POLYTECHNIQUE MONTRÉAL

affiliée à l'Université de Montréal

Traitement électrolytique de la liqueur noire de Kraft avec production de soude caustique et précipitation de la lignine

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Traitement électrolytique de la liqueur noire de Kraft avec production de soude caustique et précipitation de la lignine

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RÉSUMÉ

L'initiative de bio raffinerie de l'industrie des pâtes et papiers vise principalement à diversifier l'offre de produits incluant les biomatériaux dérivés de la lignine. La lignine peut être récupérée de la liqueur noire. L'approche chimique de précipitation de la lignine consiste à réduire le pH de la liqueur noire à l'aide de dioxyde de carbone, tels que les procédés LignoBoost™ et LignoForce™, et d'acide sulfurique servant à la laver. Une approche électrochimique est proposée pour précipiter la lignine de la liqueur noire tout en produisant de la soude caustique. Ce procédé est basé sur l'utilisation de membranes cationiques. L'électrolyse de la liqueur noire réduit le pH au point de précipitation de la lignine. L'acide nécessaire au lavage de la lignine est produit par électrodialyse du sulfate de sodium qui génère de la soude caustique comme sous-produit. Le procédé ne requiert aucun produit chimique de source externe et ne génère aucun effluent additionnel. La technologie offre une augmentation de production de pâte pour les usines kraft normalement limitées par la capacité de la chaudière de récupération et le système de recaustification.

Dans la première partie de cette étude, nous avons étudié l'effet de divers paramètres d'opération sur la performance du procédé d'électrolyse de la liqueur noire incluant en particulier les réactions électrochimiques se déroulant aux électrodes, la distribution de la densité de courant et la contribution des différentes composantes individuelles de la cellule au voltage total du réacteur électrochimique.

En second lieu, le transfert de masse des ions les plus pertinents (Na^+ et H^+) migrant à travers la membrane ont été soigneusement modelés en se basant sur l'équation de transport de Nernst-Planck tout en tenant compte de l'équilibre ionique de Donnan entre deux milieux différents. Les profils de la concentration du sodium dans la membrane ainsi que les ions H^+ et le profil du pH ont été développés pour des conditions typiques d'opération. La performance de ce procédé membranaire a été évaluée à l'aide du coefficient de transfert de masse et de la productivité de la soude caustique.

Dans la troisième étape du projet, l'effet des paramètres d'opération les plus importants ont été identifiés et étudiés. Ces paramètres sont : la densité de courant, la concentration de soude caustique, le pH final de la liqueur noire ainsi que différents types et sources de liqueur. L'objectif ultime était d'optimiser les conditions d'opération.

Les résultats de ce travail montrent que l'intégration d'une bio raffinerie dans une usine de pâte kraft implique plusieurs étapes dont inévitablement un atelier de lignine. Ainsi, chacune des sous-étapes de la récupération de la lignine obtenue de l'électrolyse de la liqueur noire a été étudiée en détails, à savoir la coagulation, la précipitation, la filtration et le lavage du produit final. Les résultats expérimentaux ont montré que le taux de filtration du produit était relativement faible (64 kg/(h·m^2)), mais que l'addition de sulfate de sodium (120 g/L de Na_2SO_4) à l'étape de coagulation augmente le taux de filtration par un facteur de 7.5. Un temps de coagulation prolongé (4-5 h) améliore aussi la filtrabilité. La lignine récupérée peut être utilisée comme matière première par l'industrie chimique et comme bio-carburant dans le four à chaux à la place des combustibles fossiles comme l'huile lourde et le gaz naturel. Cette lignine, une fois lavée, possède une qualité adéquate pour la fabrication de polyuréthane. Si son contenu en sodium est de 0.64 % en poids après une seule étape de lavage, il est estimé qu'il serait possible de remplacer près de 50 % du combustible fossile du four à chaux par une telle lignine. Étant donné la sensibilité du four à chaux au contenu en sodium, une étape additionnelle de lavage permettant de faire chuter le taux en sodium pourrait conduire à substituer plus de 90 % du combustible fossile par cette lignine purifiée. Un bilan complet des composantes majeures (solides, sodium et soufre) a été effectué fournissant les données essentielles pour l'intégration du procédé au circuit de récupération des produits chimiques de l'usine.

La dernière partie de cette étude a permis de démontrer la faisabilité technique du traitement électrolytique de la liqueur noire (30 %) utilisant la cellule commerciale FM-21 qui a été développée originalement pour l'industrie du chlore-alkali. Cette démonstration peut être considérée comme une première mondiale dans le traitement de la liqueur noire. La cellule a été opérée pour un total de 38 heures durant lesquelles l'influence de la densité de courant (de 1.5 à 3.9 kA/m^2), la concentration de la soude caustique produite (de 5.4 à 9.5 %) et la température (de 62 à 71 °C) sur les performances de l'électrolyse ont été étudiées. Il a été démontré que la densité de courant est le paramètre principal qui détermine la performance du procédé. La meilleure productivité en termes de volume de liqueur noire traitée a été de 171 L/(h·m^2) en opérant à une densité de courant de 3.9 kA/m^2 et une température de 70 °C. La performance de l'électrolyse a aussi été déterminée par le taux de production de la soude caustique et l'énergie consommée pour produire une tonne de NaOH. Dans les conditions optimales d'électrolyse indiquées ci-dessus, la cellule produisait 6.0 kg of NaOH/(h·m^2) à une concentration de 5 % et consommait 4 030 kWh/t NaOH. Ces résultats sont comparables à ceux obtenus avec la cellule

de laboratoire. Il est recommandé de procéder à un lavage à contre-courant du compartiment anodique (liqueur noire) sur une base régulière avec de la soude caustique diluée afin de prévenir l'encrassement de l'anode et de la membrane et la perte de performance à long terme.

ABSTRACT

The biorefinery initiative in the pulp and paper industry aims at diversifying its product offering to include value-added biomaterials from lignin. The chemical approach to precipitate lignin from black liquor consists of reducing the pH using carbon dioxide such as LignonoBoost™ and LignoForce™ processes and, sulfuric acid to wash the lignin. We have developed an electrochemical technique to precipitate lignin from black liquor and simultaneously recover caustic soda. This proposed electrolytic treatment is based on the use of cationic exchange membrane. The electrolysis of black liquor reduces its alkalinity electrochemically to the point of lignin precipitation. It does not require chemicals from an external source and does not generate additional effluents. The technology entails an increased pulp production for Kraft mills that are limited by their recovery boiler capacity or their causticizing system.

First, in this study, the effects of various basic operating parameters on the performance of the electrolysis of black liquor were investigated; in particular the electrochemical reactions taking place in the cell, the current density distribution and the contribution of individual cell components to the total voltage of the electrochemical reactor.

Second, the mass transfer of most important ions through the membrane during electrolysis was modelled according to Nernst-Planck transport equation and Donnan phenomenon. We report on the investigation of sodium, protons, hydroxyls ions concentration and pH profiles across the membrane under typical operating conditions. This membrane process performance was evaluated based on mass transfer coefficient and caustic soda productivity.

In a third step, the effect of the most important operating parameters were investigated including current density, caustic soda strength, end pH and others during the electrolytic treatment of different types of BLs with the aim of optimizing the process.

The integration of a bio-refinery to a kraft mill site includes inevitably a lignin recovery plant. In a fourth step, the technical aspects of lignin precipitation from electrolysed BL were investigated: coagulation, precipitation, filtration and washing of the lignin product. The experimental results showed that the filtration rate is relatively low (64 kg/(h·m^2)), but adding Na_2SO_4 (120 g/L) during the coagulation step improves the rate by a factor of 7.5. A longer coagulation time (4-5 h) increases filtration rate as well. The lignin can be used as a feedstock for the chemical industry or as bio-fuel for the lime kiln. The washed lignin has an adequate purity for utilisation

in the chemical industry, for example, for making polyurethane. On the other hand, given the sensitivity of the lime kiln to sodium, it is estimated that the electrolysed lignin containing 0.64 % of residual sodium after one single water wash could replace about 50 % of the lime kiln fossil fuel. However, it can be expected that one additional water wash of the lignin cake would achieve a lower sodium level allowing for almost total replacement of fossil fuel.

A complete mass balance of the major components providing the required data for future work on the simulation of the integration of this process into a kraft mill has also been developed.

The last experimental work demonstrated the technical feasibility of the electrolytic treatment of black liquor from a kraft mill using the commercial FM-21 membrane cell that was developed originally for the chlor-alkali industry. This electrolytic treatment involves simultaneous desalkalinisation of 30 % solids black liquor at the anode and co-production of NaOH at the cathode. The cell was operated for a total of 38 hours during which the impact of current density (from 1.5 to 3.9 kA/m^2), NaOH strength (5.4 to 9.5 %) and temperature (62 to 71 °C) were investigated. The current density had the most impact on the process performance. The best productivity achieved in terms of black liquor treatment was 171 L of BL /(h·m^2) while running at 3.9 kA/m^2 and about 70 °C. Under these conditions, the cell was producing 6.0 kg of NaOH/(h·m^2) at 5 % NaOH strength and the energy consumption was 4 030 kWh/t NaOH. These results are compared to the experiments performed with a laboratory cell. It is recommended that the anode compartment being backwash on a regular basis with dilute caustic soda to prevent long term fouling of the anode and membrane.

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LISTE DES SIGLES ET ABRÉVIATIONS

A	Area
Ä	Angtröm
a_{H2}	Partial pressure of H_2
A_n	Anode
a_{O2}	Partial pressure of O_2
a_{OH-}	Chemical activity of OH^-
atm	Atmosphere
BL	Black liquor
BLS	Black liquor solids
BME	Bipolar membrane electrodialysis
C	Cathode
C	Concentration
CCC	Concentration critique de coagulation (Critical coagulation concentration)
C/D	Convection/Diffusion
CE	Current efficiency
cm^2	Centimètre carré (Square centimeters)
cm^2	MBP Membrane bipolaire
COV	Coefficient of variation
D	Diffusion coefficient
ΔC	Concentration gradient
ºC	Degré Celsius (Degree Celsius)
ºK	Degré Kelvin (Degree Kelvin)
ΔP	Pressure differential
ΔP_c	Pressure across the cake

ΔP_{fm}	Pressure drop through the filter medium,
ΔG^R	Gibbs free energy
$\Delta G°_{25}$	Gibbs free energy at 25 ºC
Δl	Anode or cathode compartment gap
ΔVol	Change of volume
DLVO	Derjaguin, Landau, Verwey, et Overbeek
DLCA	Diffusion limited cluster-cluster aggregation
D_H	Hydraulic diameter
ED	Électrodialyse (Electrodialysis)
E_e	Equilibrium reaction voltage
EL	Électrolyse (Electrolysis)
F	Faraday's constant
F(95 %)	95 % confidence level
g	Gramme (Gram)
GES	Gaz à effet de serre
GHG	Green house gas
h	Heure (Hour)
H	Cake thickness
HHRR	Hearth heat release rate
HW	Hardwood
HWBL	Hardwood black liquor
I	Current
J_{Na}	Flux of Na
κ	Electrolyte conductivity
K_B	Boltzman constant

kg	Kilogramme (Kilogram)
kJ	kilojoule
K_m	Mass of cake is proportional to the volume of filtrate
k_{Na}	Sodium transfer coefficient
kPa	Kilopascal
kW	Kilowatt
kWh	Kilowatt heure (Kilowatt hour)
L	Inter-electrode gap
L	Litre (Liter)
LN	Liqueur noire
m	Meter
M	Molaire (Molar)
mA	Milliampères (Milliamperes)
MC	Membrane cationique
M/C	Migration/Convection
M/D	Migration/Diffusion
meq	Milli-équivalent (Milli-equivalent)
mS	Millisiemens
N	Flux of species
N	Normale
N	Number of observations
N	Number of moles
$[Na^+]_{BL}$	Concentration of Na^+ ions in black liquor
$[Na^+]_{BL,M}$	Concentration of Na^+ ions in black liquor at the membrane interface
$[Na^+]_{M,BL}$	Concentration of Na^+ ions in the membrane at the black liquor interface

$[Na^+]_{NaOH}$	Concentration of Na^+ ions in caustic soda solution
NOSWBL	Non oxidized softwood black liquor
N_{Wa}	Wagner number
$[OH^-]_{BL,M}$	Concentration of OH^- ions in black liquor at the membrane interface
$[OH^-]_{M,BL}$	Concentration of OH^- ions in the membrane at the black liquor interface
OSB	Oriented strand board
OSWBL	Oxidized softwood black liquor
P_e	Peclet number
PPES	Poussières du précipitateur électrostatique
P(0.01)	Probability at 99% confidence
Q	Flow
Q	Flow rate
R	Coefficient of correlation
R	Gas constant
R	Electrical cell resistance
Re	Reynold number
REA	Residual effective alkali
RLCA	Rapid diffusion limited cluster-cluster aggregation
R_{Na}	Hydrated radius of sodium ion
rpm:	Révolution par minute (Revolution per minute)
s	Seconde (Second)
s	Standard deviation
Sc	Schmidt number
Sh	Sherwood number
SHE	Standard hydrogen electrode

SLCA	Slow reaction limited aggregation
$[SO_3^-]_{M,BL}$	Concentration of SO_3^- in the membrane
SW	Softwood
SWBL	Softwood black liquor
t	Tonne métrique (Metric ton)
T	Température (Temperature)
™	Trade mark
t_{Na}	Transport or transference number
t/V	Temps par unité de volume (V) de filtration (Time per unit V of filtration)
u	Electrolyte velocity in direction of flux
V	Voltage
v	Velocity
V_{BL}	Voltage drop across the black liquor compartment
V_D	Decomposition voltage
V_{BLML}	Voltage across the black liquor boundary layer next to the membrane,
V_M	Voltage across the membrane
V_{NaOHML}	Voltage drop through the caustic boundary layer at the membrane interface
V_{NaOH}	Voltage drop across the caustic compartment
Vol	Volume
V_{Tot}	Total cell voltage
W	Watt
WSA	Waste gas sulfuric acid
x	Distance
v	Electrolyte velocity
z	Charge number of a given species (Valence)

α_H	Specific filtering resistance
α_m	Cake resistance
β	Resistance of the filter media
δ	Film thickness
$\boldsymbol{\varepsilon}$	Over all compartment voidage
ρ	Density
Ω	Ohm
η_{An}	Anode overvoltage
η_{Cat}	Cathode overvoltage
$\emptyset$	Filter diameter
Φ	Potentiel électrique (Field potential)
Ψ	Potentiel chimique (Chemical potential)
$\psi_{BL,M}$	Chemical potential of black liquor at the membrane interface
$\psi_{M,BL}$	Chemical potential in the solid membrane phase at the BL interface
μ	Dynamic viscosity
ν	Kinematic viscosity

CHAPITRE 1 INTRODUCTION

L'introduction du bioraffinage dans l'insdustrie des pâtes et papiers comprend une approche d'optimisation d'intégration de procédés pour mieux rentabiliser cette industrie au Canada [1]. Cette industrie a toujours été à la recherche de nouvelles sources de revenus visant la production de bioproduits à haute valeur ajoutée. En effet, le concept de bioraffinage dans le secteur des pâtes et papiers n'est pas récent et date même de quelques décennies. Magdzinski [2] rapporte quelques exemples de bioraffineries intégrées aux usines de pâte et papier datant des années 1940 et 1950. Dès 1942, West Virginia Pulp and Paper Company (Westvaco, maintenant WestRock) à Charleston en Caroline du Sud opérait un atelier de lignine produisant de l'Indulin® [3] En 1944, la compagnie Howard Smith Co. produisait de l'éthanol et de la vanilline à partir des liqueurs usées du procédé de mise en pâte au sulfite. À cette même époque, cette compagnie avait développé un produit appelé Arborite™ [4] fabriqué à partir de lignine précipitée de la liqueur noire. Sous la direction de Domtar, le procédé de mise en pâte au sulfite fut converti à la mise en pâte kraft et la compagnie construisit un atelier de récupération de lignine sur le site de leur usine de pâte située à Cornwall en Ontario.

Cette tendance de diversification a récemment repris de l'intérêt dans le cadre du développement durable et de l'économie circulaire [5]. Le développement durable est une conception de la croissance économique qui s'inscrit dans une perspective de long terme et qui intègre les contraintes liées à l'environnement et au fonctionnement de la société. L'économie circulaire est un concept économique qui s'inscrit dans le cadre du développement durable et qui s'inspire notamment des notions d'économie verte, d'économie de l'usage ou de l'économie de la fonctionnalité, de l'économie de la performance et de l'écologie industrielle.

Cette diversification se fait particulièrement présente dans les usines de mise en pâte chimique de type kraft. L'usine de Thurso au Québec appartenant à Fortress Advanced Bioproducts (Fortress AB) Inc., une division de Fortress Global, s'est lancée dans la fabrication de xylitol, un édulcorant hypocalorique, produit à partir de la conversion des sucres d'hémicellulose extraits des copeaux de bois [6]. Ce nouveau produit permet de transformer l'usine de pâte kraft en une bio raffinerie alimentée en matière première de source organique renouvelable.

Domtar a annoncé la construction d'un bioparc comprenant une bio-raffinerie près de son usine de pâte kraft située à Windsor au Québec. La biomasse générée par la papetière sera transformée

en biomatériaux tel que la cellulose nanocristalline [7] ainsi que la production de bio-carburants pour maintenir sa compétitivité [8].

La lignine constitue de 18 à 35 % de la composition des copeaux de bois dépendamment de l'espèce et cette ressource naturelle est très convoitée pour alimenter les bios raffineries. La liqueur noire produite par le procédé de mise en pâte kraft est une source de matière première pour la production de biomatériaux à base de lignine. Un consortium norvégien composé de trois compagnies Preem, RenFuel et Rottneros a développé un bio-carburant à base de lignine, le lignol, pouvant servir de substitut au diesel. Une étude de faisabilité est en cours pour construire une usine de transformation de la lignine en bio combustible, une première mondiale [9].

En 2013, Domtar a démarré son usine de lignine située à Plymouth en Caroline du Nord aux États-Unis, d'une capacité de 75 t/jour d'un produit de lignine appelé BioChoice® Lignin [10]. Stora Enso produit de la lignine à l'échelle industrielle depuis 2015 à son usine de Sunila en Finlande [11]. C'est le plus grand producteur de lignine (140 t/jour) dans le monde, une partie en est utilisée pour fabriquer du Lineo, un substitut du phénol. La compagnie West Fraser Timber produit de la lignine (30 t/jour) à son usine de pâte kraft située à Hinton Alberta depuis mars 2016 [12]. Cette lignine sert de matière première pour la fabrication de colle utilisée dans la manufacture de panneaux à lamelles minces orientées (OSB)[1] [13].

Les procédés les plus répandus pour la récupération de lignine à partir de la liqueur noire sont : (1) la technologie LignoBoost [14] brevetée par LigninBoost AB et commercialisée par Valmet[2], et (2) LignoForce [15] développée par FPInnovations[3] qui est offerte par NORAM[4]. Ces deux technologies sont basées sur le procédé chimique de carbonatation de la liqueur noire qui en réduit le pH au point de précipitation de la lignine [16-18].

Ces procédés chimiques utilisant du CO_2 comme agent d'acidification font partie de la première génération de technologies de récupération de lignine et nécessitent des produits chimiques de sources externes comme l'acide sulfurique pour le lavage de la lignine et de la soude caustique comme appoint de sodium. Cette approche chimique souffre de limitations majeures pour leur

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[1] OSB : Oriented Strand Board
[2] http://www.valmet.com/products/pulping-and-fiber/chemical-recovery/lignin-separation/
[3] https://fpinnovations.ca/ResearchProgram/Pages/research-program-biorefinery-energy.aspx
[4] http://www.noram-eng.com/news-room/lignoforce.html

intégration durable dans une usine de pâte kraft particulièrement en ce qui concerne le circuit de liqueur de procédé affectant le bilan du soufre et du sodium [19].

La deuxième génération de technologies de récupération de lignine repose sur une approche électrochimique plutôt que chimique sans utilisation de produits chimiques de source externe [19]. L'électrolyse permet de réduire l'alcalinité et le pH de la liqueur noire au point de précipitation de la lignine. L'acide sulfurique requis dans l'étape de lavage provient du traitement du sulfate de sodium par électrodialyse à membranes bipolaires tout en produisant de la soude caustique utilisable directement pour combler les besoins de l'opération. Conséquemment, l'intégration de cette technologie dans une bio raffinerie élimine le besoin d'approvisionnement externe en produits chimiques en accord avec les principes du développement durable.

À date, aucune étude de l'électrolyse de la liqueur n'a été effectuée permettant de déterminer les phénomènes de transfert de masse dans la membrane et de fournir les données nécessaires pour le design et l'intégration judicieuse en usine de la technologie d'électrolyse pour la précipitation de la lignine. Cette présente étude porte sur le développement d'un procédé de traitement électrolytique de la liqueur noire comme moyen électrochimique de produire de la lignine à partir de la liqueur noire d'une usine de pâte kraft. La liqueur noire de bois résineux et de feuillus, soit oxydée ou non oxydée sera alors traitée dans une cellule d'électrolyse munie d'une membrane pour réduire le pH au point de précipitation de la lignine. Ensuite, cette liqueur électrolysée est soumise à une étape de coagulation suivie d'une filtration et d'un lavage de la lignine récupérée.

Les travaux de cette étude permettront de mieux comprendre les phénomènes de transfert de masse impliqués, d'optimiser les conditions d'opération et de générer les données nécessaires pour le design d'une installtion commerciale et de déterminer l'impact des bilans massique et énergétique sur le circuit de récupération. De plus, cette étude expérimentale permettra ultérieurement de positionner l'approche électrolytique par rapport à l'approche chimique de précipitation de la lignine.

Dans la première étape du présent projet, les phénomènes électrochimiques impliqués lors du traitement électrolytique sur le fonctionnement de la cellule seront été étudiés. Les réactions chimiques prenant place durant l'électrolyse seront analysées et interprétées. Le profil de la densité de courant le long de la cellule sera modélisé. La distribution du voltage total entre les

composantes individuelles de la cellule, les solutions et les réactions chimiques impliquées incluant l'influence du pH de la liqueur noire sur les performances de l'électrolyse seront étudiées.

Dans la deuxième étape du programme expérimental, les principaux phénomènes de transfert de masse impliqués dans ce procédé électro-membranaire seront étudiés en détails en utilisant l'équation de Nernst-Planck et en considérant l'équilibre de Donnan à l'interface des solutions et de la membrane. Le transport des ions sodium, des protons, des ions hydroxyles et le profil de leur concentration et du pH à travers la membrane cationique sera modélisé en utilisant des conditions expérimentales typiques d'opération.

Les travaux de la troisième partie de cette étude porteront sur l'optimisation du traitement électrolytique de la liqueur noire. L'effet des paramètres suivants sur la performance du procédé sera investigué : le type de liqueur noire, le pH d'opération, la densité de courant, la concentration de la soude caustique produite, la température des solutions et l'addition de sulfate de sodium à la liqueur. Les paramètres de performance qui seront évalués comprennent: l'efficacité du courant, la productivité de soude caustique et le débit de liqueur noire traitée par unité de temps et de surface de membrane.

Le quatrième volet du développement de la technologie portera sur la précipitation et la récupération de la lignine de la liqueur noire électrolysée incluant les étapes de coagulation, de filtration et de lavage. L'emphase sera portée sur la performance de l'étape de filtration et de lavage du produit final de lignine. L'effet des variables suivantes sur le taux de filtration sera investigué : (1) le temps de coagulation (2), le type de liqueur noire (3), la température (4), le niveau de vide (5), le pH final and (6), l'addition de sulfate de sodium. Les résultats de la performance de la filtration de la lignine seront comparés aux autres méthodes de précipitation telles que le CO_2 et l'acide sulfurique. Les résultats obtenus avec la lignine seront aussi comparés aux taux de filtration du $CaCO_3$ récupéré comme sous-produit dans l'atelier de caustification. La qualité de la lignine après lavage à l'acide et à l'eau sera déterminée. Un bilan détaillé des étapes d'électrolyse, de filtration et de lavage sera fourni dans le but de recycler et d'intégrer les filtrats au circuit de liqueur de l'usine kraft.

L’électrolyse de la liqueur noire se fera dans une cellule FM-21, fabriquée par Ineos, ont été désignées pour la production de chlore et de soude caustique et pour la production d’hydrogène en milieu alcalin.

La cinquième et dernière partie de cette étude consistera à démontrer la faisabilité technique du traitement électrolytique de la liqueur noire en utilisant la cellule commerciale FM-21 et à déterminer sa performance pour cette application. Les effets de la densité de courant, de la température et de la concentration de soude caustique sur la performance du procédé seront étudiés. Les paramètres de mesure de performance comprendront l’efficacité de courant, la consommation d’électricité, la productivité de soude caustique ainsi que le débit de liqueur noire traité par unité de surface de membrane et de temps. Les résultats obtenus avec la cellule commerciale FM-21 seront comparés à ceux de la cellule de laboratoire.

CHAPITRE 2 REVUE CRITIQUE DE LA LITTÉRATURE

2.1 Bref historique de la fabrication du papier

Le produit de papier a évolué de papyrus, à parchemin et finalement à papier [20]. Les premières feuilles de papier (dérivé de papyrus) sont fabriquées en Égypte antique à partir de fines bandelettes de papyrus. Toutefois, le processus moderne de transformation de la pâte en papier a été inventé en Chine à peu près au début de notre ère. Lorsque cette technique migre vers l'Europe à la fin du premier millénaire, les peaux d'animaux sont le matériau de choix pour fabriquer le papier qu'on appelle parchemin. Leur coût élevé mène à la recherche de matières premières plus abordables, à savoir de vieilles guenilles de coton et de lin. Au XIXe siècle on choisit le bois comme matériau plus économique. Les procédés de mise en pâte de la fibre de bois s'étendent de la séparation physique (mécanique) des fibres à la dégradation chimique et l'enlèvement de la lignine. Ils peuvent se diviser en trois grandes catégories : la mise en pâte chimique, la mise en pâte mécanique et la mise en pâte des fibres recyclées. Cette présente étude concerne le procédé de mise en pâte chimique kraft inventé par Dahl en 1879 dont le brevet a été publié en 1884 [21]. La première usine de pâte utilisant cette technologie fut ouverte en Suède en 1890 [22]. L'invention de la chaudière de récupération par G.H. Tomlinson [23] à la fin des années 1930 a été une étape importante dans l'avancement du procédé kraft. Elle a permis la récupération et la réutilisation des produits chimiques de façon qu'une usine de pâte à papier fonctionne presque en circuit fermé mise à part l'atelier de blanchiment.

Les pâtes chimiques sont utilisées largement dans la fabrication du papier mais sont aussi transformées en une vaste gamme de produits tels que les mouchoirs, le papier hygiénique. Dans le cadre de l'initiative de bioraffinage [1], de nombreuses recherches sont en cours visant la production de bioproduits à valeur ajoutée tels que les nanofibres, les biocombustibles et certainement la lignine.

2.2 Le procédé de mise en pâte kraft

Le procédé kraft consiste en une mise en pâte chimique reposant sur la cuisson de copeaux de bois dans un réacteur appelé "lessiveur" [24]. La cuisson s'effectue en présence d'une solution de sulfure de sodium (Na_2S) et d'hydroxyde de sodium (NaOH) à une température maintenue

entre 150-180 °C pendant une durée d'environ 2 à 3 heures. Le but de ce procédé est de réduire le contenu en lignine de la pâte pour en faciliter le blanchiment. Le rendement varie d'environ 42 à 55% due aux pertes de lignine et hémicellulose, dépendamment de l'espèce de bois et surtout de son contenu en lignine. La présence de sulfure de sodium dans la solution de cuisson améliore les propriétés physiques de la pâte ainsi que le rendement par rapport au procédé à la soude caustique. Certaines modifications ont été apportées au procédé kraft pour en améliorer le rendement : entre autres l'addition d'anthraquinone, de polysulfures et la délignification prolongée [24].

La pâte kraft blanchie est surtout utilisée dans la fabrication du papier d'écriture : livres, revues, photocopies et comme agent de renforcement dans d'autres papiers tels que le papier journal et le papier d'annuaires alors que la pâte non-blanchie est utilisée pour la fabrication de sacs et de boîtes de carton pour l'industrie de l'emballage.

2.3 Le système de récupération des produits chimiques

La liqueur usée provenant de la cuisson et les eaux de lavage d'une usine de pâte kraft sont récupérées pour former la liqueur noire faible qui est alimentée à l'entrée du système d'évaporation [25]. Cette liqueur contient les substances organiques dissoutes durant la cuisson et les produits chimiques essentiels pour la cuisson. Les deux principaux objectifs du système de récupération d'une usine kraft sont de produire de la vapeur à partir de la combustion des organiques et de convertir les produits chimiques de la liqueur noire pour en faire la liqueur de cuisson. Les principales unités d'un système conventionnel de récupération sont représentées à la Figure 4.1. Elles comprennent l'évaporation et la concentration de la liqueur noire, la combustion dans la chaudière de récupération, la caustification de la liqueur verte et la production de chaux nécessaire à l'étape de caustification [25, 26]. La chaudière de récupération est le cœur du système de récupération. Elle produit presque toute la vapeur de l'usine ainsi que de l'électricité grâce au système de cogénération.

La liqueur noire faible qui contient environ 15% de solides est alimentée dans le train d'évaporateurs à effets multiples pour en sortir avec une teneur en solides d'environ 50%. Cette solution plus concentrée appelée "liqueur noire forte" est alors soumise à une étape d'épaississement dans un concentrateur spécialement conçu pour amener la teneur en solides à

environ 70-75%. À une telle teneur en solides, la liqueur noire peut alors être brûlée comme un combustible dans la chaudière de récupération.

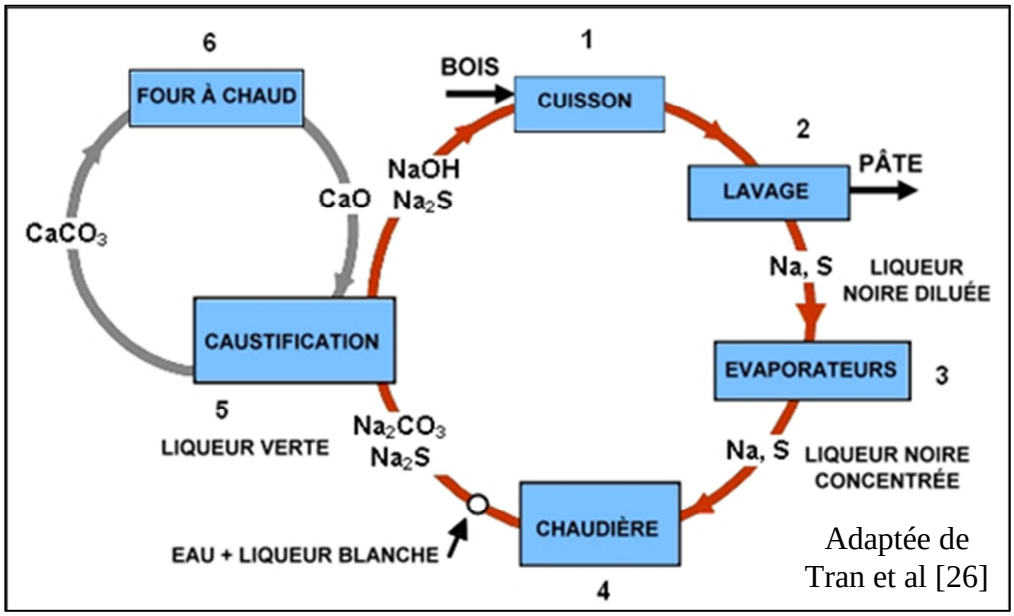

Figure 2.1 : Schéma du système de récupération d'une usine de pâte kraft

L'environnement réducteur maintenu au bas de la chaudière permet de convertir les composés oxydés de soufre de sodium (Na_2SO_4, $Na_2S_20_3$) en Na_2S. Le CO_2 produit par la combustion des matières organiques réagit avec les vapeurs de sodium pour produire du Na_2CO_3. La majorité de la quantité des deux sels fondus (Na_2S et Na_2CO_3) récupérés à la sortie de la chaudière sont dissous dans l'eau pour former la liqueur verte. Cette liqueur verte est alors alimentée au système de caustification où la chaux ajoutée convertit le Na_2CO_3 en NaOH et $CaCO_3$ selon la réaction suivante :

$$Na_2CO_3 + CaO \rightarrow NaOH + CaCO_3 \qquad (1)$$

La solution de Na_2CO_3 et de NaOH sortant de la caustification forme la liqueur blanche ou liqueur de cuisson. Le $CaCO_3$ est récupéré et traité dans un four pour produire de la chaux selon l'équation (2) :

$$CaCO \rightarrow CaO + CO_2 \qquad (2)$$

La partie des sels qui s'échappe avec les gaz de combustion est capturée par le précipitateur électrostatique pour être recyclé dans le circuit de liqueur noire. En bref, grâce au système de

récupération, la liqueur noire est reconvertie en liqueur de cuisson avec production de vapeur et, d'électricité pour les usines équipées d'un système de cogénération.

2.4 Options de précipitation de la lignine

La chaudière de récupération doit traiter la totalité de la liqueur noire provenant du procédé de la mise en pâte. La production de pâte des usines kraft est souvent limitée par l'engorgement thermique de cet équipement dispendieux. Dans certains cas, la charge de matières solides est une contrainte additionnelle à l'augmentation de production.

Le coût très élevé d'une nouvelle chaudière de récupération (au-delà de 100 M$ pour une usine de 1000 t/j de pâte) est un obstacle majeur pour répondre à une demande de production additionnelle. Il est pratiquement impensable de remplacer cette unité de façon rentable. Il est plus économique pour l'usine de maximiser la production en améliorant le système de récupération déjà existant à l'aide de technologies d'ajout telles que la précipitation de la lignine. L'extraction d'une partie de la lignine de la liqueur noire réduit la charge thermique entrant à la chaudière. Cette réduction de charge est alors compensée par une augmentation de la production de pâte générant une quantité additionnelle suffisante de liqueur noire pour rétablir la charge thermique à la chaudière. Plusieurs approches ont été proposées pour récupérer la lignine de la liqueur noire dont certaines ont été commercialisées. L'extraction de la lignine peut être accomplie par la réduction du pH de la liqueur noire au point de précipitation (pH 9.0-10.0) [14-17]. Elles peuvent être regroupées en deux approches majeures : l'acidification chimique et l'acidification électrochimique de la liqueur noire.

L'acidification chimique a été commercialisée bien que le nombre d'installations demeure limité. Elle consiste à neutraliser l'alcalinité de la liqueur noire par l'addition d'agents acidifiants tels que l'acide sulfurique et le dioxyde de carbone. D'autre part, l'acidification électrochimique qui vise aussi à réduire l'alcalinité de la liqueur noire pour précipiter la lignine, ne nécessite aucun ajout d'agents neutralisant de source externe. Quatre options électrochimiques se présentent pour réduire le pH de la liqueur noire au point désiré de précipitation de la lignine [19]: (1) l'électrodialyse conventionnelle de la liqueur noire, (2) l'électrodialyse à membranes bipolaires, (3) l'électrolyse directe de la liqueur noire et, (4) la production électrochimique d'acide sulfurique à partir du sulfate de sodium.

2.4.1 Options chimiques

La Figure 4.2 montre l'intégration d'un système de récupération de lignine par acidification chimique au circuit de récupération de liqueur noire d'un procédé kraft. Une fraction du débit de liqueur noire contenant 30 % de solides est déviée du circuit de récupération conventionnel et alimentée dans une étape d'acidification. La précipitation chimique de la lignine consiste à ajouter des agents acidifiants à la liqueur noire tels que l'acide sulfurique (H_2SO_4) et le dioxyde de carbone (CO_2) afin de réduire le pH au point de précipitation. La lignine est alors récupérée sous forme solide par filtration. À la sortie du système de séparation, on récupère d'une part une liqueur résiduelle (filtrat) appauvrie en lignine et d'autre part la lignine partiellement déshydratée. Le filtrat est retourné dans le circuit de liqueur noire de l'usine, plus précisément en amont du système d'évaporation. La lignine peut servir de combustible dans la chaudière à écorces et le four à chaux ou comme matières premières à un atelier de transformation chimique pour la production de produits dérivés à valeur ajoutée.

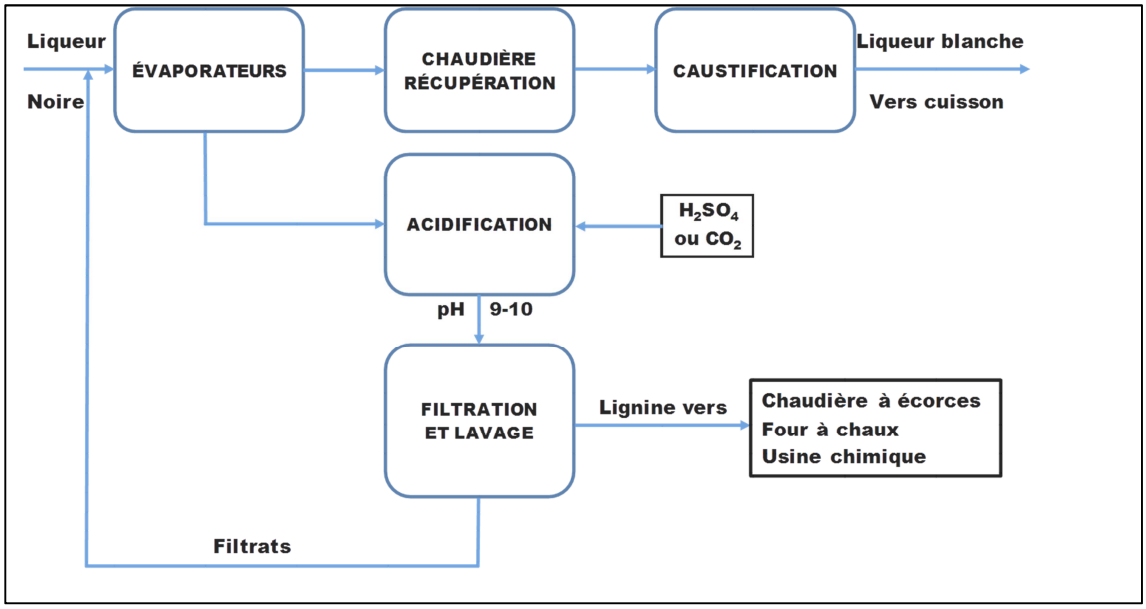

Figure 2.2 : Récupération de lignine par acidification chimique de la liqueur noire à l'aide d'acide sulfurique ou de dioxyde de carbone (CO_2)

2.4.1.1 Acide sulfurique (H_2SO_4)

L'acide sulfurique peut être utilisé comme agent d'acidification de la liqueur noire étant donné son contenu en soufre compatible avec la composante Na_2S de la liqueur de cuisson. L'acide chlorhydrique (HCl) est à éviter à cause de l'accumulation du chlore élémentaire dans le circuit

de récupération causant l'entartrage des échangeurs de chaleur de la chaudière en présence de potassium [26]. De plus, assumant que le filtrat contaminé de chlore puisse être déversé aux égouts, cette pratique génère des pertes considérables de sodium sous forme de chlorure de sodium qui doivent être compensées par l'addition de soude caustique (NaOH).

Bien que l'acide sulfurique soit acceptable dans le circuit de liqueur, toutefois il doit être accompagné de l'addition de sodium sous forme de NaOH pour maintenir le rapport Na/S spécifique à chaque usine. Cependant, la quantité d'acide permise est limitée aux pertes de soufre de l'usine. Au-delà de cette limite, la sulfidité[5] de la liqueur de cuisson dépassera les cibles opérationnelles. Alors, afin de maintenir cet équilibre (Na/S), l'excès de soufre doit être purgé en déversant aux effluents une partie des poussières récupérées par le précipitateur électrostatique traitant les gaz de combustion de la chaudière de récupération. Ces poussières essentielles au procédé de mise en pâte contiennent principalement du sulfate de sodium (94 %) et du carbonate de sodium (6 %) [27]. Cette pratique implique donc la perte simultanée de sodium qui doit être compensée par l'addition de NaOH. La rentabilité dépend fortement du coût des produits chimiques [17, 28-29].

Afin de minimiser l'impact négatif de l'utilisation d'acide sulfurique de source externe sur la sulfidité de la liqueur de cuisson, trois sources internes peuvent être considérées pour précipiter la lignine de la liqueur noire: (1) les rejets acides du générateur de dioxyde de chlore [30], (2) la conversion du soufre des gaz non condensables en acide sulfurique [31, 32] et (3), de l'acide sulfurique provenant de la conversion électrochimique du sulfate de sodium [33, 34].

Quelques vieilles usines kraft sont équipées d'un générateur de dioxyde de chlore de type Mathieson, Solvay et R2 d'ERCO[6] qui génèrent un effluent acide (GWA[7]) comme sous-produit de réaction de la production du dioxyde de chlore [35, 36]. Cet effluent peut contenir jusqu'à 500 g/L d'acide sulfurique [37] et autant de sulfate de sodium. Il sert d'appoint pour compenser les pertes de soufre et de sodium du circuit de liqueur. Cette source d'acide pourrait être déviée vers un atelier de précipitation de lignine [30, 38].

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[5] Sulfidité (%) = $Na_2S/(NaOH + Na_2S)$
[6] ERCO: http://www.ercoworldwide.com/index.php/company/company-overview/?lang=fr
[7] GWA : Generator Waste Acid

Andritz [31] a développé un procédé alternatif pour la précipitation de la lignine appelé WSA[8] lequel produit et utilise de l'acide sulfurique comme agent acidifiant. La particularité de cette approche réside dans le fait que l'acide sulfurique concentré est produite à l'usine même à partir des composés de soufre contenu dans les gaz non condensables générés durant la cuisson des copeaux de bois. Cependant, la capacité maximale d'un atelier de lignine est dictée par la production d'acide laquelle dépend directement de la quantité de composés sulfureux produite lors de la mise ne pâte et récupérée sous forme d'acide.

2.4.1.2 Dioxyde de carbone (CO_2)

L'utilisation du CO_2 comme agent d'acidification présente un avantage majeur par rapport à l'acide sulfurique. Le CO_2 lui-même n'affecte pas le bilan soufre-sodium de la liqueur. Par contre, le recyclage du filtrat de l'étape de lavage à l'acide présente le même inconvénient, mais à un moindre degré. Pour une efficacité optimale, le procédé au CO_2 doit opérer avec une liqueur contenant environ 30 à 35% de solides [16-18, 39]. Un pH final d'environ 9-10 semble être idéal pour l'étape de carbonatation donnant un rendement d'environ 65 à 75% et produisant ainsi une lignine plus facile à filtrer. En 2008, Araújo [40] rapporte une seule installation commerciale de précipitation de lignine kraft appartenant à WestRock, anciennement Westvaco, utilisant le CO_2 comme agent acidifiant. Kouisni [15] et Tomani [41] ont développé de récentes versions de cette technologie, LignoBoost® et LignoForce™ commercialisées par Valmet et NORAM, respectivement. Les différences majeures entre les deux technologies sont les suivantes : LignoBoost™ comprend une étape de remise en suspension du gâteau de lignine pour le lavage alors que dans le cas du procédé LignoForce® la liqueur noire est assujettie à une étape d'oxydation permettant d'améliorer la filtrabilité de la lignine.

En 2013, Domtar a démarré une usine de lignine appelée BioChoice® Lignin, située à Plymouth en Caroline du Nord aux États-Unis, d'une capacité de 75 t/jour [10]. Stora Enso produit de la lignine à l'échelle industrielle depuis 2015 à son usine de Sunila en Finlande. C'est le plus grand producteur de lignine (140 t/jour) dans le monde dont une partie est utilisée pour fabriquer du Lineo, un substitut du phénol [11]. La seule usine de lignine au Canada a été construite par la compagnie West Fraser Timber qui produit 30 t/jour à son usine de pâte kraft située à Hinton

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[8] WSA : Waste Gas Sufuric Acid

Alberta depuis mars 2016 [12]. Cette lignine sert de matière première pour la fabrication de colle utilisée dans la manufacture de panneaux à lamelles minces orientées (OSB) [12].

Toutefois, cette option chimique de précipitation de la lignine à l'aide du CO_2 ne s'applique pas nécessairement à toutes les usines. Certaines contraintes peuvent en limiter le potentiel tel que démontré dans le chapitre 2 de ce document.

2.4.1.3 Acides organiques

Namane et al [42] ont effectués des essais de précipitation de lignine utilisant non seulement des acides inorganiques (H_2SO_4) mais aussi des acides organiques tels que l'acide acétique, citrique et formique comme agents acidifiants. Ils ont constaté que la lignine précipitée avec les acides organiques contenait moins de soufre que celle utilisant de l'acide sulfurique, ce qui pourrait représenter un avantage pour certains produits dérivés de la lignine. Cependant, l'utilisation d'acides organiques augmente la charge thermique à la chaudière de récupération lorsque les effluents de filtrat sont retournés au circuit de liqueur. De plus, les acides organiques sont généralement plus dispendieux que les acides minéraux.

2.4.2 Options électrochimiques

La deuxième génération de technologies de récupération de lignine repose sur des traitements électrochimiques pour réduire l'alcalinité de la liqueur noire au point de précipitation de la lignine. Les procédés de traitement direct de la liqueur noire incluent : (1) le dessalement par électrodialyse conventionnelle, (2) l'électrodialyse à membranes bipolaires et (3) l'électrolyse à membranes. L'électrodialyse à membranes bipolaires et l'électrolyse récupère le sodium et le convertit en soude caustique alors que l'électrodialyse conventionnelle récupère le sodium sous forme de sels alcalins. De façon indirecte, le traitement électrochimique du sulfate de sodium est une option dérivée qui fournit l'acide sulfurique pouvant être utilisé comme agent acidifiant.

Les traitements électrochimiques tels que l'électrodialyse et l'électrolyse de liqueurs de cuisson usée de l'industrie des pâtes et papiers ont été proposés au début des années 1940 comme alternative au traitement chimique. Ces deux procédés ont été investigués dans le but de séparer et de récupérer des composés organiques d'abord de la liqueur résiduelle de la mise en pâte au sulfite [43-48] et puis de la liqueur noire de la mise en pâte kraft [49-80].

2.4.2.1 Électrodialyse conventionnelle de la liqueur noire.

La liqueur noire consiste en un mélange de matières organiques et inorganiques comprenant principalement les électrolytes alcalins suivants : NaOH, Na_2CO_3 et Na_2S [27] fournissant les cations de sodium et les anions HCO_3^-, HS^- et OH^-. L'électrodialyse (ED) conventionnelle permet une déminéralisation partielle de la liqueur noire, notamment par extraction des sels de sodium alcalins pour en réduire le pH afin de précipiter la lignine.

Contrairement à l'électrolyse, le traitement électrodialytique ne neutralise pas l'alcalinité de la liqueur noire. Il extrait les sels alcalins réduisant ainsi le pH de la liqueur noire. La cellule ED contient des membranes cationiques et des membranes anioniques (Figure 4.3) [19]. Les membranes cationiques étant chargées négativement sont perméables aux ions positifs de sodium (Na^+) et imperméables aux anions (HCO_3^-, HS^- et OH^-). Les membranes anioniques qui sont chargées positivement laissent passer les anions mais repoussent les cations. Les anions qui sont attirés vers l'anode traversent la membrane anionique pour se combiner aux ions sodium qui ont traversé la membrane cationique se déplaçant dans la direction opposée vers la cathode. Les sels extraits de la liqueur noire sont piégés entre les membranes du compartiment adjacent alimenté de liqueur noire jusqu'à leur sortie de celui-ci et contribuent à l'enrichir en sels alcalins pour ensuite être retournés au circuit de récupération. D'autre part, la liqueur noire appauvrie en sels est dirigée vers l'étape de précipitation de la lignine. Cette option du traitement électrochimique pause un problème d'entartage de la membrane anionique très sensible aux composés chargés négativement tel que la lignine. Lorsque le pH de la liqueur noire atteint 10-10.5, le voltage de la cellule augmente de façon drastique [19, 73] affectant directement la consommation d'énergie. Il est donc nécessaire de développer une méthode d'opération appropriée incluant un cycle de lavage pour éliminer ou réduire l'entartrage. De plus, l'électrodialyse qui opère à des densités de courant plutôt faibles (50 mA/cm^2) limitées par la membrane anionique comparé à l'électrolyse (300 mA/cm^2) requiert des surfaces de membranes nettement plus élevées. Par le fait même, plus d'empilements de membranes (stacks) sont requis nécessitant une plus grande surface de plancher affectant doublement les coûts d'une installation.

