIGURE 3.68 Sulfur S_{2p} peak for the 190°C/2 minutes explosion pulp

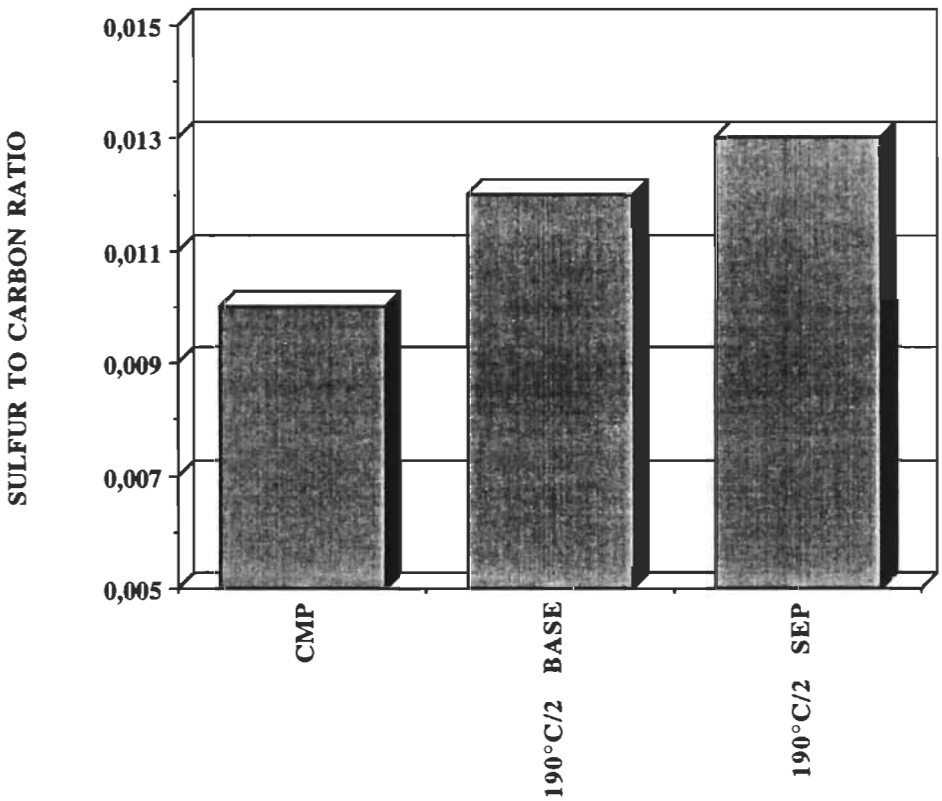


FIGURE 3.69 Sulfur-to-carbon evaluation for CMP and chemically impregnated explosion pulps prepared at 190°C/2 minutes

In conclusion, the ESCA analysis showed that explosion pulps have higher oxygen-to-carbon ratio and less C1 peak areas compared to wood or conventional CMP. This suggests that explosion pulps have more carbohydrates exposed on its fiber surface. More carbohydrates, therefore more hydrophilic groups, exposed on the surface facilitate hydrogen bonding during paper formation, and consequently improve interfiber bonding. This may explain why the paper sheet made of explosion pulp provides much greater strength than a conventional pulp. Explosion pulps also have higher degree of surface sulfonation resulting in more hydrophilic groups on the fiber surface.

3.3.3 CONCLUSION FROM THE THIRD TRIAL RESULTS

Sixteen pulps in the third experimental series covered the majority of the cooking interval for the high severity treatment as well as some conventional processes. If we look at the explosion pulps, we can conclude that:

- pulp yield has decreased proportionally with increasing severity. The mildest conditions (180°C/1 minute) resulted in yield higher than 90% and the most severe conditions (200°C/4 minutes) lowered the yield to about 83%.

- The yield drop is mainly caused by the hydrolysis of hemicelluloses. Klason lignin analysis showed that the lignin content is similar in most of the samples. Several other analyses (X-ray diffractometry, spectroscopies) have shown that the quantity of cellulose did not change, too.

- Ionic content was another proof of hemicellulose hydrolysis. Hemicellulose COOH groups are the main contribution to the carboxylic content. Their decrease with rising severity confirmed the fact, that the hydrolysis is the fastest reaction during high-temperature cook. On the other hand, the sulfonic content was increasing for the main part of the pulping interval. Only at he most extreme conditions at 200°C, the sulfonation began to decrease. This can be explained by lignin reactions and partial hydrolysis of the sulfonic groups.

- Every severity increase has improved some fiber properties. This was not quite expected since we thought that there would be an optimum with further quality decrease at exaggerated cooking conditions. The light-scattering coefficient at the most severe conditions, for example, was very close to values known for chemical pulps which have substantially lower yield. Also, the mechanical properties were best at higher severity.

- Pressurized explosion (from 25 atmospheres) showed the biggest benefit at 180°C/1 minute. Pressure increase had almost the same effect on paper quality as doubling the reaction time. In the central point, we found slightly higher breaking length and at the most severe conditions (200°C/4 minutes) we did not see any improvement at all. This confirms our previous findings

(from the first and second experimental series) that the pressurization to 25 atmospheres has a positive effect only at lower severity or lower or insufficient chemical treatment.

Several analytical analyses helped to explain better performance of explosion pulps. The X-ray diffraction confirmed higher cellulose crystallinity and thicker crystals with increasing severity. As we explained in the first series, when we talk about bonding properties, the ordered cellulose I is the highest quality material possible. Water retention value analysis showed better surface fibrillation for explosion pulps. Pressurized explosion improved the WRV by about 15% in all cases, which demonstrated another benefit of explosive pulp release. ESCA analysis showed some important differences in fiber surface. In comparison with conventional processes (CMP), the surface cellulose exposure was substantially higher in the case of explosion pulps. Also, higher surface sulfonation of explosion pulps helped to reduce the hydrophobic lignin character and increased mechanical properties.