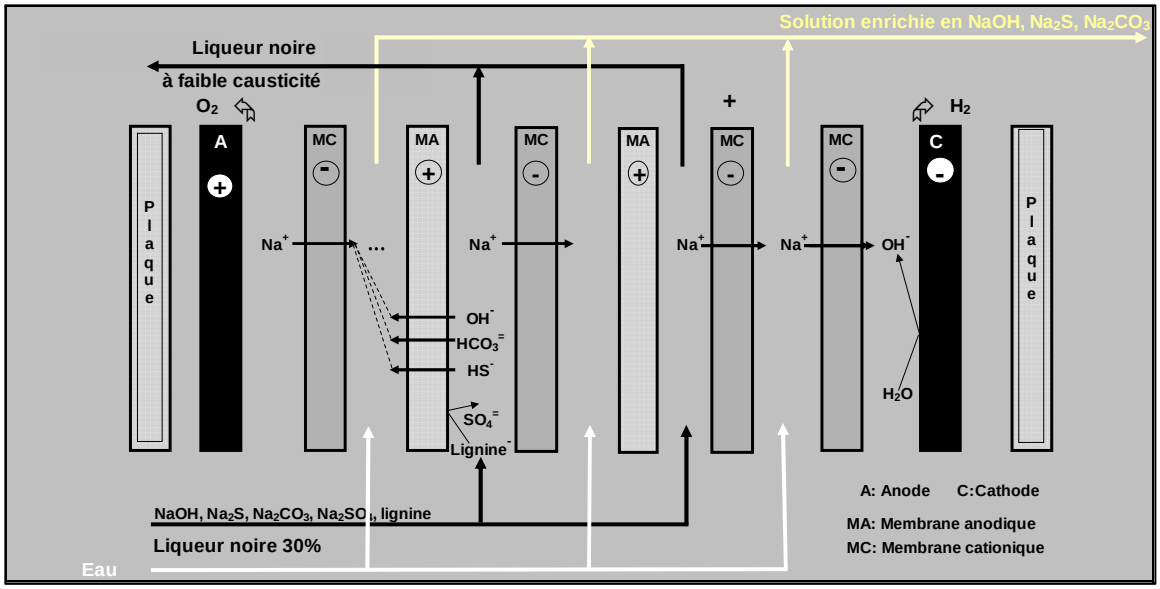

Figure 2.3 : Arrangement interne d'une cellule d'électrodialyse conventionnelle

2.4.2.2 Électrodialyse à membranes bipolaires

L'électrodialyse par membranes bipolaires est une option de traitement de la liqueur noire qui permet de baisser le pH à partir des ions H^+ générés par la membrane bipolaire (Figure 4.4). Cette membrane composite est formée d'une membrane anionique et d'une membrane cationique qui sont collées dont l'interface comprend un catalyseur. À cette interface, grâce au catalyseur, la molécule d'eau est séparée en ions hydroxyles (OH^-) d'une part qui traversent la membrane anionique pour se joindre aux ions Na^+ pour former de la couse caustique et d'autre part en ions H^+ qui traversent la membrane cationique pour neutraliser l'alcalinité de la liqueur noire. Il faut souligner que cette option ne requiert pas de membranes anioniques mais seulement des membranes bipolaires et cationiques moins susceptibles au colmatage en milieu organique. La faisabilité technique a déjà été démontrée dans les années 1990 [62]. Depuis, les membranes bipolaires se sont beaucoup améliorées. Cependant, selon l'étude de Haddad [77] pour l'acidification de la liqueur noire, le problème d'entartage causant une augmentation drastique de voltage s'est avérée similaire à l'application de l'électrodialyse conventionnelle malgré l'absence de membranes anioniques. Il est donc de mise d'étudier davantage ce phénomène pour développer une meilleure compréhension du mécanisme de colmatage.

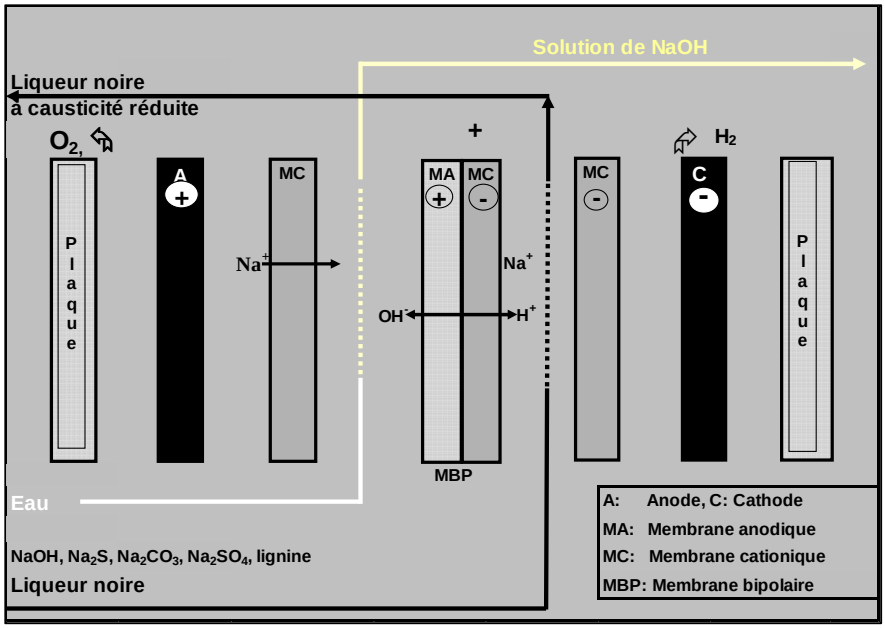

Figure 2.4 : Principe de l'électrodialyse de la liqueur noire à membranes bipolaires

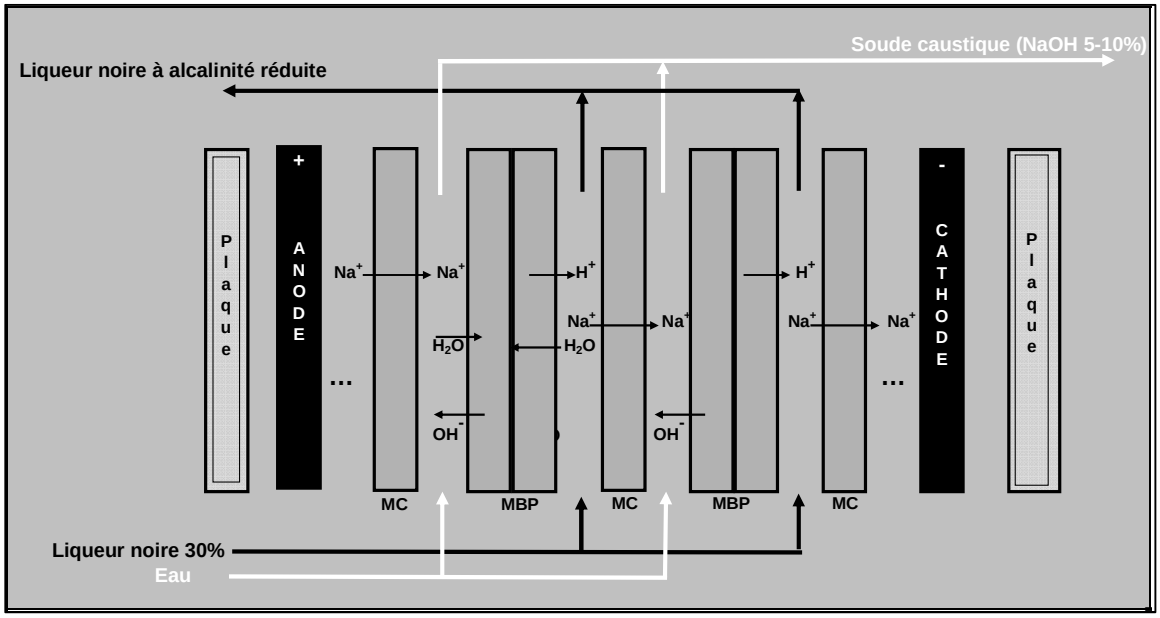

Figure 2.5 : Arrangement interne d'une cellule avec membranes bipolaires et cationiques pour le traitement de la liqueur noire (MBP : membrane bipolaire, MC : membrane cationique)

2.4.2.3 Électrolyse de la liqueur noire

Le pH de la liqueur noire peut être réduit par un traitement électrolytique en vue de la précipitation de la lignine. L'électrolyse de la liqueur est alors effectuée dans une cellule

comprenant une anode, une membrane cationique et une cathode (Figure 4.6). Un empilement (stack) peut contenir plusieurs dizaines de cellules unitaires (Figure 4.7). Dans ce procédé, l'alcalinité de la liqueur noire est réduite suite à la réaction des ions hydroxyles (OH^-) à la surface de l'anode formant de l'eau [81]. Cette réaction de désalcalinisation contribue à réduire le pH au point de précipitation de la lignine. Plusieurs études sur l'électrolyse de la liqueur noire ont été revues [19] rapportant l'effet de la densité de courant, du pH final, du type d'anode, du type de liqueur noire, de l'addition de sels, de la température et de la concentration du NaOH produit. La faisabilité technique du procédé a aussi été démontrée en opération continue [68, 74].

L'électrolyse de la liqueur noire joue deux rôles. D'abord, elle permet la précipitation de la lignine par désalcalinisation électrochimique. Simultanément, elle extrait le sodium de la liqueur noire pour le convertir sous forme de soude caustique. Il est à noter qu'avec l'électrolyse directe, il y a production d'hydrogène à la cathode et d'oxygène à l'anode. L'hydrogène peut être utilisé comme combustible dans le four à chaux alors que l'oxygène peut servir à oxyder la liqueur noire ou encore à l'atelier de blanchiment pour la délignification de la pâte [24].

Toutefois, malgré les nombreux bénéfices, les difficultés d'opération en mode continu et d'intégration au système de récupération conventionnel, semblent avoir été un frein à la commercialisation de cette technologie. Il est impératif d'avoir recours à un design de cellule adapté spécifiquement [65] à la liqueur noire à cause de son grand potentiel de colmatage. La cellule électrolytique doit pouvoir tolérer la présence de particules solides de lignine et le système doit aussi permettre le dégazage de la solution, voir le dégagement de l'oxygène formé à l'anode ainsi que le CO_2 généré suite à la décomposition du carbonate de sodium [74].

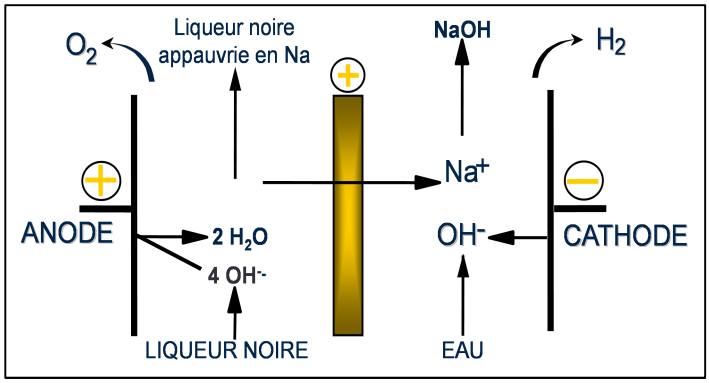

Figure 2.6 : Principe de l'électrolyse directe de la liqueur noire

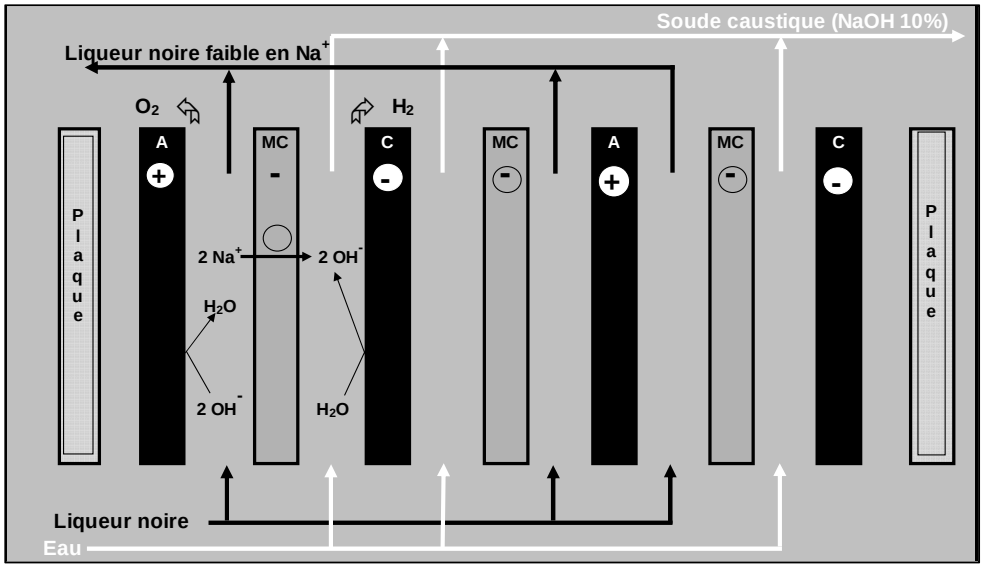

Figure 2.7 : Arrangement interne d'une cellule d'électrolyse pour le traitement de la liqueur noire (A : Anode, C : Cathode, MC : Membrane cationique)

2.4.2.4 Acide sulfurique de source électrochimique (Na_2SO_4)

La précipitation de la lignine peut être réalisée en abaissant le pH de la liqueur noire par l'ajout d'acide sulfurique tel que décrit à la section 1.4.1.1. Mais, l'acide peut être produit en usine par la conversion électrochimique du sulfate de sodium. Il existe deux sources de sulfate de sodium dans une usine kraft : a) les poussières collectées par le précipitateur électrostatique de la chaudière de récupération et, b) le résidu salin du générateur de dioxyde de chlore (ClO_2) [82]. La quantité totale de sels peut atteindre 180 kg/t dans les usines de pâte blanchie et non blanchie (Tableau 2.1). Dans les usines de pâte blanchie, les pertes de sel sont compensées par le recyclage d'une partie des rejets du générateur de ClO_2 alors que l'usine de pâte non blanchie doit combler ses pertes par un approvisionnement externe.

Tableau 2.1 : Sources de sulfate de sodium (t/j) dans une usine de pâte kraft

Sources	Usine de pâte non blanchie		Usine de pâte blanchie	
	Min	Max	Min	Max
PPES[9]	50	140	50	140
ClO_2	-	-	20	40
Appoint	20	40	-	-
Total	70	180	70	180

[9] PPES : Poussières du précipitateur électrostatique

Deux procédés de nature électrochimique peuvent être considérés pour la production d'acide sulfurique à partir de sulfate de sodium. Il s'agit de l'électrolyse membranaire et de l'électrodialyse à membranes bipolaires. Ces procédés impliquent la production simultanée d'acide sulfurique et de soude caustique. Seule l'option d'électrolyse est considérée ici produisant un acide de concentration suffisante. En effet, l'électrolyse peut produire de l'acide suffisamment concentré, jusqu'à 25 à 40 % [33, 82-83] alors que l'électrodialyse à membranes bipolaires est limitée à moins de 10 %, concentration au-delà de laquelle l'efficacité de courant est réduite en bas de 50 % [84] rendant l'application non rentable. Cependant, dans le contexte de la récupération de la lignine, cet acide bien que dilué, serait de concentration suffisante pour combler les besoins d'acide de l'étape de lavage de la lignine.

L'électrolyse du Na_2SO_4 produit de l'acide sulfurique, de la soude caustique, de l'oxygène et de l'hydrogène utilisable dans l'usine. L'acide peut être utilisé pour la précipitation de la lignine pour augmenter la production de pâte d'une usine dont la production est limitée par l'engorgement de la chaudière de récupération. La soude caustique et l'oxygène peuvent servir dans les étapes de blanchiment et l'hydrogène brûlé au four à chaux. La rentabilité du procédé de conversion du sel en produits chimiques seulement, sans l'option de précipitation de la lignine peut offrir un investissement intéressant dont la rentabilité dépend fortement du prix de l'acide et de la soude caustique [85]. L'utilisation de l'acide pour la précipitation de la lignine dans le but d'augmenter la production de pâte est une valeur économique ajoutée au procédé.

Il est important de souligner que la production d'acide et de lignine à partir du sulfate de sodium est limitée par la quantité de sel disponible dans l'usine. La disponibilité de sulfate de sodium est d'environ 0.1 t par tonne de pâte produite. Basé sur un taux de conversion de 60% du sel et une consommation d'acide de 0.6 t par tonne de lignine, on peut estimer que la quantité d'acide produite permettrait de précipiter 0.07 tonne de lignine par tonne de pâte. Cela signifie une augmentation potentielle maximale de production de l'ordre de 7%, en supposant que chaque tonne de lignine produite permet d'augmenter la production d'une tonne de pâte additionnelle. On peut donc conclure que l'utilisation du sulfate de sodium comme source d'acide offre un potentiel d'augmentation de production plutôt limité.

2.4.2.5 Design de cellules spécialisées pour le traitement de la liqueur noire

L'électrolyse peut être utilisée pour traiter la liqueur noire dans le but soit (1) de précipiter la lignine tel que décrit dans la section 4.4.2.3 ou (2), de l'oxyder en produits dérivés. Quant à l'électro-oxydation anodique, elle vise à modifier la lignine par dépolymérisation [76, 78] dans le but de la transformer en produits à valeur ajoutée tels que des acides organiques entre autres l'acide vanillinique et l'anthraquinone [71, 76].

Une première tentative du traitement électrolytique de la liqueur noire a été rapportée par Dyfverman en 1942 [49]. Depuis, quelques designs de cellules ont été proposés pour l'application dédiée spécifiquement à la liqueur noire. Le traitement électrolytique de la liqueur noire représente un plus grand défi technologique que les applications électrochimiques conventionnelles telles que la production de chlore ou d'hydrogène. Durant le traitement électrolytique de la liqueur noire, la lignine tend à précipiter sous forme de particules colloïdales [18, 86] pouvant causer l'entartrage du compartiment anodique. Il est alors essentiel que le design de la cellule assure une vitesse suffisante du fluide pour maintenir les particules en suspension pour prévenir la sédimentation dans le compartiment et éventuellement le blocage de celui-ci.

Le premier concept breveté du traitement électrolytique de la liqueur noire pour précipiter la lignine a été attribué à Kennedy and Jernigan en 1959 [50]. L'équipement proposé comprenait un tambour rotatif servant d'anode lequel est trempé partiellement dans un bassin de liqueur noire. Lorsque le courant est appliqué à l'électrolyte, une mince couche de matériel ligneux se dépose sur l'anode. Le film de lignine est arrosé avec de l'eau pour le ramollir et est subséquemment enlevé à l'aide d'un grattoir. Aucune application commerciale de ce dispositif n'a été rapportée.

La cellule électrolytique développée par Edel et al [59] comprend un compartiment anodique séparé de la cathode par une membrane. La liqueur noire alcaline est désalcalinisée à l'anode où le pH descend au point de précipitation de la lignine. Une mousse brune légère est formée et flotte à la sortie de la cellule où la lignine est récupérée. La particularité de ce design est la flottation du produit de lignine dans le compartiment anodique alors que l'on fait appel à la sédimentation dans les procédés conventionnels de précipitation de la lignine. Aucune application commerciale de ce design de cellule n'a non plus été rapportée.

Azarniouch et Prahacs [64] ont proposé un procédé électrolytique pour extraire la lignine de la liqueur en utilisant deux étapes d'électrolyse. Leur brevet repose plutôt sur les conditions de traitement et les bénéfices de la technologie sans mention du type de cellule ni des détails sur le design de la cellule utilisée. Par contre, subséquemment, Cloutier et al [66-68] ont repris le concept pour investiguer la performance du procédé utilisant la cellule de laboratoire MP fabriquée par ElectroCell A/S[10]. L'inconvénient majeur de cette cellule est la consommation plus élevée d'énergie dû d'abord aux compartiments anodiques et cathodiques plus épais causant un voltage plus élevé et puis la présence d'un promoteur de turbulence qui a tendance à s'encrasser de particules de lignine.

Herron et al. [65] ont développé une cellule d'électrolyse spécifiquement pour le traitement de la liqueur noire. La particularité de la cellule repose sur un design à haute turbulence à la surface de la membrane avec un changement continu de direction créé par la forme ondulée du compartiment anodique. La cellule comprend une rangée d'anodes tubulaires entourées par deux membranes cationiques. Cette configuration crée un passage étroit (4 mm) pour la liqueur noire et un écoulement turbulent permettant de maintenir les particules colloïdales de lignine en suspension. Des essais pilote en usine ont été effectués [87], mais aucune installation commerciale n'est connue à date.

Stiefel et al. [76] proposent un design unique de cellule pour le traitement de la liqueur noire dont le but est la dépolymérisation de la lignine. Leur objectif n'est donc pas simplement de précipiter la lignine mais plutôt de briser les molécules de lignine et de récupérer des produits dérivés à valeur ajoutée. La cellule comprend deux anodes cylindriques et une membrane tubulaire de nano-filtration en céramique. Une membrane anionique entoure la membrane de céramique entre la cathode et le perméat contenant le produit dérivé de lignine. Ce design requiert des efforts additionnels de développement avant d'atteindre la commercialisation.

Belo et al. [80] revendique d'avoir développé un nouvel électrolyseur pour le traitement de la liqueur noire qui permet de récupérer la lignine par électrodéposition. Cet électrolyseur est basé sur le design de la cellule électrochimique de type filtre-presse. Le principe semble similaire au design de Kennedy [50] où la lignine se dépose sur l'anode. Un grattoir est nécessaire pour

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[10] http://www.electrocell.com/products/electrochemical-flow-cells/electro-mp-cell

enlever la lignine de la surface de l'anode. Comme avantage, il apparaît que cette approche ne requiert pas de système de filtration. Il n'y a aucune mention de la méthode de récupération et de lavage de la lignine. Il est évident que cette technologie est encore au stade expérimental.

2.4.2.6 Le choix de la cellule commerciale FM-21

Aucune des cellules électrolytiques décrites précédemment ont le stade de la commercialisation pour le traitement de la liqueur noire. Par contre, la cellule FM-21 semble être un candidat d'électrolyseur commercial approprié pour le traitement de la liqueur noire grâce à sa praticabilité et sa versatilité [88, 89]. Cet électrolyseur a été développé par ICI (maintenant INEOS) dans les années 1980 pour la production de chlore et est offert par INOVYN [89], une filiale d'INEOS. Quelques aspects de sa praticabilité incluent : (1) un design compact, (2) des électrodes uniques de type lanterne, légères et faciles à remplacer sans le besoin d'un pont roulant pour les soulever, (3) les lanternes sont fabriquées en pressant une feuille métallique simplifiant le surfaçage et, (4) le design innovant des électrodes lanternes permet de remplacer la plomberie externe par un collecteur interne des écoulements dans la cellule. La versatilité des applications comprend entre autres : la production de chlore et de soude caustique, de chlore et d'hydroxyde de potassium (KOH), de polysilicone, d'hypochlorite de sodium [89] et, d'acide sulfurique et de soude caustique à partir du sulfate de sodium [33, 82].

La cellule FM-01 (64 cm^2 par unité cellulaire) représente la version laboratoire de la cellule commerciale FM-21 (2 100 cm^2 par unité cellule unitaire) correspondant à un facteur de mise à l'échelle de 33. Les résultats expérimentaux peuvent être facilement extrapolés à la version commerciale avec confidence selon le concept de similarité développé par Sulaymon [90] et basé sur les similarités : (1) géométriques, (2) cinétiques et, (3) de distribution de courant et de potentiel électrique.

Les cellules FM01 et FM-21 ont fait l'objet de nombreuses études pour diverses applications [91, 92]: du lignosulfonate à la vanilline [93], l'oxydation des ions cérium [94], les dérivés de la catecholamine [95], l'oxydation des composés de crésol [96], l'oxydation destructive des teintures indigo dans l'industrie du textile [97-99] du crésol et de la vinasse [100], l'enlèvement de l'arsenic [101], la réduction des ions de ferricyanide en ions ferrocyanide [102] et, la réduction des ions de cuivre [103]. Ces deux cellules ont été grandement caractérisées en termes

d'hydrodynamique, de mélange turbulent, de transfert de masse, de performance et de mise à l'échelle [90, 92, 104-118].

2.5 La modélisation des phénomènes de transport dans la membrane

Le transport de masse dans les cellules électrochimiques est le résultat de trois phénomènes : (1) la diffusion, (2) la migration due au potentiel électrique et, (3) la convection [81]. Le transport d'ions dans une membrane échangeuse d'ions est décrit par l'équation de Nernst-Planck [12]. Carlberg [119] propose un modèle simplifié de transport de masse basé sur l'équation de Nernst-Planck dans laquelle il réduit le nombre de dimensions dans la géométrie et le nombre de variables. Il a développé trois rapports adimensionnels pour caractériser chacun des phénomènes impliqués dans le transport d'ions : (1) le rapport convection/diffusion (C/D) correspondant au nombre de Péclet, (2) le rapport migration/diffusion (M/D) et (3) le rapport migration/convection (M/C). Cette simplification lui a permis de développer une solution analytique permettant de développer le profil de la concentration des ions à travers la membrane en opération de régime permanent.

Tel que proposé par Moshtari Khah [120], les calculs du profil de la concentration des ions dans la membrane doivent absolument tenir compte de l'effet Donnan qui sévit aux interfaces solutions-membrane causant un saut de concentration entre les deux media. Ce phénomène concerne le comportement des particules chargées proches d'une membrane semi-perméable qui parfois ne sont pas distribuées également de chaque côté de la membrane. La cause principale est la présence de différentes substances chargées qui ne peuvent pas traverser la membrane (protéines ou ions non diffusibles), ce qui crée une charge électrique inégale. L'effet Donnan crée ce gradient subi de la concentration entre le liquide et la membrane selon le potentiel d'équilibre chimique. L'équilibre de Donnan est basé sur le fait que le potentiel chimique (ψ), par exemple, dans la phase liquide à l'interface liquide-membrane est égal au potentiel chimique dans la phase solide de la membrane à cette interface.

Moshtarikhah [121] rapporte que la différence dans la composition de l'anolyte affecte la conductivité de la membrane et donc la perte de voltage à travers celle-ci. En effet, l'auteur a observé que lors des essais avec des concentrations différentes de l'anolyte et du catholyte, la concentration de l'anolyte avait une forte influence sur la conductivité de la membrane. De plus, une augmentation de la concentration de la solution de NaOH résulte en une baisse de la

conductivité de la membrane et augmente ainsi la chute de voltage à travers la membrane. La conductivité de la membrane atteint un maximum à une concentration de NaOH de 15 % correspondant à la conductivité typique de la soude caustique. Concernant l'effet de la température sur l'efficacité de courant du procédé d'électrolyse à membranes, Moshtarikhah [121] explique qu'une température plus élevée augmente la mobilité des ions favorisant le transport des ions.

2.6 La précipitation et la filtration de la lignine

2.6.1 Coagulation brownienne

La précipitation et récupération de la lignine de la liqueur noire requiert une étape de coagulation sans égard à la technique utilisée: l'acidification au CO_2, à l'acide sulfurique, la désalcalinisation par électrodialyse conventionnelle ou électrolyse ou, l'acidification par électrodialyse à membranes bipolaires. En fait, la lignine commence à précipiter de la liqueur noire à pH 10.5-11.0 [86] formant de fines particules colloïdales. Ces particules sont très difficiles sinon impossibles à filtrer bloquant les pores du filtre. Une étape de coagulation est nécessaire pour promouvoir la croissance de gros flocs volumineux facilitant la filtration.

La coagulation et la précipitation de la lignine sont causées par un mouvement aléatoire continu des particules qui entrent en collision pour finalement se coller ensemble, appelé la coagulation brownienne et formant ainsi une agglomération de grosses particules [122]. Le phénomène consiste en un processus physique de collisions inélastiques et de l'attachement de particules les unes sur les autres [123]. Le mouvement brownien thermique de particules accompagné de turbulence, de champs de cisaillement, et de forces externes telles que gravitationnelle et électrique peuvent causer la coagulation [123]. Heine et al. [124] ont rapporté que plus la concentration de particules en suspension est élevée (jusqu'à 35 %) meilleur est le taux de coagulation dû à la plus grande probabilité de collisions. Kannangara [18] explique que durant l'acidification de la liqueur noire au CO_2, la lignine est déstabilisée et que les particules colloïdales portant des charges électriques commencent à se former à pH 10.8.

Le taux de coagulation de la lignine peut être prédit par la théorie DLVO[11] développée à la fin des années 1940 par Derjaguin et Landau en 1941 et Verwey et Overbeek en 1948 [123]. Trefalt [125] a formulé un sommaire du concept DLVO. Il y est postulé que les forces d'interactions dans une suspension aqueuse colloïdale peuvent être approximées par une superposition des forces de Van der Waals et des forces inhérentes à la double couche lesquelles doivent être réduites afin de favoriser l'agrégation des particules. Norgren [86] a appliqué ce concept à une solution de lignine kraft et mentionne que l'efficacité de la coagulation de la lignine dépend de la température, de la force ionique et du pH. Le taux de coagulation peut être amélioré en augmentant la force ionique de la solution par l'addition d'un sel à la concentration critique de coagulation (CCC) [86, 126] laquelle varie d'un sel à l'autre.

Durant l'étape de coagulation, une agitation légère doit être maintenue en opérant l'agitateur à faible vitesse durant la coagulation afin de garder un régime laminaire dans la solution. Par contre, le niveau d'agitation doit être suffisamment élevé pour favoriser la collision des particules contribuant à la formation de gros flocs sans les briser mais pas trop lent pour éviter la sédimentation et maintenir les particules de lignine en suspension [127-129]. Lors de l'optimisation de l'étape de filtration, Kannangara [18] rapporte qu'une vitesse de rotation de 122 révolutions/min fournit la meilleure performance de filtration.

Deux régimes de cinétique ont été identifiés pour expliquer l'agrégation causée par le mouvement brownien : (1) diffusion rapide limitée par l'agrégation de grappes et (2) l'agrégation limitée par la vitesse de réaction. La CCC est en fait déterminée au point de changement de régime passant d'un processus limité par la réaction tranquille à un processus limité purement par la diffusion. Cette transition de régime a été bien illustrée par l'addition de 1.3 M NaCl à une solution de lignine de type Indulin® Kraft at pH 10.5 and 70°C [18, 86]. À plus grande force ionique de la solution de plus gros agrégats sont formés favorisant le taux d'agrégation. Norgren [86] a aussi rapporté qu'une augmentation de la température diminue la CCC. Malheureusement, l'utilisation de NaCl n'est pas acceptable dans une usine kraft. Les chlorures en présence de potassium peuvent causer un entartrage sévère des échangeurs de chaleur de la chaudière de récupération [26, 27]. En pratique, le Na_2SO_4 disponible en grande quantité et déjà présent dans la liqueur noire serait d'usage acceptable et inoffensif pour la chaudière de récupération. Mais, sa

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[11] DLVO : Derjaguin, Landau, Verwey, et Overbeek

concentration doit être maintenue en dessous de sa solubilité pour éviter sa cristallisation dans les évaporateurs [29].

2.6.2 Théorie et modes de filtration

L'équation fondamentale de filtration dérivée de la loi de Poiseuille et Darcy décrit l'écoulement d'un fluide à travers un médium poreux [130-131]. Quatre modèles sont proposés par Ripperger et al [130]: (1) filtration par le gâteau, (2) filtration bloquante, (3) filtration en profondeur et, (4) filtration tangentielle. Le mode de filtration par le gâteau lui-même est le modèle le plus utilisé. Dès que la première couche de gâteau est formée sur le filtre, la filtration est accomplie par le gâteau lui-même et le filtre joue un rôle de support physique seulement. Ce modèle présente les avantages suivants: (1) simplicité, (2) un seul et unique filtre pour la filtration, le lavage et l'essorage, (3) application d'une pression négative ou positive sur le gâteau. Dans le cas d'une filtration sous vide, la différence de pression est évidemment limitée conséquemment le taux d'humidité du gâteau est plus élevé qu'avec un filtre à pression [130].

Ripperger [130] propose une méthode simple pour estimer la résistance du médium filtrant et celle du gâteau. Il s'agit de tracer les données de t/V vs V obtenues lors d'un essai de filtration, où t est le temps pour collecter le volume V de filtrat. Normalement, la courbe représente une ligne droite, mais cette courbe peut dévier de la linéarité dépendamment du mode de filtration. Dans le cas de la filtration du $CaCO_3$, un produit commun et familier à l'atelier de caustification d'une usine de pâte kraft, la courbe de filtration dévie d'une droite au-delà d'une certaine épaisseur du gâteau [131]. Selon Ripperger [130], cela signifie que l'opération comprend une combinaison de modes de filtration. Il explique cette déviation par la présence de fines particules se déplaçant à travers le gâteau et bloquant les pores de celui-ci ou celles du filtre. Le processus peut être caractérisé comme une filtration bloquante au-delà d'une certaine épaisseur de gâteau provenant du volume correspondant de filtrat collecté.

Ripperger [130] suggère aussi la formulation d'un indice pour évaluer la filtrabilité d'un produit. Cet indice consiste au produit de la résistance du gâteau par la viscosité du filtrat. Il a déterminé que la plage de l'indice varie de 10^8 pour une filtration rapide à 10^{13} pour un produit pratiquement non filtrable. Il est connu que la filtration de la lignine peut être lente dépendamment des conditions de coagulation et de filtration. De nouvelles techniques se sont

développées pour améliorer le taux de filtration. Entre autres, Kouisni [15] a démontré que l'oxydation avancée de la liqueur noire permet d'améliorer substantiellement la filtrabilité.

Le pH final de la liqueur noire acidifiée affecte le taux de filtration de la suspension de lignine et son impact a été minutieusement investigué [15, 40, 132]. Par exemple, Öhman [132] a montré que plus le pH est élevé plus la résistance de filtration est importante et conséquemment, plus le taux de filtration est faible. Cependant, Kannangara [18] rapporte que le pH a relativement peu d'influence sur le taux de filtration.

La plupart des gâteaux sont compressibles se caractérisant par une porosité qui décroît et une résistance à la filtration qui augmente avec la pression. La compression du gâteau est causée par la contrainte de compression sur la structure des particules, laquelle est causée par les forces de traînée du liquide [130]. La compressibilité peut être démontrée expérimentalement en variant le niveau de vide ou de pression appliqué au gâteau. Si le gâteau est compressible, une augmentation de la différence de pression d'un facteur x se traduit par une augmentation du taux de filtration d'un facteur inférieur à x.

La qualité de la lignine est très importante pour son utilisation comme matières premières et dépend essentiellement de l'efficacité des étapes de lavage. Selon Heiskanen [133], une lignine de haute pureté devrait contenir moins de 1.0 % de cendres et préférablement moins que 0.5 % pour certaines utilisations.

Après filtration de la suspension de lignine, la remise en suspension du gâteau a été proposée pour améliorer l'efficacité de lavage produisant ainsi une lignine de haute pureté avec une faible teneur en sodium. Öhman et al [132] ont développé une nouvelle méthode de lavage produisant une lignine de haute pureté. Il recommande que le pH final des eaux de lavage acides soit inférieur à 3.75 pour une meilleure efficacité de lavage. Une plus faible teneur en sodium peut aussi être obtenue en augmentant le nombre d'étapes de lavage [30, 41, 132, 134] ou en soumettant le gâteau de lignine à un champ électrique [133].

2.7 L'impact sur l'opération de l'usine

L'intégration d'une bioraffinerie dans une usine de pâte kraft comprenant un atelier de récupération de lignine affecte la plupart des unités opérationnelles spécialement si une augmentation de production de pâte est considérée. Plusieurs usines souhaiteraient augmenter

leur production de pâte mais la capacité de la chaudière de récupération à brûler la liqueur noire additionnelle est limitée par la charge thermique. La solution la plus convoitée par l'industrie est de réduire la charge organique donc thermique. La méthode la plus commune est l'extraction de la lignine puisque parmi les composés de la liqueur, la lignine représente le constituant majeur (30-45%) de la liqueur avec un pouvoir calorifique le plus élevé (25 110 à 26 900 kJ/kg) après les substances extractibles (16 220 à 37 710 kJ/kg) [27]. Quant aux substances extractibles, elles ne constituent que 3 à 5 % de la composition de la liqueur noire et leur présence n'est pas en quantité suffisante dans la plupart des usines puisque la teneur dépend des espèces de bois.

2.7.1 Chaudière de récupération

Il existe certaines limites physiques à pousser la capacité d'une chaudière de récupération à brûler de la liqueur noire. La surface du foyer de la fournaise, le volume de la cavité et la dimension du tambour à vapeur imposent des limites pratiques au débit de liqueur noire que peut traiter une chaudière [135]. Välimäki et al [136] ont trouvé que le taux de dégagement de chaleur du foyer (HHRR[12]) et la température adiabatique de la chaudière sont des paramètres critiques qui déterminent la quantité maximale de lignine qui peut être extraite basée sur le pouvoir calorifique minimum de la liqueur résiduelle à brûler. Cependant, l'ultime limite d'une chaudière est la production de vapeur dont le maximum est dicté par la capacité nominale du design original qui a parfois été bonifié. Cette limite ne peut être dépassée en aucun temps pour des raisons de sécurité et d'assurance. En pratique, cela se traduit par une charge thermique maximale qui limite le débit de liqueur noire entrant dans la chaudière et conséquemment plafonne la production de pâte.

L'une des stratégies adoptées consiste à extraire la lignine de la liqueur noire pour en abaisser la valeur calorifique et réduire ainsi la charge thermique à la chaudière [17-18, 30]. Cependant, cette approche réduit la puissance disponible créant un déficit de vapeur pour l'opération. La puissance énergétique nominale de la chaudière est alors rétablie en augmentant la production de pâte générant ainsi une quantité additionnelle de liqueur noire suffisante mais toutefois sans dépasser la charge thermique maximale permise.

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[12] HHRR : Hearth heat release rate

Benali et al [137] ont établi que la valeur calorifique minimale de la liqueur noire qui garantit une opération efficace et sécuritaire de la chaudière est d'environ 12.5 kJ/kg. Basé sur cette limite calorifique inférieure, on estime qu'il est possible d'atteindre les 15 % d'augmentation de production de pâte. Cependant, il faut s'assurer que la valeur limite inférieure du HHRR établie à 2.5 W/m^2 et la température adiabatique minimum opérable de 1 450 °C soient respectées [136].

Les taux d'extraction peuvent atteindre 60 % selon la limite physique des équipements [136]. Cependant, à 30 % d'extraction, la partie inférieure de la chaudière de récupération commence à montrer des signes de problèmes opérationnels. À 40 % d'extraction, la limite du surchauffeur est atteinte [138]. À 50 % d'enlèvement de la lignine, il est possible de maintenir la température adiabatique requise, mais le débit du salignon en fusion (smelt[13]) devient un facteur limitant [136]. Afin de maintenir la limite inférieure du taux de dégagement de chaleur du foyer, on ne peut dépasser un taux d'extraction de lignine de plus de 50 %. Vakkilainen, and Välimäki (2009) [138] ont étudié l'effet d'augmenter le débit de liqueur noire dans la chaudière pour conclure que la limite des surchauffeurs pouvait tolérer 60 % d'extraction de lignine. Cependant, pour des taux d'extraction élevée de la lignine dépassant les 10-15 %, il est possible que des modifications majeures s'imposent dans les unités adjacentes de production.

2.7.2 Évaporateurs

L'augmentation seule de production de pâte de 10 ou 15 % génère autant de liqueur noire faible additionnelle créant une surcharge équivalente aux évaporateurs. À cette charge additionnelle s'ajoutent les eaux de lavage de la lignine si elles sont retournées au circuit de liqueur noire. La pratique actuelle des installations existantes utilisant le CO_2 comme agent acidifiant est de les déverser à l'effluent dû au problème de bilan de soufre et sodium engendré par l'utilisation au lavage d'acide sulfurique de source externe tel que discuté antérieurement. Dans le cadre du développement durable, l'option électrochimique [19] bénéficie de l'avantage de pouvoir recycler les eaux de lavage. Conséquemment, la charge additionnelle aux évaporateurs sera d'autant plus élevée et nettement supérieure à celle rapportée par Périn-Levasseur [139]. Cependant, l'approche électrochimique de précipitation de la lignine peut compter sur le bénéfice de

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[13] Smelt : sels fondus récupérés de la combustion de la liqueur au bas de la chaudière de récupération pour former la liqueur verte

réduction de la viscosité suite au traitement électrolytique [86] et de la réduction de la teneur en lignine [140] pour récupérer une certaine capacité d'évaporation. Le traitement électrolytique peut réduire la viscosité de la liqueur noire concentrée par un facteur de dix [87]. Une réduction de la viscosité de la liqueur noire par un facteur de cinq double la valeur du coefficient de transfert de chaleur (U, $W/m^2 \cdot °C$) ainsi donc de la capacité d'évaporation [141]. D'autre part, la viscosité du filtrat de l'étape d'extraction lorsque 70 % de la lignine a été enlevée est réduite de 2 à 100 fois dépendant de la teneur en solide et de la température comparées à la valeur correspondante de la liqueur noire originale [142]. Bien que la charge additionnelle d'eau provenant de l'augmentation du débit de liqueur noire et des eaux de lavage soit substantielle, le coefficient de transfert de chaleur pourrait être nettement amélioré suite à une baisse globale de viscosité. En cas de limite de la capacité des évaporateurs, une unité de compression mécanique de la vapeur pourrait s'avérer nécessaire pour combler les besoins manquants [143].

Dans le cas de l'option chimique de précipitation de la lignine, le CO_2 qui est barboté dans la liqueur pour en réduire le pH réagit avec l'hydroxyde de sodium formant ainsi du carbonate de sodium (Na_2CO_3). Cette réaction implique inévitablement une augmentation de la concentration en carbonate et la formation de burkeite ($2\ Na_2SO_4 \cdot Na_2CO_3$). La concentration pourrait excéder la limite de solubilité [29, 144-147] et causer un entartrage des échangeurs de chaleur des évaporateurs suite à une cristallisation du sel. Cette situation démontre à nouveau l'importance de porter attention à tout changement de la composition de la liqueur noire lors de l'intégration d'un atelier de production de lignine, d'où l'intérêt et les bénéfices de l'approche électrochimique ne nécessitant aucun produit chimique de source externe.

2.7.3 Système de caustification

L'atelier de caustification comprend deux unités majeures : le réacteur ou extincteur de chaux pour la conversion du Na_2CO_3 de la liqueur verte en NaOH pour produire la liqueur blanche ou liqueur de cuisson et, le four à chaux qui sert à convertir le $CaCO_3$ en chaux vive (CaO) Figure 4.1). Lors de l'installation d'un atelier de récupération de lignine avec augmentation de production de pâte, ces deux unités sont directement affectées. Une augmentation de production génère un débit additionnel de liqueur verte et une quantité de $CaCO_3$ qui peuvent surcharger l'extincteur de chaux et le four à chaux, respectivement. De plus, avec l'option chimique de précipitation de la lignine, le CO_2 utilisé comme agent acidifiant de la liqueur noire convertit le

NaOH de celle-ci en Na_2CO_3 ajoutant une charge additionnelle au système de caustification. La consommation de combustible fossile sera augmentée ainsi que les émissions de GES.

Quant à l'intégration de l'option électrochimique de précipitation de la lignine, le système de caustification n'est pas aussi sollicité et n'est pas soumis à un engorgement de production. Les besoins additionnels de soude caustique peuvent être fournis par l'étape d'électrolyse de la liqueur noire ou de l'électrodialyse du Na_2SO_4.

Le four à chaux demeure la seule et dernière unité opérationnelle d'une usine kraft qui consomme du combustible fossile. Il a été proposé à maintes reprises d'utiliser la lignine pour remplacer soit l'huile lourde ou le gaz naturel comme combustible. À cet égard, Richardson [148, 149] a démontré avec une unité pilote de four à chaux que la lignine séchée était un combustible aussi efficace sinon meilleur que le gaz naturel. Öhman [150] a obtenu un brevet concernant la combustion de la lignine dans un four à chaux. Cependant, la teneur en sodium de la lignine limite son utilisation dans le four à chaux. Basé sur un bilan de sodium, Uloth et Wearing [30] ont calculé que la lignine précipitée à pH 9.0 et soumise à deux étapes de lavage à l'acide ne contenait que 0.3 % de sodium. Elle pouvait donc fournir plus de 98 % des besoins de combustible du four à chaux sans causer de problème de formation d'anneaux de dépôts de sel de très grande dureté sur les parois du four. Berglin et al [142] ont effectué des essais de combustion de lignine dans un four à pleine échelle. Ils ont réussi à opérer avec 100 % de lignine comme combustible. Cependant, ils ont observé qu'au-delà de 90 % de substitution, les émissions de SO_2 provenant du soufre de la lignine ont augmenté rapidement. Dans leur étude de combustion de la lignine, Moosavifar et al [151] recommande de mélanger la lignine avec de la chaux au niveau de saturation (0.8 mmol Ca/g de lignine) permettant de réduire de 50 % les émissions de soufre.

2.7.4 Bilans massique et énergétique

Tel que montré précédemment dans cette section, l'intégration d'un atelier de production de lignine dans une usine de pâte kraft affecte la plupart des unités opérationnelles. Les équipements existants seront davantage sollicités et les quantités de solides sont appelés à augmenter ainsi que les besoins énergétiques. Il est donc important d'examiner l'impact d'un atelier de production de lignine sur les bilans massiques et énergétiques de l'usine.

2.7.4.1 Bilan massique

Lorsque l'atelier de production de lignine est accompagné par une augmentation de production de pâte, la plupart des équipements de l'usine sont appelés à manipuler des quantités accrues de solides au point d'atteindre leur limite physique. Cette situation d'engorgement des unités est propre à chaque usine. Par contre, le respect des bilans de sodium (15-20%) et de soufre (3-5 %) et leur proportion respective (Na/S = ~3-4) [27] dans la liqueur de cuisson est fondamentale et intrinsèque au bon fonctionnement du procédé de mise en pâte kraft. L'excès de soufre provenant de la récupération des eaux de lavage de la lignine à l'acide sulfurique doit être obligatoirement purgé, soit en déversant une partie des poussières du précipitateur ou une fraction additionnelle du sulfate de sodium sous-produit du générateur de ClO_2 normalement retourné au circuit liqueur noire pour compenser les pertes de sodium et de soufre. Selon l'approche chimique de récupération de la lignine utilisant le CO_2 comme agent acidifiant où l'acide sulfurique de source externe est utilisé pour le lavage de la lignine, il est de pratique courante de déverser aux égouts les eaux de lavage pour être conditionnées par le système de traitement des effluents afin de rencontrer les normes environnementales. D'autre part, il a été démontré que l'approche électrochimique promet de maintenir le bilan de sodium et de soufre sans changer la composition de la liqueur noire ni celle de la liqueur de cuisson [19] sans rejet additionnel aux égouts.

2.7.4.2 Bilan énergétique

L'aspect énergétique de l'intégration d'une bioraffinerie comprenant un atelier de production de lignine a fait l'objet d'études de l'impact sur la chaudière de récupération, le système d'évaporation et le four à chaux menant à l'optimisation et la réduction des besoins énergétiques [152-153]. Benali [136] et Périn-Levasseur et al [138] ont déterminé la valeur calorifique minimum (12.5 kJ/k) de la liqueur pour soutenir une combustion efficace dans la chaudière de récupération. Par contre, cette liqueur à faible valeur calorifique pourrait être accompagnée d'une baisse de production de vapeur de l'ordre de plus de 20 % selon certaines études dépendamment de la composition initiale de la liqueur noire. Les travaux de Périn-Levasseur et al [139, 154] ont démontré que l'intégration du procédé de la précipitation acide de la lignine dans une bioraffinerie d'une usine kraft a un impact significatif sur la demande de vapeur laquelle pourrait atteindre 27 % créant une contrainte majeure sur les besoins énergétiques des

évaporateurs. Les auteurs suggèrent de réviser la stratégie énergétique de l'usine. Ce besoin additionnel de vapeur pourrait être compensé par la récupération de chaleur interne au procédé kraft, par la récupération des produits chimiques et par le recyclage de l'eau. Afin de rétablir partiellement le bilan énergétique de l'usine, Kannangara [18] a revu quelques études de cas et propose de débuter un programme de révision énergétique avec une analyse de pincement pour identifier les nouvelles opportunités d'économie d'énergie.

La lignine extraite de la liqueur noire utilisant la technologie LignoBoost a été testée avec succès dans plusieurs applications de combustion telles qu'un four à chaux, une chaudière à lit fluidisé au charbon et une chaudière à écorces. Selon les estimés de Tomani et al [155] provenant de la modélisation du bilan énergétique, si la lignine extraite de la liqueur noire était brûlée dans une chaudière à biomasse telle que la chaudière à écorces, la production de puissance une fois la chaudière optimisée serait supérieure de 20 à 25 % par rapport au cas de référence sans extraction de lignine indiquant que le bilan énergétique global peut être rétabli.

CHAPITRE 3 PROBLÉMATIQUE ET SOLUTION PROPOSÉE

3.1 Problématique

La rentabilité d'une usine de mise en pâte kraft repose en grande partie sur le système de récupération des produits chimiques sans lequel ce procédé n'est pas rentable. La production de pâte de plusieurs usines kraft est souvent limitée par la capacité de la chaudière de récupération, composante principale du système de récupération. L'une des raisons pour laquelle l'utilisation maximale de capacité requiert autant d'effort est la difficulté excessive d'augmenter la capacité d'une chaudière existante. À cette limite, s'ajoutent occasionnellement celles des capacités de l'atelier de caustification, du train d'évaporateurs et du système de traitement des effluents. Étant donné le coût élevé d'un système de récupération, il est impératif de tirer le maximum de bénéfice de cet investissement majeur et d'en maximiser la rentabilité en développant des solutions novatrices implantant des améliorations technologiques incrémentielles telle que la récupération de lignine. L'approche conventionnelle de précipitation de la lignine par des moyens chimiques présente des limites techniques qui peuvent être résolues par une approche électrochimique.

3.1.1 Engorgement des principales unités

Le coût très élevé d'une nouvelle chaudière de récupération est un obstacle majeur pour répondre à une augmentation de production de pâte afin de répondre à une croissance du marché. Il est plus économique pour l'usine de maximiser la production en améliorant le système de récupération déjà existant à l'aide de technologies d'ajout telle que la précipitation de la lignine.

Il existe certaines limites physiques à pousser la capacité d'une chaudière de récupération. La surface du foyer de la fournaise, le volume de la cavité et la dimension du tambour à vapeur imposent des limites pratiques au débit de liqueur noire que peut traiter une chaudière.

L'ultime limite d'une chaudière est la production de vapeur dont le maximum est dicté par la capacité nominale du design original. Cette limite ne peut être dépassée en aucun temps pour des raisons de sécurité et d'assurance. Cela se traduit par une charge thermique maximale qui limite le débit de liqueur noire entrant dans la chaudière et conséquemment la production de pâte.

La capacité de la chaudière peut aussi être limitée par la quantité de solides de liqueur noire à brûler. Une quantité excessive de solides provoque un entraînement dans les gaz de combustion

des particules qui n'ont pas eu le temps de brûler complétement. Cette condition d'opération cause inévitablement un encrassement des tubes des échangeurs de chaleur affectant la production de vapeur.

Le système de caustification comprend deux unités principales qui peuvent aussi limiter la production de liqueur de cuisson et conséquemment celle de la pâte : (1) le réacteur qui convertit le carbonate de sodium en soude caustique par addition de chaux produisant ainsi la liqueur de cuisson et (2), le four à chaux qui convertit le carbonate de calcium, sous-produit de l'étape précédente, en chaux servant à la réaction. Cette boucle de recyclage à l'intérieur du système de récupération est essentielle et se doit de fonctionner à pleine efficacité pour fournir la quantité de liqueur de cuisson requise pour l'opération.

Toute usine de mise en pâte kraft est munie d'un train d'évaporateurs à effets multiples comprenant habituellement 5 à 6 effets. La liqueur usée de cuisson ou liqueur noire faible contenant 15 à 18 % de solides et les eaux de lavage de la pâte sont concentrées jusqu'à environ 50 % par le système d'évaporation. Puis, la teneur en solides de ce mélange concentré est bonifiée davantage (à plus de 70 %) dans un cristallisoir et cette liqueur à haute teneur en solides est alors brûlée dans la chaudière. La capacité d'évaporation est affectée principalement par la viscosité de la solution affectant le transfert de chaleur et la teneur en burkeite (2 $Na_2CO_3 \cdot Na_2SO_4$) qui risque de cristalliser sur les tubes des échangeurs de chaleur si la concentration excède la solubilité, réduisant ainsi la surface d'échange.

Le système de traitement des effluents d'une usine est dimensionné en fonction de la production de pâte. Une augmentation de production apporte nécessairement une charge additionnelle au système de traitement. De plus, l'implantation d'un système conventionnel de récupération de lignine au CO_2 déverse incontestablement une charge supplémentaire de matières organiques provenant du déversement des eaux de lavage de la lignine. L'unité de traitement des effluents peut alors représenter une limite quant à la capacité de production d'un atelier de récupération de lignine.

3.2 Solution proposée

Afin d'offrir une augmentation substantielle de production de pâte dans une usine dont la production est limitée par la capacité du système de récupération des produits chimiques et afin

de surmonter les limites de l'approche conventionnelle de précipitation de la lignine par des moyens chimiques, il est proposé d'évaluer une approche électrochimique consistant en l'électrolyse de la liqueur noire comme alternative.

3.2.1 Limitations de l'approche chimique

La première génération de technologies de récupération de lignine de la liqueur noire utilisant le dioxyde de carbone (CO_2) soufre de limitations majeures. Le CO_2 qui est barboté dans la liqueur pour en réduire le pH au point de précipitation de la lignine réagit avec l'hydroxyde de sodium formant ainsi du carbonate de sodium (Na_2CO_3). Cette réaction implique inévitablement une augmentation de la concentration en carbonate et la formation de burkeite ($2Na_2SO_4{\cdot}Na_2CO_3$) dont la concentration pourrait excéder la limite de solubilité et causer une cristallisation sur les échangeurs de chaleur des évaporateurs. De plus, cette quantité additionnelle de carbonate de sodium augmente la charge à l'atelier de caustification et conséquemment les émissions de GES. De surcroît, la lignine précipitée doit être lavée avec de l'acide sulfurique pour réduire la teneur en sodium et autres impuretés. Après neutralisation, les eaux de lavage acides sont soit déversées aux égouts causant une surcharge au système de traitement soit recyclé au circuit de récupération. Dans ce dernier cas, le rapport sodium-soufre du circuit de liqueur est débalancé par l'excès de soufre provenant de l'acide sulfurique. Afin de rétablir l'équilibre, on doit purger l'excès de soufre en rejetant une partie des poussières récupérées par le précipitateur électrostatique des gaz de combustion ou déverser aux égouts le sulfate de sodium du générateur de ClO_2 normalement récupéré comme appoint chimique. Les rejets du générateur ainsi que des poussières sont composées principalement de sulfate de sodium. Le fait de purger le soufre sous cette forme implique une perte inévitable de sodium qui doit être comblé par l'addition de soude caustique contribuant aux coûts additionnels d'opération. Dans le cas où les eaux de lavage sont retournées au circuit de récupération, la teneur en cendres de la liqueur noire augmente et conséquemment sa valeur calorifique est diminuée affectant sa combustibilité et limitant alors le potentiel de récupération de lignine et d'augmentation de production de pâte.

3.2.2 Avantages de l'approche électrochimique

La deuxième génération de technologies de récupération de lignine repose sur des traitements électrochimiques pour réduire l'alcalinité de la liqueur noire au point de précipitation de la lignine. Ces procédés incluent : (1) l'électrodialyse conventionnelle de dessalement, (2)

l'électrodialyse à membranes bipolaires et (3) l'électrolyse à membranes. L'électrodialyse conventionnelle extrait les sels alcalins de la liqueur réduisant ainsi le pH. L'électrodialyse à membranes bipolaires réduit le pH suite à la génération d'ions H^+ par la membrane bipolaire. Durant l'électrolyse, l'alcalinité est réduite suite à la réaction des ions hydroxyles (OH^-) de la liqueur à la surface de l'anode formant de l'eau. Cette réaction de désalcalinisation contribue à réduire le pH au point de précipitation de la lignine.

L'approche électrochimique de récupération de la lignine par électrolyse de la liqueur noire présente les avantages suivants par rapport aux technologies chimiques:

(1) Aucun besoin d'approvisionnement en acide sulfurique et soude caustique de source externe à l'usine n'est requis

(2) Les eaux résiduelles des étapes de lavage à l'acide et à l'eau peuvent être ajoutées au circuit de récupération sans affecter le bilan de sodium et de soufre,

(3) Aucune charge additionnelle de matières organiques au système de traitement des effluents,

(4) Une réduction de la teneur en inorganique (cendres) de la liqueur due à l'extraction de sodium sous forme de NaOH ce qui contribue à augmenter la valeur calorifique de la liqueur avant l'étape de précipitation offrant un potentiel plus élevé de production de lignine et de pâte,

(5) Un désengorgement du système de caustification souvent surchargé et réduction des émissions de GES,

(6) Une oxydation directe in-situ des sulfures de sodium dans le compartiment anodique éliminant la formation de H_2S indésirable lors de l'étape de lavage à l'acide et,

(7) Une réduction significative de la viscosité de la liqueur traitée pouvant aller jusqu'à 10 fois la valeur normale contribuant à absorber les besoins additionnels d'évaporation des eaux de lavage.

La technologie proposée élimine l'approvisionnement en acide sulfurique et soude caustique de source externe. Ces produits chimiques sont fournis par le sulfate de sodium présent à l'usine (poussières du précipitateur et sous-produit du générateur) qui est soumis à l'électrodialyse à membranes bipolaires. En outre, de la soude caustique est aussi récupérée de l'étape d'électrolyse de la liqueur noire.

Cette approche électrolytique permet d'ajouter toutes les eaux de lavage de la lignine au circuit de liqueur puisque le soufre contenu dans l'acide sulfurique pour le lavage provient du sulfate de sodium de source interne n'affectant pas le bilan de sodium-soufre de la liqueur. Le recyclage en entier des eaux de lavage dans le circuit de liqueur élimine alors la charge additionnelle organique au système de traitement des effluents.

Contrairement à l'approche chimique qui nécessite l'ajout de produits chimiques (H_2SO_4, NaOH et CO_2) à la liqueur contribuant à augmenter le taux de cendres et diminuer la valeur calorifique, l'électrolyse extrait du sodium de la liqueur noire sous forme de soude caustique (NaOH) réduisant ainsi la teneur en matières inorganiques. Cela contribue à maintenir une valeur calorifique plus élevée après traitement permettant de récupérer plus de lignine pour une cible donnée du pouvoir calorifique assurant une bonne combustibilité.

La récupération de soude caustique de la liqueur noire et du sulfate de sodium offre une solution élégante lorsque le système de caustification est surchargé permettant de produire plus de pâte en réduisant les GES.

Un autre avantage de l'électrolyse est l'oxydation des composés de soufre, entre autres le sulfure de sodium (Na_2S). L'oxygène produit à l'anode oxyde les sulfures en composés plus stables éliminant la formation de H_2S toxique durant l'étape de lavage de la lignine à l'acide.

Finalement, le traitement électrolytique réduit considérablement la viscosité de la liqueur noire offrant une opportunité d'absorber en partie la charge additionnelle d'évaporation des eaux de lavage retournées au circuit de liqueur noire.

CHAPITRE 4 OBJECTIFS, MÉTHODOLOGIE ET ORGANISATION DE LA THÈSE

4.1 Objectif principal de cette étude

L'objectif principal de la présente étude consiste à développer une meilleure compréhension des mécanismes réactionnels et de transfert de masse impliqués lors du traitement électrolytique de la liqueur noire pour précipiter la lignine et, d'amener la technologie à l'étape de pré-commercialisation. Il est essentiel de mieux comprendre les enjeux électrochimiques qui sont actuellement très peu connus et étudiés, d'approfondir les connaissances de cette application et d'optimiser la performance du procédé. Il est essentiel de minimiser l'impact de l'intégration de cette technologie de récupération de la lignine sur les opérations d'une usine de pâte kraft, particulièrement le système de récupération. Cette étude fournira les données fondamentales nécessaires pour le design et l'intégration de la technologie dans une bio-raffinerie.

4.2 Objectifs spécifiques

Les objectifs spécifiques de cette investigation sont regroupés en deux catégories :

1. le traitement électrolytique de la liqueur noire
2. la récupération de la lignine

4.2.1 Traitement électrolytique de la liqueur noire

Les objectifs détaillés de cette première partie qui concerne le traitement électrolytique de la liqueur noire sont les suivants :

1. Développer une meilleure compréhension des réactions chimiques et du transfert de masse impliqués lors de l'électrolyse de la liqueur noire
2. Valider la faisabilité technique de la désalcalinisation de la liqueur noire pour la précipitation de la lignine utilisant l'électrolyse à l'échelle laboratoire,
2. Étudier l'effet des principaux paramètres (densité de courant, température, concentration de la soude caustique, etc.) du traitement électrolytique et les phénomènes de transfert d'ions (Na^+) affectant la performance du procédé;

3. Confirmer la faisabilité technique du traitement électrolytique de la liqueur noire à l'aide d'une cellule de dimension industrielle (FM-21) permettant d'amener la technologie au niveau de maturité technologique de pré-commercialisation.

4.2.2 Récupération de la lignine

Les objectifs détaillés de cette deuxième partie reliée à la récupération de la lignine de la liqueur noire électrolysée sont les suivants :

1. Déterminer les meilleures conditions (pH, température, temps de coagulation, etc.) pour précipiter et récupérer la lignine de la liqueur noire électrolysée
2. Optimiser les paramètres de la filtration et de lavage de la lignine pour obtenir un produit de lignine de qualité acceptable pour l'utilisation dans le four à chaux.
3. Comparer la performance de filtration de la lignine de la liqueur noire électrolysée à celle de l'option chimique au CO_2.

4.3 Méthodologie

Le programme expérimental a compris trois parties distinctes. La première partie se préoccupe du traitement électrolytique de la liqueur noire et de l'optimisation du procédé en laboratoire. La seconde partie couvre l'investigation de la récupération de la lignine de la liqueur noire électrolysée comprenant les étapes de coagulation, de précipitation, de filtration et de lavage. Et, la troisième partie consiste à démontrer et confirmer la faisabilité technique de traiter la liqueur noire avec la cellule électrolytique commerciale FM-21. La méthodologie utilisée est illustrée à la Figure 3.1.

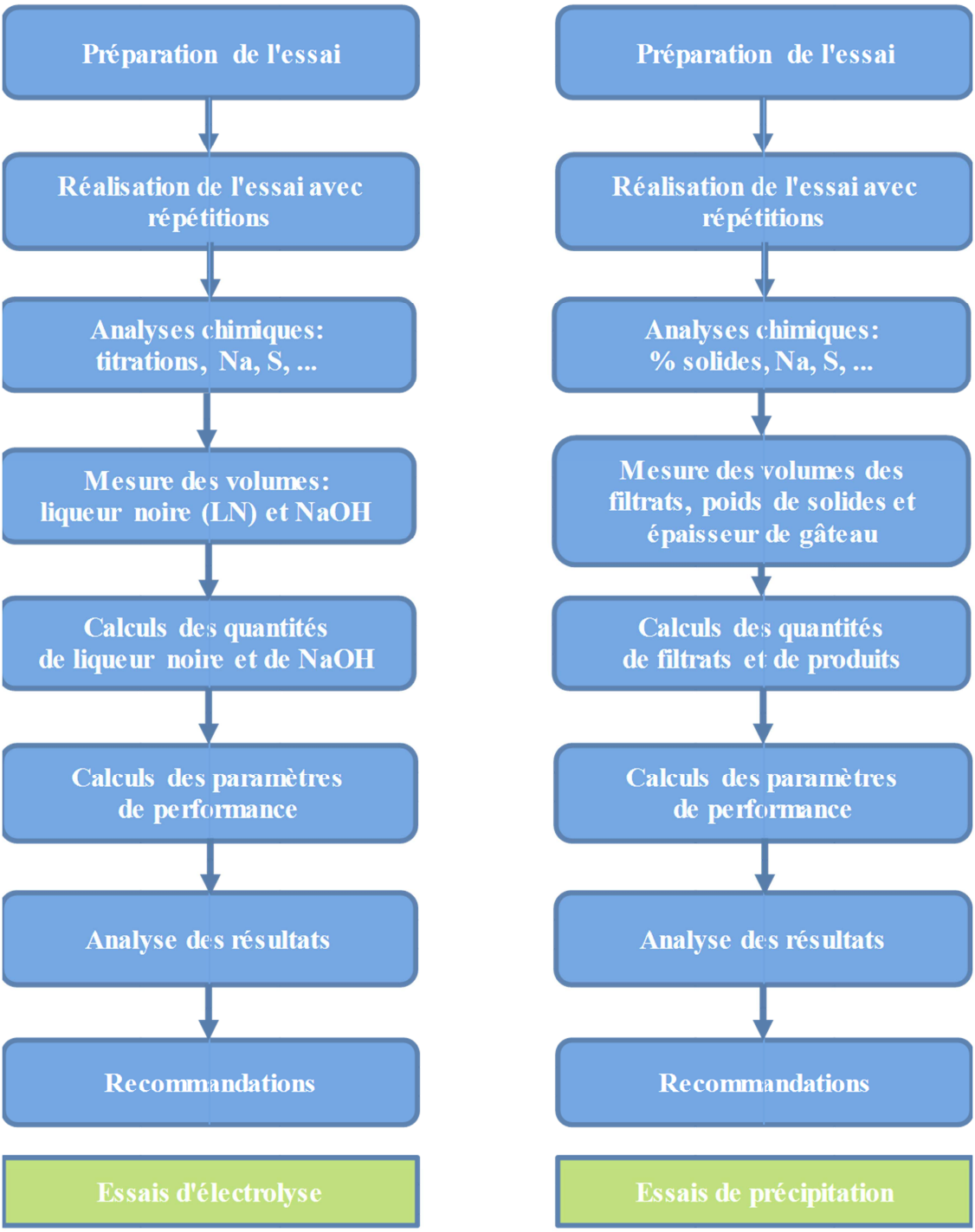

Figure 3.1 : Schéma illustrant la méthodologie utilisée pour les essais d'électrolyse de la liqueur noire et de filtration de la lignine

4.3.1 Traitement électrolytique de la liqueur noire à l'échelle de laboratoire

Les essais d'électrolyse de la liqueur noire ont été effectués avec la cellule de laboratoire ELSEP comprenant 10 anodes (358 cm^2) tubulaires de 2.54 cm de diamètre et 14 cm de longueur, deux membranes et deux cathodes.

Le système d'électrolyse est opéré en mode d'alimentation continue et de purge (feed and bleed) à pH constant maintenu par l'addition de liqueur noire. La concentration de soude caustique est mesurée par la sonde de conductivité qui est maintenue constante par l'addition d'eau. La cellule opère en mode galvanostatique, i.e. à courant constant avec le voltage fluctuant. Les paramètres suivants ont été mesurés et enregistrés à chaque minute : voltage, courant, température et conductivité des deux solutions. La liqueur noire et la soude caustique sont alimentées dans la cellule en mode co-courant et à température constante. Les réactions chimiques impliquées durant l'électrolyse ont été détaillées et le profil de transfert des ions à membrane a été modélisé utilisant l'équation de Nernst-Planck et bonifié en tenant compte du phénomène d'équilibre des ions à l'interface de deux milieux (liqueur noire-membrane-soude caustique) développé par Donnan.

La performance du traitement électrolytique sous différentes conditions expérimentales a été déterminée pour l'efficacité de courant exprimée en pourcent, la production de soude caustique en kg NaOH/h·par m^2 d'anode, de la consommation d'énergie en kWh/t de NaOH produite et le débit de liqueur par heure par unité de surface d'anode ($L/(h \cdot m^2)$. Ces paramètres de performance reliés à la soude caustique sont basés sur la quantité produite dans un lapse de temps suffisamment long pour assurer un régime permanent. Le montant de soude caustique a été calculé à partir de la titration de la solution de NaOH produite multipliée par le volume recueilli durant l'essai. Le débit de liqueur noire traité est basé sur la différence de volume dans le réservoir d'alimentation entre le début et la fin de l'essai divisé par la durée de l'essai. Les résultats sont présentés sous forme graphique montrant les barres d'erreurs calculées à partir de la déviation standard des valeurs mesurées. Une matrice des coefficients de corrélation a été

développée rapportant la relation qui existe entre les différentes variables dépendantes et indépendantes déterminée à l'aide du logiciel EXPLORE développé par CANMET[14].

4.3.2 Récupération de la lignine

Les essais de précipitation et de récupération de lignine ont été effectués dans un réacteur de 2 L muni d'un agitateur opéré à 100 rpm et un contrôle de température pour l'étape de coagulation. Par la suite, la solution de lignine précipitée a été filtrée sur un filtre à l'aide d'une pompe à vide. Le gâteau de lignine est lavé avec un volume d'acide sulfurique (0.5 N) équivalent au volume du gâteau suivi d'un lavage à l'eau de même volume. Les volumes de filtrat récupérés ont été mesurés et les débits calculés. Le gâteau de lignine a été séché à l'air libre pour une période de 24 h et le poids de solide sec mesuré. Un échantillon de lignine a ensuite été analysé pour son contenu de sodium, d'humidité, de lignine et de cendres. Les paramètres de performance ont compris le débit de filtrat par unité de surface de filtre exprimé en $L/(h \cdot m^2)$ et le taux de filtration de lignine exprimé en $kg/(h \cdot m^2)$. L'efficacité de récupération de lignine a aussi été déterminée. Un bilan massique global du procédé est présenté permettant de valider l'essai.

4.3.3 Traitement électrolytique de la liqueur noire avec la cellule commerciale FM-21

Les essais d'électrolyse de la liqueur noire effectués avec la cellule commerciale FM-21 ont été soumis à la même méthodologie utilisant le même montage expérimental et soumis au même protocole expérimental que ceux exécutés avec la cellule de laboratoire. Par contre, la surface d'anode et de membranes était nettement supérieure avec la cellule FM-21 qui avait une surface de 2 100 cm^2 d'anode et de membranes comparées à quelques centaines de cm^2 avec la cellule de laboratoire. Les débits de liqueur noire étaient 20 fois plus élevés en proportion de la surface d'anodes. Les courants étaient aussi beaucoup plus élevés (jusqu'à 1 600 ampères) par rapport à 100 ampères avec la cellule ELSEP. Bien que les courants étaient plus importants, les densités de courant étaient similaires, de quelques milliers d'ampères/m^2.

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1. https://www.nrcan.gc.ca/sites/www.nrcan.gc.ca/files/canmetenergy/files/pubs/EXPLORE-brochure_%20EN.pdf

4.4 Organisation de la thèse

Cette thèse doctorale, organisée sous la forme d'une thèse par articles, comporte dix chapitres. Le premier chapitre comprend l'introduction qui présente le problème étudié et les buts poursuivis. Le deuxième chapitre décrit la problématique de l'engorgement des composantes majeures du système de récupération des produits chimiques d'une usine de mise en pâte kraft ainsi que les limitations de la technologie chimique de précipitation de la lignine de la liqueur noire utilisant du CO_2. Les avantages de l'approche électrochimique basée sur l'électrolyse de la liqueur noire y sont présentés. Le chapitre 3 définit les objectifs de cette étude, la méthodologie utilisée et l'organisation de la thèse. Le chapitre 4 couvre la revue critique de littérature relative à l'intégration d'un atelier de production de lignine dans une bioraffinerie d'une usine de pâte kraft.

La section des résultats comporte les 5 chapitres suivants:

Chapitre 5 - Article #1: Effect of the basic electrochemical cell operating parameters on the performance of the electrolysis of kraft pulping black liquor,

Chapitre 6 – Article 2: Electrolytic processing of kraft black liquor- Mass transfer investigation

Chapitre 7 – Article #3: Electrolytic treatment of Kraft black Liquor- Process optimisation

Chapitre 8 – Article #4: Precipitation and washing of lignin from electrolysed black liquor

Chapitre 9 – Article #5: Electrolytic processing of Kraft black liquor using the FM-21 commercial cell.

Le chapitre 5 (Article #1) porte sur l'étude des phénomènes électrochimiques fondamentaux pertinents au traitement électrolytique de la liqueur noire. Cela inclut les items suivants : (1) les réactions chimiques anodiques et cathodiques, (2) la distribution de la densité de courant le long de la cellule d'électrolyse et (3) l'analyse de la contribution des différentes composantes de la cellule au voltage total. Ces composantes comprennent : (1) les anodes, (2) les membranes, (3) les cathodes, (4) les solutions comprenant la liqueur noire et la soude caustique et (5) les réactions électrochimiques aux électrodes. La modélisation de la densité de courant a permis de recommander de réduire le diamètre des anodes pour obtenir une meilleure distribution du courant. Cet article a été publié en 2017 dans le journal intitulé Electrochemical Society Transactions.

Le chapitre 6 (Article #2) porte sur les phénomènes de transport prenant place durant l'électrolyse de la liqueur noire. Le transfert des ions sodium et des protons à travers la membrane a été modélisé ainsi que leur profil de concentration et celui du pH. Les résultats ont conduit à la recommandation d'opérer à pH alcalin du côté de la liqueur noire pour éviter la précipitation des cations divalents dans la membrane. Cet article a été soumis pour publication dans la revue Journal of New Materials for Electrochemical Systems.

Le chapitre 7 (Article #3) consiste à l'optimisation du procédé d'électrolyse de la liqueur noire en termes d'efficacité de courant, de consommation d'énergie et de productivité de soude caustique et de débit de liqueur noire traité per unité de surface. L'effet des paramètres suivants a été étudiés : (1) la source et le type de liqueur noire, (2) le pH de l'étape d'électrolyse, (3) la densité de courant, (4) la concentration du NaOH produit, (5) la température et l'addition de sulfate de sodium à la liqueur noire. Cet article a été soumis pour publication dans la revue Journal of New Materials for Electrochemical Systems.

Le chapitre 8 (Article #4) rapporte les résultats des essais de coagulation, de précipitation, de filtration et de lavage de la lignine récupérée de la liqueur noire électrolysée. L'analyse des données expérimentales se concentre principalement sur la performance de l'étape de filtration et la qualité du produit de lignine après lavage. L'effet des variables suivantes a été étudié : (1) le temps de coagulation, (2) le type de liqueur, (3) la température, (4) le niveau de vide, (5) the pH final et (6) l'addition de sulfate de sodium. Les résultats de performance de la filtration sont comparés avec ceux des méthodes de précipitation de la lignine de la liqueur noire utilisant le CO_2 et l'acide sulfurique. La performance de filtration est aussi comparée à celle du carbonate de calcium, un sous-produit de l'atelier de caustification qui semble avoir un comportement similaire à la lignine. La pureté de la lignine lavée est rapportée et un bilan massique des éléments critiques est fourni pour l'intégration éventuelle à l'opération de l'usine. Cet article a été soumis pour publication dans la revue Journal of New Materials for Electrochemical Systems.

Le chapitre 9 (Article #5), le dernier de la section des résultats, confirme la faisabilité technique de l'électrolyse de la liqueur noire avec la cellule commerciale FM-21 et rapporte que la performance de cette cellule est comparable à celle de l'unité de laboratoire. Les essais ont compris l'étude des paramètres suivants : (1) la densité de courant, (2) la température et (3) la concentration de la soude caustique produite sur la performance de la cellule. Cette dernière a été

caractérisée par l'efficacité de courant, la consommation d'énergie, la productivité de NaOH et du débit de liqueur noire traitée par unité de surface. Cet article a été soumis pour publication dans la revue Journal of New Materials for Electrochemical Systems.

Finalement, au chapitre 10, on retrouve les conclusions de cette étude et quelques recommandations pour des travaux futurs.

CHAPITRE 5 ARTICLE 1: EFFECT OF THE BASIC ELECTROCHEMICAL CELL OPERATING PARAMETERS ON THE PERFORMANCE OF THE ELECTROLYSIS OF KRAFT PULPING BLACK LIQUOR

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The biorefinery initiative in the pulp and paper industry aims at diversifying its product offering to include value-added biomaterials from lignin. We have developed an electrochemical technique to precipitate lignin from black liquor and simultaneously recover caustic soda. Our approach, which is based on the electrolysis of black liquor, reduces its alkalinity electrochemically to the point of lignin precipitation. It does not require chemicals from an external source and does not generate additional effluents. The technology entails an increased pulp production for Kraft pulp mills that are limited by their recovery boiler capacity or their causticizing system. In this study, we investigated the effect of various basic operating parameters of on the performance of the electrolysis of black liquor; in particular the electrochemical reactions taking place in the cell, the current density distribution and the contribution of individual cell components to the total voltage of the electrochemical reactor.

5.1 Introduction

The biorefinery initiative is a part of a roadmap to exploit Canada's natural advantage in the pulp and paper industry. Black liquor from the Kraft pulping process is a source of raw material for the production of biomaterials based on lignin [1]. Nowadays, lignin is recovered by acid precipitation using carbon dioxide technologies, such as LignoBoost [2] patented by LignoBoost

AB and commercialized by Valmet[15], and LignoForce [3] developed by FPInnovations and offered by NORAM[16].

These first generation lignin recovery technologies suffer from major limitations. The carbon dioxide sparged into the liquor to reduce the pH to the point of lignin precipitation reacts with the sodium hydroxide to produce sodium carbonate. This implies a higher carbonate content and the formation of additional burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$), which may exceed the solubility in the evaporator. This additional sodium carbonate increases the load on the causticizing plant and greenhouse gas emissions. Moreover, the precipitated lignin must be washed with sulfuric acid to reduce its sodium content and other impurities. After neutralization, the residual acid washings can either be discharged to the effluent treatment system adding to its load and operating costs or be returned to the chemical recovery system. In the second case, the sodium-sulfur balance is disturbed and the appropriate amount of sodium sulfate, either electrostatic precipitator (ESP) dust or ClO_2 generator saltcake, needs to be discarded to the effluent to retain the chemical balance. If the residual washing stream is returned to the chemical recovery system, the black liquor ash content increases and reduces its calorific value, which affects combustibility limiting the lignin recovery potential.

The second generation of lignin recovery technologies relies on electrochemical processes to reduce the alkalinity of black liquor to the point of lignin precipitation. These processes include: (1) conventional desalting electrodialysis, (2) bipolar membrane electrodialysis and (3) standard electrolysis. Conventional desalting electrodialysis selectively removes the alkaline salts from the liquor and reduces its pH [4, 5]. Bipolar membrane electrodialysis reduces the pH of the electrolyte by the action of the H^+ ions generated by the bipolar membrane [6]. During the electrolysis of the black liquor, the OH^- ions of the liquor are neutralized by the reaction at the anode of the cell. This reaction contributes to decreasing the liquor's alkalinity with a drop of its pH [5, 7] to the desired value.

There are significant advantages of the electrochemical approach to precipitate lignin from a Kraft mill versus the chemical precipitation process. First, it is not necessary to use chemicals, like caustic soda and sulfuric acid, from an external source since they can be obtained in situ in

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[15] http://www.valmet.com/products/pulping-and-fiber/chemical-recovery/lignin-separation/
[16] http://www.noram-eng.com/news-room/lignoforce.html

the electrochemical reactor by splitting the sodium sulfate present in the electrostatic precipitator (ESP) dust or in the by-product salt cake from the ClO_2 generator. Part of the caustic soda can also be provided by the electrolysis of black liquor. Secondly, the proposed process generates no additional discharge to the effluent treatment since the acid washings can be returned entirely to the black liquor without modification of the Na/S balance. Thirdly, contrarily to the chemical approach, which adds external inorganics to the black liquor reducing its calorific value, the electrochemical process extracts sodium and lowers the inorganic content of the electrolyte. Consequently, the black liquor calorific value is increased prior to lignin precipitation during the black liquor electrolysis.

The electrochemical process offers a fourth advantage because additional lignin can be extracted from the liquor at the same level of the minimal calorific value required for sustaining combustibility. The recovery of caustic from black liquor offers a solution to overloaded causticizing systems allowing more pulp to be produced with less GHG emissions. The sodium sulphide component of the black liquor (Na_2S) is oxidized into more stable sulfur compounds at the anode [8] eliminating the H_2S formation during the acid wash of lignin. On the other hand, the electrolytic treatment of black liquor can also help pulp mills with overloaded evaporators since it can reduce the liquor's viscosity by as much as tenfold [9].

This study is concerned with the electrolytic treatment of black liquor to reduce its pH to the point of lignin precipitation or lower. We investigated the fundamentals of the electrochemical phenomena involved and have reported on the specific functioning of the cell. The electrochemical reactions taking place, the current density distribution and the analysis of the individual cell components' contribution to total voltage are topics that will be examined in this study.

5.2 Background

This separation process relies on the selective affinity of the Nafion® membrane for sodium ions.

5.2.1 Membrane Structure and Properties of Nafion® 324

In this work, Nafion® 324 based membranes, which contain two sulfonate films that differ in equivalent weights and thicknesses (Table 5.1) are used. It is known that the ion exchange

capacity of that membrane is between 0.91 to 1.0 meq per g, and we found that it is well suited for the electrochemical splitting of salt applications [10].

Table 5.1 : Properties of the Nafion® 324 membranes used in this work

Property	Nafion® 324	Reference
Polymer matrix	PTFE (Teflon)	10
Ion exchange	PFSA[17]	10
Layer	2	11-13
Equivalent weight, g/mole Anolyte side layer Catholyte side layer	 1 100 1 500	11
Exchange capacity (meq g^{-1})	0.91-1.0	11
Electrical resistance (Ohm-cm^2)	4.5 0.6 M KCl	11-13
Thickness, cm (in) Anolyte side layer Catholyte side layer	 0.01270 (0.005") 0.00254 (0.001")	14
Cation affinity	$Ba^{2+}>Pb^{2+}>Sr^{2+}>Ca^{2+}>Mg^{2+}>Ag^{+}>K^{+}>NH^{4+}>Na^{+}>Li^{+}$	14

The Nafion® 324 features a special cluster type structure containing aqueous ions imbedded in a continuous fluorocarbon phase (Figure 5.1) [14]. The clusters of an estimated diameter of 40 Ä and distanced by 50 Ä are interconnected by narrow channels (10 Ä) that determine the transport properties (Figure 5.2) [15]. The microstructure consists of a strong hydrophobic fluorocarbon/polytetrafluoroethylene backbone with sidechains ending with hydrophilic sulfonic acid (SO_3^-) represented by the following molecular formula $[OCF_2CF(CF_3)_2]_nOCF_2CF_2SO_3H$ [11,15].

[17]PFSA: perfluorosulfonic acid cation exchange

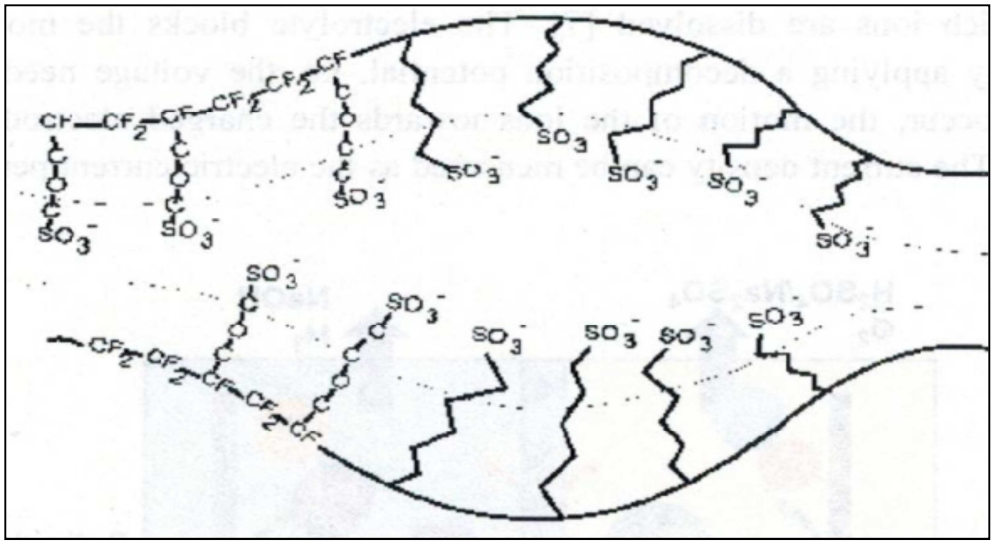

Figure 5.1 : Cluster network model of Nafion®membrane

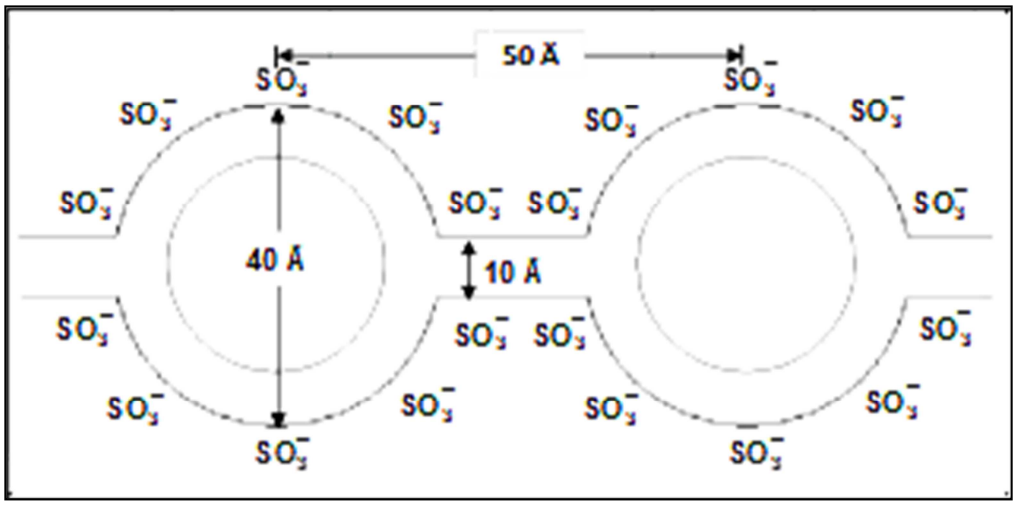

Figure 5.2 : Membrane cluster network dimensions

5.2.2 Current Efficiency and Energy Consumption

Current efficiency and energy consumption are the main performance indicators of an electrochemical process. They impact the economic viability of an industrial application.

Current or Faradaic efficiency is the ratio of moles of product made from an electrolyte to the maximum theoretical production, i.e., the equivalent number of moles of electrons passed [14]. At constant volume, it is expressed as follows:

$$CE = (z \cdot n \cdot F)/(I \cdot t) \cdot 100 \quad [1]$$

Where:

z is the valence (=1 for Na^+),

n = number of moles produced (Vol·ΔC),

F = Faraday's constant (96 485 A s/mole),

Vol = volume (L),

I = current (Amps),

t = time (s) and

ΔC = incremental product concentration (Mole/L). At constant concentration, the expression becomes:

$$CE\ (\%) = (z \cdot F \cdot C \cdot \Delta Vol)/(I \cdot t) \cdot 100 \quad [2]$$

In our case, the overall current efficiency is based on the amount of NaOH produced. It depends on the performance of the reactions at the electrodes and the selectivity of the membrane for sodium. Undesired reactions in the cell as well as the back-migration of hydroxyl ions influence the current efficiency negatively.

Energy Consumption

The energy consumption is expressed in kWh/kg of NaOH product and is calculated as follows:

$$E\ (kWh/kg\ NaOH) = V \cdot A \cdot t/(3\,600 \cdot 40 \cdot C\Delta Vol) \quad [3]$$

where:

V is the cell voltage

A, the current in amperes

C, the concentration in moles

t, the time in seconds and

ΔVol, the change of volume collected in litre.

The effect of current efficiency is taken into account by the total amperes used (A t) and the quan0tity of NaOH produced.

The Nafion® 324 is commonly used in the chlor-alkali industry and has been proposed for sodium sulfate splitting. It delivers a current efficiency of close to 90% for the electrolysis of sodium chloride producing chlorine gas and NaOH with a strength of 10-20%.

That membrane was also tested to split sodium sulfate into sulfuric acid and caustic soda. The current efficiency and the energy consumption are strongly dependent on the product concentration (Table 5.2). A two compartment cell configuration can be used to split sodium sulfate producing acid that contains residual sodium sulfate. In that particular case, beyond a 50% salt conversion rate, the current efficiency is very sensitive to the acid concentration as demonstrated by Jörissem [16]. The membrane changes to an acid state because of the H^+ ions that cross the membrane and moves to the catholyte where they neutralize hydroxyl ions. In order to obtain a higher current efficiency while making more concentrated products, Martin [17, 18] suggested to keep the acid stream saturated with sodium sulfate to maintain the favourable Na^+/H^+ ratio as high as possible. That technique increases current efficiency to the vicinity of 90% while producing acid and NaOH with strengths of around 20%. By taking advantage of salt saturated acid, Cloutier et al. [19] demonstrated that the addition of sodium sulfate reduces conductivity and increases the cell voltage. The lowest energy consumption (3 700 kWh/t NaOH) was achieved while producing acid and NaOH at strengths of 13 and 21% respectively with a cell voltage of 5.2 V delivering a current efficiency of above 90%.

5.2.3 Influence of Impurities [14]

The counter-ion exchange affinity sequence (Table 5.1) indicates that larger monovalent cations have a greater affinity than sodium ions or multivalent cations to the negatively charged fixed sulfonate groups in the interior of the membrane. It can be intuitively assumed that this will affect the desired sodium transport negatively by decreasing the current efficiency. Also based on the pH, the presence of impurities can lead to precipitations inside or on the surface of the membrane. In our application, this can be avoided by operating and maintaining alkaline the pH of the black liquor therefore preventing the dissolution of divalent metals.

Table 5.2 : Performance of Nafion® 324 in chlor-alkali production and sodium sulfate splitting using a two compartment cell configuration

Application	Value	Reference
Chlor-alkali: NaCl (315 g/L) → Cl_2 + NaOH (10, 14, and 20 %)		
Cell voltage, V	3.53, 3.53 and 3.5	11-13
Current efficiency, %	88, 88 and 84	
Na_2SO_4 (38 %)→ H_2SO_4 (20.9 %)/Na_2SO_4 : NaOH (22.0 %)		
Current efficiency, %	87.3	17-19
Cell voltage, V	7.23	19
Energy consumption, kWh/t NaOH	5 563	19
Na_2SO_4 (35 %) → H_2SO_4 (13.3 %)/Na_2SO_4: NaOH (20.8 %)		
Cell voltage, V	5.2	19
Current efficiency, %	94.2	
Energy consumption, kWh/t NaOH	3 704	

5.2.4 Sodium Transfer Mechanism

Carlberg [14] developed an ion transfer model through a Nafion® membrane for the electrolysis of sodium sulfate producing sulfuric acid and sodium hydroxide. The Nafion® membrane promoted the selective transport of cation sodium ions through the polymer by exchanging them with the proton from the sulfonic acid and it acts as a barrier against anions by repelling them with negatively charged sulfonate groups [14]. The model is derived from the Nernst-Planck equation, which describes the molar flux of ions through the membrane combining diffusion, migration and convection:

$$N = - D\, dc/dx - DczF/RT \cdot d\Phi/dx + cu \qquad [4]$$

N: The flux of species (Na^+) across a plane perpendicular to x direction (kmole $m^{-2} \cdot s^{-1}$)

D: Diffusion coefficient of Na^+ ($m^2 \cdot s^{-1}$)

c: Concentration of Na^+ ($kmole \cdot m^{-3}$)

x: Distance (m)

z: Charge number of species

F: Faraday constant (96 485 kC/kequiv)

Φ: Potential field (V)

T: Temperature (K)

R: Gas constant (8.31 $kJkmol^{-1} \cdot K^{-1}$)

u: Electrolyte velocity in direction of flux ($m \cdot s^{-1}$)

The diffusion term is derived from Fick's law and represents the flow of species due to a concentration gradient. Migration is caused by the gradient of electrical potential and the convective part is induced by the bulk movement. The author found that the main modelling parameters were the bulk concentration and diffusivity of ions. His findings were based on a model mainly concerned with the migration of sodium and H^+ ions through the membrane during sodium sulfate splitting. Our application is also concerned with the conversion of sodium salts but with a very low concentration of H^+ for the recovery of sodium as sodium hydroxide.

5.2.5 Nafion® Membrane Performance

To optimize the NaOH product concentration, the solution on the anode side of the cation exchange membrane (CEM) must remain at a high enough pH to prevent the CEM from entering an acidic state and the formation of an acidic boundary layer on the cathode side of the CEM [10]. However, a trade-off between the current efficiency and NaOH concentration can be mitigated by increasing the thickness of the CEM but at the expense of a higher overall cell voltage. The new trade-off results in a higher product concentration and current efficiency with high cell potential or a lower product concentration and current efficiency with a lower cell potential [10].

DuPont, the membrane manufacturer, specifies that the Nafion® CEMs should be operated at a current density range of between 150 and 600 $mA \cdot cm^{-2}$. Above the maximum current density, physical damage occurs and current efficiency is lost. Below the minimum current density, the membrane will not be damaged but the current efficiency will decline [10]. Membrane current

efficiency depends on the ion exchange capacity which must be as high as possible, but the electrical resistance of the membrane also increases [20].

Table 5.3 : Performance of Nafion® 324 in chlor-alkali production and sodium sulfate splitting using a two compartment cell configuration

Application	Value	Reference
Chlor-alkali: NaCl (315 g/L) → Cl_2 + NaOH (10, 14, and 20 %)		
Cell voltage, V	3.53, 3.53 and 3.5	11-13
Current efficiency, %	88, 88 and 84	
Na_2SO_4 (38 %)→ H_2SO_4 (20.9 %)/Na_2SO_4 : NaOH (22.0 %)		
Current efficiency, %	87.3	17-19
Cell voltage, V	7.23	19
Energy consumption, kWh/t NaOH	5 563	19
Na_2SO_4 (35 %) → H_2SO_4 (13.3 %)/Na_2SO_4: NaOH (20.8 %)		
Cell voltage, V	5.2	19
Current efficiency, %	94.2	
Energy consumption, kWh/t NaOH	3 704	

5.3 Experimental procedure

5.3.1 Black Liquor Electrolysis

Electrolysis is an alternative process in development to recover lignin from black liquor. The dual compartment electrolysis cell is composed of an anode and a cathode separated by a cationic membrane, such as Nafion® 324. The liquor is circulated through the anode compartment where the alkalinity is reduced until the pH reaches the point of destabilizing the lignin and forcing its precipitation out of the solution. In this section, the electrolytic cell, the sodium transport mechanism through the membrane and the electrochemical reactions involved are described and discussed.

5.3.2 Electrochemical Principle

The principle of the electrochemical reduction of the alkalinity and pH consists of circulating the black liquor through the anode compartment. The application of voltage between the anode and the cathode forces the positive sodium ions to move out of the black liquor and cross the membrane towards the negative cathode (Figure 5.3). In order to maintain electroneutrality in the anodic and cathodic compartments, the hydroxyl ions are oxidized to water at the anode and the water is reduced at the cathode producing hydroxyl ions. Consequently, the black liquor alkalinity and pH are reduced while OH^- ions are formed at the cathode and combine with sodium ions to produce NaOH.

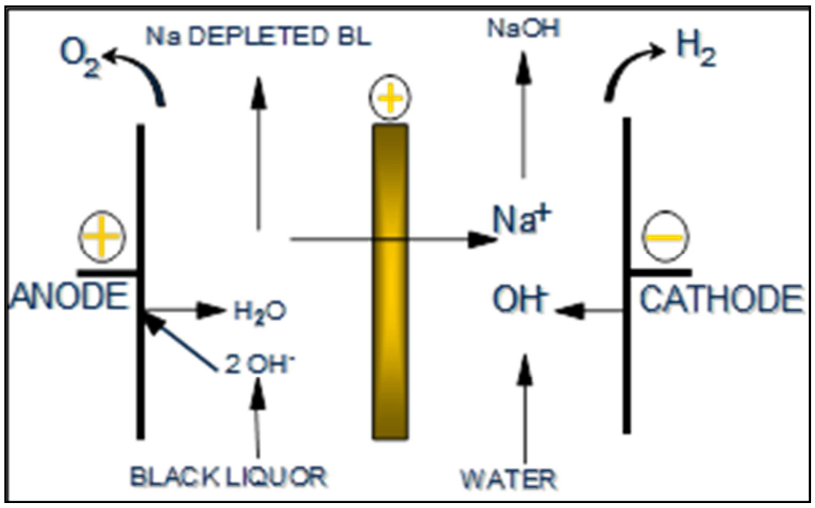

Figure 5.3 : Illustration of the principle of black liquor electrolysis lowering its pH

5.3.3 Electrochemical cell for the current potential polarisation curves

The cell used in our investigation had an unusual configuration (Figure 5.4) compared to the more standard plate and frame design common in the electrochemical industry. The anodes were tubular, the membrane adopted a wave-like shape and the cathode was flat. The cell we used can accommodate a set of 10 tubular anodes (1.27 cm outside diameter) 14 cm in length offering a total surface area of 56 cm^2 each [21]. The anodes are bordered by two Nafion® 324 membranes that are firmly maintained in place by a triangular support creating a waved channel that promotes flow turbulence in a crossflow manner.

The design of an electrolytic cell plays an important role in the distribution of potential and current density, which affects the process performance, such as mass transfer, yield and energy

consumption. Unwanted products may be generated as a result of an uneven distribution of potential and current density on the working electrodes [20]. The cell design parameters and operating conditions are shown in Table 5.4 and 5.5. The experimental set-up was operated in a feed and bleed mode on both streams: black liquor and caustic soda [7].

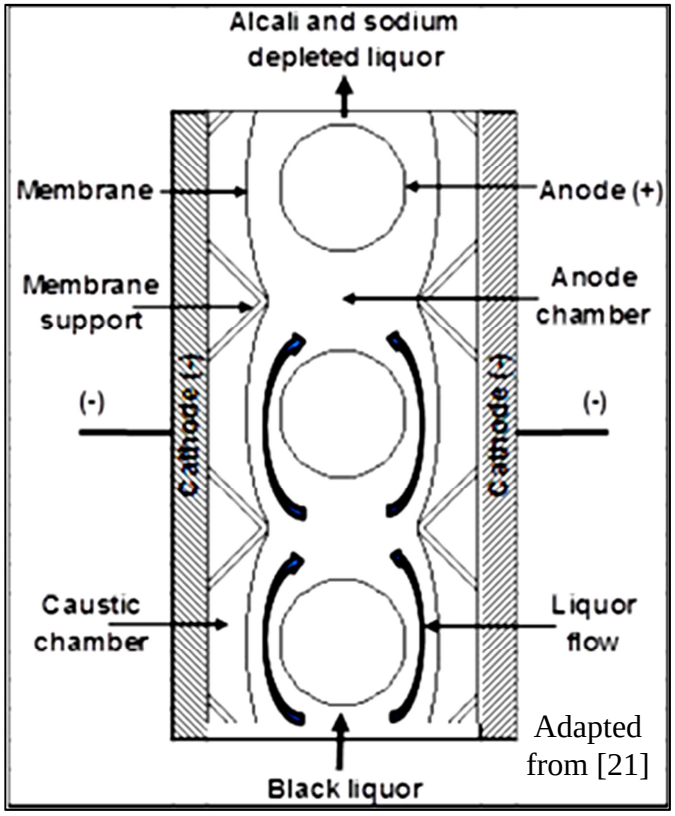

Figure 5.4 : Internal design of the ELSEP electrolysis cell

Table 5.4 : Cell design characteristics

Anode material	Ti/IrO_2-Ta_2O_5
Anode diameter, cm	1.27
Anode length, cm	14.0
Anode area, cm^2	55.9
Anode-membrane gap, cm	0.40
Cathode-membrane gap, cm	0.40
Distance between anodes, cm	1.73
Anode-anode center distance, cm	3.00
Membrane thichness, cm	0.015
Effective membrane length, cm	30.0
Effective membrane width, cm	14.0
Number of Nafion® 324 membrane	2
Membrane effective area, cm^2	840

Table 5.5 : Cell operating conditions

Anode current density, mA/cm^2	0-180
Cell voltage, V	0-4.85
NaOH, %	5.4
Temperatrure, °C	71.5
Black liquor solids, %	30.0
Black liquor flow, L/min	30.9
Black liquor conductivity, mS	117
Black liquor pH	9.0
Caustic flow, L/min	16.3
Caustic conductivity, mS	357
Black liquor inlet pressure, kPa	67.5
Black liquor outlet pressure, kPa	12.4
Caustic inlet pressure, kPa	137.8
Caustic outlet pressure, kPa	101.3

5.4 Experimental Results and Discussion

5.4.1 Current and Potential Distribution

Based on the cell design parameters (Table 5.4) and operating conditions (Table 5.5), it is possible to illustrate the distribution of current density (Figure 5.5) along the cell and in the vicinity of the anode (Figure 5.6) using the COMSOL software[18].