4 MATHEMATICAL EVALUATION OF OBTAINED RESULTS

With a new process development, it is very important to analyze its performance by comparing all the important outcomes to existing processes. In the case of ultra-high yield pulps, the most important parameters are the cost evaluation (mostly represented as the refining energy) and paper properties. It is very difficult to compare process conditions of high severity pulping and conventional methods, such as the CTMP and CMP, since the operating conditions and chemical charges added are completely different. Carrasco et al. [42, 53, 155] suggested that it would make no sense to compare the properties of pulps resulting from processes, working at such different temperatures, times, pressures and impregnation conditions based on one single parameter only (such as the yield, sulfonation, etc.). When he tried to explain or predict the pulp and paper properties with one parameter only, the regression coefficients were very low (for yield, for example: from 0.04 to 0.53 for the refining energy and mechanical properties, 0.56 to 0.73 for optical properties). This is also the situation in this work: most of the figures are presented as a function of temperature. In fact, the temperature was not chosen as a single important parameter - it was chosen to demonstrate increasing cooking severity, which increases with rising temperature. Also, the temperature was chosen for better result visualization, because it did not cause many challenges in understanding of the figures. It is really essential to determine which and how many parameters can be taken as reference variables. These parameters should represent the severity of different pulping processes.

As a first step in this evaluation, we tested the result reproducibility. We cooked 100 explosion pulps at 190°C/2 minutes. Based on randomly generated

numbers, we prepared 10 pulp samples with 10 cooks in each of them. With these samples, we did most of the analyses performed throughout this work. For the yield, density, porosity, breaking length, stretch, burst, brightness, opacity and light-scattering coefficient, the relative standard deviation at 100 ml CSF was in 2 to 5% interval. The two parameters with higher spread were the relative specific refining energy (6%) and tear (7%).

For every pulping condition in the first, second and third experimental series, every cook was repeated 15 times and cooked pulps were mixed together. From this mixture, pulps were refined to at least three freeness values. Pulp yield, sulfonic and carboxylic content, relative refining specific energy and the Bauer-McNett fiber classification were measured 4 times, all other parameters were measured at least 10 times.

The experimental error defined as the relative standard deviation for each measurement is presented in the tables with experimental results (chapter 3).

The interdependence between processing pulping conditions and characteristic pulp and paper properties is illustrated in Figure 4.1. It is clear that specific refining energy and paper properties depend on operating conditions. But the pulp parameters also influence paper properties and could explain the energy consumed to obtain certain paper quality. Then, it is possible to relate y variables (paper quality) to x variables (pulp characteristics) without considering the operating conditions (z variables) because the overall influence of the latter will be included in the intermediate variables x. Therefore, the determination of mathematical equations of the type $y = f(x)$ instead of $y = f(z)$ is an attempt to correctly compare processes having two or more operating conditions. Equation of the type $x = f(y)$ could be also useful.

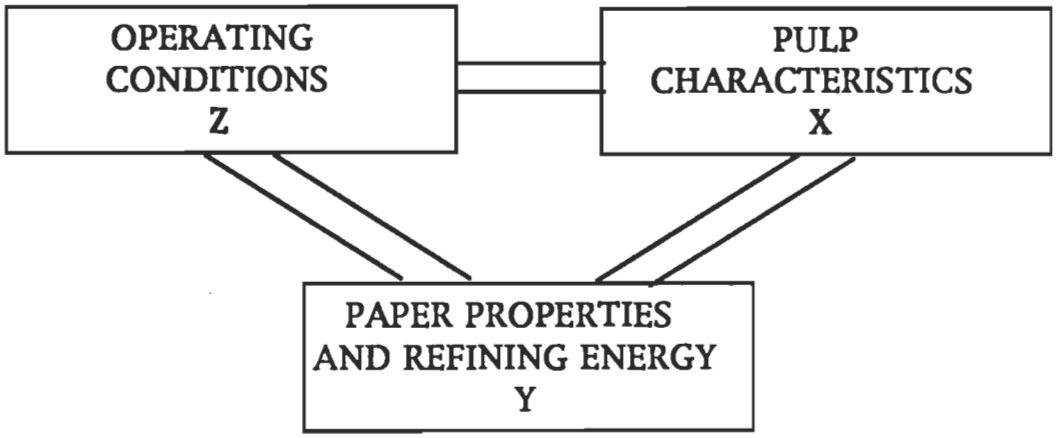


FIGURE 4.1 Schematic diagram of the interrelations between operating conditions and variables representing pulp and paper quality

In our study, we considered the following variables:

Cooking condition parameters (z):
- Cooking temperature
- Cooking time
- Cooking pressure

Pulp parameters (x):
- Yield
- Sulfonic content
- Carboxylic content
- Total ionic content

Refining energy and paper parameters (y):
- Relative specific refining energy
- Refining time
- Density
- Porosity
- Breaking length

- Stretch
- Burst index
- Tear index
- Light-scattering coefficient
- Brightness (60 g/m^2)
- Brightness (150 g/m^2)
- Opacity

To determine the most significant pulp parameters affecting the values of specific refining energy and paper properties, we used the following mathematical model:

$$y = a + \sum b_i.x_i$$

where a is the intercept and b_i are slopes. In our case, i can be one to four (we have four parameters for evaluation).

4.1 EVALUATION BASED ON PULP PROPERTIES

For each dependent variable, a systematic and complete linear regression was performed by considering all the possible combinations between these variables (4 one-x, 9 two-x, 3 three-x and 1 four-x model). The most significant regressions are shown in Tables 4.1 to 4.8. One sole parameter is clearly not enough for reliable property prediction. Neither yield, nor ionic content (sulfonic, carboxylic or total) gave correlations over 90 or 95%. If we look at all the individual influences (Tables 4.1 to 4.4), we can see that the least regression coefficients were found for the carboxylic content. Total ionic content gave correlations somewhat higher and the yield correlated to about 60% (with the exception of optical properties). Sulfonic content had best correlations and confirmed results of several other studies emphasizing the importance of good sulfonation [42, 44, 53, 64, 89].

TABLE 4.1 Regression analysis of pulp quality: the influence of yield

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF YIELD				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.80	0.79	0.57	0.57
REL. REF. ENERGY	0.74	0.78	0.69	0.71
DENSITY	0.60	0.76	0.70	0.67
POROSITY	0.73	0.75	0.41	0.45
BREAKING LENGTH	0.91	0.91	0.75	0.80
STRETCH	0.61	0.70	0.67	0.67
TEAR	0.75	0.80	0.69	0.72
BURST	0.86	0.87	0.74	0.79
BRIGHTNESS 60 g/m^2	0.68	0.81	0.06	0.02
BRIGHTNESS 300 g/m^2	0.79	0.86	0.09	0.00
OPACITY	0.71	0.34	0.39	0.54
LSC	0.81	0.84	0.74	0.76

TABLE 4.2 Regression analysis of pulp quality: the influence of sulfonic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF SUFONIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.73	0.68	0.88	0.91
REL. REF. ENERGY	0.60	0.46	0.80	0.84
DENSITY	0.42	0.31	0.78	0.87
POROSITY	0.61	0.59	0.86	0.86
BREAKING LENGTH	0.82	0.65	0.83	0.86
STRETCH	0.43	0.23	0.80	0.88
TEAR	0.59	0.51	0.87	0.89
BURST	0.81	0.67	0.75	0.78
BRIGHTNESS 60 g/m^2	0.40	0.26	0.60	0.68
BRIGHTNESS 300 g/m^2	0.55	0.29	0.58	0.71
OPACITY	0.64	0.64	0.63	0.65
LSC	0.70	0.62	0.84	0.88

TABLE 4.3 Regression analysis of pulp quality: the influence of carboxylic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF CARBOXYLIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.23	0.35	0.03	0.04
REL. REF. ENERGY	0.29	0.41	0.10	0.14
DENSITY	0.20	0.44	0.24	0.38
POROSITY	0.24	0.37	0.11	0.13
BREAKING LENGTH	0.44	0.54	0.23	0.32
STRETCH	0.58	0.54	0.17	0.26
TEAR	0.43	0.53	0.22	0.29
BURST	0.45	0.54	0.20	0.27
BRIGHTNESS 60 g/m^2	0.38	0.60	0.48	0.48
BRIGHTNESS 300 g/m^2	0.36	0.57	0.61	0.62
OPACITY	0.29	0.11	0.56	0.59
LSC	0.28	0.41	0.15	0.23

TABLE 4.4 Regression analysis of pulp quality: the influence of total ionic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF TOTAL IONIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.08	0.17	0.52	0.66
REL. REF. ENERGY	0.15	0.27	0.43	0.58
DENSITY	0.10	0.34	0.41	0.64
POROSITY	0.11	0.21	0.67	0.76
BREAKING LENGTH	0.24	0.35	0.40	0.54
STRETCH	0.21	0.47	0.43	0.63
TEAR	0.29	0.38	0.46	0.60
BURST	0.25	0.34	0.33	0.44
BRIGHTNESS 60 g/m^2	0.32	0.54	0.22	0.41
BRIGHTNESS 300 g/m^2	0.21	0.48	0.20	0.42
OPACITY	0.13	0.01	0.33	0.34
LSC	0.13	0.24	0.45	0.61

From the more-x models, we concentrated on several two-x results. This type of analysis gave good correlations and this is also logically best choice, since there are just two types of variables: yield and a certain form of ionic content. Interaction terms (product of two or more variables) did not produce any significant improvement, so we used a two-x model equation:

$$y = a + b1x1 + b2x2$$

Results and correlation factors are in Tables 4.5 to 4.8. As we can see, the best results with best correlations can be interpreted as a combination of yield with sulfonic or total ionic content. For these parameters, the correlation coefficient r^2 was around 90% for most of studied properties. When we created prediction equations, it was confirmed that the properties increase and refining energy decreases with rising sulfonic/total ionic content and decreasing yield.

TABLE 4.5 Regression analysis of pulp quality: the combined influence of yield and sulfonic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF YIELD AND SUFONIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.82	0.86	0.94	0.93
REL. REF. ENERGY	0.75	0.78	0.95	0.91
DENSITY	0.60	0.77	0.90	0.90
POROSITY	0.73	0.79	0.86	0.86
BREAKING LENGTH	0.93	0.93	0.97	0.97
STRETCH	0.61	0.74	0.89	0.91
TEAR	0.75	0.81	0.95	0.95
BURST	0.89	0.90	0.92	0.92
BRIGHTNESS 60 g/m^2	0.72	0.84	0.82	0.78
BRIGHTNESS 300 g/m^2	0.80	0.89	0.89	0.89
OPACITY	0.72	0.64	0.70	0.85
LSC	0.82	0.87	0.96	0.96

TABLE 4.6 Regression analysis of pulp quality: the combined influence of yield and carboxylic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF YIELD AND CARBOXYLIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.96	0.95	0.58	0.57
REL. REF. ENERGY	0.82	0.85	0.76	0.75
DENSITY	0.69	0.80	0.89	0.86
POROSITY	0.84	0.85	0.50	0.49
BREAKING LENGTH	0.95	0.94	0.93	0.94
STRETCH	0.61	0.70	0.79	0.78
TEAR	0.76	0.81	0.85	0.85
BURST	0.87	0.88	0.90	0.90
BRIGHTNESS 60 g/m^2	0.69	0.81	0.56	0.56
BRIGHTNESS 300 g/m^2	0.84	0.87	0.64	0.65
OPACITY	0.76	0.48	0.88	0.92
LSC	0.92	0.94	0.85	0.85