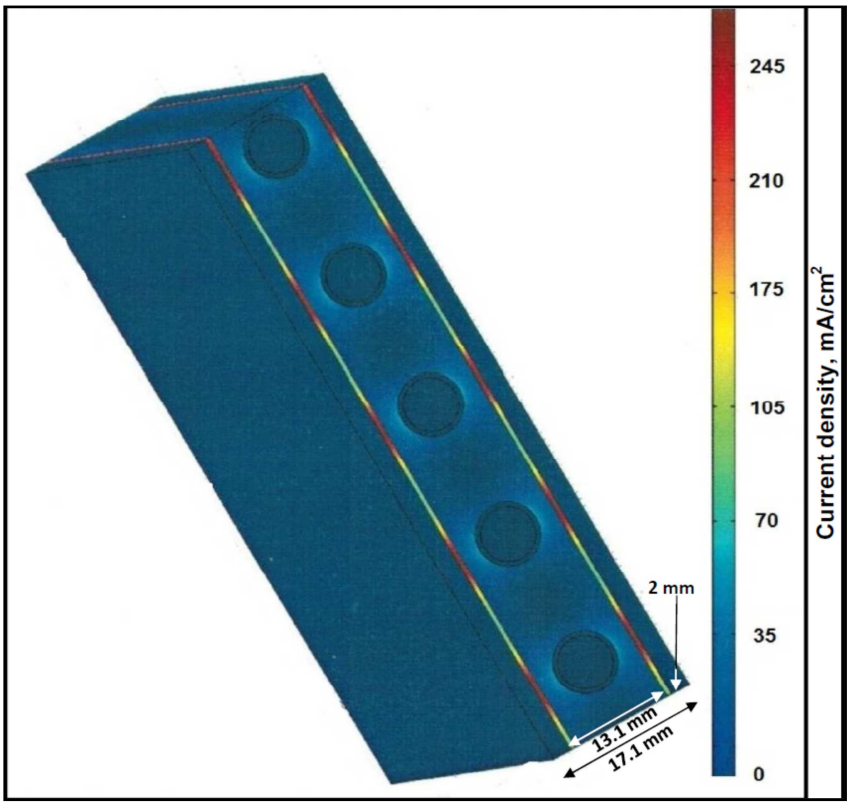

Figure 5.5 : Distribution of current density (mA/cm^2) along the cell when a total voltage of 4.5 V is applied to the cell.

For the purpose of the simulation, a current of 80 amps was applied to the 10 anodes with 8 amps per electrode corresponding to an average anodic current density of 142 mA/cm^2. As a consequence, the total voltage measured across the cell was 4.5 V. It can be observed that the current density was not uniform along the cell (Figure 5.5). Higher values (dark red segment)

[18]https://www.comsol.com/

existed on the outer surface of the anode facing the membrane. The simulation results also show that the entire perimeter of the anode was active in distributing the current through the surface exposed to black liquor but with more intensity on the surface closer to the membrane (Figure 5.6). Therefore, the current density varied considerably along the cell presenting a wave-like shape (Figure 5.7). At 0.05 cm from the outer anode surfaces, the current density reached a maximum value of 233 mA/cm^2. In the sections where the membrane is facing the non-occupied space between the anodes, the value dropped to 87 mA/cm^2 corresponding to a factor of 2.7. Moving away from the anode (0.2 cm) towards the membrane, the amplitude of the current density variation was reduced by a factor of 1.9. At such a position, the distance is halfway between the membrane and the outer surface of the anode. Each membrane supported an average current density of approximatively 73.0 mA/cm^2 [19,] but it is submitted to a higher density in the sections of membrane facing the anodes. Consequently, at these positions, the membranes transferred a higher flux of sodium from the black liquor to the caustic stream, which could be a limiting factor of the membrane's life expectancy.

The results show that from 0.05 cm to 0.20 cm distance from the anode, a factor of four, the peak current density is reduced by 25 % and the minimum value increases by 10 %. Assuming that the same factor would apply from 0.20 to 0.8 cm, we estimate a peak current density of 155 mA/cm^2 and a minimum value of 110.5 mA/cm^2 at the cathode. In a similar manner, we can estimate that the membrane located at 0.4 cm would be submitted to a peak density of 173.0 mA/cm^2 and a minimum value of 105.1 mA/cm^2.

Theoretically, each membrane supports an average current density of approximatively 95.2 [20,] mA/cm^2 but it is submitted to a higher density in the sections of membrane facing the anodes. Consequently, at these positions, the membranes transferred a higher flux of sodium from the black liquor to the caustic stream, which could be a limiting factor of the membrane's life expectancy.

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[19]Total amperage/(membrane length x width x No. of membranes) = 8 000 mA/(30 cm x 14 cm x 2) = 73.0 mA/cm^2
[20]Total amperage/(membrane length x width x No. of membranes) = 80 A x 1 000 mA/A x/(30 cm x 14 cm x 2) = 95.2 mA/cm^2

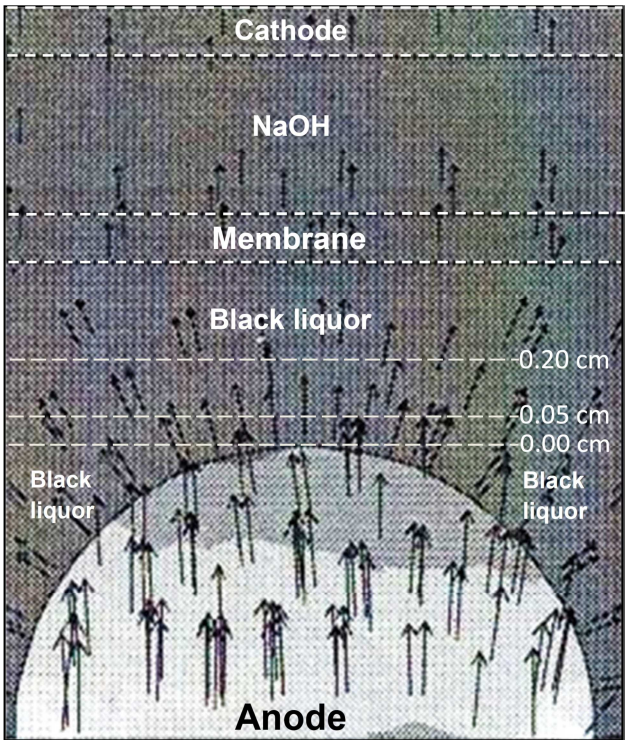

Figure 5.6 : Current density in the vicinity of the anode

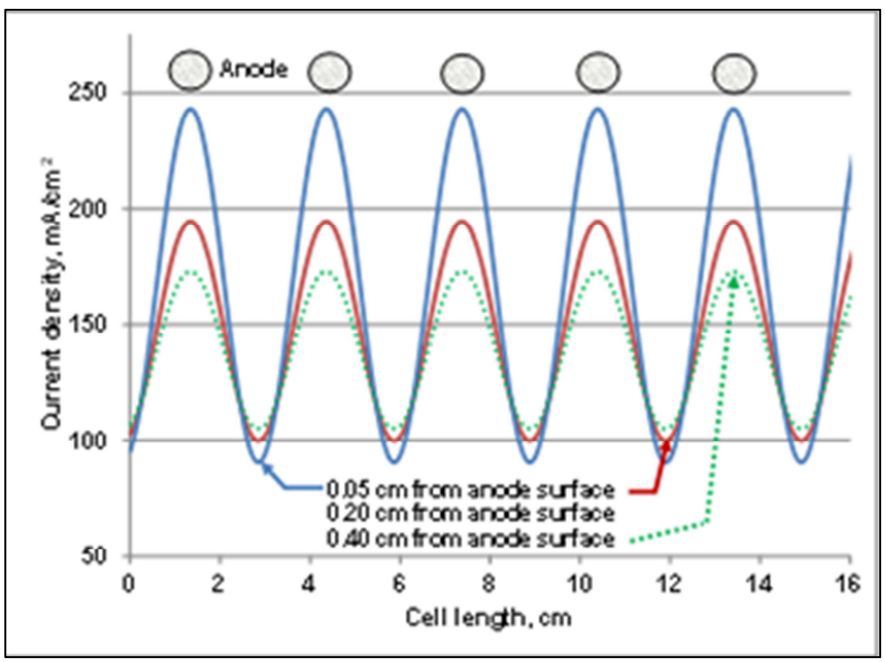

Figure 5.7 : Current density along the cell at 0.05, 0.20 and 0.40 cm from the anode surface

The profile of the current distribution is generally influenced by the cell geometry but in some cases it could also be related to the overvoltage η of the working electrode, which is related to the

current density [20]. Therefore, the current distribution was obviously influenced by the electrode polarization. This behaviour can be described by the dimensionless Wagner number (N_{Wa}) [22], an important parameter which helps to determine the effect of the potential polarization on the current distribution. The Wagner number expresses the ratio of the polarization resistance at the electrochemical interface over the ohmic resistance in the electrolyte [23-Sulaymon et Abbar] and is defined as:

$$N_{Wa} = (dV/dI) / (\kappa \cdot L) \qquad [5]$$

where κ is the electrolyte (black liquor) conductivity (S/cm), dV = the interface electrode potential, dI = the current density , L = the inter-electrode gap and dV/dI represents the slope of the polarization curve.

The current distribution became more uniform when the slope b of the polarization curve increased. Hine [20] demonstrated that a more uniform current density can be achieved for $\mathbf{N_{Wa}}$ greater than 1. An important criterion in the scale-up of electrochemical reactors is the electrical similarity that is respected when the $\mathbf{N_{Wa}}$ numbers have the same value at any site of the two reactors [23].

The current density profile along the cell used in this work could be improved by modifying the geometry. For example, if we decrease the diameters of the anodes and increase their number per unit length, that will shorten the distance between them and decrease the anode-membrane gap (L) as well. Therefore, a more uniform current density could be obtained. The experimental results reported by Sulaymon [24] for a cadmium recovery process confirm this assumption. The results could be explained through the understanding of electrochemical reactions, the current efficiency and energy consumption, the mechanism of sodium transfer and the Nafion® membrane performance.

5.4.2 Electrochemical Reactions During the Electrolysis of Black Liquor

5.4.2.1 Electrolysis of Black Liquor And Salt Conversion.

Kraft black liquors contain a large amount of sodium (20%) from the cooking liquor and a small fraction (1%) of potassium originating from the wood [8]. These liquors are mixtures of inorganic compounds, principally sodium salts, such as NaOH, Na_2CO_3, Na_2SO_4, Na_2S, and

sodium salts of organic material along with a low level of potassium salts. It is estimated that the sodium is evenly distributed between inorganic and organic salts [7].

Due to alkaline salt components, the pH of black liquor is rather high (13.0-14.0) [25]. In order to precipitate lignin, the liquor is submitted to an electrolytic treatment that can drop the pH to the point of initiating lignin precipitation (pH 9.5-10.0) and possibly much lower (2.0-4.5) [8, 26]. During electrolysis, the sodium leaves the anolyte compartment to be transferred to the catholyte producing NaOH. With regard to maintaining electro neutrality in the liquor compartment, as long as the liquor is alkaline, OH^- ions are oxidized at the anode causing a drop of the pH. This oxidation reaction occurs according to the following equation [27]:

$$4\ OH^- \rightarrow 2\ H_2O + O_2 + 4\ e^- \quad E_e^o = +0.40\ V\ vs\ SHE \qquad [6]$$

When the electrolysis time increases, the pH decreases and water produced in equation [7] reacts with the sodium carbonate to give sodium bicarbonate (eq. 7) and then carbonic acid (eq. 8). Finally, at a pH lower than 5.0, carbon dioxide is released from the solution (Figure 5.8) according to equation 9.

$$Na_2CO_3 + 2\ H_2O \rightarrow NaHCO_3 + NaOH + 1/2\ O_2 + H_2 \qquad [7]$$

$$NaHCO_3 + 2\ H_2O \rightarrow H_2CO_3 + NaOH + 1/2\ O_2 + H_2 \qquad [8]$$

$$H_2CO_3 + H_2O \rightarrow CO_2 + H_2 + 1/2\ O_2\ (pH<5) \qquad [9]$$

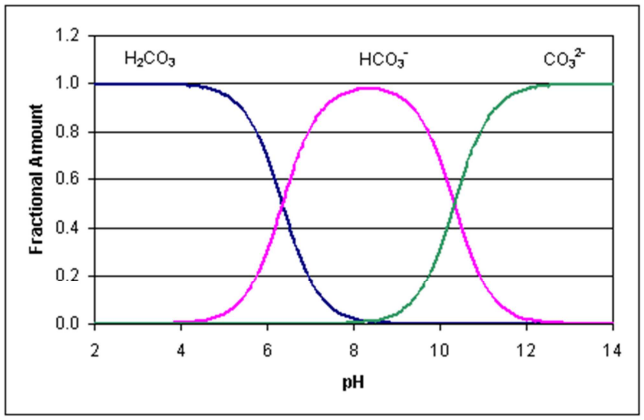

Figure 5.8 : Distribution of carbonate and bicarbonate species[21] as a function of pH

Initially, the anodic reaction proceeds via equation (6) in an alkaline medium while it transfers to equation (10) in an acidic solution where the water is being oxidized to oxygen and proton ions:

$H_2O \rightarrow 2\ H^+ + 1/2\ O_2$ (Anode reaction) [10]

As the pH decreases with the continuous generation of H^+ ions, salts are converted to their acid form. For example, sodium sulfate is converted to sulfuric acid and organic salts to their respective organic acids, such as vanillin to vanillic acid [26] and caustic soda.

5.4.2.2 Sulfide Ion Oxidation.

The residual black liquor still contains 80% of the sodium sulfide brought in with the cooking liquor. In the solution, the sodium sulfur is hydrolyzed according to the following reaction:

$2\ Na_2S + H_2O \rightarrow 2\ NaSH + 2\ NaOH$ [11]

At the high pH (13.9) value of the liquor, the sulfur species are mainly HS^- (50%) and S^{-2} (50%) (Figure 5.9) [28]. As the pH drops to the 10.0-11.0 range, all the sulfur ions are present as HS^-. If, however, the pH of the liquor is reduced to 9 or lower, the HS^- ions are transformed to undesirable H_2S gas.

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[21]http://ion.chem.usu.edu/~sbialkow/Classes/3600/Overheads/Carbonate/CO2.html

It has been a common practice in Kraft mills to submit the black liquor to an oxidation step using air or oxygen prior to its concentration in multiple-effect evaporators [29]. This results in the formation of more stable sulfur compounds reducing sulfur emissions [30]. Depending on the authors, the sodium sulfides could be converted to polysulphides, thiosulfates or sulfates [30--32], which are more stable sulfur compounds, reducing H_2S emissions and helping to meet regulations.

Both non-oxidized and oxidized black liquor contain residual sulfides. Non-oxidized black liquor at 15% solids contains about 8.3 g/L (As S^{2-}) [33] while oxidized liquor at 30 % solids contains about the same concentration (8.1 g/L) [7]. That means that only half of the sulfide ions have been converted to thiosulfate. The presence of residual sulfide ions in black liquor could be an issue when the pH drops to low acid values generating H_2S gas (Figure 5.9) [28]. It would create the formation of undesirable H_2S during the acid wash of precipitated lignin [4].

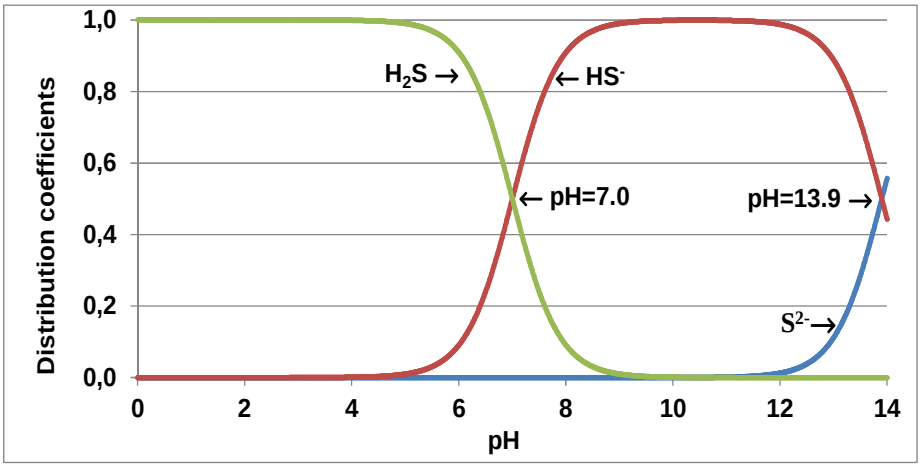

Figure 5.9 : Sulfur species distribution coefficients as a function of pH

The electrochemical oxidation of sulfides in black and white liquors has been studied [26, 34-37]. The oxidized product depends on the anode material [38]: S_0 and S_x^{2-} on graphite, intermediate sulfur compound on platinum, SO_4 on boron doped diamond anode or polysulfide on Ti/Ta_2O_5-IrO_2 at low current density. At low current density (<35 mA/cm^2), the sulfide ions are oxidized to polysulfide. When the electrode potential increases along with current density, oxygen evolution significantly increases [36]. At a higher current density (>100 mA/cm^2) where oxygen production is predominant, the sulfides are oxidized to thiosulfates and sulfates [35]. As

previously shown (equations 1-5), the electrochemical conversion of salts generates oxygen at the anode at high current densities. That oxygen is available to oxidize the sulfur compounds of the black liquor, such as Na_2S to sodium thiosulfate ($Na_2S_2O_3$). The overall reaction can be written as:

$$2\ Na_2S + 2\ O_2 + H_2O \rightarrow 2\ Na_2S_2O_3 + 2\ NaOH \qquad [12]$$

Fortunately, by the time the electrolyzed black liquor has reached a pH of 8.5, all the sodium sulfide has been oxidized to a more stable product ($Na_2S_2O_3$) preventing undesirable H_2S gas formation (Figures 5.10 and 5.11) [8].

If electrolysis is pursued below pH 8.5, the oxidation reaction continues and the thiosulfate can then be oxidized to sodium sulfate (eq. 13) [31, 32] according to the following reaction:

$$Na_2S_2O_3 + 2\ NaOH + 2\ O_2 \rightarrow 2\ Na_2SO_4 + H_2O \qquad [13]$$

In brief, regardless of the final oxidation product, sulfide ions are converted to more stable sulfur compounds eliminating the formation of undesirable H_2S gas at an acidic pH.

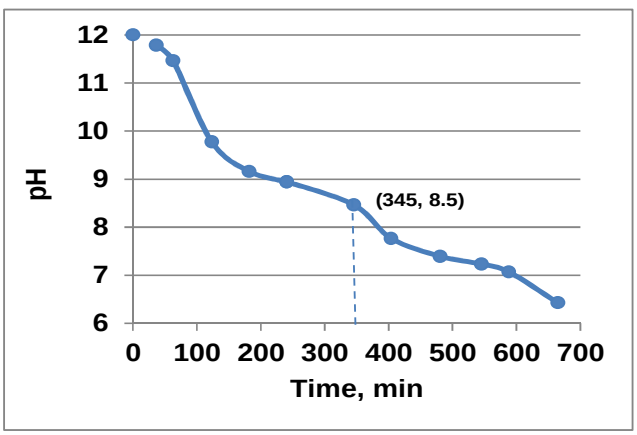

Figure 5.10 : Change in pH as electrolysis proceeds

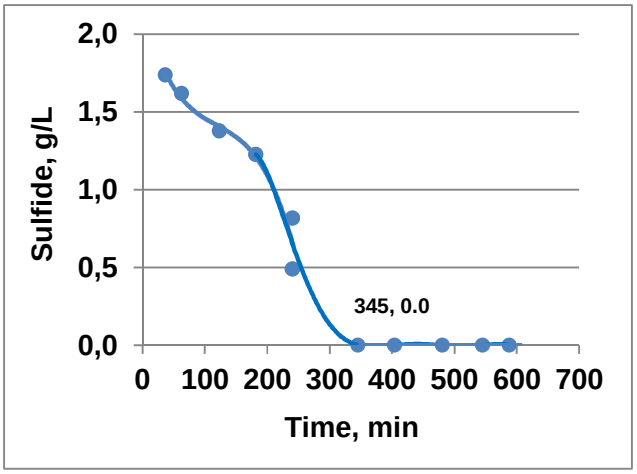

Figure 5.11 : Oxidation of sulphide ions as electrolysis proceeds

5.4.3 Voltage Cell Balance

The current density profile expressed as a function of the total voltage for a 30% black liquor solution was developed based on two pH values and two caustic concentrations (Figure 5.12). At pH 9.0 for the treated black liquor, the caustic concentration had only little impact (6.6%) on the curve slope. We noticed that, in the 5.4% NaOH case, the curve slope decreased slightly in the vicinity of 4 V (3.8 to 4.2 V) and returned to its initial value. No explanation can be provided for that bend in the curve other than a possible deposit blocking sodium transfer. However, reducing the pH from 9.0 to 6.0 reduced productivity by 32% based on the current density at a constant voltage. By dropping the pH to an acidic value (pH 6.0), the electrochemical equilibrium reactions change and carbon dioxide would start to form (Figure 5.8) increasing cell ohmic resistance. On the other hand, the limiting current density is dependent on the pH which determines the level of residual sodium. Based on the continuous progression of current density as the voltage increases, we can conclude that at pH 9.0, where less than 40% of the sodium is removed from black liquor [8], the sodium content of the liquor is high enough (approximately 48 g/L) so the process operates below the limiting current density and is not sodium-transfer limited. However, in a previous study, it was shown that at pH 6.0 where 56.4% of the sodium was removed from black liquor making the concentration drop to 28 g/L, a limiting current density was observed around 200 mA/cm^2 [7].

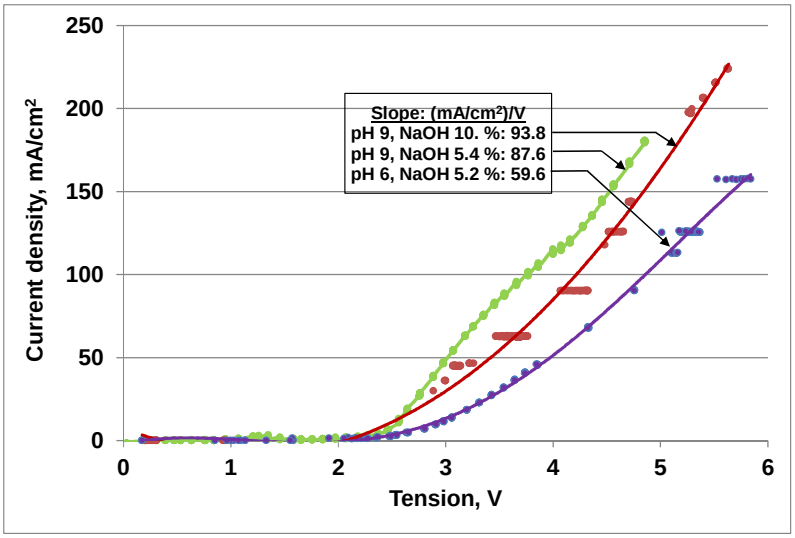

Figure 5.12 : Current density profile as a function of total cell voltage

The terminal or total voltage V_{Tot} of the cell during the electrolysis of black liquor comprises three major contributions: (1) the equilibrium reaction voltage E_e, (2) the total polarization, anode and cathode overvoltages (η_{An} and η_{Cat}) and the sum of the ohmic voltage drops (Σ I·R) (Figure 5.13). The experimental values of the equilibrium reaction potential and the overvoltage are in agreement with the values determined theoretically below.

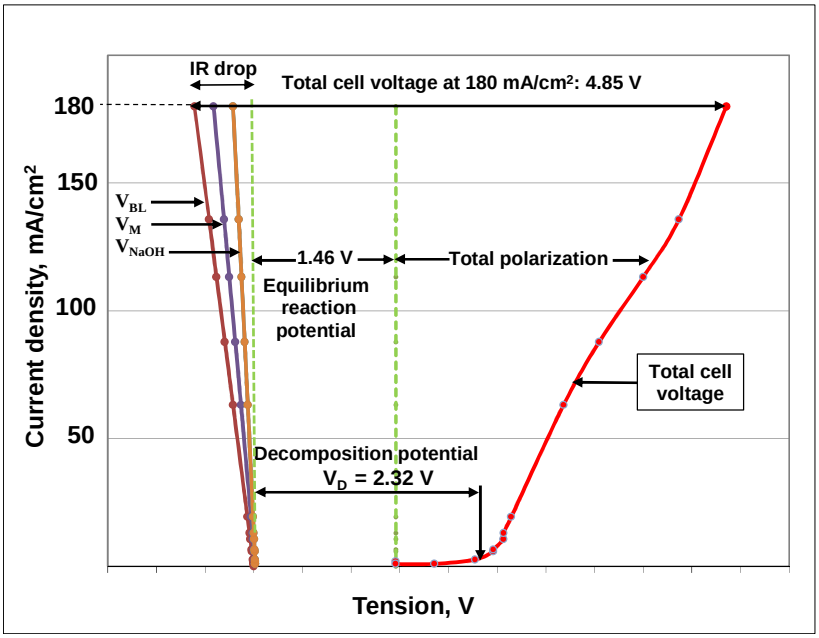

Figure 5.13 : Cell components' contribution to total cell voltage during the electrolysis of black liquor at pH 9.0 and 73 °C while producing 5.4% NaOH

5.4.3.1 Equilibrium Reaction Potential (E_e).

The equilibrium reaction potential is the minimum voltage at which the electrochemical reaction takes place [38]. In our application, as mentioned previously, the electrolysis of water was the dominant reaction producing oxygen and hydrogen. The overall reaction is represented by the following equation:

$$H_2O\ (l) \rightarrow H_2(g) + 1/2\ O_2(g) \qquad [14]$$

The potential of the reaction can be determined using equations 15 to 18 for water electrolysis.

$$\Delta G^R = \Delta G°_{25} + RT\ Ln\ (K) \qquad [15]$$

$$\text{where } K = a_{H2}\ a^{1/2}_{O2} / a_{H2O} \qquad [16]$$

$$E_e = \Delta G^R/(2 \cdot F) \qquad [17]$$

Both ΔG^R and E_e vary depending on the concentration and temperature because the activities of the chemical species involved in the reactions are related to their concentration and temperature [21]. The operating conditions of the temperature and pressure in both compartments are listed in Table 5.5. The values of the parameters employed are given below:

$\Delta G°_{25}$=236 330 J/mole

T = 73 °C (346 °K), R = 8.314 J/(mole·K),

a_{H2O} = 1.0, a_{H2} = 0.60 atm, the partial pressure of H_2, and a_{O2} = 0.66 atm, the O_2 partial pressure.

Under these conditions, we calculate that E_e = 1.20 V. However, at that voltage, one must add the electromotive force related to the concentration gradient of anion OH^- across the membrane, expressed as follows:

$$E_{OH-} = R\ T\ Ln\ (a_{OH\text{-}cathode}/a_{OH\text{-}anode})/F \qquad [18]$$

In order to proceed with the computations of E_{OH-} using Equation 148, the concentration of hydroxyl anion as the chemical activity for each of the cell compartments must be taken into consideration. For example, at a typical concentration of 1 M for OH- in the catholyte, the value of $a_{OH\text{-}cathode}$ is equal to 1. The value of $a_{OH\text{-}anode}$,can be estimated based on the pH of the anolyte black liquor and its temperature. At pH 9.0 and T= 73 °C, and pK_{H2O} = 12.8, it can be determined that a_{OH-} = 1.65E^{-4} mole/L and then, according to eq. [18], E_{OH-} = 0.26 V. Adding this

value to the 1.20 V calculated previously, a thermodynamic electromotive force (E_e) of 1.46 V is obtained.

5.4.3.2 Electrode Overvoltages.

In this work, the anodic overvoltage was estimated by means of the data from Jin et al. [26] for various electrolysis systems including black liquor. From cyclic voltammetry and anodic polarization curves, we observed a slope of 280 mV/decade in the oxygen evolution region (Figure 5.14) in the case of black liquor electrolysis conditions. As mentioned by the authors, the oxygen evolution reaction starts at 0.79 V instead of 0.57 V for a sodium hydroxide solution. The complex composition of black liquor has an inhibiting effect. Assuming that black liquors exhibit similar behaviour, we estimate that the anode overvoltage in the higher current density region 180 mA/cm^2) considered with our situation would be around 0.6 V. This is in agreement with experimental values obtained here as indicated in Table 5.6.

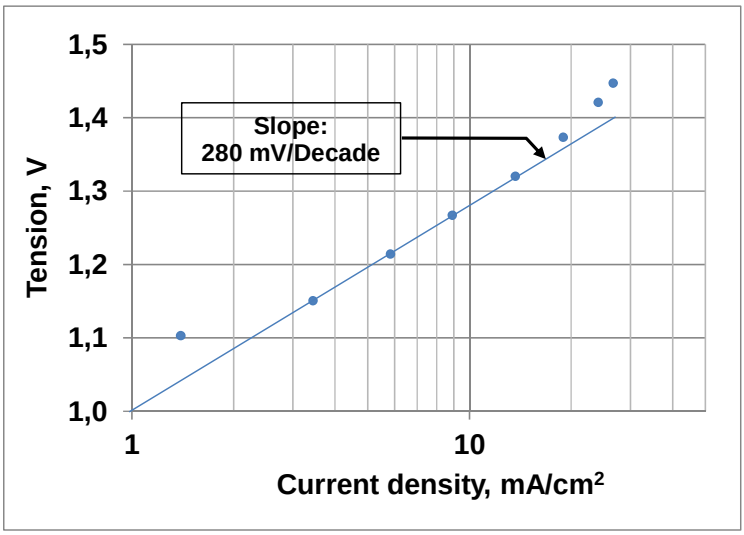

Figure 5.14 : Anodic overvoltage from cyclic voltammetry test with black liquor

Low carbon steel cathodes were used in chlor-alkali and alkaline water electrolysis due to their low cost, easy availability and low overpotential (about 300mV) at a current density of 200-300 mA/cm^2 at 80°C [39]. Olivares-Ramirez et al. [40] studied the hydrogen evolution in alkaline medium on different stainless steel cathodes. They concluded that SS-316 is the best cathodic electrode due to its higher nickel content with respect to other stainless steel electrodes. According to their cyclic voltammagram in 1 M NaOH, the slope of the current density vs voltage is 300 mV/decade. At an operating cathodic current density of 180 mA/cm^2, the cathode

overvoltage of the hydrogen evolution reaction in 1.44 M NaOH was estimated at 0.54 V. This value is also in agreement with the experimental data obtained here.

5.4.3.3 Ohmic Voltage Drop.

The total ohmic voltage of the cell comprises the following constituents:

$$\Sigma\, I \cdot R = \mathbf{V_{BL}} + \mathbf{V_{BLML}} + \mathbf{V_{M}} + \mathbf{V_{NaOHML}} + \mathbf{V_{NaOH}} \qquad [19]$$

Where:

V_{BL} is the voltage drop across the black liquor compartment,

V_{BLML} = the voltage across the black liquor boundary layer next to the membrane,

V_{M} = the voltage across the membrane,

V_{NaOHML} = the voltage drop through the caustic boundary layer at the membrane interface and V_{NaOH} = the voltage drop through the caustic compartment.

Based on Carlberg's findings [14], the terms $\mathbf{V_{BLML}}$ and $\mathbf{V_{NaOHML}}$ can be overlooked.

The conductivities of the electrolyte solutions are key properties influencing the cell voltage drop negatively impacting the energy consumption. Trinh et al. [33] studied the factors affecting the conductivity of kraft black liquor. They found that it depends on the concentration of inorganic compounds, such as NaOH, Na_2S, Na_2CO_3, as well as the pulping conditions, such as cooking time, caustic charge and temperature. The effect of temperature on conductivity profile was found to be different for various concentrations of black liquor, which was also reported by Cloutier [7]. Typically, the conductivity reaches a maximum between 25 and 30% solids depending on the temperature. We determined that black liquor electrolyzed at pH 9.0 also reaches a maximum conductivity at around 30% solids (Figure 5.15).

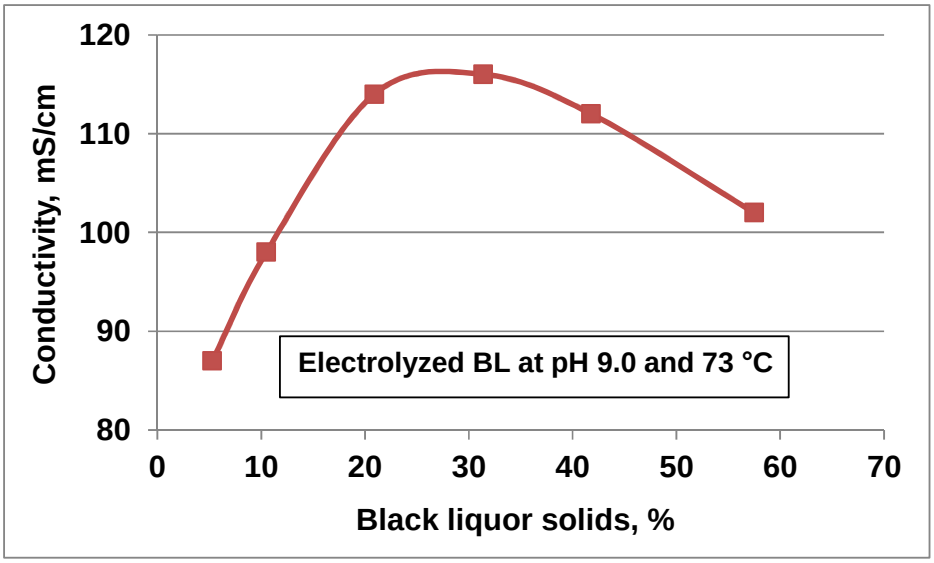

Figure 5.15 : Conductivity of electrolyzed black liquor (pH 9.0) as a function of solids

The conductivity of 30% black liquor at pH 9.0 (117 mS/cm) is much lower compared to 357 mS/cm for the 1.44 M (5.4%) NaOH solution produced in the catholyte compartment. In fact, since it represents one third of the caustic conductivity, the voltage IR in the black liquor compartment is 3 times lower than in the NaOH compartment.

The ohmic voltage drop across the black liquor and NaOH compartments is calculated as follows:

V_{BL} = J (83 mA/cm^2) x Δl (0.4 cm)/κ (117 mS/cm) x 2 compartments = 0.57 V [20]

V_{NaOH} = J (83 mA/cm^2) x Δl (0.4 cm)/κ (357 mS/cm) x 2 compartments = 0.19 V[21]

where J is the current density,

Δl = the anode or cathode compartment gap and

κ = the solution conductivity.

The ohmic voltage drop of both electrolyte solutions (black liquor and caustic) totalizes 0.76 V.

The voltage drop across the membrane could be estimated based on Ohm's law (V= R·I). By using the membrane conductivity reported in literature (73.0 mS/cm) [25] and assuming a linear relationship, at a current density of 180 mA/cm^2, the voltage drop is estimated at 0.18 V. Using a resistance of 4.5 Ω·cm^2 provided by the manufacturer (in 0.6 M KCl), 0.81 V is obtained. The method tends to overestimate the voltage drop especially in the high ranges of current density.

On the other hand, Moshtarikhah [41] determined experimentally that the voltage drop across the membrane does not follow a linear relationship with current density. His results indicated that the voltage increases up to a current density of 500 mA/cm^2 and then levels off (Figure 5.16). It is observed that the slope corresponding to the membrane resistance increases linearly at low current density but stabilizes at higher current densities. He suggests that increasing the current density results in the swelling of the membrane due to an increase in the channel diameter and the number of pores taking part in ion transport.

We applied the results of his findings to our situation and determined that, at the current density that each membrane is exposed to (83 mA/cm^2), the voltage drop would be 0.14 V (Figure 5.16) for each membrane and 0.28 V for both. This value is more representative since it is based on experimental measurement as opposed to theoretical calculations.

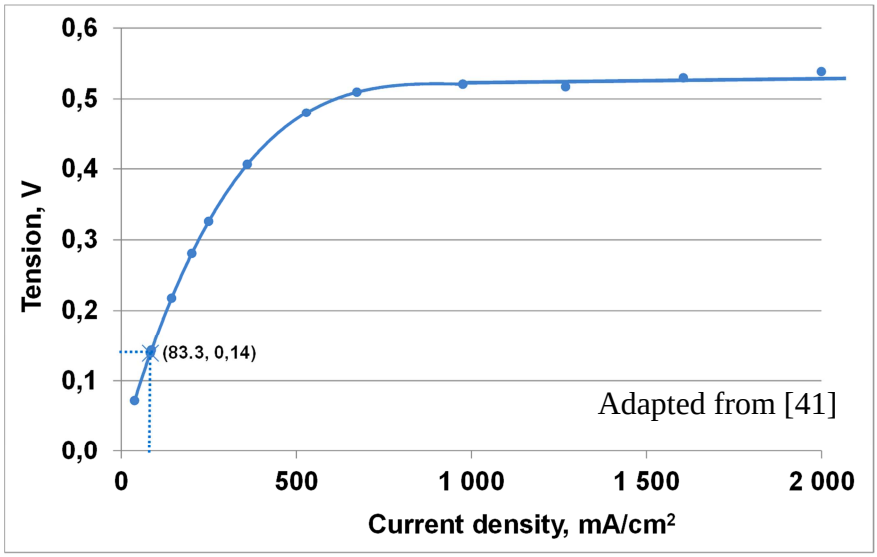

Figure 5.16 : Measured voltage through a Nafion® membrane as a function of current density.

Gas bubbles, oxygen at the anode and hydrogen at the cathode are formed during the electrolysis of black liquor. These bubbles disperse in the solutions causing the streams to become two-phase flows. The bubble effects are classified as (1) the surface area reduction on the electrodes, and (2) the generation of a gas void fraction in the electrolytic solutions thereby increasing its resistivity [20]. The gas void fraction is closely related to the bubble size and current density. During water electrolysis in a 20% NaOH solution, the voltage drop due to bubble effects is estimated at 5% of the total cell voltage. According to our experimental results, when operating at a current density of 180 mA/cm^2, the total cell voltage is 4.85 V (Figure 5.13). Based on the

similarity of the solution composition in our application and the electrode reactions, we estimate the contribution of bubbles to be 0.24 V.

The voltage contribution of each cell constituent is shown in Table 5.6. In order to balance the sum of the contributions with the total voltage, we added a hardware IR drop as suggested by Hine (1.4%) [20] and other contributions accounting for a total of 0.16 V. The other contributions could be secondary electrochemical reactions unaccounted for outside the predominant reaction of water electrolysis due to the complex composition of black liquor.

Table 5.6 : Cell voltage distribution at a current density of 180 mA/cm^2

Constituent	Voltage	
	V	%
Decomposition potential, V_D	2.32	47.8
Estimated electrode overvoltage		
Anodic overvoltage, η_{an}	0.50	10.4
Cathodic overvoltage, η_{cat}	0.54	11.1
Sub-total (1)	1.04	21.5
Solution IR drop		
Anolyte (black liquor), V_{BL}	0,57	12.5
Catholyte (NaOH), V_{NaOH}	0,19	4.1
Sub-total (2)	0.81	16.7
Membrane IR drop, V_M	0.28	5.7
Bubble effect	0.24	5.0
Hardware effect and others	0.16	3.3
Total	4.85	100.0

It is clear that the decomposition voltage (48%) is the major contributor to the cell voltage followed by both hydrogen and oxygen overvoltages (21.5%). The solutions account for 16.7% of the voltage drop with the black liquor having a voltage drop three times higher than the NaOH solution since its conductivity is about one third of the caustic solution. Due to the internal cell configuration, the membranes are exposed to a low current density and consequently their voltage drop contribution is only 5.7%. The energy consumption of this process would benefit primarily from lower overvoltage electrode materials and increasing the black liquor's conductivity.

5.5 Conclusion

The electrochemical treatment of black liquor is proposed as an alternative to recover lignin from kraft black liquor and is a priority in the biorefinery initiative for the pulp and paper industry. A special feature of the electrochemical process is the use of electric energy as a driving force for the chemical reactions to replace the use of chemicals. The fundamental electrochemistry of cell operation was investigated. The membrane acts as a selective media for sodium ions moving towards the catholyte compartment under the influence of the electric field.

Based on experimental results complemented by data from the literature, the cell operation and the electrochemical reactions encountered were elucidated and it was shown that the principal reaction was the decomposition of water and the production of caustic soda from the sodium recovered from the black liquor. Secondary reactions include the complete oxidation of sulfide ions to thiosulfate and the transformation of sodium carbonate to bicarbonate and eventually carbon dioxide.

It was demonstrated, in our tubular anode cell-design electrolyser, that the current density distribution is unevenly distributed along the cell presenting a sinusoidal-like shape with a maximum at the anode surface and a minimum in the area between the anodes. However, the current density becomes more and more uniform as the distance between the anode and the membrane and the flat cathode was increased. In order to reduce that current variation, it was proposed to downsize the anode diameter and install more anodes per unit length.

The influence of the black liquor pH on cell voltage as a function of current density was studied. It showed similar curve shapes but with different slopes compared to what is proposed in the literature. At a high pH (9.0), we obtained a better current density at the constant voltage indicating a more productive condition for water splitting than at a pH value of 6.0.

The distribution of the estimated voltage contributions of cell components revealed that the major contributors were the decomposition reaction (48%) followed by the electrode overvoltages (21.5%). The ohmic voltage drop of the electrolytes and the membranes accounted for 22.4%, or 16.7% and 5.7% respectively. The energy consumption of the proposed process would benefit the most from lower overvoltage electrode materials and increasing the black liquor conductivity.

5.6 Acknowledgments

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CHAPITRE 6 ARTICLE 2: ELECTROLYTIC PROCESSING OF KRAFT BLACK LIQUOR- MASS TRANSFER INVESTIGATION

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The chemical approach to precipitate lignin from black liquor consists of reducing the pH using carbon dioxide and sulfuric acid to wash the lignin. We have developed an electrochemical avenue for lowering pH while recovering caustic and acid from salts. It includes electrolytic treatment of black liquor that reduces its alkalinity to the critical point of lignin precipitation without using chemicals of external source. This electrolytic treatment is based on the use of cationic exchange membrane. In this study, we modeled the mass transfer phenomena of most important ions through the membrane during electrolysis. We report on the investigation of sodium, protons hydroxyls ions and pH profiles across the membrane under typical operating conditions. We evaluated this membrane process performance based on mass transfer coefficient and caustic productivity.

6.1 Introduction

The recovery of lignin from kraft black liquor (BL) to make value-added biomaterials is a part of the biorefinery initiative in the pulp and paper industry [1]. The industry presently relies on acid precipitation (Carbon dioxide) using commercial technologies, such as LignoBoost [2] and LignoForce [3].

That first generation of lignin recovery technologies suffers from major limitations, mainly (1) the additional load to the effluent and (2) the recausticizing system, (3) the disturbance of the black liquor Na/S balance and (4) the lower limit of the lignin production capacity [4]. In that regard, the second generation of lignin recovery technologies relying on electrochemical processes eliminates many of the above issues [5, 6-8].

We proposed an electrochemical approach to precipitate lignin from BL making the technology more environmentally friendly while supporting sustainable development where electricity is provided from a renewable source. A special feature of electrochemical processes is the use of electricity as a driving force for the chemical reaction and the electrons are considered a feedstock rather than a utility [9]. The advantages of the electrochemical approach to precipitate lignin are the following: (1) no chemical requirement from an external source, (2) no additional discharge to the effluent treatment, (3) no disturbance of the Na/S balance, (4) a reduction in the inorganic content of BL by extracting the sodium, which results in an increased black liquor calorific value, (5) off-loading the overloaded causticizing system and a reduction of GHG emissions, (6) oxidation of sulfide ions, thus eliminating H_2S formation and (7) a significant increase in the evaporation capacity of a kraft mill since it will be able to reduce liquor viscosity by tenfold [10].

In our previous experimental study [4] we reported on the fundamentals of electrochemistry occurring during the electrolysis of black liquor, including electrochemical reactions, current density distribution along the electrolytic cell that leads to recommendations for improving cell design, the influence of black liquor pH on the cell voltage as a function of current density and, finally, the contribution of the individual cell components to the total voltage [4].

This study is on the mass transport involved during the electrolytic treatment of black liquor to reduce its pH to the point of lignin precipitation or even lower, if desirable. Specifically, we modeled the mass transfer phenomena related to the ion exchange membrane of the electrochemical cell used for the electrolytic treatment. We reported on the transport of sodium ions, protons, hydroxyl ions and thus the pH profile across the membrane under typical operating conditions.

6.2 Theoretical aspects on mass transport phenomena

6.2.1 General aspects

Lowering the pH of BL electrochemically relies on electrolysis membrane technology. An electric potential is applied across the anode and the cathode separated by a

membrane to split sodium salts. This electric potential forces the Na^+ ions to move out of the liquor in order to maintain electroneutrality in the compartment where OH^- ions are reduced to water and oxygen. The sodium ions that are attracted toward the negative cathode migrate through the membrane to reach the catholyte compartment where they combine with cathode-generated OH- ions to make caustic soda. The process performance is based on the selectivity of the membrane favoring the passage of sodium and blocking the back migration of hydroxyl ions toward the liquor.

In this study, we consider transport phenomena related to Na^+, H^+ and OH^- ions under acidic or basic operating states of the membrane. Under the influence of the electric potential, the Na^+ and H^+ ions are moving from the anolyte to the catholyte compartment passing through the membrane while the OH^- ions are back migrating in the opposite direction. We assume that the membrane consists of a homogeneous solid phase (in the form of a flat sheet) in contact with the BL (anolyte) on one side and a caustic soda solution (catholyte) on the other side.

The membrane within the electrolysis cell is surrounded by two film layers: one at the BL interface and the other at the NaOH solution interface (Figure 6.1). A typical Na^+ concentration profile is also shown as an illustration comprising a Na^+ concentration gradient across the thickness of the membrane, a step concentration at each of the membrane layer interfaces, and at last, a Na^+ concentration gradient in each of the film layers. For each of the layer-membrane interfaces, we assume a two-phase equilibrium with the membrane taking into account the so-called Donnan effect.

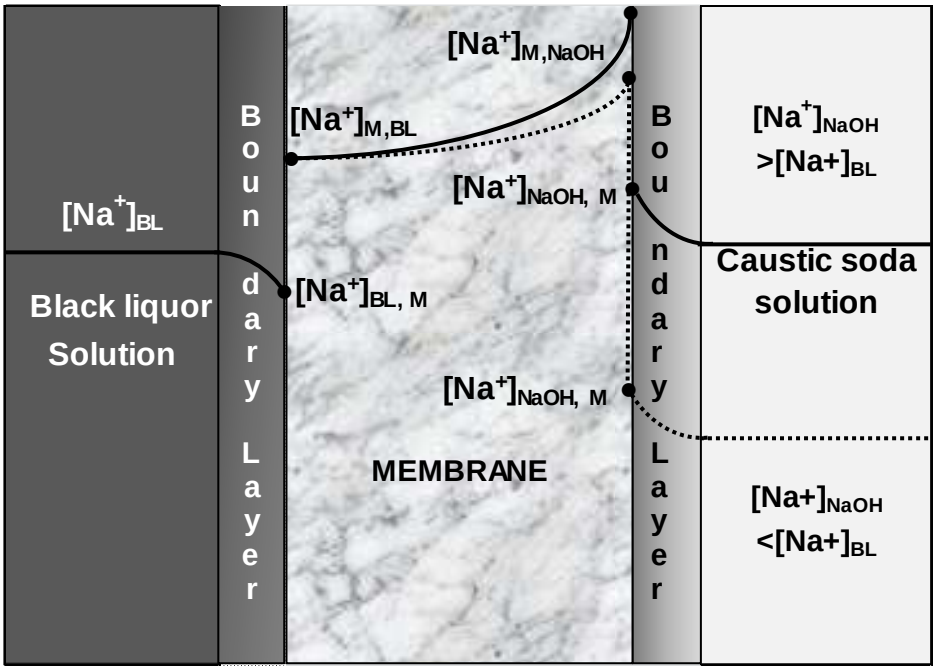

Figure 6.1 : Illustration of the sodium concentration profile across the membrane applied to electrolysis of black liquor taking into account the so-called Donnan effect.

6.2.2 Modelling of transport phenomena in the membrane

Mass transport in electrochemical cells is caused by three phenomena: (1) diffusion, (2) migration from electro-potential, and (3) convection [11]. The complete Nernst-Planck equation for modeling the transport of an ion in an ion-exchange membrane can be written in the following vectorial form [12:

$$J = - D\cdot \nabla C - D\cdot z\cdot C\,(F(/R\cdot T))\cdot \nabla \Phi + v\cdot C \qquad [1]$$

Assuming a negligible impact of the convection term, which is demonstrated later, and the transport in one direction through the membrane only, i.e., the transport of ions from the anolyte to the catholyte at a steady state regime, the equation is simplified to (the x-direction is normal to the membrane):

$$J = -D\cdot \partial C/\partial x - D\cdot z\cdot C\cdot (F/(R\cdot T))\partial \Phi/\partial x \qquad [2]$$

J: flux of species across a plane perpendicular to the x direction (mole $m^{-2}\cdot s^{-1}$)

D: Diffusion coefficient ($m^2\cdot s^{-1}$)

C: Concentration ($mole \cdot m^{-3}$)

x: Distance (m)

z: Charge number of a given species

F: Faraday constant (96 485 $A \cdot s/mole$)

Φ: Electrical potential (V)

T: Temperature (K)

R: Gas constant (8.31 $kJkmol^{-1} \cdot K^{-1}$)

v: Electrolyte velocity in the direction of flux ($m \cdot s^{-1}$)

The diffusion term comes from Fick's law and represents the flow of species due to a concentration gradient. The migration is due to the gradient of electrical potential and the convective part is induced by the bulk movement and affected by the osmotic pressure and electro-osmotic effects [13, 14].

This equation (2) is usually strictly applicable only in dilute solution (<0.01 M) but still commonly used for all conditions [12] because of its high complexity at high concentration. Carlberg [15] proposed a simplified mass transport model based on the Nernst-Planck equation by reducing the number of dimensions in the geometry and the number of independent variables. He developed three dimensionless ratios to characterize each of the three phenomena mentioned above concerning ion transport: (1) convection/diffusion (C/D) ratio corresponding to the Peclet number (P_e), (2) migration/diffusion (M/D) and (3) migration/convection (M/C) or :

$$Convection/Diffusion = P_e = \upsilon \cdot L/D_i \quad [3]$$

$$Migration/Diffusion = z_i \cdot F \cdot \Delta\Phi/(R \cdot T) \quad [4]$$

$$Migration/Convection = z_i \cdot F \cdot D_{i,m} \cdot \Delta\Phi / (R \cdot T \cdot \upsilon \cdot L) \quad [5]$$

where indices i and m refer to a specific ion and the membrane respectively, L is the thickness of the membrane, and $\Delta\Phi$ is the voltage drop across the membrane assuming $\partial\Phi/\partial x$ is equal to $\Delta\Phi/L$.

Then, the author estimated the three ratios with the objective of comparing the relative significance of each transport mechanism in the overall transfer process. He demonstrated which mechanisms are the most important for ion transport through the membrane and any that can be neglected due to their insignificance.