TABLE 4.7 Regression analysis of pulp quality: the combined influence of yield and total ionic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF YIELD AND TOTAL IONIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.96	0.97	0.94	0.93
REL. REF. ENERGY	0.80	0.83	0.93	0.93
DENSITY	0.66	0.78	0.93	0.93
POROSITY	0.82	0.85	0.90	0.90
BREAKING LENGTH	0.95	0.95	0.98	0.98
STRETCH	0.61	0.71	0.89	0.91
TEAR	0.75	0.81	0.94	0.94
BURST	0.89	0.89	0.91	0.91
BRIGHTNESS 60 g/m^2	0.68	0.82	0.83	0.79
BRIGHTNESS 300 g/m^2	0.83	0.86	0.91	0.92
OPACITY	0.78	0.62	0.70	0.85
LSC	0.91	0.94	0.98	0.97

TABLE 4.8 Regression analysis of pulp quality: the combined influence of sulfonic and carboxylic content

REGRESSION ANALYSIS OF COOKING RESULTS THE INFLUENCE OF SUFONIC AND CARBOXYLIC CONTENT				
R^2 FOR VARIABLE	SEP (9 pulps)	SEP + N EXP (12 pulps)	ALL PULPS (16 pulps)	SEP + CONV PULPS (11 pulps)
REFINING TIME	0.74	0.71	0.91	0.91
REL. REF. ENERGY	0.60	0.57	0.85	0.86
DENSITY	0.42	0.50	0.84	0.87
POROSITY	0.61	0.65	0.86	0.87
BREAKING LENGTH	0.83	0.78	0.91	0.91
STRETCH	0.47	0.55	0.85	0.89
TEAR	0.63	0.68	0.92	0.92
BURST	0.82	0.80	0.87	0.86
BRIGHTNESS 60 g/m^2	0.47	0.61	0.74	0.72
BRIGHTNESS 300 g/m^2	0.57	0.60	0.75	0.76
OPACITY	0.64	0.65	0.67	0.75
LSC	0.70	0.69	0.90	0.90

4.2 EVALUATION BASED ON PULPING PARAMETERS

As the purpose of this work is not only the evaluation of cooking intermediates (pulp quality) but mainly pulping conditions, we applied this very same mathematical approach towards cooking parameters. Since the H factor (as used in the case of chemical pulping) cannot be used for high yield processes, the only previous attempt to use cooking parameters was the K constant or K factor [31]. K factor is a product of cooking time and cooking temperature and has very limited interpretation. In our trials, we were able to use one-, two- and three-variable models in evaluation of cooking conditions and resulted paper properties and refining energy requirements. The results are presented in Tables 4.9 to 4.15.

Tables 4.9 to 4.11 show that neither of three cooking variables provides reasonable correlation all by itself. From two-z variables models (Tables 4.12 to 4.14), the best results were obtained for the time/temperature combination. If we look at the complete three-z evaluation at the Table 4.15, the correlations are very good for the explosion pulps with or without pressurized explosion. If we add the CTMP and CMP processes, the correlations drop significantly. This is due to very different cooking conditions for high severity and conventional pulping. Also, if we talk about the short span of condition used in explosion pulping, we can consider the influence of individual parameters as linear. However, if we include other pulps produced at very different time and temperature values, we must realize that these influences are not linear. In spite of trying other non-linear models, we were not able to obtain reasonably better outcome.

If we concentrate on the high severity interval and cooking temperatures between 180 and 200°C, cooking times between 1 and 4 minutes and pressures ranging from 9.9 to 25 atmospheres, we can see that our correlations are over 90% in the predictions of yield, relative specific refining energy, breaking length, burst, light-scattering coefficient and the brightness. From this point of view, we have covered most of the important parameters: yield, refining energy, mechanical and optical properties. Based on these considerations, Table 4.16 shows the equations for parameter estimate. We can see, that increasing cooking temperature decreases pulp yield, carboxylic and total ionic content,

refining energy, porosity, LSC and optical properties. It also helps to increase sulfonation, density and all the mechanical properties. The very same tendency was found with increasing cooking time. Thus we have also mathematical proof of our experimental conclusions.

Figure 4.2 provides a visual way to evaluate the goodness of proposed model. It consists of plotting the predicted values resulting from the mathematical equations (Table 4.16) as a function of experimental data. When the model is appropriate, points must be the nearest possible from the diagonal. This type of representation gives more information than just reporting regression coefficient values: it also allows to detect if points are randomly distributed above and below the diagonal line for each series of operating conditions. Figures 4.2 and 4.3 clearly indicate that the breaking length is accurately predicted. Plots of residuals against estimated values indicated that for each dependent variable, residuals were randomly scattered. Thus, the assumptions inherent to multiple linear regression models were satisfied.

TABLE 4.9 Regression analysis of pulping conditions: the influence of pulping temperature

REGRESSION ANALYSIS OF COOKING PARAMETERS TEMPERATURE			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.58	0.67	0.42
SULFONATES	0.39	0.39	0.65
CARBOXYLATES	0.56	0.62	0.00
TOTAL IONIC CONTENT	0.48	0.48	0.32
REFINING TIME	0.35	0.48	0.56
REL. REFINING ENERGY	0.17	0.32	0.65
DENSITY	0.64	0.70	0.52
POROSITY	0.62	0.70	0.48
BREAKING LENGTH	0.59	0.67	0.50
STRETCH	0.49	0.53	0.50
TEAR	0.60	0.69	0.52
BURST	0.60	0.68	0.56
BRIGHTNESS 60 g/m^2	0.56	0.62	0.36
BRIGHTNESS 300 g/m^2	0.24	0.38	0.14
OPACITY	0.23	0.18	0.09
LSC	0.46	0.58	0.58

TABLE 4.10 Regression analysis of pulping conditions: the influence of pulping time