Carlberg [15] developed an analytical solution for eq. [2] assuming that the convective term was negligible (*Conv/Diff* >> 1 and *Conv/Diff* << 1), which is reasonable for electrolysis with a membrane cell. The final solution describing the profile of the ion concentration across the membrane at a steady state is expressed as follows:

$$C_x = C_1 + \frac{(C2-C1)}{[e(-zF\Delta øx)/RTL) - 1)]} \cdot [e^{(z \cdot F \cdot \Delta ø)/R \cdot T \cdot L \cdot x)} - 1] \qquad [6]$$

where the indice 1 refers to the inner part of the membrane on the anode side (x = 0) and 2 refers to the inner part of the membrane on the cathode side (x = L). For instance, C_1 represents $[Na^+]_{M.BL}$ and C_2, $[Na^+]_{M,NaOH}$. Equation [6] can be used to predict the concentration profile of ions Na^+ and the pH profile across the membrane.

6.2.3 Effect of the acid or alkaline membrane state on transport phenomena

Jörissem and Simmrock [16] studied a phenomenon whereby there is a loss in the membrane's current efficiency with the electrolysis of Na_2SO_4 following an increase in the concentration of both products: H_2SO_4 and NaOH. They proposed two models (Figure 6.2) to explain the phenomena, one when the membrane operates in an acidic state and the other one when the membrane is in an alkaline state.

The acidic state prevails when the concentration of H^+ ions surpasses the Na^+ ions. The membrane affinity for H^+ ions is three times higher than for sodium [17]. When the membrane operates in an acidic state, the H^+ ions cross the membrane and move toward the catholyte where they neutralize hydroxyl ions making the current efficiency very sensitive to the acidic concentration [16]. When the membrane operates in an acidic membrane state, the hydroxyl concentration in the catholyte has no influence on the current efficiency because hydroxyl ions have already been neutralized in the acid boundary layer [16, 18]. Hydrogen ions pass through the membrane when the acid concentration is high and the sodium hydroxide concentration in the catholyte is low [17].

However, under the alkaline membrane state, the hydroxyl ions pass through the membrane when the acidic concentration is low and the sodium hydroxide concentration is high [16]. The acidic concentration in the anolyte has no influence on the current efficiency because hydrogen ions have already been neutralized in the acidic boundary layer [16, 18] and cannot reach the membrane itself. If membrane type, current density and temperature are fixed, the current efficiency depends on the caustic soda concentration in the cathode compartment only [16].

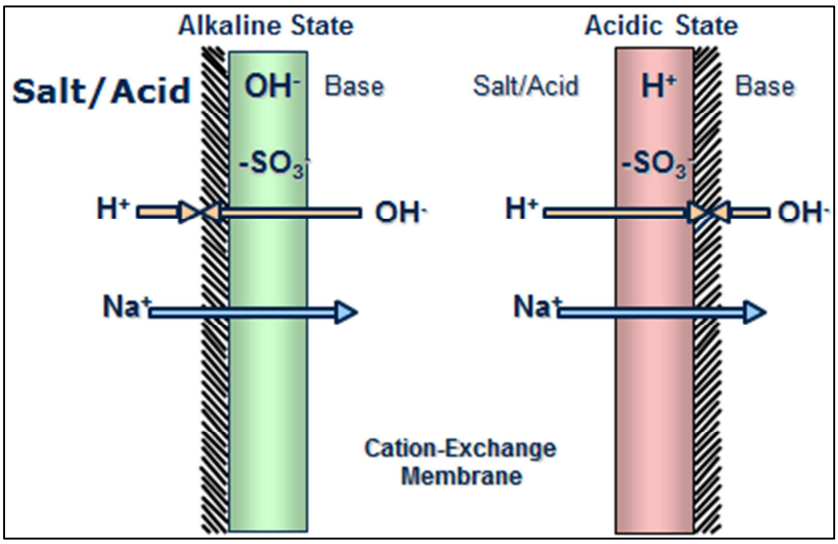

Figure 6.2 : Model of the alkaline membrane state (to the left) and the acid membrane state (to the right) of a cation exchange membrane

The above-mentioned results can be explained by the model shown in Figure 6.2 [16]. At a high caustic soda concentration in the catholyte and a low concentration of acid in the anolyte, losses in current efficiency are caused by the migration of OH- ions. This assumption has been confirmed experimentally [19] and is supported by the result that in the case of an acidic anolyte containing some impurities of multivalent metals subjected to precipitation under caustic conditions, soluble earth alkaline hydroxides precipitated on the membrane surface on the anode side [20].

6.2.4 Ions concentration at the solutions-membrane interfaces

As proposed by Moshtari Khah [14], calculations of an ionic concentration profile should consider the Donnan effect occurring at membrane-solution interfaces, explaining the step increase of sodium concentration between the two Medias. The Donnan effect

creates a step concentration between the liquid and the membrane media (boundary layer and the membrane) based on the chemical potential equilibrium (Figure 6.1).

We propose considering the membrane as a homogenous medium containing fixed charges of SO_3^- ions and at equilibrium, sodium ions and H+ or OH^- diffusing through the membrane. The chemical activities of OH^- (or H+) and Na^+ can be represented by their respective molar concentration (M). The Donnan equilibrium is based on the fact that the chemical potential (ψ), for example, in the liquid phase at an interface liquid-membrane is equal to the chemical potential in the solid membrane phase at this interface. Let us consider for instance the membrane-BL interface of a membrane under alkaline conditions. The chemical potential of black liquor at the interface ($\psi_{BL,M}$) is equal to the chemical potential in the solid membrane phase at this interface.–($\psi_{M,BL}$). We have:

$$\psi_{BL,M} = RT \ln [Na^+]_{BLM} + RT \ln [OH^-]_{BL,M} \quad [7]$$

$$\psi_{M,BL} = RT \ln [Na^+]_{M,BL} + RT \ln [OH^-]_{M,BL} \quad [8]$$

The Donnan equilibrium principle says that $\psi_{BL,M}$ equals $\psi_{M,BL,}$ which gives the following expression for the sodium ion concentration in the membrane at the black liquor interface:

$$[Na^+]_{M,BL} = [Na^+]_{BL,M} \cdot [OH^-]_{BL,M}/[OH^-]_{M,BL} \quad [9]$$

On the other hand, to respect the electroneutrality principle in the membrane at the black liquor-membrane interface, we must have:

$$[Na^+]_{M,BL} = [SO_3^-]_{M,BL} + [OH^-]_{M,BL} \quad [10]$$

Assuming that the black liquor is maintained at alkaline condition, we can neglect the concentration of H+ ions. Therefore, by solving equations [9] and [10], and manipulating the variables, we can calculate $[Na^+]_{M,BL}$ and $[OH^-]_{M,BL}$ from known values for $[Na^+]_{BL,M}$ and $[OH^-]_{BL,M}$ that would be previously calculated.

6.2.5 Modelling of transport phenomena in each of the boundary layers

Ionic concentrations in each of the boundary layers at the membrane-layer interface can be calculated from the bulk concentration and mass transfer coefficients. For each of the

boundary layers, for a given ion, the concentration gradient is related to the flux according to eq. [11]:

$$|J| = k\,|C_b - C_m| \qquad [11]$$

Where k is the mass transfer coefficient, indices b refer to a bulk concentration and indice m refers to the interface membrane-layer but at the side of the liquid film (boundary layer). For example, looking at Figure6.1, in the case of Na^+ in the boundary layer of the BL, C_b is $[Na^+]_{BL}$ while C_m is $[Na^+]_{M,BL}$.

In order to estimate the mass transfer coefficient in a fully developed region, Goodridge et al [21] proposed the Chilton-Colburn correlation for such a system relating the Sherwood number to the Reynolds and Schmidt numbers allowing the calculation of the mass transfer coefficients k_i for a specific ion i, in the case of a turbulent regime:

$$S_h = 0.023 \cdot Re^{0.8} \cdot S_c^{1/3} \qquad [12]$$

where

$$R_e = \upsilon \cdot D_H / \nu \text{ and} \qquad [13]$$

$$S_c = \mu / (\rho D_i) = \nu / D, \qquad [14]$$

$$S_h = k_i \cdot D_H / D_i \qquad [15]$$

D_H is a hydraulic diameter or a characteristic length, μ is the viscosity and D is the diffusivity, ν the kinematic viscosity and ρ the density.

By combining eq. [12], [14] and [15], and referring to the Na^+ species, we obtain eq. [16] allowing for the calculation of the Na^+ transfer coefficient for each of the two boundary layers adjacent to the membrane.

$$k_{Na} = 0.023 \cdot Re^{0.8} \cdot S_c^{1/3} \cdot D_{Na}/D_H \qquad [16]$$

Then the film thickness can be calculated:

$$\delta = k_{Na} / D_{Na} \qquad [17]$$

Boundary layers (film resistance) on each side of the membrane play an important role in the transfer of ions from the anolyte to the catholyte via the membrane. It could affect

the concentration profiles developed in the boundary layers and within the membrane. The thickness of the boundary layers depends on the flow regime, which is determined by the Reynolds number [12] and the characteristics of the liquid and flow conditions in the channel [22].

6.3 Experimental method and methodology

6.3.1 Experimental set-up

The experimental set-up and method used in the process development were detailed in a previous publication along with the operating conditions and the composition of the BL as well [5, 7]. The dual compartment electrolysis cell is composed of a bundle of cylindrical anodes (10), two flat plate cathodes and two separated by the cationic membrane Nafion® 324 (Figure 6.3). The characteristics of BL and caustic soda solutions and cell design are described in Table 6.1. The BL (anolyte) is circulated through the anode compartment where the alkalinity is reduced until the pH reaches the point of destabilizing the lignin and forcing its precipitation out of the solution. During electrolysis, the sodium is transferred from the anolyte to the catholyte compartment to make caustic soda. The set-up is operated in a feed and bleed mode for both streams. The pH of the anolyte loop is maintained constant by the addition of fresh black liquor at high pH. The caustic soda concentration is controlled by conductivity measurement demanding the addition of water when over target.

6.3.2 Black liquor characteristics

In this work, we recommended using black liquor at about 30 % solids. At this concentration, the electrolyte exhibited a maximum conductivity [4, 7, 8]. The other reasons supporting the choice of this composition of the electrolyte are in the following. At the above solids level, black liquor is also considered to have a Newtonian fluid behaviour [24, 25, 26, 27]. Moreover, once electrolysed, the black liquor viscosity could be reduced by one order of magnitude depending on the solids content. At 30 % solids

and 70 °C, Caro [10] reported a kinematic viscosity of 0.0116 cm^2/s equivalent to 1.356 cP[22], a value we retain for our calculations since we operate under similar conditions.

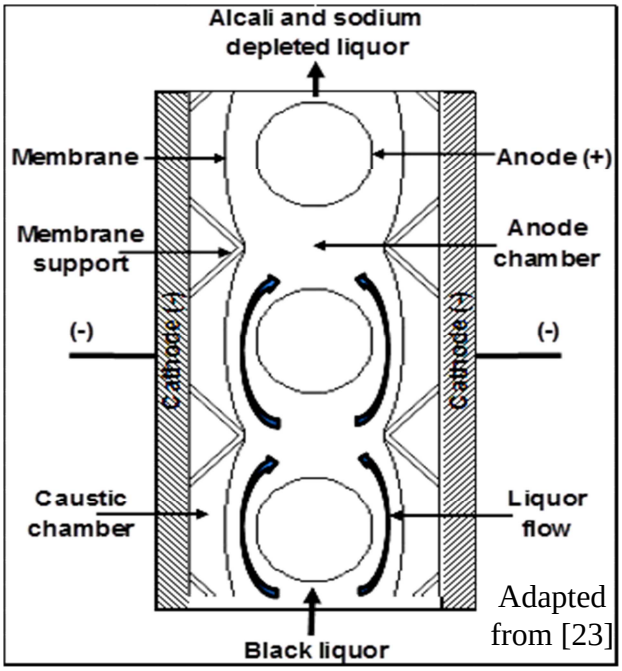

Figure 6.3 : Internal design of the ELSEP electrolysis cell

6.3.3 Reynolds (R_e) number calculations

The Reynolds number (Re) is an important parameter that describes whether flow conditions lead to laminar or turbulent flow, a characterization needed to evaluate the mass transfer performance. Given the irregular shape of the internal channels of the cell we used, we considered various methods to calculate R_e numbers. For simplification, we assume that both streams (anolyte and catholyte) are flowing in a channel considered to be composed of two parallel walls for which we determine the equivalent hydraulic diameter (D_H). On the black liquor side, we identified four ways to calculate the flow R_e number all using eq. [13] [12]. In the equation, velocity v is based on the volumetric flow (Q) and the definition of the cross section area (A) between the membrane and the anode is defined as:

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[22] $\mu=\nu\cdot\rho=cm^2/s\cdot m^2/cm^2$ x kg/m^3 x cPoise/(kg/(m·s)) = 0.01163 x $1/(100)^2$ x1 166 x 1 000/1 = 1.356 cP

$$v = Q/A \quad [18]$$

The anode compartment can be represented as a rectangular channel containing a bank of tubes (Figure 6.3). The four methods that were considered are as follows:

a) A is defined by the minimum rectangular passage between an electrode and the membrane and D_H and velocity are calculated accordingly;

b) A is defined by a rectangle characterized by D_H equals to the diameter of the cylindroids anodes [30];

c) Velocity is the so-called mean superficial velocity, i.e., the average velocity that would occur if the tubes were removed [30];

d) A is defined by the cross sectional with the full width channel of 2.07 cm (membrane to membrane).

On the caustic soda side, the R_e number calculation is computed according to a simple rectangular shape like channel characterized by an equivalent hydraulic diameter (D_H).

Table 6.1 : Experimental conditions and cell characteristics

Parameter	Black liquor (Anolyte) compartment	NaOH (catholyte) compartment	Reference
Solids content, %	29,3	6,43	This work, Herron [23]
Sodium content, %	5,31	3,70	Cloutier [7]
Sodium [Na^+], M	2,69	1,66	Cloutier [7]
Temperature, °C	70	70	This work
Current density, kA/m^2 of electrode	1,26	0.835	This work
Current density, kA/m^2 of membrane	0,835		This work
Density, g/cm^3	1,166	1,071	Cloutier [7] Liquiflo [28]
Viscosity kinematic , cm^2/s	0,012	0,005	Caro [710]
Flow, L/min	30,9	16,3	Cloutier [7]
Anode length, cm	14,0	-	Cloutier [7], Herron [23]
Number of anodes	10	-	This work
Number of cathodes	-	2	This work
Anode surface, cm^2	559	-	This work
No of membrane Nafion 324	2		
Membrane area, cm^2	840		Cloutier [7], Herron [23]
Membrane thickness, cm	0.01524		
Membrane density, g/cm^3	1,95		Sigma [29]
Exchange capacity, meq/g	1,00		Sigma [29]
[SO_3^-] in membrane[23]	1,95		Sigma [29]

[23] [SO_3^-], Mole/L = eq/L = g/cm^3· meq/g· eq/meq· cm^3/L = 1.95 x 1.0 x 1/1 000 x 1 000 = 1.95 M

6.3.4 Ionic fluxes and concentration gradient across boundary layers

Ionic fluxes were obtained from measurements and mass balances for a typical run of electrolysis of BL with the experimental set-up. Then the concentration gradient for each of the boundary layers was estimated from the ionic flux and the value of mass transfer coefficients. The mass transfer coefficients were calculated according to eq. [12] presented above. Finally, we proceeded with the calculations of the thickness of the boundary layer on each side of the membrane with eq. [17]. The diffusivity of Na^+ ion in black liquor and in the NaOH solution was estimated using the Stokes-Einstein relationship [12]:

$$D_{Na} = K_B \cdot T/(4 \cdot \Pi \cdot \mu \cdot R_{Na}) \qquad [19]$$

where D_{Na} is the diffusion coefficient in cm^2/s, K_B the Boltzman constant ($1.38\ 10^{-23}$ $m^2 \cdot kg)/(s^2 \cdot K)$, T in K, Π = 3.1416, μ is the solution viscosity in $kg/(m \cdot s)$ and R_{Na} the hydrated radius of sodium ion ($3.12 \cdot 10^{-10}$ m) [31].

It is worth mentioning that the effect of multiphase flows (liquid and gas) is not incorporated in the modelling. The author assumed that single phase modelling is sufficient for his case since the bulk concentration should not be significantly affected when the electrolyte is considered well mixed and the gradient concentration across the boundary layer is considered negligible. We followed his recommendation for our application given the turbulent flow regime.

6.3.5 Concentration profile across the membrane and Donnan equilibrium

Knowing the ion concentrations in the liquid phase for each of the interface liquid-membranes, we can calculate the ion concentration in the membrane for each of the liquid-membrane interfaces solving eq. [9] and [10]. Starting from these values, we plotted the ion concentration profiles based on equation [6] at different values of $\Delta\Phi$ across the membrane. It is understood that this variable is directly related to the current density. We previously reported a $\Delta\Phi$ of 0.27 V when the membrane is submitted to a current density of 0.835 kA/m^2 [4].

6.3.6 Remarks regarding purity of the caustic soda produced

As mentioned earlier in this study, we considered only transport of Na^+ and H^+ or OH^- depending on the acidic state of the membrane. Despite the fact that the caustic soda produced in the catholyte (NaOH) compartment comes from the sodium recovered from the black liquor, it contains some impurities, although at low levels. It is said that other species may diffuse through the membrane but the transport of these species was not considered.

6.3.6.1 Organics traces in the caustic soda

Black liquor contents high concentration of organics including lignin, hemicellulose and sugars. In fact about 50 % of dry black liquor solids are constituted of organic matter of which 80 % is lignin. That organic material has the potential to diffuse through the membrane to the caustic soda stream depending on the operating conditions of the electrolytic process. But previous work [32] has shown that the level of total organic carbon in the caustic soda was very low, less than 100 ppm, demonstrating that the Nafion® membrane acts as a selective filter preventing organic matter to cross over. Despite the dark color of black liquor, the high selectivity of the membrane allows to produce a colorless caustic soda suitable for bleaching operation.

6.3.6.2 Sulfate ions traces in the caustic soda.

The black liquor also contains sulfate ions (1.47 %) that could leak as well through the membrane and contaminate the caustic soda, even though its presence is not detrimental to its use in the mill. Earlier work [33] on the electrolysis of concentrated sodium sulfate demonstrated that the Nafion® 324 could produce caustic soda containing a very low level of sulfate (<10 ppm) at 70 °C when the acidity is low. Given the much lower levels of sulfate and low acidity in the black liquor, we would expect less than 10 ppm of sulfate ions in the caustic soda when operating at 70 °C.

6.3.6.3 Low concentration of potassium ions in the caustic soda.

Black liquors contain a high level of sodium (19-20 % on a dry basis) mostly coming from the cooking liquor [7, 34] but also a fraction of potassium (1%) as well coming from the wood chips. During electrolysis, the potassium ions are transferred along with

the sodium across the membrane to generate potassium hydroxide in the caustic soda stream. Potassium hydroxide is a chemical as valuable as sodium hydroxide for pulping and bleaching operation.

6.4 Results

6.4.1 Predominant transfer mechanisms

The relative significance of the three transport phenomena for our application of electrolysis of black liquor was determined based on Carlberg's method [15]. The analysis is performed based on the absolute value of the dimensionless ratios and the results are compared to the values shown in Table 6.2. Given the low value of the ratio C/D (-9.8 10^{-11}), the diffusion term dominates the convection term. Therefore, the convection term can be neglected. On the other hand, the ratio M/D (9.86 10^{+1}) is too low to neglect. In fact, the ratio should be several orders of magnitude larger [11]; consequently, both terms have been kept in the model. Regarding the M/C ratio (-9.17 10^{+8}) we see that the migration term dominates by far; hence the convection term is excluded. In overall, we can conclude that the convection term can be ignored in the modelling because of negligible incidence as per the Na_2SO_4 splitting application [15].

6.4.2 Determination of flow regimes

The determination of the flow regime requires special attention and the results obtained from the various methods of calculating R_e are presented in Table 6.3. The estimated values of the R_e number for the four methods used to calculate that parameter on the black liquor side vary considerably. Indeed, the average value is 4 100 with a high coefficient of variation of 33 % due mainly to the equivalent hydraulic diameter variable. It was unexpected that the R_e number in the restricted area would be lower (3 075) than the one in the full width passage (5 511). Intuitively, you would expect more turbulence or a higher R_e number in a narrower channel, but the hydraulic diameter dictates otherwise.

Nevertheless, considering the average of the R_e numbers being above 3 000 and the geometry of the cell, we can affirm that the flow of black liquor is well agitated and runs in a well-developed turbulent regime. Moreover, according to the cell design patent [23],

once there is pressure applied to the feed stock (Black liquor) the membranes formed a serpentine flow path (Figure 6.3). Due to the continually changing direction of the fluid flow, there is a high degree of turbulence formed along the side of the membrane.

Table 6.2 : Results of dimensionless ratios analysis based on Carlberg criteria [15]

Model term	Dimensionless ratio [Carlberg]	Criteria [Carlberg]	Ratio value			Conclusion
			Na^+	H^+	OH^-	
Convection vs diffusion	$C/D=P_e=\upsilon \cdot L/D_i$	|C/D|<<1: TF=D |C/D≈1: TF=D+C |C/D>>1: TF=C	9,80E-11	3,33E-09	4,43E-09	The diffusion term dominates for all cases, thus convection term is excluded.
Migration vs diffusion	$M/D=z_i \cdot F \cdot \Delta\Phi/(R \cdot T)$	|M/D|<<1: TF=D |M/D|≈1: TF=M+D |M/D|>>1: TF=M	-9,86E+01	-9,86E+01	-9,86E+01	The ratio should be several orders of magnitude larger to drop the diffusion term. So, it is kept in the model.
Migration vs Convection	$M/C=z_i \cdot F \cdot D_i \Delta\Phi/(R \cdot T \cdot \upsilon \cdot L)$	|M/C|<<1: TF=C |M/C|≈1: TF=M+C |M/C|>>1: TF=M	-9,17E+08	-3,12E+10	-4,15E+10	The migration term dominates for all cases, thus the convection term is excluded.
C: Convenction flux, D: Difusion flux, M: Migration flux, TF: Total flux						

Table 6.3 : Estimates of Reynolds numbers in the different cell channel defined

Parameter	Black liquor compartment				Catholyte compartment (NaOH)	Reference
	Anode-membrane passage	Tube bank configuration				
		Minimum cross section	Mean superficial velocity*	Full compartment width		
Channel thickness, cm	0,40	-	2,07	2,07	0,40	[7, 23]
Flow area, cm^2	11,2	20,1	29,0	29,0	11,2	Calculated
Hydraulic diameter, cm	0,78	1,27	1,27	3,61	0,78	Calculated
Velocity, cm/s	46,0	46,0	25,6	17,8	24,3	Calculated
Reynolds No. (N_{Re})	3 075	5 021	2 794	5 511	3 715	Calculated
* Mean superficial velocity, i.e., the average velocity that would occur if the tubes were removed [30]						

Despite turbulent regimes, both stream flows could be increased to enhance process performance. In that regard, Tzanetakis [35] suggested a corrugated membrane to

promote turbulence. Moreover, Khan et al [36] proposed to reduce the diameter of the tubes, the longitudinal pitch (the distance between two consecutive tubes) and the benefits of a staggered arrangement of the tubes should be evaluated as well compared to an in-line configuration. These improvements would enhance mass transfer.

6.4.3 Sodium ions flux

Based on the sodium balance (Figure 6.4), we can estimate the sodium mass transfer flux and the sodium hydroxide productivity when electrolyzing black liquor. Indeed, in a typical experiment, we determined that the amount of sodium transferred was 49.6 g/h. Given a membrane surface of 840 cm^2, we calculate the sodium flux to be 0.59 kg/h-m^2 or 25.7 mole/h-m^2 therefore making 1.03 kg of NaOH/($m^2 \cdot h$). At a current density of 0.835 kA/m^2, the process delivered an average measured current efficiency of 80.7 % based on five measurements with a low coefficient of variation (2.2 %) compared to a theoretical calculated value of 82 %[24]. A better sodium transfer coefficient would translate to a higher sodium flux through the membrane and higher sodium hydroxide productivity. In terms of process performance, it means that less electrode and membrane area would be required reducing the capital cost. That aspect of process performance improvement is presently under investigation.

According to the mass balance (Figure 6.4), the amount of sodium entering the process was 154.6 g/h while delivering 49.6 g of Na/h or 86.3 g/h as caustic soda. Based on the caustic soda produced, we determined that the sodium recovery was 32 %. From that particular example at the above specified operating conditions (Table 6.1), we can affirm that we need to remove one third of the sodium from the black liquor in order to bring the liquor to pH 9.0, the point of lignin precipitation.

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[24] Current efficiency measurements: 78.5 %, 78.7 %, 81.5 %, 82.0 %, 82.7 %, average = 80.7 %, standard deviation = 1.76 and coefficient of variation (COV) = standard deviation/average x 100 = 2.2 %

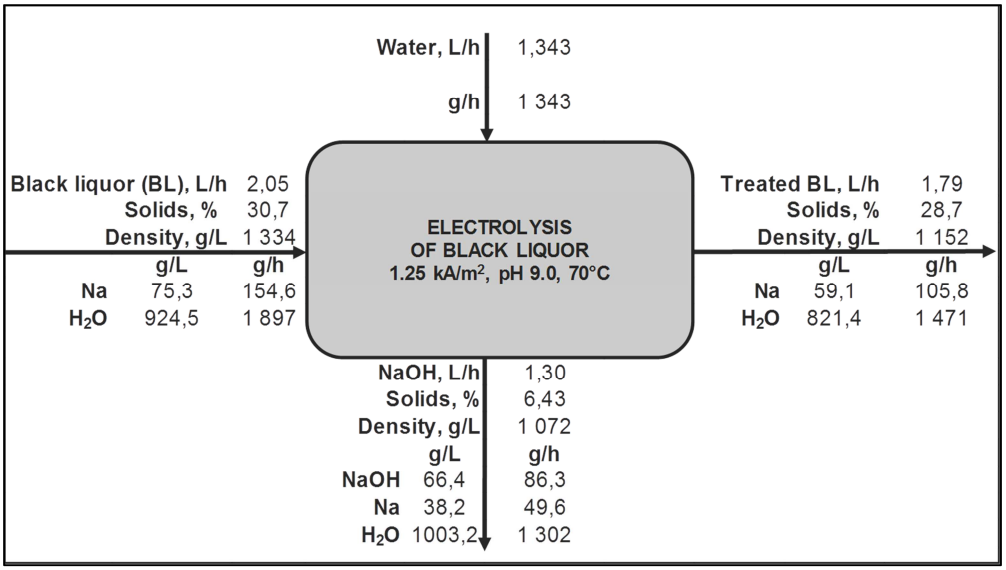


Figure 6.4 : Typical sodium and water balances

6.4.4 Estimate of sodium diffusivity D_{Na} and transfer coefficient (k)

The diffusivity of Na^+ ion in black liquor and the NaOH solution was estimated using equation [19] (Table 6.4). The values obtained were compared to the values reported in the literature for sodium salt solutions encountered in the pulp and paper industry, such as NaCl [37, 38], $NaClO_3$ [39] and sodium sulfate/sulfuric acid mix [11] (Table 6.2) at a similar concentration (2.7 M). We noticed that the estimated D_{Na} for black liquor (0.890 10^{-5} cm^2/s) is similar to the values in salt solutions (1.056-1.3339 10^{-5} cm^2/s). However, it is much higher, indeed nine times the value in the membrane (0.098 10^{-5} cm^2/s) [15].

Regarding the sodium transfer coefficient k, the value on the black liquor side is much lower, about 61 % of the value on the caustic side (Table 6.5). We can explain the difference by a lower R_e number for the BL despite a lower flow on the caustic soda stream, and a lower viscosity as well.

Table 6.4 : Diffusivity of Na (D_{Na}) in salt and NaOH solutions, black liquor and Nafion®

Medium	Na, Mole/L	T, °C	D_{Na}, $cm^2/s \cdot 10^{-5}$	Viscosity μ, kg/(m·s)	Reference
NaCl	2.7	18	1.056	-	[37-Welty]
	2.7	25	1.339	-	[38-Vitagliano]
$NaClO_3$	2,7	25	1.206	-	[39-Campbell]
Na_2SO_4/H_2SO_4	3.8	80	1.110	0.000500	[15-Carlberg]
NaOH	2.7	80	2.265	-	[15-Carlberg]
	2,7	70	2.219	0.000550	[This work]
Black liquor	2.7	70	0.890	0.001356	[This work]
Nafion® Membrane	-	80	0.098		[15-Carlberg]

The sodium transfer rate would benefit from increasing both stream flows (Figure 6.5). In fact, by doubling the flow of black liquor from 31 to 60 L/min, the R_e number would, of course, double and we estimate that the sodium transfer coefficient would rise from 13.5 to $23 \cdot 10^{-4}$ cm/s, a 70 % increase. With the same action on the caustic soda side, the sodium transfer coefficient would rise from 22.0 to $35.8 \cdot 10^{-4}$ cm/s, a 63 % improvement. Optimum conditions could be determined by taking into account that higher flows would enhance the process performance but at the expense of higher pressure drop and energy consumption.

Table 6.5 : Results of dimensionless numbers, boundary layer thicknesses (δ_L) and sodium transfer coefficient (k) during electrolysis of black liquor at 70 °C.

Parameter	Black liquor	Caustic soda
Solids, %	29.3	6.43
Q, L/min	30.9	16.3
υ, m/s	46.0	24.3
D_H, cm	0.78	0.78
ρ, kg/L	1.166	1.068
μ, kg/(m·s)	0.00136	0.00054
ν, cm^2/s	0.01163	0.00508
D_{Na}, 10^{-5} cm^2/s	0.890	2.219
Reynold number (R_e)	3 075	3 715
Schmidt number (S_c)	1 307	229
Sherwood number (S_h)	155	101
k, 10^{-4} cm/s	17.8	28.8
δ 10^{-4} cm	53.6	48,7

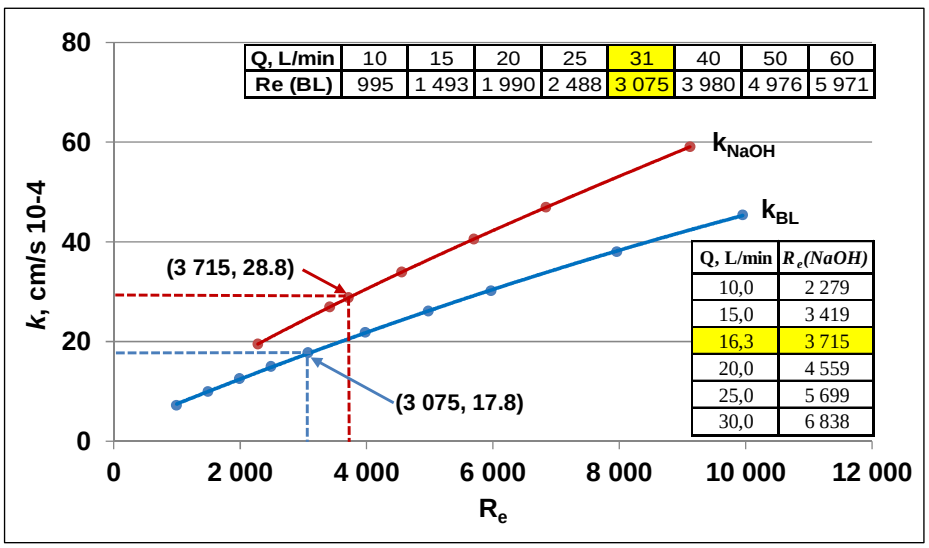


Figure 6.5 : Estimated Na transfer coefficient in black liquor and NaOH boundary layers as a function of R_e

6.4.5 Interfacial concentrations

The interfacial concentrations were calculated from the values of the ion fluxes and mass transfer coefficients by considering the Donnan equilibrium (Table 6.6). The results show that the sodium concentration at the interface of the black liquor and the membrane

($[Na^+]_{BL,M}$ = 2.6909 M) is very close to the one in the bulk ($[Na^+]_{BL}$ = 2,6913 M) and the difference is insignificant. On the caustic side, the concentration of sodium at the caustic soda and the membrane interface is also close to the concentration in the bulk. These results confirm that the turbulent flows are efficient enough and the mixing at both stream interfaces seems to be adequate.

The results (Table 6.6) show that at the black liquor-membrane interface, the OH^- concentration in the boundary layer ($1.585 \cdot 10^{-4}$ M) drops to $9.535 \cdot 10^{-5}$ M, a 40 % reduction while the Na^+ concentration goes from 2.69 M down to 1.95 M, a 28 % drop. In fact, the Na^+ concentration is practically equal to the SO_3^- concentration (1.95 M) in the membrane given the low concentration of OH^- ions in the black liquor at pH 9.0.

On the caustic soda side, the OH^- concentration in the boundary layer and inside the membrane is lower (0.95 M) than at the liquid interface (1.66 M). At the interface, the Na^+ concentration drops from 2.90 M inside the membrane to 1.66 M at the liquid interface, a factor of 1.75. In fact, we noticed that the higher level of OH^- ions affects the Na^+ concentration within the membrane according to the Donnan equilibrium and respecting electroneutrality (($[SO_3^-]$=1.95) M]+($[OH]^-$= 0.95 M) = ($[Na^+]$ = 2.90 M)).

Table 6.6 : Results of calculations of boundary layer thickness and interfacial concentrations

Black liquor		**NaOH**	
Parameter	**Value**	**Parameter**	**Value**
$[Na^+]_{BL}$ (M)	2,69130	$[Na^+]_{NaOH}$ (M)	1,6610
pH	9,00	pH	13,02
$[OH^-]_{BL,M}$ (M)	1,585E-04	$[OH^-]_{NaOH}$ (M)	1,6610
$J_{Na,}$ Mole NaOH/(s·m^2)	7,14E-03	$J_{Na,}$ Mole NaOH/(s·m^2)	7,14E-03
$[Na^+]_{BL,M}$ (M)	2,69090	$[Na^+]_{NaOH,M}$ (M)	1,66125
$[Na^+]_{M,BL}$ (M)	1,95010	$[Na^+]_{M,NaOH}$(M)	2,90113
$[OH^-]_{M,BL}$ (M)	9,535E-05	$[OH^-]_{M,NaOH}$ (M)	0.95113

6.4.6 Profile of ions concentration and pH in the membrane

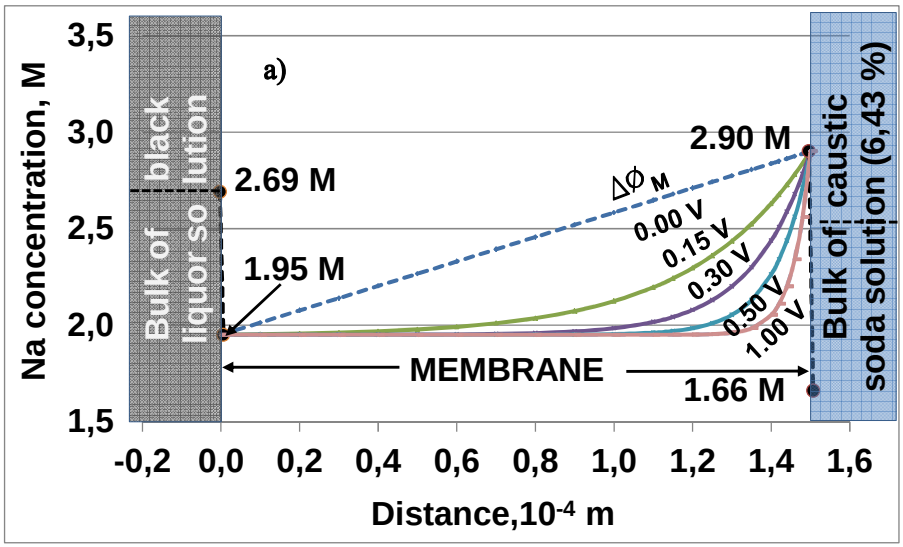
Knowing the sodium concentration at the solutions' interfaces inside the membrane, we apply the analytical solution (eq [6]) to the Nernst-Planck equation proposed by Carlberg [15] to develop the profiles of the Na^+ concentration and pH profile across the membrane. We investigated two pH levels of the black liquor and two caustic soda concentrations: 1.66 M and 2.77 M. We varied the electric potential across the membrane from 0 to 1 V.

We see (Figure 6.6a and b) that the concentration of sodium in the membrane increases exponentially as we approach the catholyte side. As we increase the electric potential across the membrane, the initial sodium concentration within the membrane (1.95 M) is initially maintained deeper and deeper within the membrane and then takes off exponentially to attain the maximum level in the membrane. At low potential, the increase in concentration starts earlier and when no potential is applied, the profile shows a straight line from the initial to the final concentration. The profiles are similar for both caustic soda cases with the difference that a higher level creates a higher concentration of sodium in the membrane (3.34 M vs 2.90 M).

The membrane also has an affinity to pass H^+ ions which compete with the sodium ions. As a matter of fact, the membrane has approximately three times more affinity for H^+ ions than Na^+ ions, especially at high acidity [11]. Contrary to the case studied by Carlberg [11] where the anolyte is strongly acidic (1.5 M of H^+ ions), for our application, we recommended keeping the black liquor pH preferably alkaline (9.0) or maybe at the most slightly acidic (6.0). The latter would accommodate mills experiencing a pulp production capacity limited by the recausticizing plant and needing to provide more caustic soda. However, that would be achieved at the expense of higher energy consumption [7]. Therefore, we simulated two cases, pH 6 and 9 while making caustic soda at 6.43 % and 10.0 % strength. The pH was calculated from the concentration of H^+ ions, which was determined using equation #6.

The pH profile within the membrane behaves similarly to the profile of sodium. We noticed that the pH of black liquor was maintained at the same level that existed in the black liquor up to a certain depth in the membrane where it then took an upward

direction. That upward turning point depended strongly on the electric potential applied across the membrane (Fig 6.7a, b). A higher potential pushes the flexion point closer to the catholyte. We observed the same profile for both pH values (6 and 9) (Figure 6.7a, b). Increasing the caustic soda concentration did not affect the pH pattern but it raised the final value accordingly [38].



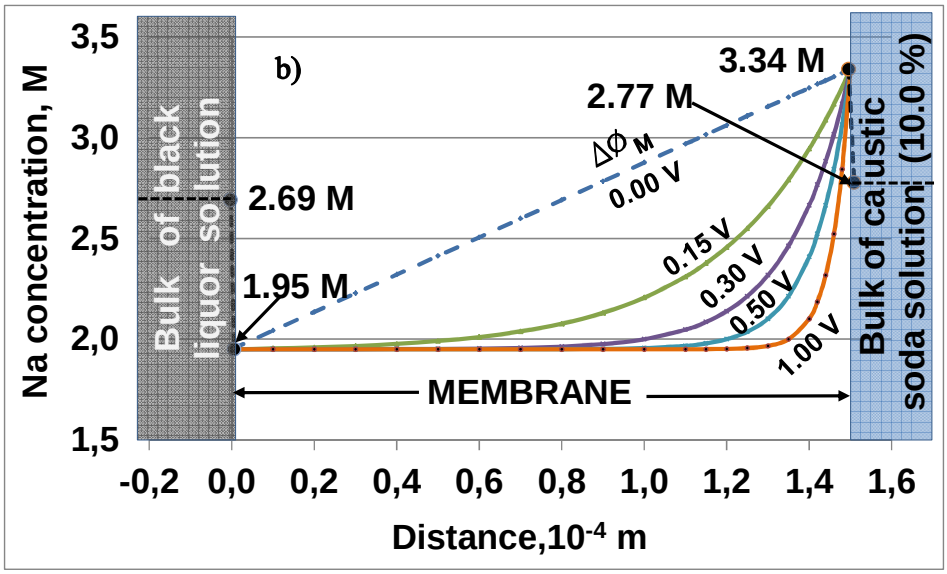
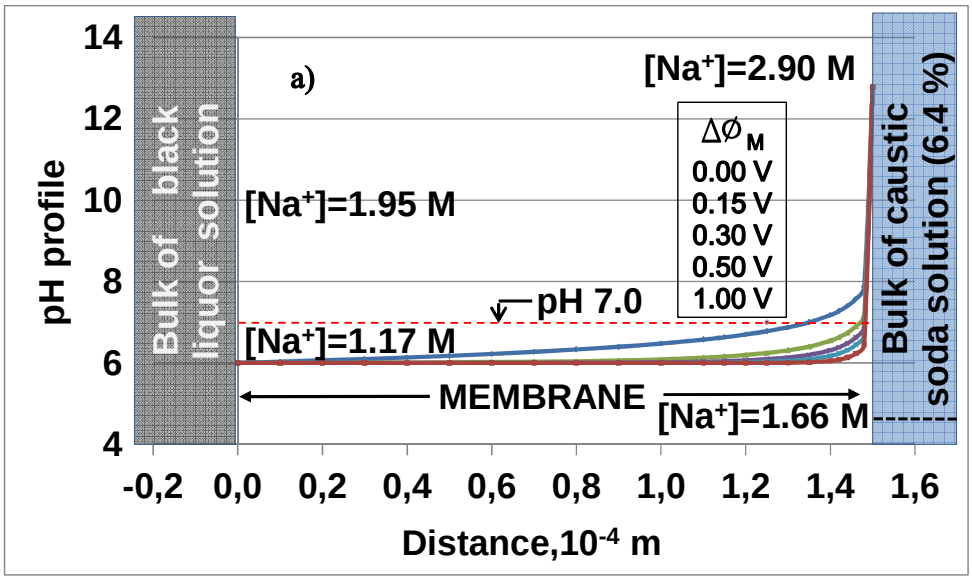


Figure 6.6 : Results of simulation of sodium concentration profile in the membrane as a function electric potential ($\Delta\emptyset_M$) across the membrane while making a) 1.66 M (6.43 %) or b) 2.77 M (10.0 %) caustic soda.



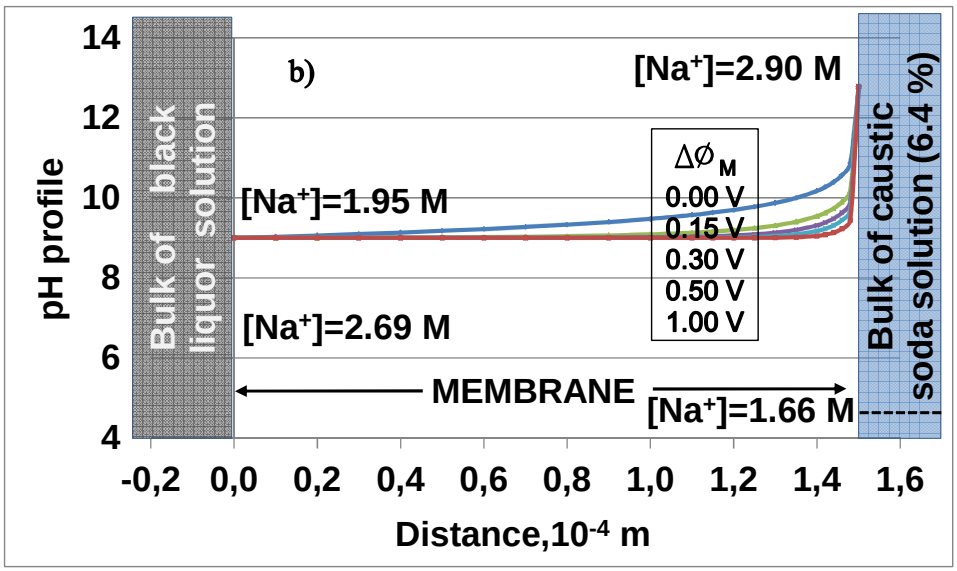


Figure 6.7 : Results of simulation of pH profile across the membrane for two levels of black liquor pHs 6 (a) and 9 (b) at different membrane voltage drops ($\Delta\emptyset_M$) while making 6.43 % caustic soda (1.66 M).

The increase of pH across the membrane could create an issue depending on the acidic or alkaline state of the membrane as proposed by the model developed by Jörissem [16]. When black liquor is maintained alkaline during the electrolysis step, the pH within the membrane remains alkaline all the way. If, however, the process was operated with slightly acidic black liquor, for example at pH 6.0, according to the simulation, more than

90 % of the membrane would also be in an acidic state depending on the electric potential. Nevertheless, that means that on the pathway through the membrane, there is a point where neutrality will be encountered (pH 7.0). At that point, some multivalent cations that were dissolved in the acidified black liquor could precipitate out thus damaging the membrane [19, 20]. It is therefore recommended to operate the electrolytic treatment of black liquor at alkaline conditions to avoid a shock of pH within the membrane that would affect its durability and performance. Otherwise, the removal of multivalent cations would be necessary in order to protect the membrane.

The Na^+ and H^+ ions are migrating towards the cathode under the influence of the electric potential applied between the electrodes while the hydroxyl (OH^-) ions are moving in the opposite direction under the influence of the electric potential and concentration gradient. It might seem contradictory to study both H^+ and OH^- profiles along the membrane, but we have to consider that the medium of the membrane is a solid polymer and not a liquid solution. The Na^+ and H^+ ions are moving from SO_3^{-2} sites to others and the OH^- ion is moving in the opposite direction. It is important to remember that at all points inside the membrane, electro-neutrality has to prevail taking into account a balance between the SO_3^{-2} sites of the membrane and the OH^-, Na^+ and H^+ ions.

6.4.7 Water balance

During electrolysis, some water is transferred from the black liquor (anolyte) and migrates across the membrane to the catholyte (Caustic soda). That water can be transported through the ion exchange membrane in three ways [15, 40]: coupling with the electric current passing the membrane due to the electrical potential gradient (electro-osmosis), transported due to a flux of ions with a hydration shell, and transported due to a chemical potential gradient, i.e., concentration gradient, of the solvent (osmotic flux). In general, the water flux depends on the current density, concentration gradient, and perm-selectivity of the ion exchange membrane where the three terms can be of varying importance [15].

If the membrane is in an acidic state, the transport number of water represents the number of water molecules (about three) transported by one mole of sodium. In an

alkaline state, it was reported that more than four moles of water are transferred with each mole of sodium and the amount depends on the current density and the sodium concentration in the solution [17], the lower the concentration the higher the number.

Along with a sodium balance, a water balance was also performed for a typical trial at pH 9.0 on the liquor side while making caustic soda of 6.4 % strength in the cathode compartment (1.7 M) (Figure 6.4). The sodium balance closes at 0.5 % meaning that we can account for 99.5 % of all the sodium entering the process with the black liquor and leaving with the treated liquor and the caustic soda made (Table 6.7). However, the balance indicates that some water is missing (13.5 %). We concluded that the water shortage is due to the evaporation of anolyte and catholyte. Indeed, both black liquor and caustic recirculation tanks were ventilated for the safe evacuation of the oxygen and hydrogen separately.

Table 6.7 : Sodium and water balances[25] during electrolysis of black liquor at pH 9.0.

Component	In				Out						Δ	
	BL in	2 $OH^- \rightarrow H_2O$	Water in NaOH	Total in	BL out	NaOH out	$H_2O \rightarrow OH^-$ +1/2 H_2	O_2	H_2	Total out	g/h	%
Na, g/h	154	-	0,0	154	105	50	-	-	-	155	0,8	0,5
H_2O, g/h	1 897	77	1 343	3 318	1 521	1 302	-38	37	48	2 869	-448	-14

In order to complete the water balance, the water sources and losses of the process were investigated. The two major sources of water entering the system are the black liquor (1 897 g/h) and the water added to the caustic soda loop (1 343 g/h) to maintain the concentration constant.

A small amount of water is also generated from the reaction occurring at the anode:

$$4\ OH^- \rightarrow 2\ H_2O + O_2 \qquad [31]$$

To maintain electroneutrality in the anolyte compartment, for every mole of sodium transferred to the catholyte, there was one mole of OH^- being converted to water and oxygen. According to equation #31, four moles of hydroxyl ions were neutralized

[25] https://en.wikipedia.org/wiki/Vapour_pressure_of_water

making two moles of water. Since every mole of sodium transferred implies the neutralization of one mole of hydroxyl, there was one mole of water generated per two moles of sodium transferred.

On the other hand, the water outputs of the process are: (1) the treated black liquor, (2) the caustic soda stream, (3) the water evaporated from both electrolytes, and (4) the water split at the cathode according to this reaction:

$$H_2O \rightarrow OH^- + 1/2\ H_2 \qquad [32]$$

Similarly, to maintain electroneutrality in the catholyte compartment, one mole of hydroxyl was formed for every mole of sodium transferred consuming two moles of water for every mole of sodium transferred.

Some of the water lost by evaporation can be estimated from equations 9 and 10 and considering the oxygen and hydrogen stream was saturated with water. It represents, however, a small fraction (3 %) of the total water (2 869 g/h) exiting the system, 37.2 g/h and 48.1 g/h. It helps the water balance but does not close it. Indeed, there is still a deficit of 13.5 %, which cannot be attributed to the water transferred with the sodium alone because that would correspond to 11.6 moles of water per mole of sodium, which is three times higher than the values of 4.0 moles reported in the literature [17]. We believe that air was entrained with both gas streams enhancing evaporation beyond oxygen and hydrogen mass flows. The experimental set-up could be improved by installing a cooling of the exhausts preventing evaporation and allowing for an accurate estimate of water transfer by hydration with sodium [41].

Therefore, for design purposes, it would be reasonable to assume that at least 4.0 moles of water were transferred per mole of sodium. The transfer of water from black liquor to caustic soda will help the mill water balance in two ways. First, it allows returning a more concentrated stream of electrolyzed liquor to the recovery system minimizing the water load to the evaporators. Second, a smaller flow of water is needed to make the caustic soda therefore contributing to reduce the capital and operating costs of the water treatment system.

6.5 Conclusions and discussions

In this study, the mass transfer process involved in the electrolytic treatment of black liquor to precipitate lignin was investigated. The analytical solution to the simplified Nernst-Planck equation was applied to develop the concentration profile of sodium, H^+ and OH^- ions along with the profile of pH within the membrane. The Na^+ concentration tended to be constant at the level encountered in the black liquor most of the distance through the membrane and adjusted itself to attain the sodium level, either higher or lower, prevailing in the caustic soda compartment. It was shown that the pH profile followed the same pattern. When the black liquor pH was slightly acidic (pH 6.0), the membrane operated in an acidic state almost all the way. At one point before reaching the caustic soda side, the pH became neutral, which means that any divalent metals would precipitate, thus damaging the membrane. It is therefore strongly recommended to keep the black liquor alkaline preferably above 8.0 to protect the membrane.