REGRESSION ANALYSIS OF COOKING PARAMETERS TIME			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.39	0.54	0.03
SULFONATES	0.34	0.32	0.39
CARBOXYLATES	0.07	0.23	0.01
TOTAL IONIC CONTENT	0.01	0.13	0.34
REFINING TIME	0.55	0.63	0.33
REL. REFINING ENERGY	0.80	0.78	0.20
DENSITY	0.13	0.32	0.15
POROSITY	0.23	0.37	0.10
BREAKING LENGTH	0.37	0.49	0.12
STRETCH	0.17	0.31	0.17
TEAR	0.26	0.39	0.18
BURST	0.32	0.44	0.15
BRIGHTNESS 60 g/m^2	0.16	0.35	0.12
BRIGHTNESS 300 g/m^2	0.67	0.70	0.04
OPACITY	0.65	0.41	0.02
LSC	0.44	0.57	0.18

TABLE 4.11 Regression analysis of pulping conditions: the influence of pulping pressure

REGRESSION ANALYSIS OF COOKING PARAMETERS PRESSURE			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.55	0.08	0.25
SULFONATES	0.33	0.02	0.33
CARBOXYLATES	0.51	0.03	0.02
TOTAL IONIC CONTENT	0.45	0.12	0.18
REFINING TIME	0.34	0.02	0.31
REL. REFINING ENERGY	0.17	0.11	0.44
DENSITY	0.69	0.10	0.36
POROSITY	0.63	0.01	0.28
BREAKING LENGTH	0.58	0.11	0.36
STRETCH	0.59	0.16	0.41
TEAR	0.56	0.09	0.36
BURST	0.55	0.08	0.35
BRIGHTNESS 60 g/m^2	0.58	0.10	0.11
BRIGHTNESS 300 g/m^2	0.28	0.11	0.04
OPACITY	0.24	0.00	0.09
LSC	0.45	0.04	0.39

TABLE 4.12 Regression analysis of pulping conditions: the combined influence of pulping temperature

REGRESSION ANALYSIS OF COOKING PARAMETERS TEMPERATURE AND TIME			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.97	0.97	0.51
SULFONATES	0.73	0.57	0.67
CARBOXYLATES	0.63	0.71	0.20
TOTAL IONIC CONTENT	0.49	0.52	0.40
REFINING TIME	0.90	0.89	0.57
REL. REFINING ENERGY	0.97	0.91	0.66
DENSITY	0.79	0.84	0.52
POROSITY	0.85	0.88	0.52
BREAKING LENGTH	0.96	0.94	0.52
STRETCH	0.66	0.68	0.50
TEAR	0.86	0.88	0.53
BURST	0.92	0.91	0.58
BRIGHTNESS 60 g/m^2	0.72	0.79	0.37
BRIGHTNESS 300 g/m^2	0.91	0.88	0.12
OPACITY	0.87	0.49	0.09
LSC	0.90	0.92	0.59

TABLE 4.13 Regression analysis of pulping conditions: the combined influence of pulping temperature and pressure

REGRESSION ANALYSIS OF COOKING PARAMETERS TEMPERATURE AND PRESSURE			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.58	0.67	0.43
SULFONATES	0.45	0.45	0.65
CARBOXYLATES	0.58	0.62	0.03
TOTAL IONIC CONTENT	0.49	0.50	0.33
REFINING TIME	0.34	0.49	0.57
REL. REFINING ENERGY	0.17	0.35	0.68
DENSITY	0.71	0.70	0.55
POROSITY	0.64	0.72	0.49
BREAKING LENGTH	0.59	0.68	0.53
STRETCH	0.72	0.57	0.55
TEAR	0.61	0.69	0.56
BURST	0.61	0.68	0.58
BRIGHTNESS 60 g/m^2	0.58	0.63	0.37
BRIGHTNESS 300 g/m^2	0.31	0.41	0.15
OPACITY	0.24	0.18	0.11
LSC	0.46	0.58	0.60

TABLE 4.14 Regression analysis of pulping conditions: the combined influence of pulping time and

REGRESSION ANALYSIS OF COOKING PARAMETERS TIME AND PRESSURE			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.94	0.61	0.25
SULFONATES	0.68	0.32	0.48
CARBOXYLATES	0.58	0.30	0.02
TOTAL IONIC CONTENT	0.46	0.25	0.37
REFINING TIME	0.89	0.65	0.43
REL. REFINING ENERGY	0.97	0.89	0.46
DENSITY	0.82	0.42	0.37
POROSITY	0.86	0.38	0.28
BREAKING LENGTH	0.95	0.60	0.36
STRETCH	0.76	0.47	0.42
TEAR	0.81	0.48	0.39
BURST	0.88	0.52	0.37
BRIGHTNESS 60 g/m^2	0.73	0.45	0.15
BRIGHTNESS 300 g/m^2	0.95	0.81	0.05
OPACITY	0.88	0.42	0.09
LSC	0.89	0.60	0.38

TABLE 4.15 Regression analysis of pulping conditions: the combined influence of pulping temperature, time and pressure

REGRESSION ANALYSIS OF COOKING PARAMETERS TEMPERATURE AND TIME AND PRESSURE			
	SEP (9 pulps)	SEP + N-EXP (12 pulps)	ALL PULPS (16 pulps)
VARIABLE	R^2	R^2	R^2
YIELD	0.97	0.98	0.53
SULFONATES	0.79	0.62	0.67
CARBOXYLATES	0.66	0.71	0.05
TOTAL IONIC CONTENT	0.50	0.55	0.40
REFINING TIME	0.90	0.89	0.58
REL. REFINING ENERGY	0.97	0.96	0.69
DENSITY	0.84	0.85	0.56
POROSITY	0.86	0.89	0.53
BREAKING LENGTH	0.96	0.95	0.56
STRETCH	0.89	0.74	0.56
TEAR	0.87	0.88	0.56
BURST	0.93	0.91	0.60
BRIGHTNESS 60 g/m^2	0.73	0.81	0.37
BRIGHTNESS 300 g/m^2	0.98	0.93	0.15
OPACITY	0.88	0.49	0.11
LSC	0.90	0.92	0.61

TABLE 4.16 Regression analysis of pulping conditions: pulp and paper quality prediction equations for explosion pulps

REGRESSION ANALYSIS OF COOKING PARAMETERS FOR THE STEAM EXPLOSION PULPS (180 TO 200°C) (12 pulps)

VARIABLE	R2	INTERCEIPT	TEMPER [K]	TIME [s]	PRESSURE [atm]
YIELD	0.98	195	- 0.223	- 0.021	- 0.400
SULFO	0.62	- 20.1	0.155	0.012	- 0.082
CARBOXYL	0.71	397	- 0.541	- 0.026	- 0.056
TOTAL IONIC	0.55	384	- 0.402	- 0.016	- 0.158
REF TIME	0.89	836	- 1.620	- 0.218	0.117
REF ENERGY	0.96	23.8	- 0.039	- 0.012	- 0.046
DENSITY	0.85	- 910	3.050	0.184	0.651
POROSITY	0.89	1540	- 3.180	- 0.188	0.659
BL	0.95	- 25.6	0.068	0.006	0.020
STRETCH	0.74	- 2.25	0.008	0.001	0.005
TEAR	0.88	- 23.7	0.063	0.005	0.012
BURST	0.91	- 18.5	0.047	0.004	0.008
BR 1.2g	0.81	140	- 0.163	- 0.012	- 0.047
BR 3g	0.93	106	- 0.078	- 0.017	- 0.067
OPACITY	0.49	114	- 0.055	- 0.012	0.011
LSC	0.92	187	- 0.313	- 0.033	- 0.021

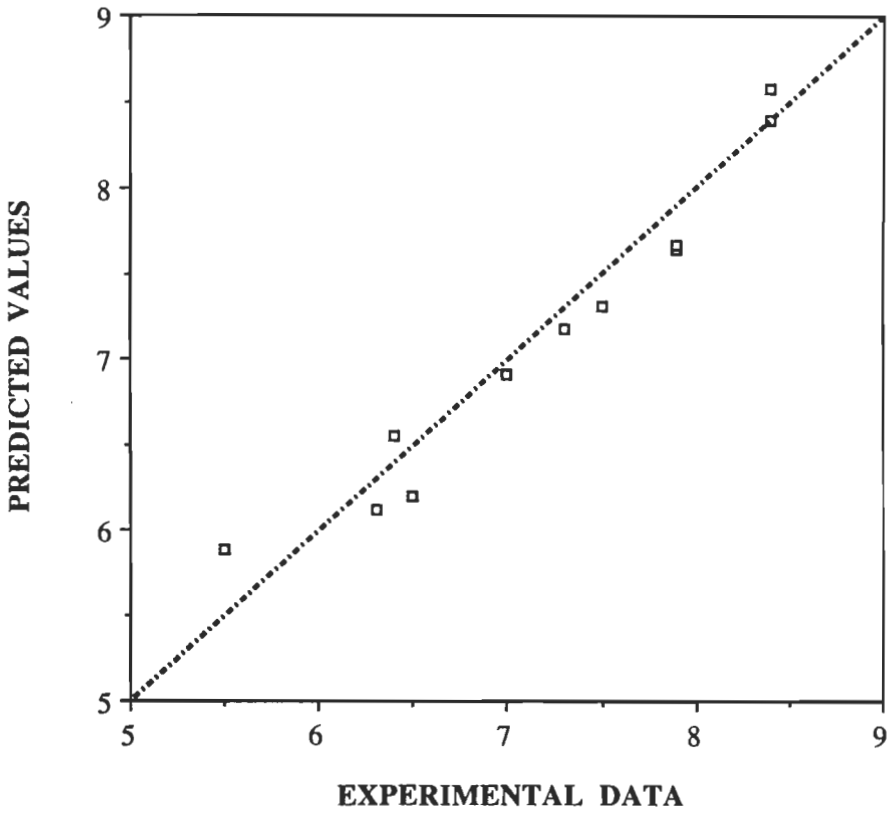


FIGURE 4.2 Comparison between predicted values and experimental data with a three parameter model for the breaking length