It was demonstrated that the thickness of the boundary layer on the caustic side was slightly lower (9 %) than the one calculated on the black liquor side in the narrow channel between the anode and the membrane. Consequently, the sodium transfer coefficient was higher (+62%) on the caustic soda side due mostly to a lower viscosity and higher diffusivity of sodium. However, the thickness of the boundary layer calculated for the full width section (membrane-membrane) on the black liquor side located between the anodes was 3.5 times larger than the restricted passage (anode-membrane) due to a channel 5 times wider and lower velocity, which suggests increasing the flow to improve mass transfer in that part of the cell.

We found that in order to bring the liquor to pH 9.0, corresponding to the point of lignin precipitation, we needed to remove one third of the sodium from the black liquor. Under the operating conditions investigated, we estimated the sodium mass transfer flux from the anolyte (Black liquor) to the catholyte (caustic soda) to be 0.59 kg of $Na/(m^2 \cdot h)$ making 1.02 kg of $NaOH/(m^2 \cdot h)$ based on the anode surface. Optimization of the operating parameters is under investigation.

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CHAPITRE 7 ARTICLE 3: ELECTROLYTIC TREATMENT OF KRAFT BLACK LIQUOR- PROCESS OPTIMISATION

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The integration of a bio-refinery to a kraft mill site includes inevitably a lignin recovery plant. The lignin is usually recovered using commercially available processes based on a chemical approach, which precipitates lignin from black liquor by lowering the pH using carbon dioxide and sulfuric acid. Recently, we have developed an electrochemical avenue consisting of an electrolytic treatment of black liquor that reduces its alkalinity to the critical point of lignin precipitation. The process converts some of the sodium salts in the black liquor and sodium sulfate waste to valuable caustic soda and sulfuric acid while avoiding the usage of chemicals from a source external to the mill. In this study, we investigated the effect of the most important operating parameters, such as current density, caustic soda strength, end pH and others during the electrolytic treatment of different types of BLs with the aim of optimizing the process.

7.1 Introduction

In the context of sustainable development and a circular economy, we have developed an electrochemical approach to provide lignin to a biorefinery based essentially on the judicious use of electricity compared to the chemical approach in which LignoBoost [1] and LignoForce [2] technologies which rely on acid precipitation using carbon dioxide and sulfuric acid from a source external to the mill. Both technologies are commercially available from Valmet[26] and NORAM[27], respectively. The new approach proposed in

[26] https://www.valmet.com/pulp/chemical-recovery/lignin-separation/
[27] http://www.noram-eng.com/groups/pulp-group-technologies.html

this work entails the electrolytic treatment of black liquor (BL) to reduce its alkalinity to the critical point of precipitating lignin while the sodium recovered from the BL is converted to valuable caustic soda [3]. This electrochemical technology presents many advantages [4]:

(1) No chemicals are provided from an external source but rather from splitting Na_2SO_4,

(2) No additional discharge to the effluent treatment is necessary,

(3) The acid and water washings can be returned entirely to the chemical recovery system without disturbing the Na/S balance,

(4) A reduction of inorganic content of the black liquor is resulting from the extraction of sodium, therefore increasing the BL calorific value prior to lignin precipitation and allowing for additional lignin recovery,

(5) Off-loading the causticizing plant which is often overloaded, while reducing GHG emissions,

(6) The oxidation of the sulfide ions eliminates H_2S formation during the acid wash and

(7) A significant increase in the evaporation capacity is expected from a reduction of liquor viscosity [5].

In an earlier paper [6] that reviewed the literature on the subject of lignin precipitation, we reported on the fundamentals of electrochemistry occurring during the electrolysis of black liquor were presented, including electrochemical reactions, current density distribution along the electrolytic cell and cell voltage contributors and balance. We found that the energy consumption of the proposed process would benefit most from lower overvoltage electrode materials and by increasing BL conductivity. In a previous paper [7] focused on the mass transfer of ions through the membrane. We modeled the sodium, protons, hydroxyl ions concentration profiles and pH across the membrane based on the analytical solution of the Nernst-Planck equation for mass transport calculations in an electrochemical cell. Based on the model of the membrane state, we determined that the black liquor pH should be kept alkaline in order to prevent the precipitation of divalent cations within the membrane which affects its performance and life expectancy.

We estimated experimentally the sodium transfer coefficient and flux for the production of caustic soda.

The present study investigates the effect of the following operating parameters during the electrolytic treatment of BL: the source and type of BL, the pH during electrolysis, the current density, the NaOH concentration, the temperature and the addition of sodium sulfate to the black liquor to optimize the process performance.

7.2 Experimental methodology

7.2.1 Experimental set-up

The experimental set-up and the method used in this work were reported in detail in previous publications and are summarized in this paragraph [4, 6]. The dual compartment electrolysis cell is composed of a bundle of tubular anodes (a maximum of 10) surrounded by two cationic membranes of the Nafion® 324 type isolating the anodes from the two flat plate cathodes. The BL (anolyte) is circulated through the anode compartment where the alkalinity is reduced until the pH reaches the point of destabilization of the lignin and forcing its precipitation out of the solution. During electrolysis, the sodium is transferred from the anolyte to the catholyte compartments to make caustic soda. The set-up is operated in a feed and bleed mode for both streams. The pH of the anolyte loop is maintained constant by the addition of fresh BL at high pH (~13). The caustic soda concentration is controlled by measuring the conductivity and by the addition of water to maintain concentration on target. We investigated the process performance according to: (1) current efficiency, (2) energy consumption, (3) productivity of NaOH and (4) lignin productivities, and (5) specific flow of BL fed to the electrolysis unit. The calculations of these performance parameters are based on titration of the NaOH stream, the volume produced in a certain period of time, and the BL volume accumulated during that same period.

7.2.2 Experimental conditions

The experimental program comprised the investigation of seven independent variables (Table 7.1) on thirteen dependent variables (Table 7.2) pertaining to the process performance and design. The independent variables are those that we varied and

controlled to investigate their effect on the dependent variables which were measured or calculated. The flows of black liquor and caustic soda in the recirculation loop through the cell were not varied. Furthermore, each of the electrolyte recirculating pumps was operated at maximum capacity. The experimental work comprised 54 runs with 2 to 5 replicates. We reported 163 measurements for most of process performance parameters: cell voltage, current efficiency, energy consumption and NaOH productivity. A total of 56 measurements of black liquor feed rate were done as well as 41 measurements of the black liquor flow out of the system. On the caustic soda side, 130 flow measurements were taken and 23 measurements of water flow feeding the caustic soda compartment.

Table 7.1 : Independent variables

No.	**Variables**	**Unit**	**Range**
1	Type of black liquor (BL)	-	Hardwood/Softwood
2	Source of BL	-	Oxidized/non-oxidized
3	Final pH of treated BL	-	5.0-10.0
4	Current density	kA/m^2	0.35-1,89
5	NaOH concentration	%	1.25-13.9
6	Temperature	°C	61-84
7	Na_2SO_4 added to BL	-	None/Saturation

There are two types of black liqour depending of the wood species entering the mill: softwood and hardwood BLs. We also had access to two sources of softwood BL, oxidized and non-oxidized. The oxidized BL came from a vintage kraft mill still equipped with a direct contact evaporator [8].

The experimental set-up was equipped with a control system that maintains the BL at a specified pH target varying from 5.0 to 10.0. The current density is reported as the average anodic current density, which was calculated by taking into account the total surface area of the tubular anodes. Each anode was 0.5 cm in diameter and 14 cm long. However, it was demonstrated that due to the tubular configuration of the anode, the anodic current density is not evenly distributed and is much higher on the surface facing the membrane than the one at 90 ° to the membrane along the BL flow [6]. The

concentration of the NaOH produced was varied from 1.25 to 13.9 %. It is worth mentioning that caustic soda n is a valuable chemical to a kraft mill even at low concentration and could be used in place of water to dilute the 50 % strength solution delivered to the mill. Even though it is recommended to limit the temperature of the process in order to prolong the life of the anode, we evaluated the process performance between 60 and 84 °C. Since sodium sulfate is in abundance in a kraft mill, we investigated the effect of saturating the black liquor with the salt expecting to improve process performance, especially the voltage and current efficiency.

Table 7.2 : Dependent variables

No.	Variable	Units
1	BL conductivity	mS/cm
2	Current efficiency	%
3	Cell voltage	V
4	Energy (NaOH)	kWh/t NaOH
5	Energy (Black liquor)	kWh/ m^3 of BL
6	Energy (Lignin)	kWh/t of lignin
7	NaOH Productivity,	$kg/(h \cdot m^2)$
8	Lignin productivity	$kg/(h \cdot m^2)$
9	BL flow in,	$L/(h \cdot m^2)$
10	BL flow out,	$L/(h \cdot m^2)$
11	Ratio BL flow out/in	-
12	NaOH flow produced	$L/(h \cdot m^2)$
13	Water flow in	$L/(h \cdot m^2)$

7.2.3 Black liquor characteristics

We performed numerous chemical analyses of black liquor samples obtained from hardwood (HW) and softwood mills (SW) as well as oxidized and non-oxidized liquors (Table 7.3). The different black liquors were labeled as followed: non oxidized softwood (NOSW), oxidized softwood (OSW) and non-oxidized hardwood (NOHW). Oxidized hardwood liquor is not available in the province of Québec. We received the liquors from the mills at about 50 % solids and diluted them to the 30 % range where

conductivity is maximal [4]. It is worth noting that the liquors contain a large amount of various dissolved organics (119 to 188 g/L) where lignin is the dominant component (116 to 140 g/L). The lower fraction of lignin in the HW liquor can be explained by its lower content (20-25 %) in hardwood than in softwood species (25-30 %) [9]. Unexpectedly, the thiosulfate had a higher concentration in the non-oxidized HW than in the oxidized SW. Usually, oxidized liquor should contain more thiosulfate from the oxidation of sulfides [6]. The OSW sample #2 contains a high level of sulfate probably due to over-oxidation at the mill. The residual effective alkali (REA) is composed of NaOH and Na_2S[28] [10], usually expressed as Na_2O but it can be converted to NaOH equivalent according their molecular weight[29]. We observed a higher REA value in the NOHW liquor than in the NOSW liquor and that could explain the higher conductivity (121 vs 111 mSiemen (mS)/cm). BL liquors also contain a low level of chlorides coming from the wood chips. The calorific value mostly due to the lignin content is lower for the HW liquor because it contains less lignin at a lower heating value (25 110 kJ/kg) than SW lignin (26 900 kJ/kg) [8]. At 95 % confidence interval, the statistical Student test revealed no significant difference in concentration for any of the component concentrations between the NOSW and OSW black liquors. Concerning the comparison of NOHW and NOSW black liquors, the percent solids and conductivity were significantly different at the 95 % confidence interval, but not significant at the 99 % level. It is surprising that the percent solids are statistically different but not the solids expressed in g/L. This is perhaps due to the difference in density, which could not be compared due to insufficient data. The mean of many parameters could not be compared due to a lack of chemical analyses in some samples. We can confirm that the mean values of the component concentration are not statistically different with a 99 % confidence interval and therefore conclude that there is no significant difference in composition between the different types of black liquors tested.

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[28] REA = NaOH + ½ Na_2S (as Na_2O)
[29] NaOH (g/L) = Na_2O (g/L) x g NaOH/g Na_2O

7.2.4 Experimental measurements for process performance evaluation

The process performance is characterized mainly by: (1) the current efficiency, (2) the energy consumption, (3) the NaOH productivity and, (4) the black liquor flow rate. The measurements required to estimate these performance parameters are based on: (1) the amount of NaOH produced in a fixed period of time, (2) the number of Faradays used during that period, (3) the volume of black liquor treated and (4) the estimated amount of lignin recovered.

The amount of NaOH produced in a determined period of time was calculated by titrating one aliquot from one liter of solution collected at the overflow to determine the NaOH concentration. In some cases, it would take up to 2.0 h to collect one liter depending of course on the concentration of NaOH produced (1.25 to 14 %), the higher the NaOH concentration the longer the sampling time. The NaOH concentration was very well controlled by measuring conductivity. We obtained a typical coefficient of variation (COV) of 0.04 % for the conductivity and 1.3 % for the NaOH concentration. From these data, we were able to estimate the number of NaOH moles produced, to calculate caustic current efficiency, energy consumption and NaOH productivity. Current efficiency is the ratio of the number of moles of NaOH produced during a fixed period of time divided by the theoretical amount that the number of Faradays used during that period. The current was controlled in a galvanostatic mode and monitored along with the cell voltage on a continuous basis. We calculated the energy consumption expressed in kWh/t of NaOH from the current, the cell voltage and the amount of NaOH produced. We estimated the specific NaOH productivity expressed in kg of NaOH/(h·m^2) from the production rate of NaOH and the anode area.

The black liquor flow entering the system and the flow coming out expressed in L/(h·m^2) were determined from the volume variation measured by the difference in height of the liquor in the appropriate reservoir from the beginning to the end of the test. The accuracy was ± 1.0 mm corresponding to ± 46 mL for flows ranging from 3.0 to 86.0 L/(h·m^2) depending on operating conditions. This corresponds to a maximum error of 1.5 % at a flow rate of 3.0 L/(h·m^2).

Table 7.3 : Results of black liquor analyses

Analyses	Oxidized Softwood (OSW)				Non-Oxidized Softwood (NOSW)				Comparing OSW vs NOSW				Non-Oxidized Hardwood (NOHW)				Comparing NOSW vs NOHW			
	#1	#2	Mean	s	#1	#2	Mean	s	Δ, %	F(95 %) = 162	t	$t_{95\ \%}$	#1	#2	Mean	s	Δ, %	F(95 %) = 162	t	$t_{95\ \%}$
Total dissolved solids, %	29,8	28,7	29,3	0,78	29,0	29,3	29,2	0,21	0,34	13,4	0,18	16,5	32,1	32,2	32,2	0,07	10,3	9,0	-120	1,56
Total dissolved solids, g/L	330,6	343,3	337,0	8,96	338,1	343,7	340,9	3,92	-1,16	5,22	-0,57	523	384,2	385,4	384,8	0,85	12,9	21,5	-5,5	98,4
Density, kg/L	1 152	1 152	1 152	-	1 166	1 173	1 170	4,95	-1,50	-	-	-	1 197	1 197	1 197	-	2,35	-	-	-
Fixed solids (ash), g/L	149,8	169,3	159,6	13,8	159,9	174,8	167,4	10,5	-4,66	1,74	-0,64	1231	-	197,7	197,7	-	18,1	-	-	-
Organic solids, g/L	180,9	174,0	177,4	4,9	118,7	168,9	143,8	35,5	23,4	0,02	1,33	164	-	187,7	187,7	-	30,5	-	-	-
Sodium, g/L	60,8	65,8	63,3	3,51	63,9	66,2	65,0	1,59	-2,66	4,86	-0,64	90,8	-	85,2	85,2	-	31,0	-	-	-
Potassium, g/L	10,1	-	-	-	3,31	3,64	3,48	0,23	-	-	-	-	-	-	-	-	-	-	-	-
Residual alkali, (Na_2O), g/L	14,2	-	-	-	13,8	19,7	16,7	4,20	-	-	-	-	18,6	18,1	18,4	0,34	9,69	152	-0,2	112
Residual alkali (NaOH), g/L	4,61	-	-	-	3,89	7,12	5,50	2,28	-	-	-	-	7,70	7,53	7,61	0,12	38,4	336	-0,8	33,2
Sulfide, g/L	<0,01	<0,01	<0,01	0,00	8,15	9,15	8,65	0,71	-	-	-	-	5,49	6,71	6,10	0,86	-29,5	1,47	4,1	10,7
Thiosulfate, g/L	4,84	9,8	7,3	3,50	2,50	2,82	2,66	0,22	175	251	1,88	82,6	-	13,8	-	-	-	-	-	-
Sulfate,g/L	2,89	11,8	7,3	6,26	4,97	5,75	5,36	0,55	36,6	130	0,44	255	-	5,74	-	-	-	-	-	-
Total S, g/L	-	13,2	13,2	9,37	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Carbonate, g/L	13,5	15,2	14,4	1,21	15,2	16,1	15,6	0,60	-8,24	3,99	-1,35	21,9	-	18,8	-	-	-	-	-	-
Chloride, g/L	1,17	-	-	-	1,56	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Conductivity at pH 9, mS/cm	110,9	110,8	110,8	0,05	113,5	114,4	113,9	0,62	-2,71	0,01	-6,98	12,7	120,9	121,3	121,1	0,28	6,3	5,1	-30,9	4,55
UV lignin, g/L	135,0	122,1	128,6	9,12	121,1	116,0	118,5	3,57	8,46	6,53	1,45	541	140,2	-	-	-	-	-	-	-
Calorific value, kJ/kg	-	-	-	-	15 400	14 720	15 060	481	-	-	-	-	-	14 581	-	-	-	-	-	-
Legend	Significance at 95 % confidence intervale						s : standard deviation:				Missing data (-)									

7.2.5 Data analysis

The data were analysed using statistical methods and graphical illustration. A correlation matrix was computed, an analysis of variance was performed on some parameters and the variance of groups of data and means of variables were compared using the F test and the Student's t-test.

The primary data were first examined and those considered blunders eliminated either because they were out of range or could not be justified based on known phenomena in electrochemistry. Examples are a current efficiency well above 100% or a lower voltage at lower temperature. A correlation matrix was computed showing the correlation coefficient between all dependent and independent variables (20). The experimental results obtained from similar operating conditions with at least two repetitions were grouped and then the Fisher and the Student tests were performed. The t test was used to compare means and determine if they are different from each other and at what confidence interval. Next, the effect of the most important dependent variables on process performance was studied in a conventional approach (one variable at a time) in order to determine the most significant parameters and occasionally suggest some potential interactions between variables. The graphical analysis of the results was complemented with error bars where replicates were available.

7.3 Results and discussion

7.3.1 The matrix of correlation coefficients

A correlation matrix (Table 7.4) was computed showing the correlation coefficient between the most pertinent variables of the process indicating how strongly two variables are related to each other. The results are colour coded and categorised as followed; weak (-0.09 to + 0.09), low ((± 0.1 to ± 0.29), moderate ((± 0.30 to ± 0.49) and strong ((± 0.5 to ± 1.0).

In some cases a very strong correlation was observed between certain variables that can be justified easily. For example, the conductivity of the NaOH solution is directly related

(R = 0.98) to its concentration and the temperatures of the black liquor and NaOH solution are both correlated (R = 0.95) because they were controlled by the same heating bath. The NaOH flow depends on the NaOH concentration (R = 0.82) that dictates (R = 0.93) the amount of water to be added. The lower the concentration the higher is the flow rate of water. The energy expressed in kWh/t of lignin is linked to the kWh/m^3 of black liquor treated (R = 1.00). The black liquor flow exiting the cell is linked to the entering flow (R = 0.96) and of course their ratio (R = 0.86 and 0.81). It was also observed that the energy consumption depends on the two energy constituents: cell voltage and current efficiency. The effect of the dependent variables on process performance varies a lot and the impact of each dependent variable will be investigated separately.

Unexpectedly, however, the number of anodes in the cells, which varied from 4 to 10, seems to have an impact on process performance, especially the current efficiency showing a relatively strong correlation (R = 0.61). A special statistical analysis is performed to determine the level of significance.

Table 7.4 : Matrix of correlation between dependent and independent process variables

No.	Variable	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	BL pH	1,00	-0,12	-0,07	0,23	-0,02	0,46	0,70	0,22	0,02	0,37	0,24	0,36	0,39	0,55	0,70	-0,55	-0,55	-0,70	0,08	0,04	0,16
2	BL temp	-0,12	1,00	0,95	-0,06	-0,18	-0,01	0,41	0,06	0,17	0,11	-0,09	0,07	0,18	0,13	-0,14	-0,17	-0,16	0,22	0,28	0,15	-0,42
3	NaOH temp	-0,07	0,95	1,00	-0,12	-0,17	-0,06	0,42	0,01	0,24	0,00	-0,19	0,07	0,15	0,09	-0,28	-0,15	-0,14	0,17	0,22	0,15	-0,36
4	NaOH, %	0,23	-0,06	-0,12	1,00	0,02	0,27	0,10	0,98	-0,57	0,10	0,56	-0,09	0,09	0,10	0,25	-0,22	-0,20	-0,19	0,07	-0,82	-0,69
5	#Anodes	-0,02	-0,18	-0,17	0,02	1,00	-0,15	-0,09	-0,04	-0,61	-0,13	0,46	-0,44	-0,23	-0,07	0,30	0,30	0,28	-0,28	-0,42	-0,08	0,00
6	Current density, kA/m^2	0,46	-0,01	-0,06	0,27	-0,15	1,00	0,31	0,29	0,10	0,70	0,23	0,84	0,58	0,59	0,53	-0,42	-0,43	-0,19	0,52	-0,05	0,34
7	BL Conductivity, mS/cm	0,70	0,41	0,42	0,10	-0,09	0,31	1,00	0,16	0,14	0,31	0,05	0,30	0,41	0,54	0,59	-0,53	-0,52	-0,72	0,03	0,15	0,08
8	NaOH Cond., mS/cm	0,22	0,06	0,01	0,98	-0,04	0,29	0,16	1,00	-0,50	0,12	0,49	-0,04	0,12	0,12	0,24	-0,24	-0,22	-0,17	0,11	-0,84	-0,68
9	Current efficiency, %	0,02	0,17	0,24	-0,57	-0,61	0,10	0,14	-0,50	1,00	0,06	-0,83	0,59	0,33	0,16	-0,13	-0,27	-0,24	0,19	0,41	0,44	0,83
10	Cell voltage, V	0,37	0,11	0,00	0,10	-0,13	0,70	0,31	0,12	0,06	1,00	0,41	0,59	0,33	0,22	0,32	-0,27	-0,29	-0,15	0,29	0,19	0,25
11	Energy, kWh/t NaOH	0,24	-0,09	-0,19	0,56	0,46	0,23	0,05	0,49	-0,83	0,41	1,00	-0,24	-0,07	-0,01	0,31	0,07	0,04	-0,27	-0,17	-0,28	-0,49
12	kg NaOH/(h·m^2)	0,36	0,07	0,07	-0,09	-0,44	0,84	0,30	-0,04	0,59	0,59	-0,24	1,00	0,64	0,50	0,32	-0,49	-0,48	-0,04	0,64	0,21	0,63
13	BL flow in, L/(h·m^2)	0,39	0,18	0,15	0,09	-0,23	0,58	0,41	0,12	0,33	0,33	-0,07	0,64	1,00	0,96	0,81	-0,81	-0,80	-0,29	0,83	0,25	0,25
14	BL flow out, L/(h·m^2)	0,55	0,13	0,09	0,10	-0,07	0,59	0,54	0,12	0,16	0,22	-0,01	0,50	0,96	1,00	0,86	-0,76	-0,76	-0,39	0,65	0,11	0,10
15	BL flow Ratio, out/in	0,70	-0,14	-0,28	0,25	0,30	0,53	0,59	0,24	-0,13	0,32	0,31	0,32	0,81	0,86	1,00	-0,79	-0,79	-0,56	0,35	-0,08	-0,04
16	Energy, kWh/m^3 of BL	-0,55	-0,17	-0,15	-0,22	0,30	-0,42	-0,53	-0,24	-0,27	-0,27	0,07	-0,49	-0,81	-0,76	-0,79	1,00	1,00	0,36	-0,65	-0,16	-0,23
17	Energy, kWh/t lignin	-0,55	-0,16	-0,14	-0,20	0,28	-0,43	-0,52	-0,22	-0,24	-0,29	0,04	-0,48	-0,80	-0,76	-0,79	1,00	1,00	0,36	-0,63	-0,17	-0,23
18	Lignin Recovery, %	-0,70	0,22	0,17	-0,19	-0,28	-0,19	-0,72	-0,17	0,19	-0,15	-0,27	-0,04	-0,29	-0,39	-0,56	0,36	0,36	1,00	0,28	-0,01	-0,12
19	kg lignin/(h·m^2)	0,08	0,28	0,22	0,07	-0,42	0,52	0,03	0,11	0,41	0,29	-0,17	0,64	0,83	0,65	0,35	-0,65	-0,63	0,28	1,00	0,19	0,16
20	Flow of NaOH, L/(h·m^2)	0,04	0,15	0,15	-0,82	-0,08	-0,05	0,15	-0,84	0,44	0,19	-0,28	0,21	0,25	0,11	-0,08	-0,16	-0,17	-0,01	0,19	1,00	0,93
21	Flow of water, L/(h·m^2)	0,16	-0,42	-0,36	-0,69	0,00	0,34	0,08	-0,68	0,83	0,25	-0,49	0,63	0,25	0,10	-0,04	-0,23	-0,23	-0,12	0,16	0,93	1,00
	Legend	Blue : Negative correlation				RED : Positive correlation				The higher the colour intensity the stronger the correlation												

7.3.2 Investigation of the effect of the independent variables on process performance

7.3.2.1 The effect of liquor type

There are two major types of black liquor generated by kraft mills located in the province of Québec. They are identified as softwood (SW) and hardwood (HW) liquors according to the corresponding wood species processed in the mill. The system was operated with a weak solution of NaOH (0.40 M) as the anolyte instead of black liquors and the cell performance was compared to processing black liquor when producing a dilute caustic soda (NaOH). Then, non-oxidized SW liquor was compared with non-oxidized HW liquor. At one of the SW mills, the black liquor is oxidized. So, the process performance was compared when treating oxidized softwood BL (OSWBL) and non-oxidized softwood BL (NOSWBL).

In order to study the impact of the anolyte composition on cell performance, an experiment was performed using a pure solution of NaOH (0.4 M, 1.5 % and 16 g/L) as the anolyte. It is worth mentioning that the BL at 29 % solids contains approximately 50 % inorganic and 50 % organic matter (Table 7.3). The organic concentration can be as much as 150 g/L. That type of feed to an electrolysis cell is quite unusual. It is much common to treat inorganic solutions usually clean and frre of particulates. Initially, the conductivity of the NaOH solution was adjusted at 117 mS/cm, as close as possible to the conductivity of the BL (114 mS/cm), a difference that was not significant at a 95 % confidence interval. It was maintained at that level by adding NaOH at 0.8 M to the anolyte recirculation loop as electrolysis proceeded. In both cases the concentration of the caustic soda produced was controlled at 4.2-4.3 % with no significant difference between the two concentrations at a 95 % confidence interval.

We can notice that the caustic soda solution had a higher pH (11.5) than the black liquor (9.0) (Table 7.5). We had decided to operate at the same conductivity rather than at a similar pH. It is also worth noticing that the 0.4 M NaOH solution has a much lower content of sodium (9.2 g/L) than the black liquor used (65 g/L) (Table 7.3).

First, we observed that the cell voltage was significantly higher (+44 %) with a 99% confidence interval ($|t| = 83.1 >> t'_{99\ \%} = 32.5$) when operating with black liquor compared to the NaOH solution. The difference existed despite the fact that the anolyte conductivities and caustic soda concentrations were similar. The conductivity values measured in the catholyte were

significantly lower (14 %) in the black liquor case than the NaOH case contributing to the higher voltage. However, this fact alone cannot explain the voltage difference (1.35 V) between the two cases. The difference in the anolyte composition impacts the conductivity of the membrane and therefore the voltage drops across the membrane as reported by Moshtarikhah [11]. Indeed, the authors reported that the experiment with different anolyte and catholyte concentrations shows that the anolyte concentration has a strong influence on conductivity. It was assumedthat the sodium in the form of free NaOH (16 g/L) and exhibiting a higher residual effective alkali, three times the level found in the BL (5.5 g/L), contributed to increasing the conductivity of the membrane resulting in a lower voltage.

However, it is quite clear that operating electrolysis with a diluted NaOH solution as the anolyte instead of the BL has the stronger effect on current efficiency. In fact, the current efficiency is only half (43.2 %) the value that was obtained with the black liquor (88.4 %) (Table 7.5). Consequently, the energy consumption was 12.7 % higher (99% confidence interval) even though the cell voltage was significantly much lower (-29.5%). It is known that the main cause for the lower current efficiency is the back migration of hydroxyl ions from the catholyte (1.11 M) to the anolyte which rate depends on the concentration gradient across the membrane, a factor of 2.8 in this particular situation. In the case of sodium sulfate splitting, it was shown that the higher the sodium concentration in the anolyte the better the current efficiency [12]; in this work, the black liquor contained 65.0 g/L of sodium (Table 7.3). Furthermore, there are side reactions [13-18] that are taking place at the anode, such as the electro-oxidation of organics, especially the lignin present at high concentration (120 g/L). Indeed, during electrolysis, lignin is cleaved to smaller molecules [18] while the phenolic groups are reduced and the carboxylic groups are concentrated [17]. Those side reactions consume electrons and do not produce hydroxyl ions but are accounted for in the calculation of current efficiency and in the specific energy consumption, which are reported here on the basis of the NaOH produced.

Hardwood and softwood black liquors have a similar composition but differ in the concentrations of their major constituents. In this study, the HW BL was more concentrated and contained a higher level of solids (32 %) than the SW BL (29 %) with a 95 % confidence interval and contained a higher level of sodium (85 vs 65 g/L) and residual alkali (7.6 vs 5.5 g/L) as well (Table 7.3). At similar operating conditions, the results showed (Table 7.6) that the cell voltage was 3.7 % higher with the HW liquor with a 95 % confidence interval despite a slightly higher

temperature (73.4 vs 69.5 °C) that contributed to a higher conductivity (121 vs 115 mS/cm) of the anolyte. The current efficiencies had about the same values (70 vs 71 %) and they were significantly different at a 95 % confidence interval but not at 99 %. The combined effect of those two parameters results into an energy consumption of 4 400 kWh/t of NaOH with no significant difference between the two liquors. However, the 2 % difference of NaOH productivities (1.62-1.66 kg/h/m^2) was significant at a 95 % confidence interval but not at 99 %. Overall, it can be concluded that under the operating conditions tested, there was no major significant difference in performance when processing either non-oxidized softwood or hardwood black liquors despite some differences in their properties and component concentrations.

Some older kraft pulp mills are still equipped with a direct contact evaporator to concentrate black liquor from approximately 50 % solids at the evaporators exit to the 70 % level before firing in the recovery boiler [8]. These mills require the oxidation of black liquor to oxidize the sulfur components in order to meet sulfur environmental emissions. In this study, the softwood BL oxidation was carried out with pure oxygen that converts sulfide ions to a more stable thiosulfate. Oxidized BL contains a low sulfide level but more thiosulfate and sulfate depending on the degree of oxidation [19].

In order to determine the impact of oxidizing BL, oxidized and non-oxidized black liquor from two different softwood mills were electrolysed at similar operating conditions. When electrolysed at pH 9.0, the conductivities of both black liquors were significantly different (95 %) as well as the cell voltage but no significant difference was detected for the current efficiency, the energy consumption and NaOH productivity. It is important to point out that the electrolytic treatment of the black liquor involves an in-situ oxidation reaction from the oxygen formed at the anode. This produces a similar effect on sulfides [6] than the conventional oxidation carried out in a reactor with pure oxygen that converts sulfide components to thiosulfate and then sulfate. Overall, the results (Table 7.7) show no difference in the process performance between these two types of oxidized and non-oxidized liquors, with a 98 % confidence interval.

Table 7.5 : Performance comparison of the electrolysis of NOSW black liquor and 0.40 M NaOH anolyte solution operating at 70 °C and a current density of 1.25 kA/m^2.

Anolyte				Catholyte		Voltage, V	Current efficiency, %	kWh/t NaOH	kg NaOH/ (h/m^2)
Liquor	**No**	**pH**	***K*, mS/cm**	**NaOH, %**	***K*, mS/cm**				
NaOH (0.4 M)	1	11,5	117,3	4,50	337,0	3,11	43,2	4 832	0,821
	2	11,5	117,3	4,25	336,9	3,07	43,1	4 775	0,818
	3	11,5	117,3	3,81	337,4	3,00	41,6	4 833	0,782
	4	11,6	117,3	4,15	337,1	3,04	44,4	4 583	0,842
	5	11,6	117,2	4,17	337,1	3,07	44,2	4 649	0,841
	6	11,6	117,3	4,40	337,3	3,07	42,9	4 794	0,799
	Mean ($\bar{x}_1$)	11,5	117,3	4,21	337,1	3,06	43,2	4 744	0,817
	Stdev (s_1)	0,02	0,04	0,24	0,195	0,04	1,01	104,0	0,023
	COV, %	0,21	0,03	5,69	0,058	1,22	2,34	2,19	2,86
NOSW BL	1	8,99	114,1	4,26	290,1	4,40	87,9	4 169	1,290
	2	9,01	114,0	4,32	290,0	4,41	88,8	4 249	1,274
	$\bar{x}_2$	9,00	114,0	4,29	290,0	4,41	88,4	4 209	1,282
	s_2	0,01	0,07	0,04	0,041	0,01	0,67	56,2	0,01
	COV, %	0,15	0,06	0,97	0,014	0,18	0,76	1,34	0,88
Change, %		-22,0	-2,78	1,83	-14,0	44,0	104,3	-11,3	56,9
F(95 %) = 230		3,28	0,25	33,0	22,4	21,9	2,3	3,4	4,3
t-test value		183	59,9	-0,8	555	-83,1	-71,6	9,2	-37,3
t-value at 95 % = 7.4									
t-value at 98 % = 17.0									
t-value at 99 % = 32.5									
Stdev (s) : standard deviation			COV: coefficient of variation = $s/\bar{x} \cdot 100$						

Table 7.6 : Comparing the performance of the electrolysis of NOSW and NOHW black liquors when operating at pH 9.0, 70 °C, a current density of 1.57 kA/m^2 and making 10 % NaOH on the catholyte side.

Anolyte (Black liquor)				Catholyte			Voltage, V	Current efficiency, %	kWh/t NaOH	kg NaOH/ h/m^2
Liquor	**No.**	**T, °C**	**κ, mS/cm**	**NaOH, %**	**T, °C**	**κ, mS/cm**				
NOSW BL	1	69,3	113,5	10,2	70,4	564,3	4,63	70,7	4 398	1,654
	2	69,6	114,1	10,0	70,4	564,6	4,65	71,3	4 379	1,663
	3	69,6	114,4	10,0	70,4	564,8	4,68	71,2	4 418	1,654
	MEAN ($\bar{x}_1$)	69,5	114,0	10,1	70,4	564,6	4,65	71,1	4 399	1,657
	Stdev (s_1)	0,17	0,454	0,11	0,02	0,245	0,02	0,31	19,52	0,005
	COV, %	0,24	0,398	1,13	0,03	0,043	0,50	0,44	0,444	0,311
NOHW BL	1	73,3	120,9	10,3	73,3	612,5	4,78	70,2	4 321	1,621
	2	73,4	121,3	10,6	73,4	612,8	4,87	70,1	4 454	1,626
	$\bar{x}_2$	73,4	121,1	10,5	73,4	612,7	4,82	70,2	4 388	1,624
	s_2	0,04	0,276	0,18	0,10	0,167	0,07	0,06	93,94	0,003
	COV, %	0,05	0,228	1,76	0,13	0,027	1,46	0,08	2,141	0,196
Change, %		5,51	6,236	3,9	4,21	8,519	3,67	-1,28	-0,245	-2,027
F(95 %) = 200.0		22,2	2,701	0,4	0,06	2,166	0,11	27,7	0,043	2,619
t-test value		-39,2	-26,8	-5,5	-144,7	-333,7	-9,82	5,02	0,58	11,1
t-value at 95 % = 4.8										
t-value at 98 % = 8.5										
t-value at 99 % = 13.3										

Table 7.7 : Comparing the performance of the electrolysis of OSW and NOSW black liquors when operating at pH 9.0, a current density of 0.94 kA/m^2 and making 10 % NaOH.

	Anolyte (OSWBL)				Catholyte						
Liquor	**No.**	**T, °C**	**κ, mS/cm**	**NaOH, %**	**T, °C**	**κ, mS/cm**	**Voltage, V**	**Current efficiency, %**	**kWh/t NaOH**	**kg NaOH/(h/m^2)**
OSWBL	1	69,5	110,9	10,3	70,5	564,7	3,99	59,6	4 485	0,838
	2	69,8	110,8	10,3	70,5	564,5	3,99	62,2	4 227	0,862
	Mean ($\bar{x}_1$)	69,6	110,8	10,3	70,5	564,6	3,99	60,9	4 356	0,850
	Stdev (s_1)	0,25	0,054	0,01	0,04	0,159	0,00238	1,90	182,5	0,017
	COV, %	0,36	0,049	0,14	0,06	0,028	0,06	3,13	4,189	2,000
NOSWBL	1	68,8	112,3	10,19	70,4	564,3	4,04	63,5	4 301	0,897
	2	68,8	112,6	10,0	70,3	564,4	4,08	61,5	4 448	0,865
	3	69,0	112,5	10,0	70,5	564,7	4,09	63,4	4 332	0,890
	$\bar{x}_2$	68,9	112,5	10,1	70,4	564,5	4,07	62,8	4 360	0,884
	s_2	0,130	0,166	0,11	0,13	0,213	0,023	1,13	77,25	0,017
	COV, %	0,19	0,15	1,13	0,19	0,04	0,57	1,80	1,77	1,93
Change, %		-0,86	1,519	-1,92	-0,097	-0,007	2,12	5,42	3,15	5,46
F(95 %) = 18.51		3,79	0,107	0,02	0,089	0,557	0,01	2,83	5,58	0,99
t-test value		4,00	-15,90	3,11	1,17	0,92	-6,11	-1,26	-0,03	-2,17
t-value at 95 % = 5.6										
t-value at 98 % = 10.7										
t-value at 99 % = 18.0										

7.3.2.2 The effect of the number of anodes

As mentioned earlier in section 7.3.1, the number of anodes in the electrolytic cell is correlated to the process performance, especially the current efficiency, with an unexpected but relatively strong coefficient of correlation (0.61). Globally, the correlation seems to be a false correlation (Figure 7.1) implying that the correlation may not entail a mutual relationship between these two variables. Therefore, we were interested in determining the significance level of the impact of that parameter on the process performance. To this effect, we regrouped data of similar operating conditions to investigate the influence of that parameter on process performance at two levels of caustic soda (5 and 10 %) (Table 7.8).

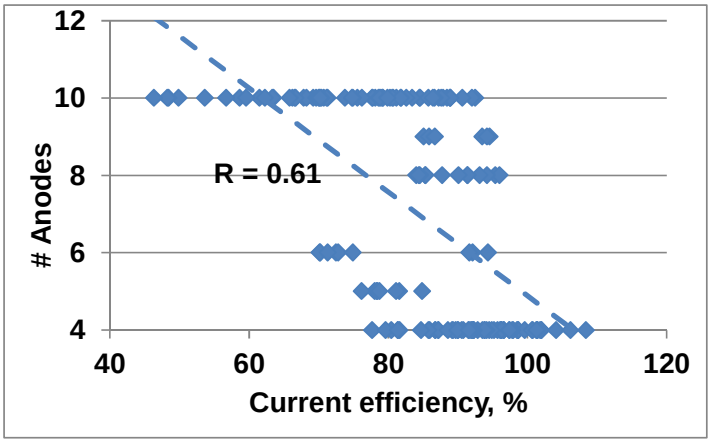

Figure 7.1 : The plot of the number of anodes as a function of current efficiency

Table 7.8 : Experimental results of the effect of the number of anodes and caustic soda strength on current efficiency at pH 9.0, 71.5 °C and 1.20 kA/m^2.

NaOH, %	# Anodes	N	Mean	Stdev, s
5	**4**	14	98,8	4,73
	8	3	91,0	0,74
10	**4**	9	87,0	6,93
	5	4	77,8	1,15
	9	3	85,9	0,82
	10	9	65,0	3,75
N : Number of observations				

The analysis of the variance (ANOVA) of the data from Table IX revealed that the NaOH concentration and the number of anodes have a significant effect on process performance, especially on the current efficiency, the energy consumption, and the productivity with a confidence interval exceeding 99 % ($P<0.001$). On the other hand, the cell voltage is not affected. The ANOVA also showed that there is a significant interaction ($p<0.001$) between those two variables concerning the energy (kWh/t of lignin) and no significant impact ($P>0.02$) on the performance of the other process parameters. It is known that NaOH strength affects the process performance due to an increased back diffusion at higher levels [20].

However, we have no fundamental justification of the effect of the number of anodes in the cell other than the impact on the current distribution, which could be altered by the number of anodes used, therefore affecting some cell and process performance parameters. Therefore, no further conclusions should be drawn as the experimental work on that subject here was limited.

The issue of current distribution was discussed previously for the particular situation where the cell contained 10 anodes [6]. This preliminary work cannot, however, provide a satisfying answer to why the number of anodes affects cell and process performance. To investigate further the phenomena, we recommend performing more elaborated simulation work that could help develop the best cell design for our application. That objective was beyond the scope of this study.

Table 7.9 : Results of the confidence interval (P) from the ANOVA analysis of the effect of NaOH concentration and the number of anodes in the cell on process performance.

Source	**Cell voltage**	**Current efficiency**	**Energy, kWh/ton**		**Productivity, kg/(h·m^2)**	
			NaOH	**Lignin**	**NaOH**	**Lignin**
NaOH, %	70.6	<0.001	<0.001	<0.001	0,002	-
# Anodes	89.5	<0.001	<0.001	<0.001	0,080	-
NaOH*# Anodes	2.1	42.9	99.4	<0.001	50.3	-

7.3.2.3 The effect of the black liquor pH during electrolysis

The black liquor from the kraft process has a high pH (12 to 13) mostly due to the residual alkali that maintains lignin in solution. However, the lignin can be precipitated by lowering the pH using either the acidification process (H_2SO_4 and CO_2) or membrane technologies, including electrolysis, conventional electrodialysis (ED), or bipolar membrane ED for reducing alkalinity [4]. When sulfuric acid is used [21, 22], the lignin recovery rate can reach 95 % at pH 3.0. Alternatively, carbon dioxide (CO_2) can also be used to lower the pH of black liquor and recover lignin but it has practical limitations. At a pH lower than 9.5 it requires an excessive amount of CO_2 because it is a weak acidifying agent and due to the buffering effect of salts, such as sodium bicarbonate. In practice, the pH is maintained above 9.5 to minimize gas consumption during lignin recovery. At that pH, a 66 to 68 % recovery rate is usually obtained with both chemicals; the acid and the gas [2, 23-25]. The electrolytic treatment can lower the pH [26] to a value

comparable (3.5) to the sulfuric acid (Figure 1). At the operating conditions using 15 % solids black liquor, 75 % of the lignin precipitated out of solution. From previous work on the electrolysis of BL [4], we recommended operating at a pH above 5.0 due to difficulty of operation caused by foaming from the excessive formation of carbon dioxide. In this study, we investigated the effect of pH during electrolysis, which varied from 6.0 to 100.

As electrolysis proceeds, the pH of the BL drops as a consequence of sodium extraction and reduced liquor alkalinity (Figure 7.2) by the conversion of hydroxyl ions to water at the anode. The conductivity drops (Figure 7.3) because of less sodium as electrolysis proceeds and due to gas formation as well [4]. Moreover, lowering the pH increases the decomposition voltage (E_d) according to the Nernst equation[30] (+0.24 V, +5.5 %). Both phenomena are contributing to the increase in cell voltage. In general, when lowering the pH from 10.0 down to 6.0 the cell voltage increased by 13 % (Figure 7.4) corresponding to 0.15 V per unit drop of pH.

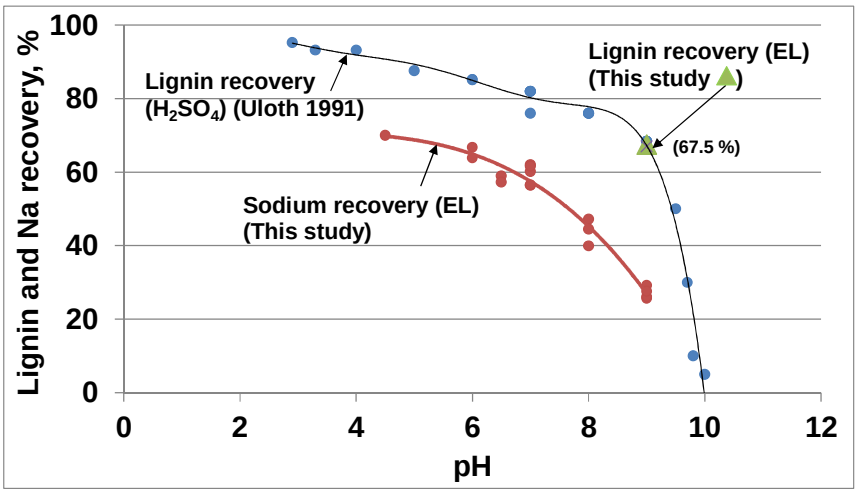

Figure 7.2 : Lignin and sodium recovery as a function of BL pH at 70 °C and at a current density of 1.3 kA/m^2

[30] At pH 9.0: E_d = 1.229-0.059 x 9 = 0.53 V and at pH 5.0: E_d = 1.229-0.059 x 5 = 0.295 V with Δ V = 0.24 V corresponding to 5.5 % increase (0.24 V/4.25 V the cell voltage) [18-Hine]

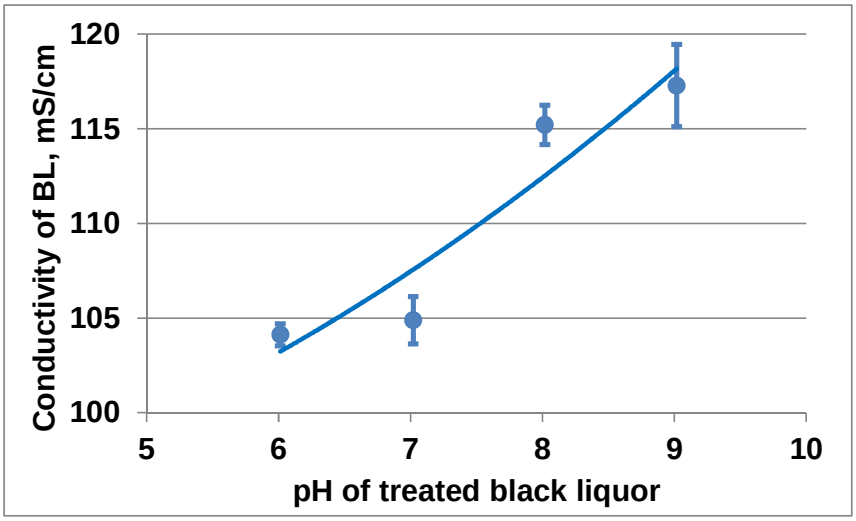

Figure 7.3 : Conductivity of BL as a function of pH and at a current density of 1.3 kA/m^2.

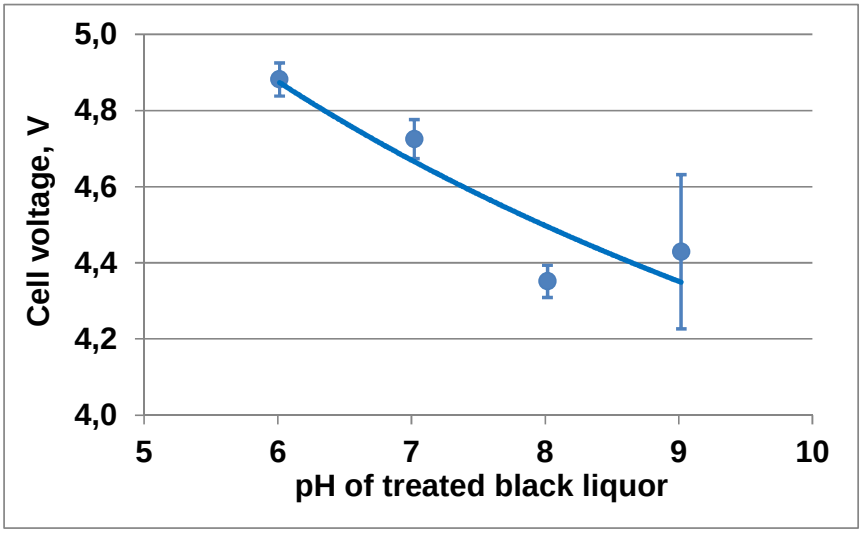

Figure 7.4 : Cell voltage as a function of BL pH during electrolysis at 70 °C and at a current density of 1.3 kA/m^2

Current efficiency is a fundamental indicator of process performance that we evaluated as a function of the black liquor pH and, caustic soda strength. The experimental results show that the concentration of caustic soda has as much an impact as the pH of the BL (Figure 7.5). Indeed, at NaOH concentration below 10 %, the current efficiency loss due to the drop in pH is similar to the contribution of the NaOH strength increase. However, above 10 %, the current efficiency loss is dominated by the NaOH strength because of back migration. It is therefore recommended to minimize the caustic soda strength where possible to maintain a higher current efficiency.

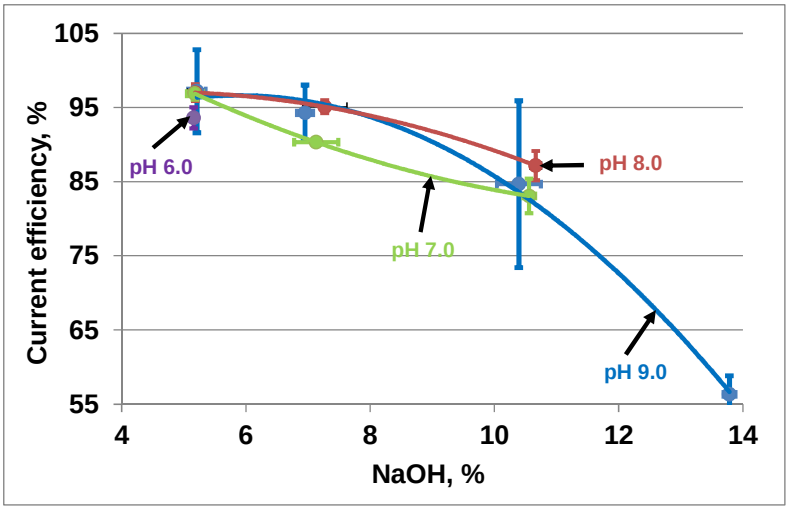

Figure 7.5 : Current efficiency as a function of BL pH and NaOH strength at 70 °C and a current density of 1.3 kA/m^2

The energy consumption of the electrolytic treatment is composed of the cell voltage and the current efficiency. We report the values on the basis of: (1) the NaOH produced in kWh/t, (2) the volume of BL treated in kWh/m^3 and, (3) the estimated amount of lignin recovered in kWh/t. The former (NaOH) allows comparing the energy utilisation of this process with the chlor-alkali industry referring to NaOH production. The latter is calculated from the energy required to treat one m^3 of BL to a target pH and using the lignin recovery rate at that pH (Figure 1) from which we can estimate the energy requirement per ton of lignin.

The energy consumption expressed in kWh/t of NaOH depends strongly on BL pH during electrolysis and the caustic strength (Figure 6). Results showed that at low NaOH concentration (5 %), the effect of pH is mitigated with high variability. As the NaOH concentration increases, the energy demand increases and at NaOH strength over 10 %, the energy consumption is dominated by the accentuated drop in current efficiency (Figure 7.4).

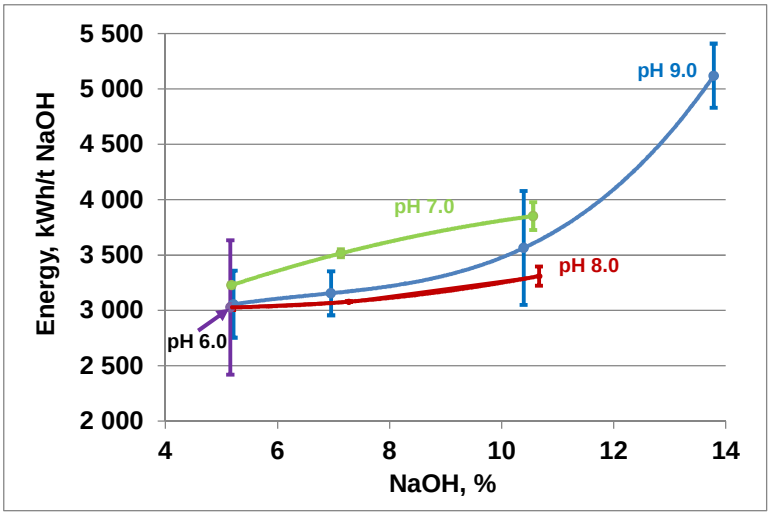

Figure 7.6 : Energy consumption in kWh per t of NaOH as a function of BL pH and NaOH strength at 70 °C and a current density of 1.3 kA/m^2

It must be noted that running at pH 6.0 requires 4 times more energy per volume of BL (Figure 7.7) than at pH 9.0. However, the sodium recovery increases from 26 to 65 % to make more sodium hydroxide. This accounts for the additional energy consumption. On the other hand, increasing the NaOH concentration contributes to higher energy usage mostly due to the loss of current efficiency.

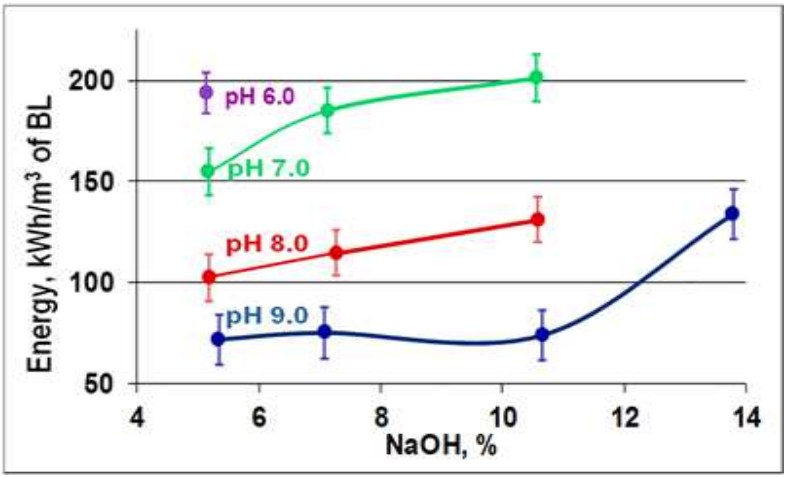

Figure 7.7 : Energy consumption per m^3 of treated BL as a function of BL pH and NaOH strength at 70 °C and a current density of 1.26 kA/m^2

It was in the early 90's that Richardson first proposed [27, 28] using the lignin recovered from the black liquor to replace fossil fuel in the lime kiln. This environmental and energy application was repeatedly investigated later by Loufti [23] and Uloth [21]. Valmet[31], Andritz[32] and Noram[33] which are major technology developers in the pulp and paper industry materialized the integration of the technology in a kraft mill. [29-31]. From that perspective, it is therefore important to minimize the energy requirement of the electrolytic step to maximize the overall process energy balance of a kraft mill. We therefore investigated the operating conditions that would offer the minimum electricity consumption per ton of lignin recovered.

The experimental results show that, after acid and water washes, black liquor electrolysed at pH 9.0 delivers a similar lignin recovery (67.5 %) to acidification with sulfuric acid (68.4 %), while Alén [32] and Merewether [33] reported lignin yields of 63.6 % and 76.6 % using CO_2 on black liquor containing 26.2 and 30.9 % solids, respectively. Based on that observation, we assumed that lignin recovery using electrolysis would have the same profile as sulfuric acid down to pH 6.0 (Figure 7.2). Accordingly, we estimated the energy consumption per ton of lignin as a function of pH at various NaOH strengths (Figure 7.8). We observed that the energy consumption increased with decreasing pH and we estimated that the amount of energy required at pH 6.0 is double the value obtained at pH 9.0. We also noticed that increasing NaOH concentration has more impact at a pH lower than 9.0, suggesting an interaction between pH and NaOH strength. However, operating at pH 9.0 offers the best energy performance (900 kWh/t of lignin) at all NaOH strengths tested. That energy usage corresponds to only 12.5 % of the high heating value of lignin, therefore giving great potential for positive energy balance in the mill. It is nevertheless worthwhile mentioning that even at lower pH (6.0-7.0) and high NaOH concentration (10 %), the technology can still achieve a positive energy balance given the fact that the energy used to precipitate the lignin (1 893 to 2 044 kWh/t of lignin) is only one quarter of its high heating value (HHV) estimated at 7 284 kWh/t.

In conclusion, it is recommended operating at pH 9.0 to maximize the energy performance of the proposed application. Moreover, operating at that pH avoids the precipitation of divalent cations

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[31]http://www.biofuelsdigest.com/bdigest/2013/11/03/metso-is-supplying-a-lignoboost-plant-to-stora-ensos-new-biorefinery/
[32] https://www.andritz.com/spectrum-en/news/tech-talk-lignin-removal
[33] http://www.noram-eng.com/pulp-paper/

within the membrane at lower pH [6], thus protecting the membrane and prolonging its life. Running electrolysis at a lower pH could only be considered in cases where mill production is limited by the causticizing plant or lime kiln creating a shortage of cooking liquor and therefore limiting pulp production. Pursuing electrolysis to lower pH will provide more NaOH to be added to the white liquor allowing for additional pulp production. However, some measures, such as ion exchange, will have to be taken to remove divalent cations.

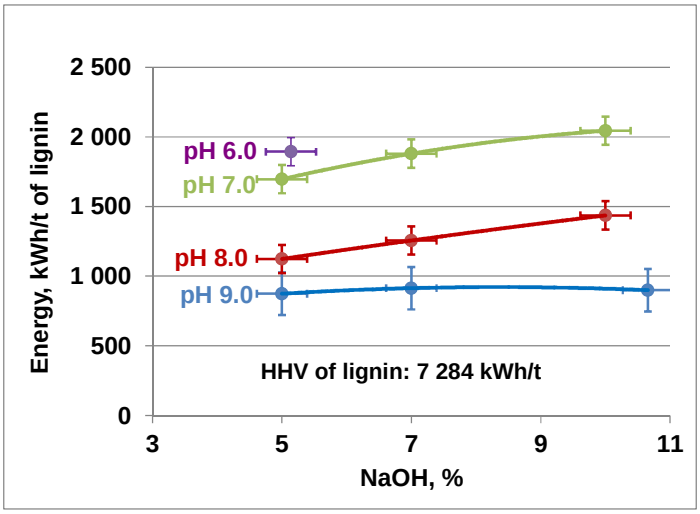

Figure 7.8 : Energy consumption in kWh per ton of lignin as a function of BL pH and NaOH strength at 70 °C and at a current density of 1.26 kA/m^2

Minimizing energy consumption by operating at a higher pH represents an opportunity to reduce operating costs. On the other hand, the process performance is also concerned with productivity to assure economic viability of the technology. The process productivity can be expressed in three ways: the NaOH production rate in kg/(h·m^2), the black liquor flow treated per unit surface of anode in L/(h·m^2) and the lignin production in kg/(h·m^2).

The NaOH productivity represents the capacity of the system to remove sodium from the BL and recovering it as caustic soda. It is moderately correlated (R = 0.5) (Table 7.4) with current efficiency. The experimental results show a decrease in productivity as pH is reduced and NaOH concentration is increased. Generally, the caustic concentration has much more impact than the pH of BL (Figure 7.9). In fact, when the NaOH strength is increased from 5 to 10 %, the NaOH productivity drops by less than 5 % (on average 4.4 %) in the pH range tested (6.0 to 9.0). On

the other hand, the productivity is estimated to be one third when the NaOH concentration increased by two fold. Above 10 % NaOH strength, the productivity drops drastically from the loss of current efficiency.

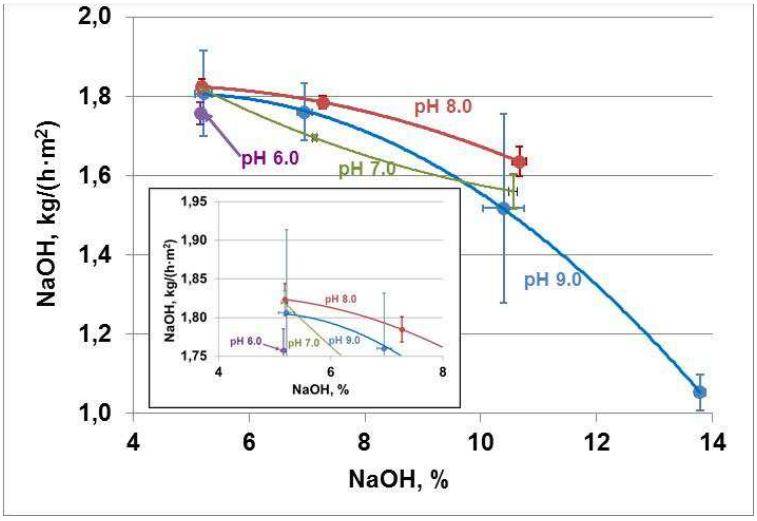

Figure 7.9 : Caustic soda productivity as a function of BL pH and NaOH strength at 70 °C and a current density of 1.26 kA/m^2

On the other hand, the lignin productivity (kg/(h·m^2) dictates the dimensioning of a lignin recovery plant from the BL. We observed that lignin productivity depends strongly on the final pH and caustic soda concentration (Figure 7.10). Indeed, the lower the pH, the lower the productivity and, a lower NaOH concentration favours process productivity. The maximum lignin productivity value is attained when electrolysing BL at pH 9.0 while making caustic soda at 5 % strength offering a lignin productivity of about 7.0 kg/(h·m^2).

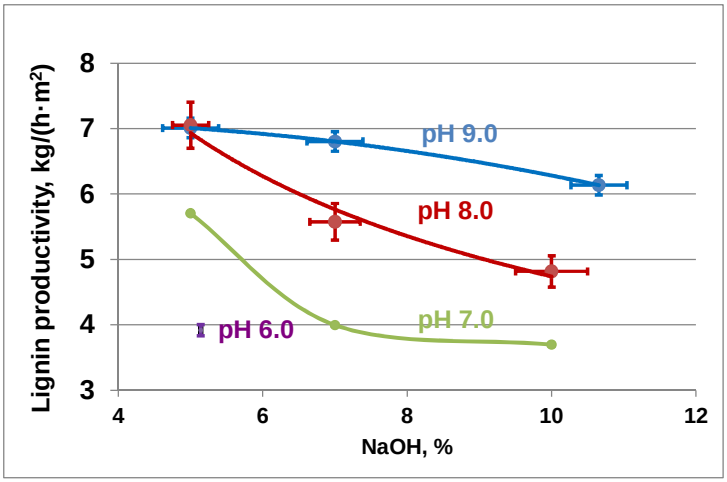

Figure 7.10 : Lignin productivity as a function of BL pH and NaOH strength at 70 °C, a current density of 1.26 kA/m^2 and lignin recovery according to Figure 7.2.

The process productivity can also be reported as the volume of BL treated per surface unit of anode and time (Figure 7.11). We can see that below 10 % NaOH strength, the flow of BL treated are the same at pH 8 and 9.0 but much lower at pH 6.0 and 7.0 due to a higher sodium recovery and lower current efficiency. At pH 9.0, increasing the NaOH concentration to 14 % brings the BL productivity flow to the same level (40 L/(h·m^2) as operating at lower pH and NaOH levels. Lignin productivity and specific BL flow are linked by the yield of lignin, which is mostly dependent on pH (Figure 7.1).

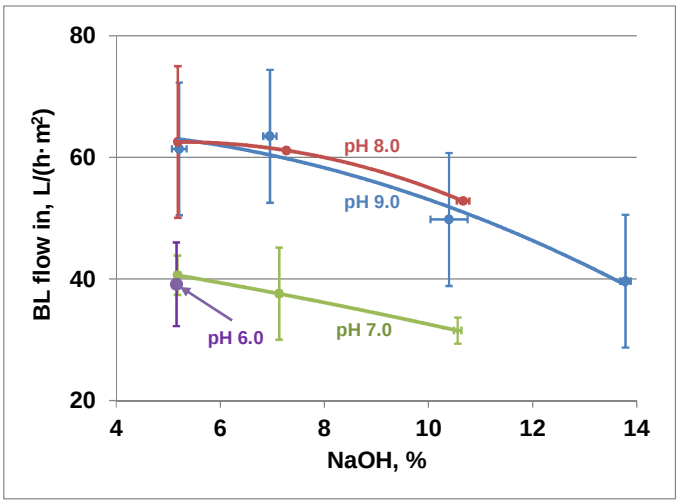

Figure 7.11 : Black liquor flow treated as a function of BL pH and NaOHstrength at 70 °C and a current density of 1.26 kA/m^2

Even though the results seem to suggest operating at pH 6-7 to maximize current efficiency (Figure 7.5) and NaOH productivity (Figure 9), it also shows that the energy consumption is higher. Furthermore, we have recommended previously that it is crucial to operate at alkaline pH (9.0) on the black liquor side to prevent precipitation of dissolved divalent cations when crossing the membrane [7].

With regards to process design and especially pipe dimensioning, it is worth mentioning that the flow of black liquor out of the system is lower than the feed flow. The ratio of these two flows shows a strong correlation (0.88) with the BL pH (Figure 7.12). At pH 10.0, the BL flow out of the cell is 90 % of the feed flow. But at pH 5.5, it is reduced to 50 %. This flow reduction is due partially to a much higher sodium recovery at low pH meaning that more water is transferred with the sodium (4 moles of water per mole of sodium) [7] from the BL to the catholyte (NaOH) compartment therefore reducing the flow exiting the cell. It is important to note that evaporation made a significant contribution as well to reduce the outlet flow [7].

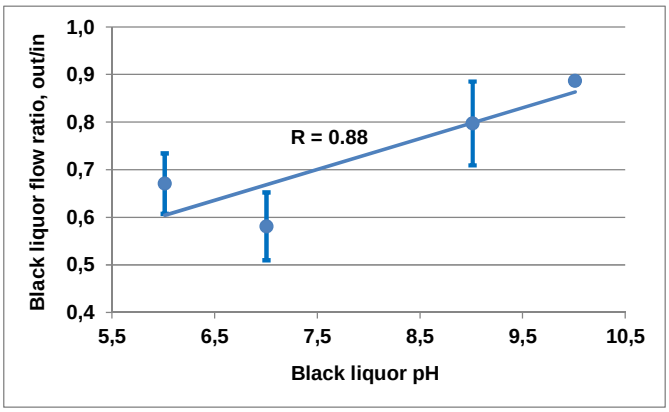

Figure 7.12 : The ratio of black liquor out of the cell over the feed flow as a function of BL pH at 70 °C and a current density of 1.3 kA/m^2

7.3.2.4 The effect of current density

We have examined the effect of pH at which we electrolysed BL in combination with the NaOH strength on the process performance. From an energy point of view, operating at pH 9.0 seems to be optimal and we select that pH value to investigate the other process parameters. While energy consumption is a major factor in the operating cost of an electrochemical process, the current density must be considered because it drives the production capacity. So, we investigated the

effect of that variable in combination with NaOH concentration on energy consumption and process productivity.

By increasing the current density, the cell voltage increases (Figure 7.13) since the electrolysis cell behaves like an ohmic resistance. By tripling the current density from 0.63 to 1.89 kA/m^2 at 10.2 % NaOH, the cell voltage increased from 3.65 to 5.1 V, an increment of 1.45 V or a 40 % increase. The cell voltage increase comes from the higher ohmic voltage drop through the anolyte, the catholyte and the membrane along with the overvoltage at the electrodes [6]. However, at a constant current density we could have expected to observe a reduction in the voltage drop as we increased the NaOH strength given the higher conductivity, but it did not show in the results. In fact, increasing the NaOH concentration in the catholyte results in a decrease of the membrane conductivity and increases the voltage drop across the membrane as demonstrated by Moshtarikhah [11]. According to this author, the maximum conductivity happened at 15 wt%, which is also typical for sodium hydroxide solutions. Making 15 % NaOH will, however, negatively affect the current efficiency cancelling the potential voltage gain. Overall, the net voltage change was negligible compared to the impact of the current density in the range tested.

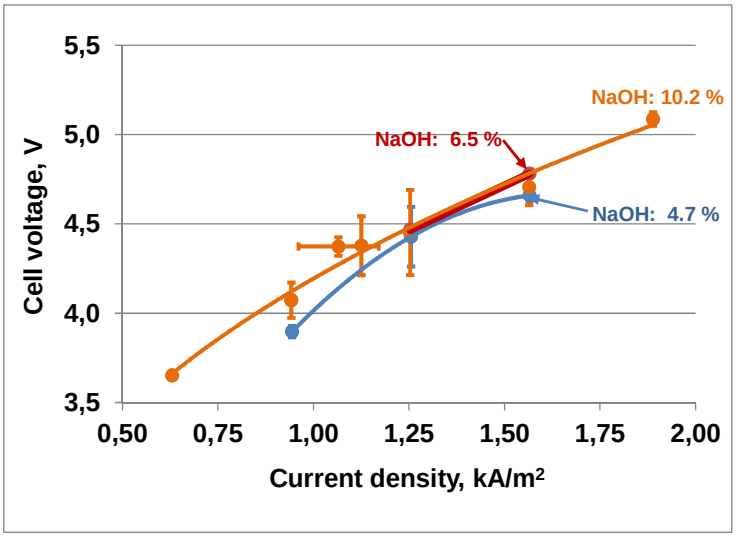

Figure 7.13 : Cell voltage as a function of current density at various NaOH strengths (Black liquor at pH 9.0 and 70°C)

Below 1.25 kA/m^2 the current density does not impact the current efficiency (Figure 7.14) but the NaOH concentration drives the current efficiency down as it increases. However, above 1.25 kA/m^2 the current efficiency tends to drop as the current density increases and this happens for the three NaOH strengths tested: 4.7, 6.5 and 10.2 %. According to Hine [20], the result of a lower current efficiency at higher current density is explained by the back diffusion phenomenon.

At higher current density the hydroxyl ions are attracted more forcefully towards the anode migrating back to the black liquor and reducing current efficiency, which is based on the production of NaOH. While making 10 % NaOH at 1.9 kA/m^2, a major decrease in current efficiency was observed therefore suggesting an interaction between NaOH strength and current density. It must be mentioned that the negative effect of current density on the current efficiency is added to the loss of hydroxyl ions migrating back to the black liquor from the higher concentration gradient existing in the catholyte than in the anolyte. These results are consistent with Moshtarikhah's findings [11] who reported that an increase of current density and sodium hydroxide concentration leads to a lower sodium transport or transference number (t_{Na}), a factor which affects negatively the current efficiency of the processes. A good transference number (t_{Na}) means that most of the electric current is carried by the sodium ions. In this case, in order to maintain the current efficiency above 90 %, the caustic soda concentration should be kept below 5 % unless a higher concentration is absolutely required for a sound mill operation.

Moshtarikhah et al [11] showed that the electrolysis membrane cells of a chlor-alkali plant can be operated at a much higher current density (up to 20 kA/m^2) than the limit of 4 to 5 kA/m^2 recommended by the manufacturer. At high current density, they experimentally demonstrated that the membrane no longer behaves as an ohmic resistor. This could have some beneficial implications for the chlor-alkali and our industrial electrolysis application as well. The increasing membrane conductivity with current density could make it possible to operate electrolysers at very high current densities considerably reducing the number of cells without excessive energy costs. Higher current density than experienced in this study should be explored, but it must keep in mind that operating at a higher current density will shorten the anode life.

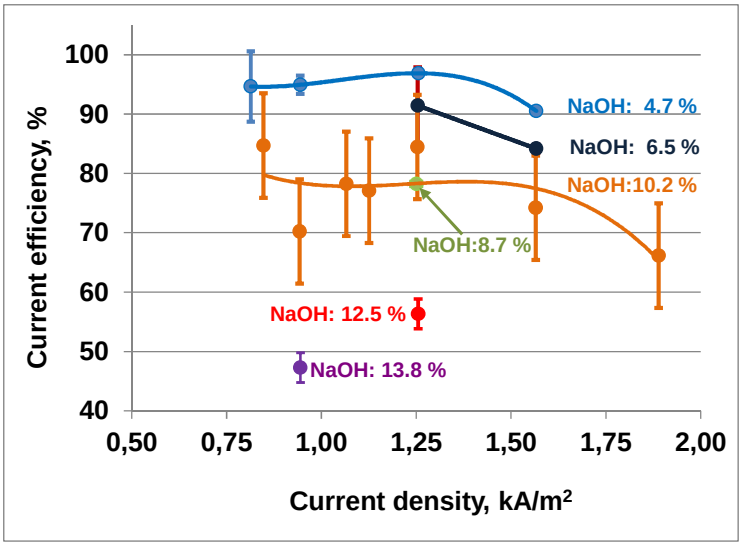

Figure 7.14 : Current efficiency as a function of current density at various caustic soda strengths (Black liquor at pH 9.0 and 70°C)

The overall impact on energy consumption (kWh/t NaOH) of increasing current density combines the effect on the cell voltage and current efficiency. For a minimum energy consumption below 3 500 kWh/t of NaOH, the recommended operating zone in blue on Figure 7.15 shows that the NaOH strength should be kept just under 5.0 % offering a 90 % current efficiency as previously found (Figure 7.14). Obviously, the energy consumption per ton of caustic soda of this process is much higher (40 %) than the caustic produced by the industrial chlor-alkali process (2 200-2 500 kWh/t) [18-Hine]. Our process asdescribed here cannot compete on the NaOH basis alone. However, it offers numerous opportunities of performance improvement in a kraft mill, including the enhancement of pulp production by debottlenecking the recovery furnace and the causticizing plant along with the production of the lignin product to be offered to speciality chemicals market or to replace the fossil fuel in the lime kiln.

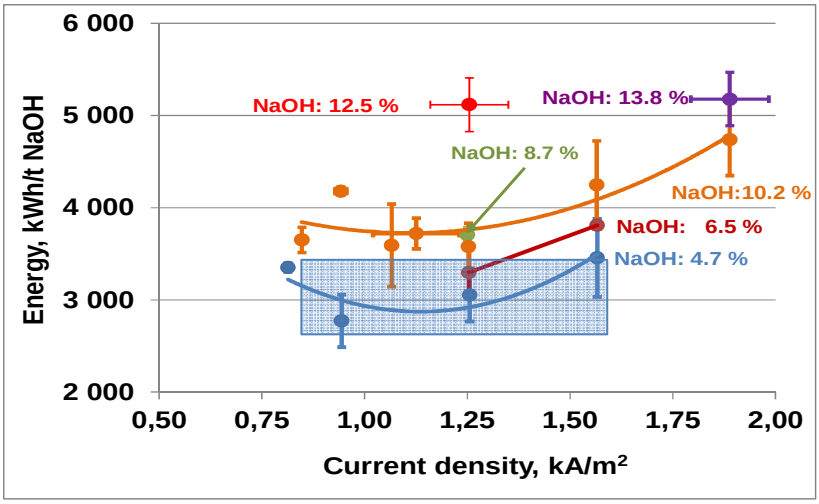

Figure 7.15 : Energy consumption (kWh/kg NaOH) as a function of current density at various caustic soda strengths (Black liquor at pH 9.0 and 70°C)

Earlier in this paper, the authors recommended that the process should be operated at a pH of about 9.0 for minimum energy consumption per ton of lignin recovered (Figure 7.8). Even though the lignin recovery is higher at lower pH, the energy required increases per incremental ton of lignin recovered. Therefore, the efforts were concentrated on optimizing the process operating conditions at that pH with regards to energy consumption. As expected, the results confirmed that the energy consumed per volume of black liquor is lower at a lower current density (Figure 7.16). With a lignin recovery of about 67 % at pH 9.0 (Figure 7.2), the energy usage can be kept below 500 kWh/t of lignin when operating at a low current density (1.0 kA/m^2) and while making 10 % NaOH (Figure 7.17). This energy value corresponds to only 7 % of the high calorific value of the lignin making the technology very attractive for a kraft mill from an energy point of view. Furthermore, from a productivity point of view, operating at low current density will require more electrodes and membrane area and more cell units for a given lignin plant capacity.

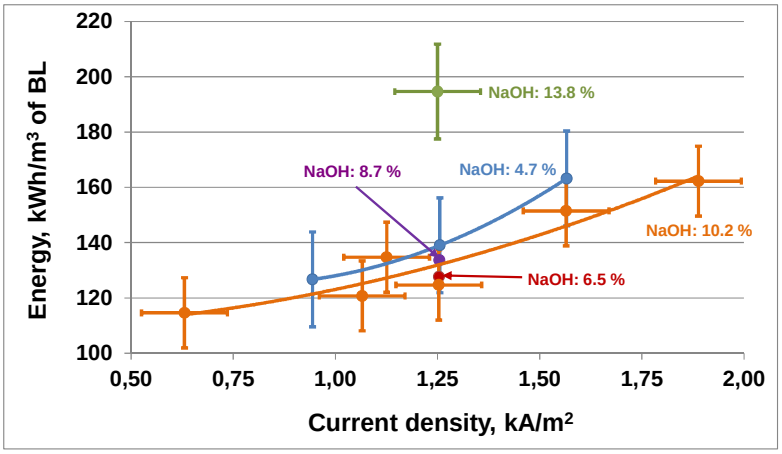

Figure 7.16 : Energy consumption (kWh/m^3 of BL) as a function of current density at various caustic soda strengths (Black liquor at pH 9.0 and 70°C)

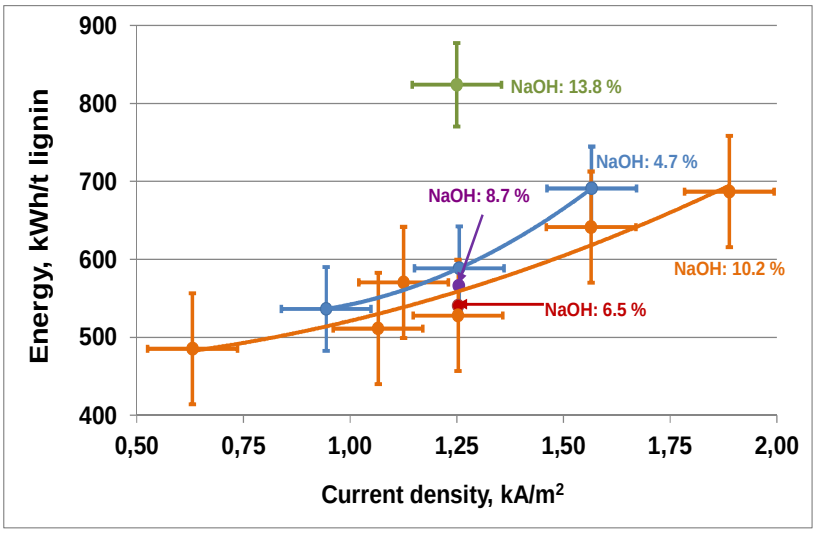

Figure 7.17 : Energy consumption (kWh/t of lignin) as a function of current density at various caustic soda strengths (Black liquor at pH 9.0 and 70°C)

This work demonstrated the effect of black liquor pH and NaOH strength on process productivity (Figure 7.9 à 7.11) at a constant current density of 1.26 kA/m^2. It is well known that the productivity of an electrochemical plant depends strongly on current density, the higher the current density the better the productivity [20]. Indeed, at 10 % NaOH, augmenting the current density by a factor of three, from 0.65 to 1.89 kA/m^2, increases the productivity by a factor of four showing the gain of productivity (Figure 7.18). Moreover, within the current density of 0.80 to 1.60 kA/m^2, the process also benefits from an average 27 % increase in productivity when the concentration of NaOH is reduced by half (from 10 to 5%) therefore offering a production rate of 2.1 kg/(h·m^2) at 1.6 kA/m^2, the maximum output obtained during the testing program.

As expected, an increase in current density has the same impact on black liquor productivity (Figure 7.19) as on NaOH production. Approximately four times more flow can be treated by increasing the current density by a factor of three when making 10 % NaOH. We observed a higher variability (Error bars) in the results that could be attributed to the measurement of the black liquor flow, which was sometimes more difficult to estimate. Contrary to the NaOH productivity, there was no benefit in reducing the concentration of the NaOH from 10 to 5 % for which no explanation could be provided except than a flow measurement inconsistency.

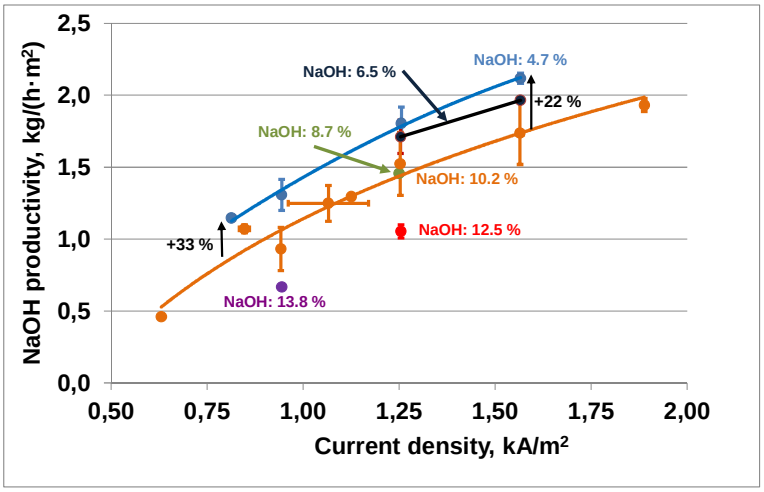

Figure 7.18 : NaOH productivity (kg/(h·m^2)) as a function of current density at various caustic soda strengths (BL pH of 9.0 and 70°C)

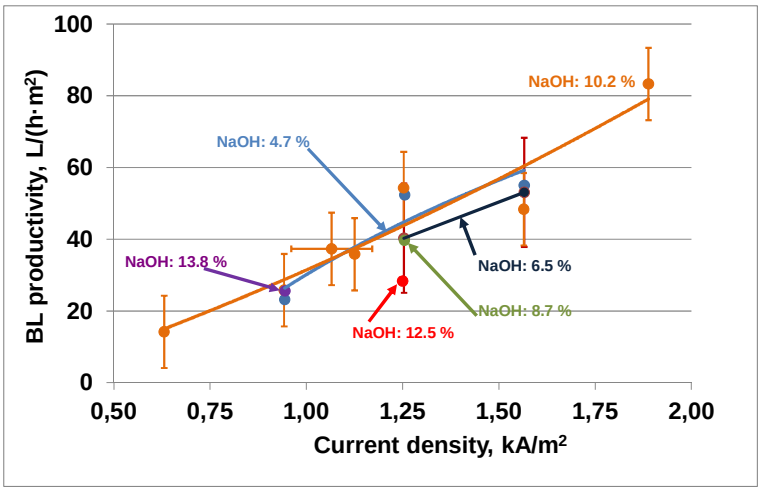

Figure 7.19 : BL productivity (L/(h·m^2)) as a function of current density at various caustic soda strengths (BL pH 9.0 and 70°C)

Lignin is the primary product of the process developed in this work and a better productivity is highly desirable. Like the NaOH recovery rate and black liquor flow, the lignin productivity which takes into account a lignin recovery of 67.5 % at pH 9.0, increases with current density (Figure 7.20) showing a similar relationship. Between 4.7, 6.5 and 10.2 % NaOH strength, the productivities vary from 11 to 18 % in the range of current densities tested (0.94 to 1.56 kA/m^2). The value at 8.7 % NaOH is lower than expected and the very low productivity at 13.8 % NaOH can be explained by the low current efficiency. Unexpectedly, based on these results, the electrolytic treatment of black liquor should be operated at the highest current density possible, while making NaOH at 10 %, without any benefit at a lower concentration.

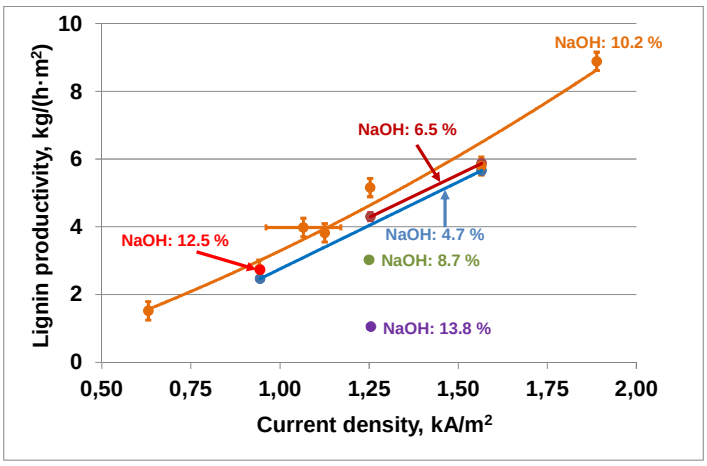

Figure 7.20 : Lignin productivity (kg/(h·m^2)) as a function of current density at various caustic soda strengths (BL pH 9.0 and 70°C

7.3.2.5 The effect of temperature

The effect of temperature on process performance was investigated in the range of 60 to 84 °C while the concentration of NaOH was varied from 5.3 to 10.4%. As expected, the conductivities of both solutions benefit from an increase in temperature (Figure 7.21). Black liquor conductivity rises by 1.7 mS/cm per °C increment and the conductivity of NaOH solutions went up by 2.9 to 5.6 mS/cm depending on the NaOH concentration. Consequently, the impact on the cell voltage drop was approximately 8 % over the temperature range studied (Figure 7.22). That corresponds to an average of 0.02 V/°C similar to the value of 0.025 V/°C reported by Moshtarikhah [11]. According to the authors, an increase in temperature results in a higher mobility of ions and a higher water content in the membrane resulting in a higher conductivity of both the membranes and the solutions as well. Moreover, it is known that at higher temperatures,

the thermodynamic potential decreases as expected from the Nernst equation and also contributing to a lower cell voltage. However, we observed that the cell voltage tends to increase with increasing catholyte concentration. This is in agreement with Moshtarikhah [11] who reported that it is due to an increase in the membrane voltage with increasing catholyte concentration due a lower conductivity of the membrane. For a more detailed explanation, we refer the reader to abovementioned study.

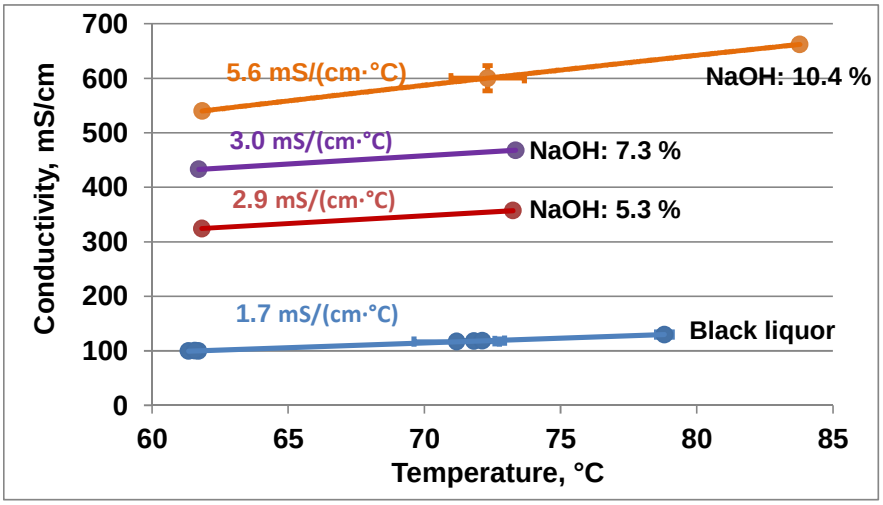

Figure 7.21 : Conductivity of black liquor and caustic soda solutions as a function of temperature at various caustic soda strengths (BL pH 9.0 and 1.26 kA/m^2) (mS/(cm·ºC)

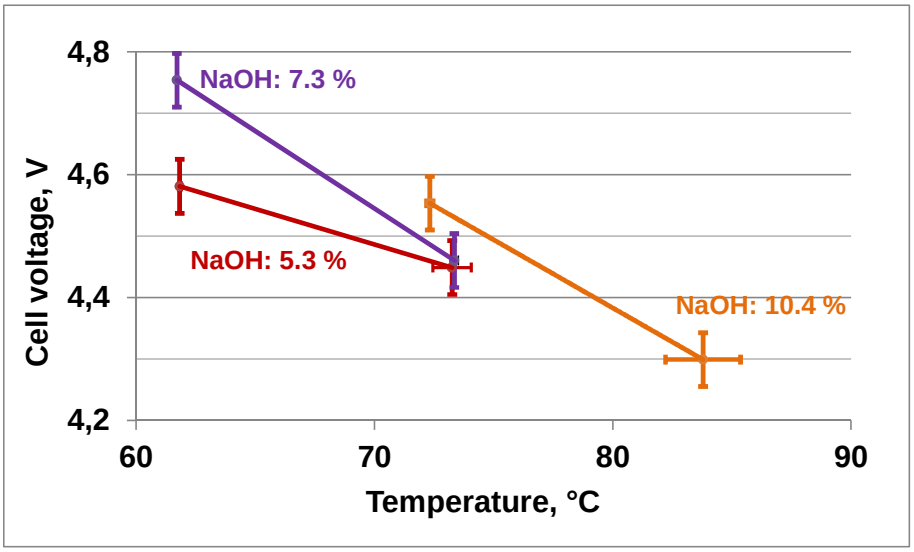

Figure 7.22 : Cell voltage as a function of temperature at various caustic soda strengths (BL pH 9.0 and 1.25 kA/m^2)

The benefit of increasing temperature is more pronounced at higher caustic soda concentration (Figure 7.23) suggesting an interaction between the two parameters. According to Moshtarikhah et al [11], this could be explained by the fact that higher temperature increases sodium ion mobility, which could result in a better gain at higher concentration.

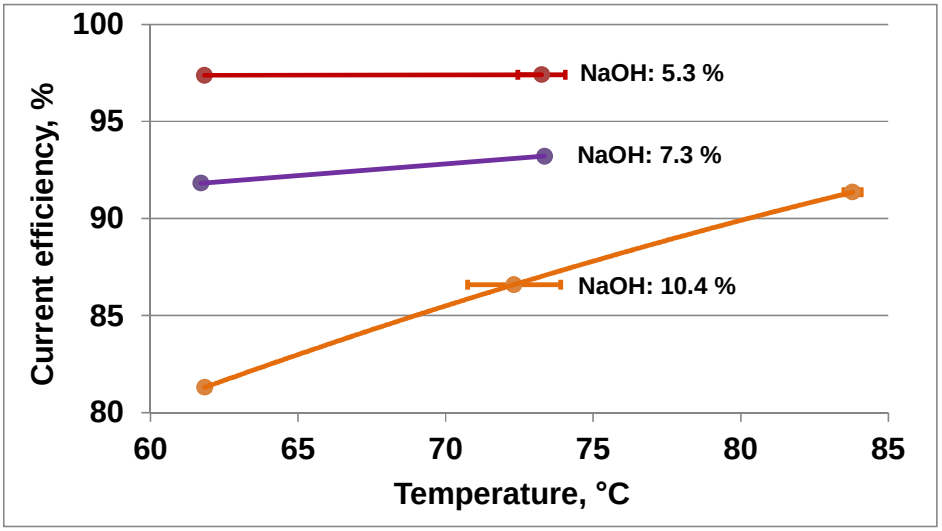

Figure 7.23 : Current efficiency as a function of temperature at various caustic soda strengths (BL pH 9.0 and 1.26 kA/m^2).

The combination of cell voltage and current efficiency dictates the energy consumption expressed in kWh/t of NaOH. It was observed that a higher temperature reduces the energy consumption at all NaOH concentrations tested (Figure 7.24). The energy gain is more significant at higher NaOH concentrations and seems to tend to a minimum value at 10 % NaOH as the temperature approaches 85 °C. According to the patent granted to Lipsztajn [34], an energy benefit can be achieved by operating the catholyte (NaOH) at 10 to 20 °C higher than the anolyte (Black liquor). That temperature differential could not be obtained with our experimental set-up since the temperatures of both streams were maintained by the same heating bath. Keeping the temperature of the anolyte lower could be achieved by cooling. In addition to the potential energy gain, a lower temperature of the anolyte would also offer the additional benefit of extending the life of the anode.

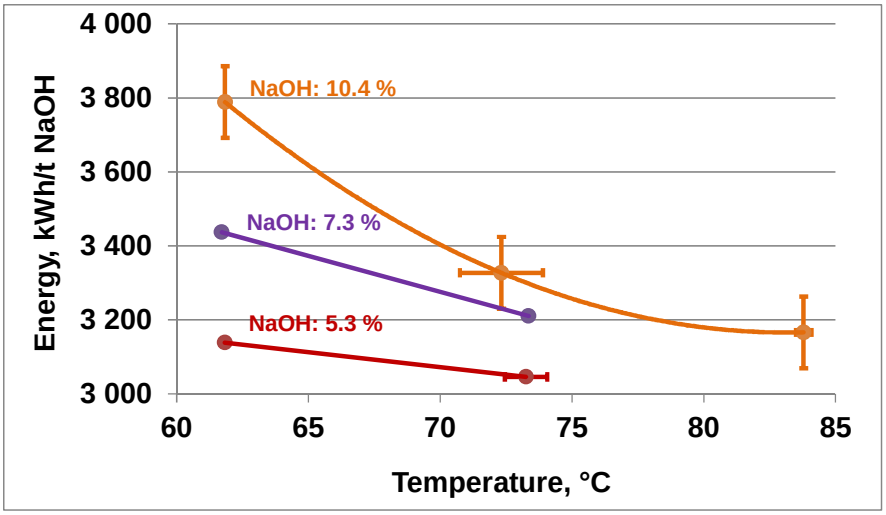

Figure 7.24 : Energy consumption as a function of temperature at various caustic soda strengths (BL at pH 9.0 and 1.26 kA/m^2)

Regarding the effect of temperature on process productivity, only the NaOH production rate is reported here. Unfortunately, the flow of black liquor was not recorded, therefore BL feed rate and lignin productivity could not be evaluated either.

An increment of 11 °C from 62 to 73 °C did not have any significant effect on NaOH productivity at lower NaOH concentrations (5.3 and 7.3 %) (Figure 7.25). On the other hand, at 10.4 % strength an overall gain of 13 % in the production rate was observed when increasing the temperature by 20 °C. That productivity benefit is due essentially to the better current efficiency (Figure 7.23) at a higher temperature.

In conclusion, according to the recommendation of the anode manufacturer to extend the anode life, we suggest to operate at 70 °C or lower given the very limited gain of performance at higher temperatures.

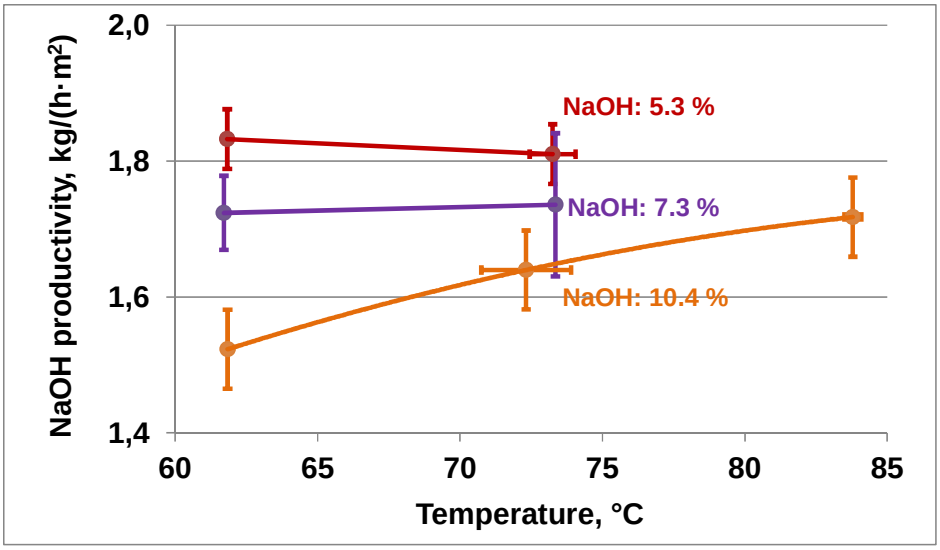

Figure 7.25 : NaOH productivity as a function of temperature at various caustic soda strengths (BL pH at 9.0 and 1.26 kA/m^2)

7.3.2.6 The effect of adding sodium sulfate to black liquor

The conductivity of 30 % solids BL is relatively low (~120 mS/cm) compared to 250 mS/cm for the sodium chloride solution[34] at a similar concentration [35] as used in the electrolytic cells of the industrial chlor-alkali plant. Higher conductivity means a lower voltage cell and, thus, lower energy consumption. Given the abundance of sodium sulfate in a kraft mill, we were interested in quantifying the improvement to the process performance from the addition of salt to the black liquor. To do so, we saturated the BL by adding salt to the black liquor at pH 9.0 in excess of saturation and let it stir overnight.

The salt addition increased the conductivity of BL from 119 to 146 mS/cm, a 23.6 % improvement that is significant at a 99 % confidence interval (Table 7.10). This increment of BL conductivity translated to a 6 % drop in voltage, which is statistically significant at 95 % only. A higher sodium level was demonstrated to be beneficial for the electrolysis of a sodium sulfate solution [36, 37]. Here, the salt addition increased the sodium level, which enhanced current

[34] 21.5/23.7 x 60 +180 + 4 x (30-26) = 250 mS/cm

efficiency by 8.5 %, but the difference was not significant at 95 %. The combination of a lower cell voltage and a higher current efficiency contributed to reduce energy consumption by 13.5 % with a 95 % confidence interval. On the other hand, the process NaOH productivity was improved by 9.6 % but the difference was not significant at 95 %. Overall, the addition of sodium sulfate seems to help productivity, which means fewer required electrolytic cells, lower capital costs, lower energy consumption and, thus, lower operating costs as well. In general, adding sodium sulfate to black liquor seems to improve process performance with limited significance.

Table 7.10 : The effect on process performance of adding sodium sulfate to black liquor

Na_2SO_4 added to black liquor		**BL conductivity, mS**	**Current efficiency, %**	**Cell voltage, V**	**Energy, kWh/t NaOH**	**Productivity, kg NaOH/(h·m^2)**
1	None	119,1	80,6	4,82	4 008	1,497
2	None	118,5	78,8	4,94	4 201	1,417
3	None	118,3	76,2	4,94	4 342	1,406
	MEAN ($\bar{x}_1$)	118,6	78,5	4,90	4 184	1,440
	STDEV (s_1)	0,40	2,18	0,07	168,0	0,05
	COV, %	0,34	2,77	1,43	4,02	3,45
1	Saturated	146,0	86,7	4,51	3 499	1,613
2	Saturated	145,4	82,6	4,59	3 722	1,526
3	Saturated	148,0	86,4	4,66	3 636	1,596
	$\bar{x}_2$	146,5	85,2	4,59	3 619	1,578
	s_2	1,37	2,28	0,08	112,79	0,05
	COV, %	0,94	2,68	1,67	3,12	2,92
	Change, %	23,5	8,5	-6,4	-13,5	9,6
	F(95 %) = 19.0	11,6	1,1	1,2	0,5	0,9
	t-test value	33,7	3,7	-5,2	-4,8	3,5
t-value at 95 % = 4.3						
t-value at 98 % = 7.0						
t-value at 99 % = 9.9						

7.4 Conclusions and discussion

In the context of sustainable development and a circular economy, we have developed an electrochemical approach that will provide lignin to a kraft biorefinery based essentially on the judicious use of electricity compared to the chemical approach of consuming carbon dioxide and sulfuric acid from an external source.

The present study reports on the effect of various operating parameters with the aim of optimizing the process performance for different sources of black liquor. Owing to abundant experimental data and replicates it was possible to draw conclusions based on statistical analysis.

The perforamnce of the process was evaluated using softwood and hardwood black liquors and, oxidized or non-oxidized softwood liquors. Despite some differences in their properties and component concentrations, it was shown that under the operating conditions tested, there is no significant difference in performance between these liquors.

Unexpectedly, the number of anodes in the laboratory cell used showed a relatively strong correlation ($R = 0.61$) with the current efficiency. The significant impact of that parameter was confirmed by an analysis of variance. However, we have no fundamental explanation justifying the effect of the number of anodes on cell performance other than the fact that it may alter the current distribution, which could consequently affect the current efficiency.