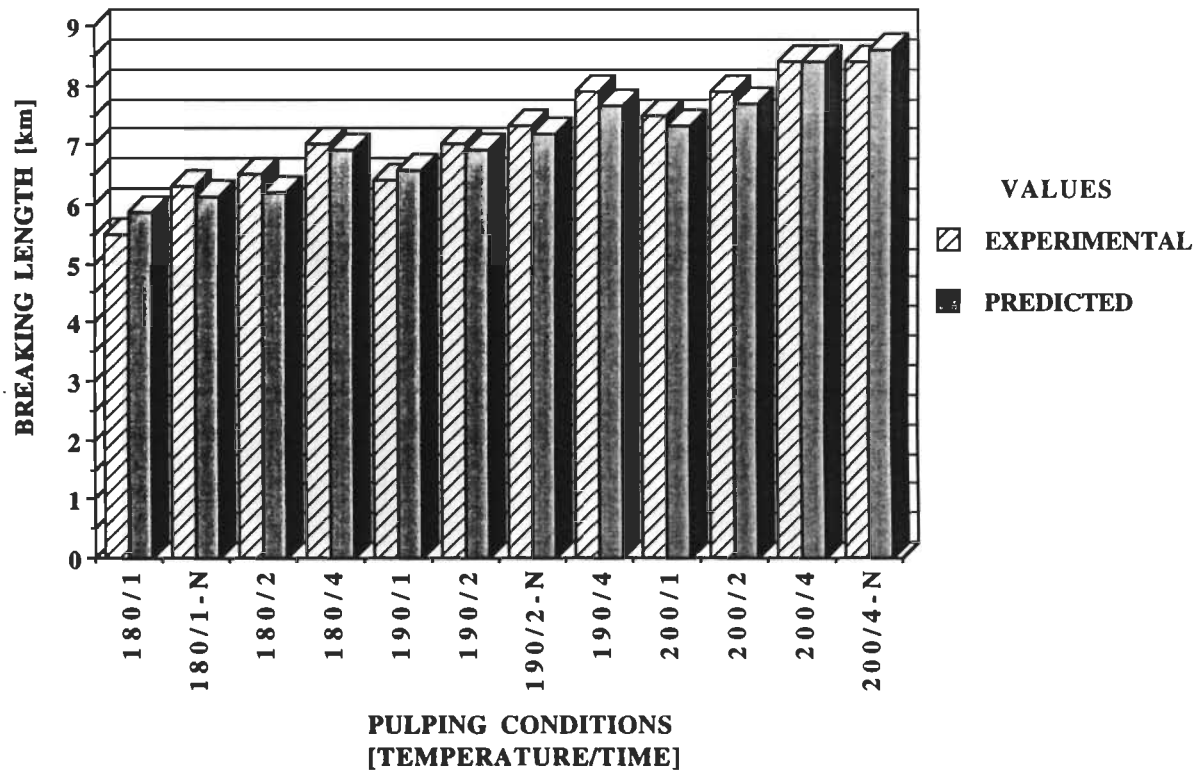


FIGURE 4.3 Visualization of the comparison between predicted values and experimental data with a three parameter model for the breaking length

Based on these equations, it is also possible to predict cooking conditions for requested pulp and/or paper property. In this case, all we need to do is to substitute the desired parameter and to choose the cooking conditions to fit the equation.

In the mathematical evaluations, we also tried to establish the kinetics of pulp sulfonation. Unfortunately, the possibility of experimental error in sulfonation measurement (lower result reproducibility) was too high to get a reasonable interpretation.

5 CONCLUSIONS

The goal of this work was to study and scientifically explain the principles of high severity (explosion) pulping process. The thesis had the following objectives: to establish a correlation between cooking conditions (temperature, time, pressure) and the physicochemical fiber changes due to vapor phase cooking, to establish a correlation between structural and chemical fiber changes and the resulting mechanical and optical pulp and paper properties and to determine the optimum cooking conditions in order to obtain required paper properties.

At the early stage of the work, we focused on the influence of cooking temperature and pressure. We adjusted the pulping conditions to eliminate some of the process variables. We cooked the explosion and conventional pulps to the same yield by using the very same chemical charge. As a result, we also obtained same ionic content for most of the pulps. However, the sulfonic group content was much higher in the case of explosion pulps (the values varied between 40 and 50 mmol/kg for the explosion pulps and 35 to 40 mmol/kg for the CMP and CTMP), cooked at higher severity. These pulps also had significantly lower refining energy (up to 50 %) in comparison to CMP and CTMP and showed improved fiber properties (Breaking length up to 7.5 km, burst 3 to 4 kPam^2/g and tear 7 to 8 mNm^2/g). The FTIR analysis showed a higher content of ordered cellulose I in exploded fibers, compared to the CMP and CTMP. The average fiber length was higher for higher temperatures and thanks to additional permanent softening, exploded fibers also had higher flexibility, density and thus better fiber contact in handsheets. This has been fully confirmed by lower values of the light-scattering coefficient and higher mechanical properties. The addition of a second impregnation agent to Na_2SO_3 enhanced the process towards significantly higher mechanical properties and lowered refining energies (at increased ionic content). With $NaHCO_3$ as second

impregnation chemical, the pulp yield of about 90% was preserved, while NaOH addition led to a yield drop (about 7% in our case). However, the property gain was the highest with NaOH. Nitrogen pressurization of the reactor prior to the explosion (up to 25 atmospheres) led to further decrease in refining energy and property improvement. When compared to the conventional pulps (CMP and CTMP, better mechanical properties and lower refining energy of the explosion pulps can be attributed to the chemical changes (higher crystallinity, better lignin softening) that occur following the high-temperature-high-pressure cook as well as the physical changes (better and easier fiber separation) that occur following high severity cook and explosive discharge from the digester.

In the second series, we concentrated on the improved impregnation system $Na_2SO_3/NaHCO_3$ and on the influence of pressure on the pulp and paper quality. We were able to prepare ten pulps with a yield of 90% (or very close to 90%) with very low refining energies (about 2.5 to 3.0 MJ/kg) and with excellent papermaking potential. Our breaking lengths reached up to 9 km, burst index was over 4.0 $kPa.m^2/g$ and the tear index was around 7 $mN.m^2/g$. Also, the brightness level exceeded 60% MgO in every case with an average value of 63% for unbleached pulps. As to the pressure influence, we did not see changes as important as in the first experimental series. The only parameter where we were able to see a pressure-related improvement was the breaking length. The reason why we did not see any important changes in the other properties is probably associated with the impregnation change. In the first series, we used one-chemical impregnation (Na_2SO_3) and most of the papermaking qualities were lower compared to this two-chemical impregnation series. If the parameters in the first series were lower, there was much more space for further improvement and the changes caused by the pressure increase prior to the explosion were evident in all three cases: 190°C/2 min; 195°C/1.5 min and 200°C/1 minute. In the second series, much of the improvement was reached by the addition of the second impregnation chemical. The resulting quality leap was probably so high that it overlapped the smaller partial improvement caused by the pressure increase.

In the third experimental trials, we fully focused on the full interval of high severity pulping. The purpose was not only to optimize the process and to find

the cooking conditions in order to reach suggested pulp properties. We also wanted to see what kind of changes (chemical, physicochemical and physical) occur or do not occur at very mild and very severe pulping conditions. We found that the pulp yield has decreased proportionally with increasing severity. The mildest conditions (180°C/1 minute) resulted in yield higher than 90% and the most severe conditions (200°C/4 minutes) lowered the yield to about 83%. The yield drop was mainly caused by the hydrolysis of hemicelluloses. Klason lignin analysis showed that the lignin content is similar in most of the samples. Several other analyses (X-ray diffractometry, spectroscopies) have shown that the quantity of cellulose did not change, either. Ionic content was another proof of hemicellulose hydrolysis. Hemicellulose COOH groups are the main contribution to the carboxylic content. Their decrease with rising severity confirmed the fact, that the hydrolysis is the fastest reaction during high-temperature cook. On the other hand, the sulfonic content was increasing for the main part of the pulping interval. Only at the most extreme conditions at 200°C, the sulfonation began to decrease. This can be explained by lignin reactions and partial hydrolysis of the sulfonic groups. Every severity increase has improved some fiber properties. This was not quite expected since we thought that there would be an optimum with further quality decrease at exaggerated cooking conditions. The light-scattering coefficient for the most severe pulping conditions, for example, was very close to values known for chemical pulps with substantially lower yield. Also, the mechanical properties were best at higher severity. Pressurized explosion (from 25 atmospheres) showed the biggest benefit at 180°C/1 minute. Pressure increase had almost the same effect on paper quality as doubling the reaction time. In the central point, we found slightly higher breaking length and at the most severe conditions (200°C/4 minutes) we did not see any improvement at all. This confirms our previous findings that the pressurization to 25 atmospheres has a positive effect only at lower severity or lower or insufficient chemical treatment.

Several analytical analyses helped to explain the better performance of explosion pulps. X-ray diffraction confirmed higher cellulose crystallinity and thicker crystals with increasing severity. As we explained in the first series, when dealing with bonding properties, the ordered cellulose I is the highest quality material possible. Water retention value analysis indicated better surface fibrillation for explosion pulps. Pressurized explosion improved the WRV by

about 15% in all cases, which demonstrated another benefit of explosive pulp release. ESCA analysis showed some important differences in the fiber surface. In comparison with conventional processes (CMP), the surface cellulose exposure was substantially higher in the case of explosion pulps. Also, higher surface sulfonation of explosion pulps helped to reduce the hydrophobic lignin character and increased mechanical properties.

Statistical analysis showed good correlation (calculated as the square regression coefficients within a 95% confidence interval) between cooking parameters, pulp properties and resulted handsheet properties. We were able not only to predict pulp properties from the cooking parameters, but also to estimate the cooking conditions based on required handsheet properties. The correlation coefficient was higher than 90% for all the important parameters (pulp yield, refining energy, breaking length...).

Laboratory results show a promise in the possibility to use the high severity explosion pulping process as an alternative to conventional methods of high yield pulping. Literature review also suggests smaller size equipment and thus lower capital investment for an industrial application (due to short cooking time). However, a full economical study would be required to confirm this suggestion. This work showed that this new approach is allowing to prepare and produce an excellent quality pulp with lower refining energy requirements and superior properties. The main feature of this process is in the high severity treatment: the combination of high cooking temperature, short cooking time and explosive pulp discharge. From this process, we obtained higher quality fibers (longer, more flexible, better fibrillated, better surface characteristics) which resulted in higher quality pulp and handsheets.

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7 AUTHOR'S TOPICAL SCIENTIFIC PRESENTATIONS

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1. **Tomasec, M.**; Kokta, B.V.: Steam explosion pulping of aspen: The effect of cooking parameters on resulting properties; In: Cellulosics: Pulp, Fibre and Environmental Aspects, Ellis Horwood series in Polymer science and technology, Part 1, chap. 7, p. 45, Ellis Horwood Publishers, 1993

2. Kokta, B.V.; **Tomasec, M.**; Sukhov, D.A.; Kaliaguine, S.; Ben, Y.; Hua, Y.; Focher, B.; Kosik, M.: Steam explosion pulping of aspen: Fundamental changes due to the high temperature; 1993 TAPPI International Mechanical Pulping Conference, Oslo, Norway (June 15-17, 1993). Proceedings, p.152

3. **Tomasec, M.**; Kokta, B.V.: High severity mechanical pulping of aspen; 1993 TAPPI International Mechanical Pulping Conference, Oslo, Norway (June 15-17, 1993) Poster Presentations, p.87

4. **Tomasec, M.**; Kokta, B.V.: Steam explosion pulping: Effects of temperature and pressure on resulting paper properties at constant yield and ionic content; *TAPPI Journal*, 74, #12, p. 119, Dec 1991

5. **Tomasec, M.**; Kokta, B.V.: Steam explosion pulping of aspen: The effect of cooking temperature and pressure on resulting paper properties at constant yield and ionic content; *1991 TAPPI Pulping Conference*, Orlando,FL (Nov 4-7,1991), Preprints Vol. 2, p. 737

14. **Tomasec, M.**; Kokta, B.V.: Steam explosion pulping of aspen: The effect of cooking parameters on resulting properties; *Cellulose'91 Conference*; a joint meeting of ACS, Cellulose, Paper and Textile Division; Cellucon Conferences; and 11th Syracuse Cellulose Conference, New Orleans, LA, (Dec 2-6, 1991), poster presentation

15. **Tomasec, M.**: Mise en pâte d'explosion pour la production papetière: L'effet des paramètres de la cuisson sur les propriétés mécaniques et optiques:.Effet de la température élevée et de la pression élevée sur la cuisson au sulfite (Explosion pulping for papermaking: The effect of cooking parameters on mechanical and optical properties. The effect of high temperature and pressure on sulphite cook); Presentation at the *Hymac scholarship of excellence*, doctorate students' section, UQTR, Trois-Rivières (April 5,1991)

16. **Tomasec, M.**: Steam explosion pulping of aspen: An overview; Presentation at the 77th CPPA Annual Meeting, section Students' seminars, Montreal (Jan 29,1991)