It is recommended operating at pH 9.0 to minimize the energy consumption per ton of lignin recovered. By operating at that pH the precipitation of divalent cations within the membrane is avoided at lower pH, thus protecting the membrane and prolonging its life. Running electrolysis at a lower pH is a possibility in cases where mill production is limited by the causticizing plant or lime kiln creating a shortage of cooking liquor and, therefore, limiting pulp production. Operating electrolysis at a lower pH will provide more NaOH that can be added to the white liquor allowing for additional pulp production. However, some measures will have to be taken to remove divalent cations such as ion exchange technology.

The current density was the second most remarkable parameter after the pH to influence the cell process performance, including energy consumption, NaOH and lignin productivities. A similar observation was reported for the chlor-alkali process with regards to energy consumption for making NaOH [38].

Given the limited benefit of operating at a higher temperature (80 vs 70 °C), it is recommended operating at 70 °C or below to obtain a longer anode life as suggested by the electrode manufacturer.

On the other hand, the addition of sodium sulfate improves productivity. This would require fewer electrolytic cells, lower capital costs, lower energy consumption, and thus lower operating costs as well. Overall, adding sodium sulfate to black liquor improves process performance.

Based on this study, the electrolytic treatment of black liquor should be operated at the highest current density, i.e., 1.89 kA/m^2 or higher, while making NaOH at 10 %. There seems to be no benefit to operate at lower NaOH concentration. It is expected that the lignin productivity would be 2.1 $kg/(h \cdot m^2)$ or higher. Although the above recommended conditions are not optimal in regards of the energy consumption, it will be essential to confirm them based on an economic analysis especially the optimum current density for the lowest cost per ton of lignin taking into account the impact of higher current density on the anode life. If the energy consumption becomes a major concern, the caustic strength can be reduced to less than 5 %.

In this study, we have determined the best operating conditions for preparing black liquor for the lignin precipitation step. A forthcoming study will consist of investigating the lignin precipitation and washing steps and the integration of the technology into a kraft mill.

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CHAPITRE 8 ARTICLE 4: PRECIPITATION AND WASHING OF LIGNIN FROM ELECTROLYSED BLACK LIQUOR

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The technical feasibility of an electrochemical process to extract lignin from black liquor (BL) thus providing a lignin product for a kraft bio-refinery has been demonstrated. The technical aspects of lignin precipitation from electrolysed BL were investigated: coagulation, precipitation, filtration and washing of the lignin product. The experimental results showed that the filtration rate is relatively low (64 kg/(h·m^2)), but adding Na_2SO_4 (120 g/L) during the coagulation step improves the rate by a factor of 7.5. A longer coagulation time (4-5 h) increases filtration rate as well. The lignin can be used as a feedstock for the chemical industry or as bio-fuel for the lime kiln. The purity of the washed lignin is adequate for utilisation in the chemical industry, for example, for making polyurethane. On the other hand, given the sensitivity of the lime kiln to sodium, it is estimated that the electrolysed lignin containing 0.64 % of residual sodium after one single water wash could replace about 50 % of the lime kiln fossil fuel. A complete mass balance of the major components providing the required data for future work on the simulation of the integration of this process into a kraft mill has also been developed.

8.1 Introduction

Lignin recovery from kraft black liquor can be accomplished by means of two commercially available chemical technologies, LignoBoost [1] and LignoForce [2], both of which use carbon dioxide as an acidifying agent for precipitating the lignin and an outsourced sulfuric acid to wash the lignin cake. Uloth et al [3] investigated lignin precipitation using the waste sulfuric acid produced by old ClO_2 generators [4]. Howell et al [5] simulated the integration of waste acid precipitation into a hardwood kraft mill. Andritz [6] has worked on the development of an alternative process called Wet gas Sulfuric Acid (WSA) in which sulfuric acid is used as an acidifying agent. The particularity of this approach is that the concentrated sulfuric acid is

produced on the mill site from the sulfur contained in the concentrated non-condensable gas (CNCG) generated during cooking [7]. However, the maximum capacity of a lignin plant is dictated by the acid production, which in turn depends on the amount of sulfur recovered or available. Namane et al [8] has investigated the use of sulfuric acid, and of organic acids, such as acetic, citric, and formic acids as acidifying agents. The authors observed that when the lignin is precipitated with organic acids it contains less sulfur than when precipitated with sulphuric acid. Lignin can also be removed by coagulants, such as aluminium sulfate [9] and as well as various chlorides and nitrate salts, exploiting the benefit of the salt-induced precipitation [10].

An electrochemical approach [11-13] was developed using electricity to bring the black liquor pH to the point of lignin precipitation and splitting sodium sulfate available at the mill to provide the acid required to wash the lignin. The fundamentals of electrolytic treatment of black liquor were previously reported [14], the mechanism of ions mass transfer through the membrane was investigated [15] and the process performance, including energy and productivity, was optimised [16].

This work is concerned with the precipitation and recovery of lignin from electrolysed black liquor, including coagulation and filtration steps. We focused on filtration performance and washing the recovered product. The effect of the following variables on the filtration rate was investigated: (1) the coagulation time (2), the type of BL (3), the temperature (4), the vacuum (5), the end precipitation pH and (6), the addition of sodium sulfate. The results of the filtration performance are compared with those of other methods for precipitating lignin from BL, including CO_2 [1, 2, 17] and waste sulfuric acid [3, 6]. Comparisons are made with the filtration of $CaCO_3$ [18] which is a by-product of the causticizing plant of kraft mills. The lignin cake was washed with dilute sulfuric acid and water. The quality of the lignin product is reported and a typical example of detailed material balance is provided to integrate the technology to a kraft mill supporting sustainable development.

8.2 Process description

The process was developed with three objectives: (1) minimum or no impact on the sodium-sulfur balance of the recovery system, (2) minimum environmental footprint and (3), concern

with circular economy and sustainable development. The economic viability is an important issue and will be discussed in a separate paper.

The entire lignin recovery process comprises 6 major steps (Figure 8.1): (1) electrolysis of black liquor to reduce pH, (2) coagulation of the lignin, (3) filtration of lignin slurry, (4) acid wash of the lignin cake, (5) water wash and (6) salt splitting. The inputs (in yellow) to the process are: (1) black liquor, (2) sodium sulfate, (3) water, and electricity. The outputs (in orange) are: (1) lignin slurry filtrate, (2) acid washing, (3) water washings (4) caustic soda and (5) lignin. Sulfuric acid is produced on site from sodium sulphate splitting and caustic soda as a by-product.

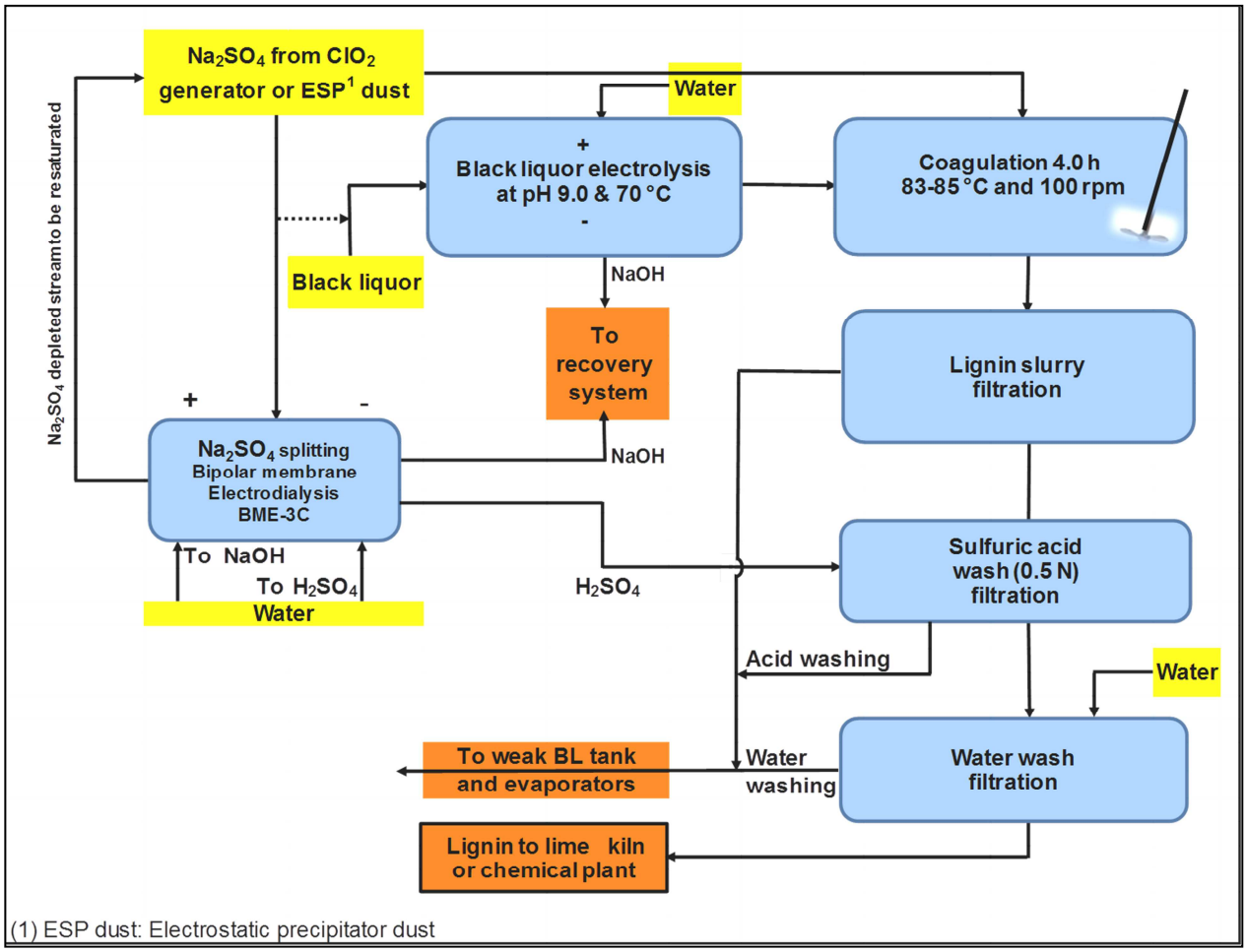

Figure 8.1 : Simplified flowsheet of electrochemical recovery of lignin from black liquor

The BL fed to the electrolytic unit is withdrawn after the second effect of the evaporator train containing approximately 30 % solids offering maximum conductivity to minimise voltage drop [13]. That liquor, once electrolysed at pH 9.0, is sent to a coagulation step in a continuous stirred

tank reactor (CSTR) where sodium sulfate is added to help the formation of larger lignin flocs by agglomeration, thus improving the filtration rate. The salt could be added to the BL prior to entering the electrolytic cell to reduce energy consumption as demonstrated in a previous publication [14]. Then, the lignin slurry is filtered, the lignin cake is recovered and, the filtrate is sent back to the weak black liquor tank of the chemical recovery system. The lignin product which contains a high level of ash and sodium is washed first with dilute sulfuric acid (0.5 N) and subsequently with water. Both wash streams are recovered and recycled to the recovery system to avoid an additional organic load on the wastewater treatment system.

To respect the requirement of sodium sulfur balance in the mill liquors, the acid is produced by splitting the sodium sulfate using electro dialysis of the ClO_2 generator by-product or the ESP dust containing mostly sodium sulfate. Both salt by-products can be captured before they are sent back to the recovery system as constituents of the black and cooking liquors. The Na_2SO_4 from the ClO_2 generator is used as chemical make-up. Using part of these by-product salts eliminates the need to purchase acid for lignin washing. Bipolar membrane electrodialysis (BME) and electrolysis also produce caustic soda as a by-product, part of which can be used to adjust the pH of the acid washing and water washing (pH 1.7) before they are returned to the weak black liquor tank. The BME produces chemicals (acid and caustic soda) on site in agreement with the circular economy trend of environmental requirements as that BME step prevents the excess sulfur from being discarded into the sewer as is the case when using purchased acid. The depleted sodium sulphate solution coming out of the BME system is returned to the ClO_2 generator to be saturated again with sodium sulphate. The clean lignin produced could replace fossil fuel in the lime kiln or be used as raw material e in a polyurethane plant.

8.3 Brownian coagulation and filtration theory

The recovery of lignin from black liquor requires a coagulation step regardless of the technology used: acidification with CO_2 [1, 2], with sulfuric acid [3, 6-8], by desalkalinisation using electrolysis or, with an electrodialysis processes [11-13]. In fact, lignin starts to precipitate from black liquor at pH 10.5-11.0 [19] forming fine colloidal particles. These particles are very difficult to filter and eventually block the filter. The coagulation step promotes the growth formation of larger flocs thus facilitating filtration.

8.3.1 Brownian coagulation

Lignin coagulation and precipitation are caused by the continuous random movement of particles that collide and stick together called Brownian coagulation forming an agglomeration of larger particles [20]. It is a physical process of inelastic collisions and of the attachment of particles onto particles [21]. The thermal Brownian motion of particles, accompanied by turbulence, shear field, and external forces, such as gravitational and electrical, may cause coagulation [22]. Heine et al. [23] reported that the more concentrated the particle suspension (up to 35 %) the better the coagulation rate due to the higher probability of collision. The BL pH drops when CO_2 is added; the lignin in solution is destabilised and colloidal particles usually carrying electrical charges start to form at about pH 10.8 according to Kannangara [17]. In the present work, lignin coagulation was initiated in the electrolysis step partially under the influence of the forces produces from the electrical field and continues progressively through the coagulation step.

8.3.2 Colloidal stability explained by the DLVO theory

The lignin coagulation rate can be predicted by the well-known DLVO theory which was established by Derjaguin, Landau, Verwey, and Overbeek in the 1940s [24, 25] and for which Trefalt [26] provided a short conceptual summary. It is assumed that the interaction forces in an aqueous colloidal suspension can be approximated by a superposition of van der Waals and double layer forces which have to be reduced in order to enhance particle aggregation. Norgren [19] applied this concept to a solution of kraft lignin and reported that lignin coagulation efficiency depends on temperature, ionic strength and pH. Coagulation rate can be enhanced by increasing the ionic strength of the solution by the addition of salt to the point of critical coagulation concentration (CCC).

Two well-defined regimes of kinetics have been identified for the aggregation caused by Brownian motion: (1) rapid diffusion limited cluster-cluster aggregation (RLCA) and (2) slow reaction limited aggregation (SLCA). The CCC is determined at the point of change of regime from still reaction limited (RLCA) to purely diffusion limited (DLCA), which was well illustrated by the addition of 1.3 M NaCl to Indulin® Kraft lignin [17] at pH 10.5 and 70°C [19]. At higher ionic strength very large aggregates are formed and the aggregation rate increases. He also reported that increasing temperature decreases CCC. Unfortunately, the use of NaCl is not

possible in a kraft mill because it causes severe fouling of the heat exchanger of the recovery boiler [27, 28]. In practice, Na_2SO_4 salt is a preferable and very suitable salt since it is already present in the black liquor causing no problem if its concentration is kept below its maximum solubility limit [29]. Furthermore, the benefits of adding Na_2SO_4 salt to BL have been demonstrated for the electrolysis step: they are a lower voltage and a better current efficiency translating to lower energy consumption [16].

8.3.3 Overview of filtration theory

8.3.3.1 Objective

The main objective of the filtration step in this work is the recovery of a maximum amount of lignin solids rather than the clarification of the liquid filtrate. The lignin slurry filtrate is recycled to the chemical recovery loop for its residual values which are the sodium and, the energy from the organic content. Returning the residual filtrate to the mill avoids an additional charge and cost to the waste water treatment plant. The quality of that filtrate is of no major concern for the recovery system as long as it does not contain an excessive concentration of burkeite (2 $Na_2CO_3 \cdot Na_2SO_4$) which could foul the evaporators by crystallisation [29].

8.3.3.2 Filtration theory

The basic filtration equation derived from the Poiseuille and Darcy law, which describes the flow of a fluid through a porous medium is presented in equation (1) [30, 31]:

$$\Delta P_c = (Q/A) \cdot H \cdot \mu \cdot \alpha_H \quad (1)$$

$$\Delta P_{fm} = (Q/A)\ \beta \cdot \mu \quad (2)$$

ΔP_c is the pressure across the cake

ΔP_{fm} is the pressure drop through the filter medium,

Q/A is the specific flow rate in $m^3/(s \cdot m^2)$,

H is the cake thickness in m,

μ is the filtrate viscosity in Pa·s,

α_H is the specific filtering resistance related to the cake thickness in m^{-2} and,

β **is** the resistance of the filter media (m^{-1}).

For convenience [30], the cake thickness can be defined in terms of solid mass m per unit filter area and the cake resistance can be represented by α_m expressed in m/kg; therefore equation (1) becomes:

$$\Delta P_c = (Q/A)\cdot(m/A)\cdot\mu\cdot\alpha_m \quad (3)$$

The pressure drop through a filtering system is:

$$\Delta P = \Delta P_c + \Delta P_{fm} \quad (4)$$

Byreplacing ΔP_c and ΔP_{fm} in equation (4), the following expression is obtained for the total pressure drop:

$$\Delta P = \alpha_m\cdot\mu\cdot(m\ Q/A^2) + \beta\cdot\mu\cdot(Q/A) \quad (5)$$

Supposing a homogeneous mix, it can be assumed that the mass of cake is proportional to the volume of filtrate following a linear relationship:

$$K_m = m/V \quad (6)$$

In equation (6), m represents the mass of the filtered cake and V, the volume of filtrate.

Combining equations (5) and (6) and considering Q = dV/dt where t is the time, equation (5) becomes:

$$\Delta P = (\alpha_m\cdot\mu\cdot\ K_m)/A^2\ V\cdot dV/dt + (\beta\cdot\mu)/A)\ dV/dt \quad (7)$$

The integration of Eqn (7) at constant pressure (ΔP) yields:

$$t = (\alpha_m\ \mu\cdot K_m)/(2A^2\ \Delta P)\cdot V^2 + \beta\cdot\mu/(A\cdot\Delta P)\cdot V \quad (8)$$

The development of these equations and a real case study are detailed in Ripperger [30].

In practice, the experimental results are plotted according to t/V = f(V):

$$t/V = (\alpha_m\ \mu\cdot K_m)/(2A^2\cdot\Delta P)\cdot V + \beta\cdot\mu/(A\cdot\Delta P) \quad (9)$$

Usually t/V is a straight line with a slope "b" containing the filter resistance (α_m):

$$b = (\alpha_m\ \mu\cdot K_m)/(A^2)/(2\cdot\Delta P) \quad (10)$$

and the intercept "a" is used to calculate the filer media resistance (β):

$$a = \beta \cdot \mu / (A \cdot \Delta P) \quad (11)$$

8.3.3.3 Filtration mode

Four idealized models were developed by Ripperger et al [30]: (1) cake filtration, (2) blocking filtration, (3) deep bed or depth filtration and (4) cross flow filtration. The cake filtration mode is the most frequently used model. As soon as the first layer of cake is formed on the filter medium, the subsequent filtration is accomplished by the cake itself and the medium becomes only a physical support. This model was used in our work for the following reasons: (1) simplicity, (2) one single filter for the three process steps of filtration, washing and dewatering (3) either a positive or a negative pressure (vacuum) through the cake. In the case of vacuum filters, the cake is freely accessible and that facilitates automatic cake handling. However, the pressure difference across vacuum filters is very limited, and the residual moisture of the filter cake is higher than with pressure filters [30].

8.4 Experimental methodology

8.4.1 Experimental set-up

The experimental set-up used to study the lignin precipitation step consisted mainly of a coagulation tank (2 L) and a laboratory vacuum filter (1L). The coagulation tank was immersed in a temperature controlled bath (Figure 8.2) and it was equipped with a single propeller type of mixer with three blades (Ø = 2.5 cm). The filtration unit used was the Buchner test kit purchased from Larox (now Outotec[35]) Model S5118-L1K2 of 5.5 cm diameter, which was connected to a vacuum pump (Figure 8.3).

[35] https://www.outotec.com/company/about-outotec/

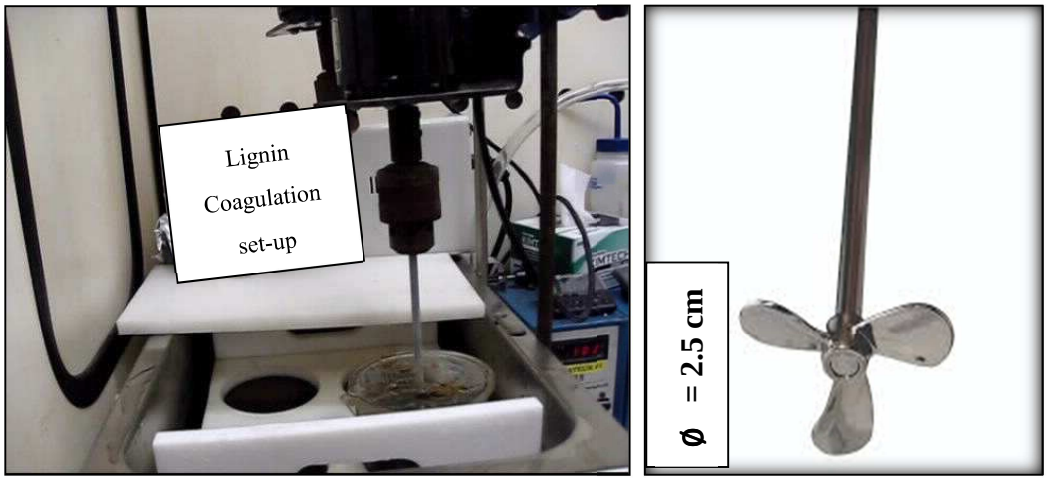

Figure 8.2 : Experimental set-up for coagulation of electrolysed black liquor

8.4.2 Experimental procedure

Once electrolysed to the desired pH (9.0), the BL is transferred to the coagulation tank. In most trials, sodium sulfate was added to promote coagulation of the lignin particles. A mild agitation was maintained from the rotational speed of the agitator, which was high enough to favour the collision of particles contributing to the growth of bigger flocs without breaking them but not too slow to maintain the lignin particles in suspension [32-34]. At 100 RPM the impeller of 2.5 cm in diameter had a radial velocity of 13.1 cm/s giving a Reynold number[36] of 922 characterising the flow of the agitation as laminar [35]. The time of reaction was varied from 0 to 5 hours and the temperature from 75 to 85 °C. The filtration rates are reported as follows: the volume (100 ml) of lignin slurry was filtered and filtration was stopped when the surface of the cake was liquid free. Then, the filtrate volume and solids recovered were measured and weighed (dry basis), which gives an average liquid filtration rate expressed in $L/(h \cdot m^2)$ and solids in $kg/(h \cdot m^2)$, respectively. The lignin cake was washed by means of the displacement method [36]. One equivalent displacement washing volume was estimated from the volume of the lignin cake calculated from the filter diameter and the thickness of the cake.

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[36] $Re = \rho \cdot N \cdot D^2/\mu = 1\,166\ kg/m^3 \times 100/60\ s \times (0.0254)^2\ m^2/0.00136\ kg/(m \cdot s) = 921.9$.

Figure 8.3 : Buchner test kit from Outotec Larox®[37]

8.4.3 Black liquor characteristics

The precipitation of lignin was experimented with two types of softwood black liquors: oxidised and non-oxidised black liquors provided by kraft mills located in the province of Québec. The detailed composition of those two black liquors has been reported previously [16]. Their constituent concentrations were similar except for the sulfide, which was much lower in the oxidised liquor that was submitted to an oxidation step using oxygen. But, according to Kouisni's patent [2] that treatment should have a positive impact on the lignin filtration rate.

8.5 Results and discussion

8.5.1 Lignin cake filtration and washing

8.5.1.1 Lignin cake resistance

We performed a filtration experiment according to the procedure described above. We plotted the results of t/V vs V (Figure 8.4) according to Ripperger's method [30] in order to estimate the filter medium resistance and determine the cake filtration resistance to be compared with

[37] https://www.youtube.com/watch?v=6gZIbz240ic p. 93:

literature data for lignin cake from other recovery processes and with $CaCO_3$ cake from the causticizing plant.

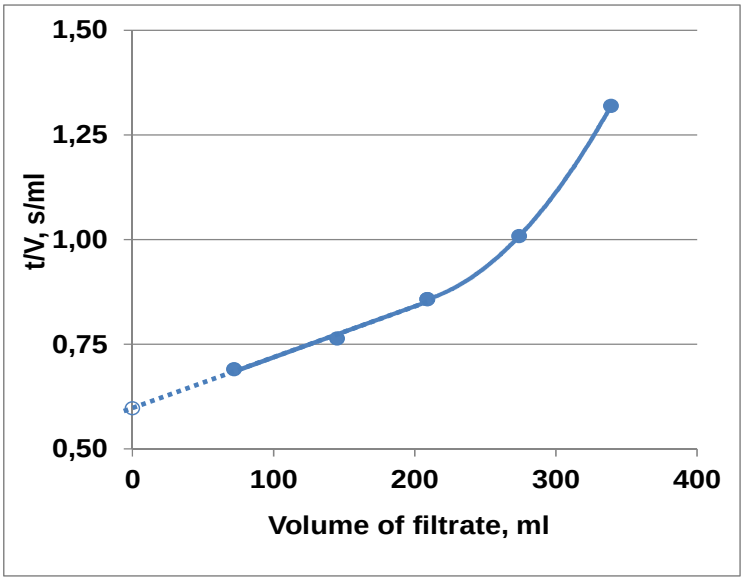

Figure 8.4 : t/V vs volume of filtrate collected for the following coagulation conditions: 3 h coagulation time, pH 9.0, 85 °C, 100 rpm, 120 g/L of Na_2SO_4 added and, filtration done at a constant vacuum of 16.9 kPa

It was noticed that the plot of t/V vs V does not follow a straight line but tends to deviate when the volume of filtrate reaches 200 ml. According to Ripperger [30], this could mean that there is a combination of filtration modes involved in the separation process. He explains that deviation by the fine particles trickling through the cake and blocking the pores of the cake or the filter medium. The process can perhaps be described as a blocking filtration at a higher volume of filtrate or cake thickness. Khean [31] reported a similar phenomenon for the filtration of $CaCO_3$ solution, which is very similar to a kraft mill. The $CaCO_3$ is formed during the causticizing step, separated from the cooking liquor, and washed prior to being fed to the lime kiln.

The resistance of the lignin cake was determined based on Khean's example [31] and was compared to the values encountered in the literature. But we retained only the linear part of the plot (Figure 4) where the mode of filtration can be considered as mainly cake filtration mode up to 200 ml of filtrate. From the interpretation of the results of that particular case, we can compute

the resistance of the cake ($\boldsymbol{\alpha_m}$) and of the filter medium (β) by modifying Eqn. (10) and (11) to obtain Eqn. (13) and (14):

$$\alpha_m = 2\cdot(b\cdot A^2\cdot\Delta P)/(\mu\cdot K_m) \quad (13)$$

$$\beta = a\cdot A\cdot\Delta P/\mu \quad (14)$$

The interpolation of the results leads to the intercept "a" and the slope "b" from the linear part of the curve (Figure 8.4):

a = 0.5970 s/ml = 5.97 x 10^5 s/m^3

b = (t/V)/V = 33 s/209 ml = 1.22 x 10^9 s/m^6

The experimental conditions of a typical filtration case and calculations of performance parameters are detailed in Table 8.1.

Table 8.1 : Details of experimental conditions and computations of performance parameters

Parameter	Symbol	Value	Parameter	Symbol	Value
Filter diameter	Ø	5.5 cm	m (dry mass)	m	0.0528 kg
Filter area	A	2.376E-3 m^2	Intercept (Figure 4)	"a"	0.5970 s/ml
Vacuum	ΔP	16 900 Pa	Slope (Figure 4)	"b"	1.219 E-3 (s/ml)/ml
Temperature	T	85 °C	Specific cake mass	K_m = m/V	22.2 kg/m^2
Cake height	H	39.0 mm	Concentration factor	-	252.67 kg/m^3
Filtrate volume	V	2.09E-4 m^3	Filter medium resistance	β	3.954E10 m^{-1}
Viscosity	μ	0.000607 Pa·s	Cake filtration resistance	α_m	1.519E9 m/kg

Ripperger [26] suggested an index consisting of the product of the cake resistance and filtrate viscosity to evaluate the filterability of a product. He determined the range of the index to be between 10^8 which is a rapid filtering and 10^{13} where the product is nearly unfilterable. When this criterion is applied to this work, the index is estimated at 7.04 10^8 which means that the lignin product filters quite easily and rapidly.

The contribution of the filter medium in this work to the total filtration resistance was estimated in order to determine potential improvement of filtration rates. We suggest comparing the

relative resistance of the two components (cake and filter medium) on the same unit basis (m/kg) according to the following ratio:

$$\alpha_{\mathbf{m}} \cdot K_w/\beta = 1.52\ 10^9 \text{ m/kg x } 22.2 \text{ kg/m}^2/(3.95\ 10^{10} \text{ m}^{-1}) = 0.854 \qquad (15)$$

According to the value of equation (15), the filtration resistance of the filter medium used in this work could not be neglected compared to the cake resistance. Indeed, according to our calculations[38], it is contributing to 46 % of the total resistance when the cake thickness reached 39 mm. Therefore, the filtration resistance of the filter medium we used could not be neglected compared to the cake resistance. A less tight filter material would help to improve the overall filterability and reduce the size of the filtration system.

8.5.1.2 Comparison to other lignin recovery processes

The filtration resistance of electrolysed lignin at pH 9.0 is compared to the cake resistance from other lignin recovery processes (Figure 8.5) such as sulfuric acid [36] and CO_2 acidification [36, 17] of black liquor at similar pH values. The electrolysed lignin offers the lowest resistance to filtration. This is in agreement with Kouisni's patent [2] claiming that the oxidation of black liquor improves the lignin filtration rate. It was previously shown that the electrolytic treatment of black liquor generates oxygen at the anode, which oxidised the liquor to the point of eliminating sulfur [14]. It can therefore be concluded that the in situ super-oxidation produces a significantly better filterability of the electrolysed lignin product.

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[38] $1.52\ 10^9 \text{ m/kg x } 22.2 \text{ kg/m}^2/(1.52\ 10^9 \text{ m/kg x } 2.22 \text{ kg} + 3.95\ 10^{10} \text{ m}^{-1}) \text{ x } 100 = 46\ \%$

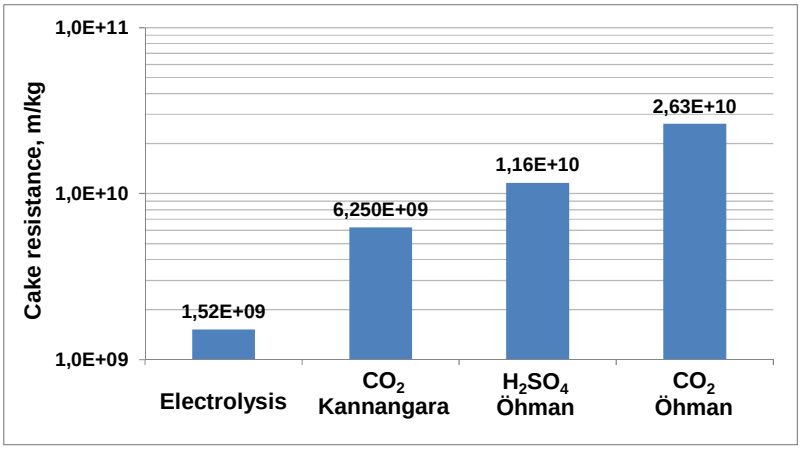

Figure 8.5 : Comparison of specific lignin cake filtration resistance for sulfuric acid and CO_2 lignin precipitation processes: Electrolysis at 70 °C, coagulation and filtration at 85 °C, H_2SO_4 and, CO_2: acidification and filtration at 80 °C.

8.5.1.3 Lignin filtration resistance compared to calcium carbonate

Comparing lignin filtration resistance to lime mud filtration ($CaCO_3$) encountered in the causticizing plant of a kraft mill gives an instructive view on the filtration process. $CaCO_3$ is formed during the causticizing step and is separated from the cooking liquor and washed prior to being fed to the lime kiln [18]. Khean [31] investigated the filtration of lime mud and reported the results of other studies (Table 8.2) as well under different pressure drops. Here again, a great variability in cake filtration resistance was observed depending on the pressure drop.

At a comparable pressure drop (70-75 000 Pa) the filtration resistance of the lignin product from H_2SO_4 and CO_2 processes is similar to the lime mud resistance (1.83 10^9-1.02 10^{10} m/kg). At a lower pressure drop (16 900 Pa) the filtration resistance of lime mud is significantly higher (2.61 10^{10} m/kg) than the electrolysed lignin (1.52 10^9 m/kg), actually 17 times higher. Over the years, lime mud filtration has been improved by increasing the filter rotational speed thus producing a thinner film, which is easier to filter and wash [18]. At the design stage, the same improvement could be applied to the lignin filtration operation.

Table 8.2 : Comparing the cake filtration resistance for different lignin recovery processes (pH~9.0) and $CaCO_3$ at different pressure drops.

Product	Process & Ref.	ΔP, Pa	α_m, m/kg	ΔP, Pa	α_m, m/kg
Lignin	**Electrolysis (Here)**	16 900	1,519E+09	-	-
	H_2SO_4 [36]	75000	1,1122E+10	75 000	1,116E+10
	CO_2 [36]	75 000	1,150E+10	200 000	2,562E+10
	CO_2 [17]	70 000	1,830E+09	70 000	1,020E+10
$CaCO_3$ [27-Khean]	**[36]**	16 900	2,611E+10	50 714	5,556E+10
	37	50 000	7,111E+10	107 143	7,722E+10
	31	90 714	4,167E+10	105 714	5,333E+10
	39	27 000	2,400E+11	140 000	2,400E+11

8.5.2 Investigation of the lignin slurry filtration rate

In the previous section, we considered a typical case study of filtration resistance of the lignin cake and compared its performance to that of other lignin recovery processes and lime mud filtration. The study of various parameters affecting the filtration rates expressed in L/(h·m^2) or kg/(h·m^2) is presented in this report. The results of this study will later be compared with studies from the literature for sulfuric acid and CO_2 processes.

8.5.2.1 The benefit of adding sodium sulfate

Norgren reported that lignin coagulation efficiency depends on temperature, ionic strength and pOH [19]. Coagulation efficiency and yield can be enhanced by increasing the ionic strength of the solution with the addition of salts [40]. It is important to note that the electrolytic treatment of black liquor reduces its salt content [16]. For example, when electrolysed at pH 9.0, about 25 to 30 % of the sodium is removed and converted to sodium hydroxide. The extracted salt reduces the liquor ionic strength thus affecting the coagulation and filtration rate [40]. The addition of sodium sulfate to black liquor before coagulation to reinforce the ionic strength after electrolysis was also investigated. The results showed that without the addition of salt, the filtration rate is very low (64 kg/(h·m^2). With the addition of 120 g/L of Na_2SO_4, which corresponds to a 56 % increase in sodium concentration, the filtration rate increased to 485 kg/(h·m^2), an improvement

factor of 7.5, which significantly reduces the filtering surface requirement and, therefore, the cost. The increase in ionic strength would significantly improve the filtration rate of the electrolysed lignin in comparison to that of the CO_2 process (246 kg/(h·m^2) [2]. Given the demonstrated benefits for the electrolysis and filtration steps, Na_2SO_4 salt should be added to the black liquor. However, it is important that the final concentration in the black liquor does not exceed the solubility limit because it would create burkeite crystallisation in the evaporator train, which depends on the levels of Na_2CO_3 and Na_2SO_4 [29, 41-43].

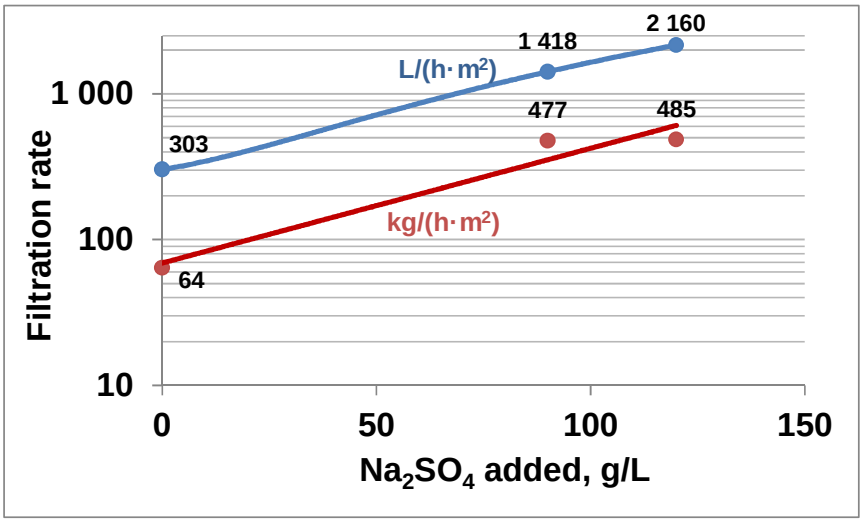

Figure 8.6 : The effect on solids filtration rate of adding sodium sulfate (Na_2SO_4) to black liquor prior to the coagulation step

8.5.2.2 The effect of final pH

The final pH of treated black liquor affects the filtration rate of lignin slurry and its impact has been thoroughly investigated [1-Tomani, 2-Kouisni, 33-Öhman]. For example, Öhman [36] showed that the higher the pH, the higher the filtration resistance and, consequently, the lower the filtration rate. On the other hand, Kannangara [17] reported that the pH has a relatively low influence on the filtration rate. In this study, we precipitated lignin from black liquor at pH between 7 and 10 (Figure 8.7). We observed that even though we added more Na_2SO_4 (175 g/L) prior to the coagulation step, the filtration rate is much lower at pH 7.0 than at 9 and at 10, it is only one third. It is known that the electrolytic treatment of black liquor reduces the ionic strength and at pH 7.0, 56 % of the sodium was removed [16]. Adding 175 g/L of salt to black

liquor electrolysed to pH 7.0 was not sufficient to re-establish the filtration rate obtained at higher pH values (9.0 and 10). However, it is worth mentioning that Kannangara [17] obtained the lowest filtration resistance at pH 9.0 when using CO_2 as an acidifying agent applied to oxidised black liquor. We observed that the cake has a lower solids content at lower pHs (Figure 8.7).

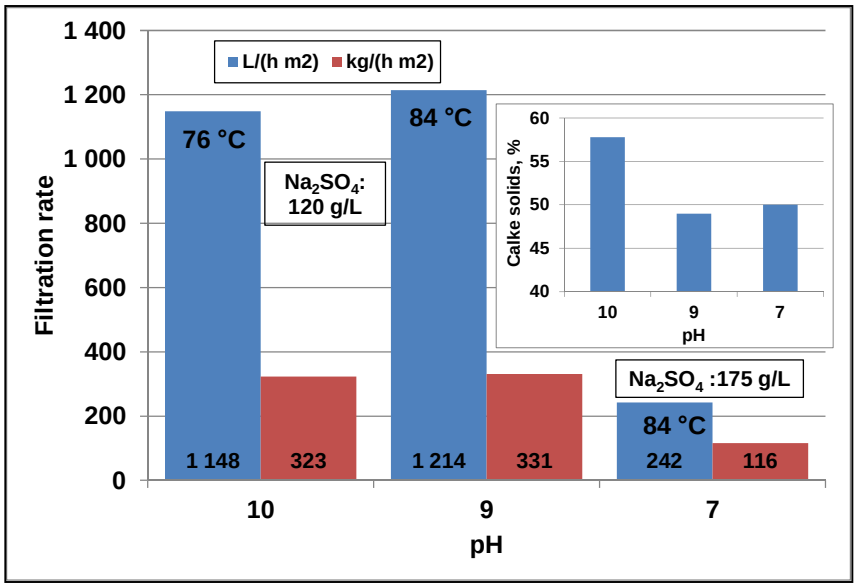

Figure 8.7 : The effect of end pH on filtration rate and cake solids

8.5.2.3 The effect of the type of liquor and coagulation time

The impact of two types of liquor on the filtration rate of oxidised and non-oxidised softwood liquors were tested at various coagulation times ranging from0 to 5 h (Figure 8.8). The results show that a longer coagulation time produces a better filtration rate. The probability of lignin particles to collide and form bigger flocs is much higher at prolonged coagulation. When coagulation time is reduced, the lignin slurry cannot be filtered in an appropriate time. It was observed that the oxidised black liquor gives a lower filtration rate, which is in disagreement with Kouisni's claim [2]. However, it can be concluded that the electrolytic treatment of black liquor is a more efficient way to improve the filtration rate than chemical oxidation. A longer coagulation time seems to favour a higher solid content of the lignin cake thus requiring less drying energy.

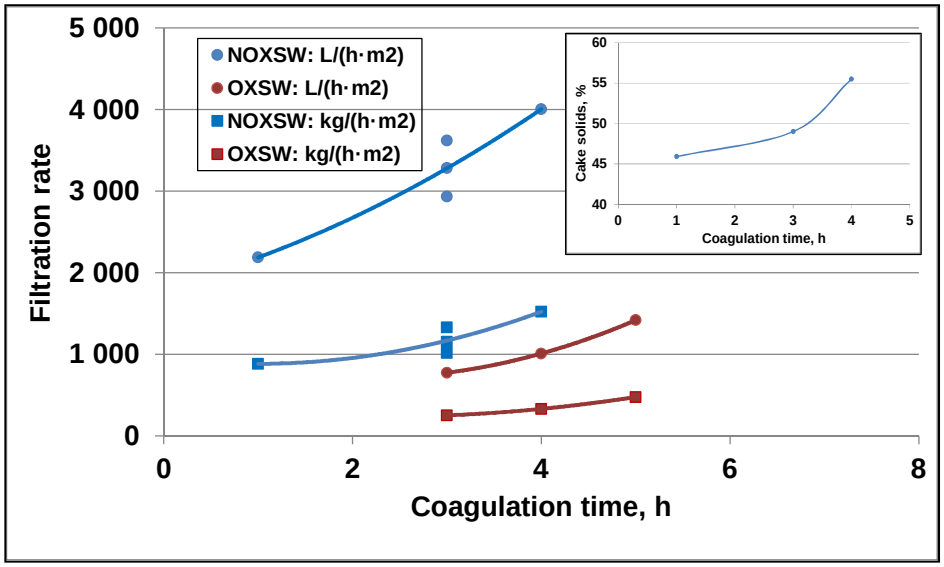

Figure 8.8 : The effect of the type of liquor and coagulation time on filtration rate and cake solids

8.5.2.4 Effect of the vacuum level on the filtration rate

Most filter cakes are compressible, therefore their porosity decreases and their resistance increases with increasing pressure. The compression of the cake is caused by the compressive stress on the particles structure, which is caused by the drag forces of the flowing liquid [31].

Experimentally, cake compressibility can be demonstrated by varying the vacuum level. If the cake is compressible, an x fold increase in filtration pressure produces a less than x-fold increase in flow rate. In the present study, the filtration rate was tested as a function of the pressure drop over a threefold range (16 900 to 50 700 Pa). Figure 8.9 shows that the filtration rate increases only by a factor of 1.85 over the pression range indicating that there is a certain degree of compressibility of the cake affecting the filtration rate (kg/(h·m^2)). It could be beneficial to keep the operating pressure across the cake to a maximum of 34 000 Pa to limit the negative effect of excessive compressing of the lignin particles. A lower pressure drop would also be beneficial to the washing steps.

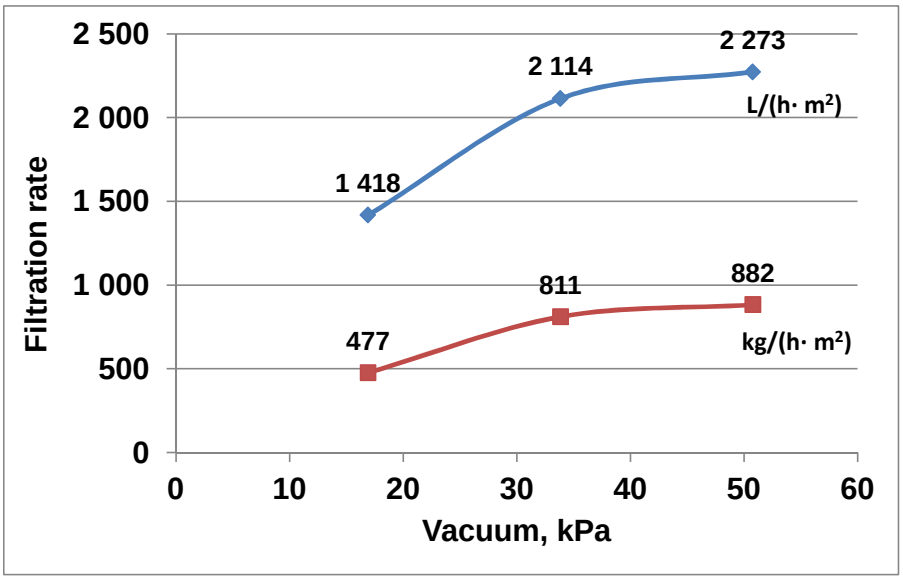

Figure 8.9 : The effect of the vacuum level on the filtration rate (85 °C)

8.5.2.5 Comparing the filtration rates (kg/(h·m^2)) of various acidification processes

It has been demonstrated that the benefits of adding Na_2SO_4 to the electrolysed black liquor prior to coagulation for enhancing the filtration rate (Figure 8.6). The cake filtration resistance was compared to data available from the literature for the CO_2 and H_2SO_4 acidification processes (Figure 8.5 and Table 8.1). It can be concluded that electrolysed black liquor, which is super oxidised, offers the lowest cake resistance under similar experimental conditions when Na_2SO_4 is added. The filtration rate rather than the cake filtration resistance was compared to other acidification processes. The data for CO_2 acidification were taken from the literature [2, 17] but the results by acidifying with H_2SO_4 or with a H_2SO_4/Na_2SO_4 mix were obtained from experimental work performed in this study. The acid/salt mix was produced from the electrolysis of Na_2SO_4 [44].

The solids filtration rates of the four acidifying methods are compared for medium concentration of black liquor solids ranging from 27 to 40% (Table 8.3). The acidification of non-oxidised black liquor using CO_2 technology gives a filtration rate similar to the electrolysed BL without the addition of Na_2SO_4. However, when salt is added to the electrolysed BL, the filtration performs better for both the non-oxidised and oxidised BL. The electrolysed BL with salt added produces a filtration rate between 2 and 6 times higher than CO_2 with oxidised BL depending on the study considered. However, within that solids range, the acidification with H_2SO_4 delivers a

filtration rate one to two orders of magnitude higher than electrolysis and CO_2 despite the fact that the BL is not oxidised. Regardless of the high content of Na_2SO_4 in the more dilute acid mix, the 60 % acid strength filtered better. Acidifying with 60% H_2SO_4 gives a better filtration rate (7 297 kg/(h·m^2)) than the acid/salt mix (2 756 kg/(h·m^2)), almost threefold higher. The acid/salt mix was composed of 15 % H_2SO_4 (160 g/L) and at that acid concentration it contains 250-262 g/L of residual Na_2SO_4 [44]. It was anticipated however that the high level of Na_2SO_4 in the acid mix would perform better based on the salt induced precipitation of lignin.

Table 8.3 : Filtration rate of lignin slurry from softwood BL using various acidification processes at similar conditions

Conditions	**CO_2**	**CO_2**	**Electrolysis (OSWBL*)**	**H_2SO_4 (NOSWBL*)** (This work)	
	OSWBL [16]	**LignoForce [2]**	(This work)	**H_2SO_4**	**H_2SO_4/ Na_2SO_4 mix**
H_2SO_4 (%)	-	-	-	60	15
BL solids, %	30-37	30-40	29-30	27.0	27.0
pH	9.4-9.8	10.0	9-10	8.7	9.3
T, °C	70-80	70-75	75-84	70	70
Vacuum, kPa	70	Pressurised	16.9	33.9	33.9
Filtration rate, kg/(h·m^2)	82-256	NOSWBL → 50-60	0 g/L** → 64.0	7 297	2 756
		OSWBL → 150-180	120 g/L → 485		

* OSWBL: Oxidised Black Liquor, NOSWBL: Non Oxidised Black Liquor
**Na_2SO_4 added to the electrolysed black liquor prior to the coagulation step: 0.0 and 120 g/L

It is important to mention that adding H_2SO_4 to the black liquor from an external source will disturb the Na/S balance of the recovery system implying that most of the filtrate would have to be discarded. To In order to overcome that issue, the acid must come from an internal source from splitting the Na_2SO_4 from the electrostatic precipitator dust or salt cake by-product from the ClO_2 generator or from the sulfur from concentrated non-condensable gas (CNCG) [6].

8.5.3 Lignin cake washing and product purity

Once the coagulation of the electrolysed black liquor has been completed, the lignin slurry produced is transferred to the filtration and the washing steps. In the first step, the lignin slurry is separated from the mother liquor to recover the precipitated lignin as a cake. The filtrate is sent

back to the black liquor circuit. In a second step, the lignin cake is washed with dilute sulfuric acid (0.5 N) to remove residual sodium. In a third step, the lignin cake is washed with water to remove residual ash and undesirable organics assuring a high purity lignin product.

8.5.3.1 Comparison of filtration rate of the lignin slurry, the acid wash and the water wash

The filtration of the lignin slurry is a critical step and the acid and water wash could add to the process complexity and increase the equipment cost. The performance of filtering the lignin slurry, the acid and the water washes are compared on the basis of two metrics: L of filtrate per h per m^2 and kg of dry solids per m^2 (Figure 8.10).

The lignin slurry has a significantly higher liquid filtration rate (2 172 L/(h·m^2)) than the acid wash filtrate (988 L/(h·m^2)) and water wash filtrate (672 L/(h·m^2)). Based on the rate of kg of solids recovered rather than liquid filtrate, the lignin slurry and water wash have a similar filtering performance. These results can be compared with the LignoForce CO_2 process [2] in which the author reported a first step filtration rate between 150 to 180 kg/(h·m^2) compared to 100 to 240 kg/(h·m^2) for the last step without re-slurring of the cake as performed in this study. These numbers support the results obtained with the filtering lignin slurry: the washed lignin obtained from electrolysed black liquor filters much faster than the LignoForce process using CO_2 with oxidised black liquor.

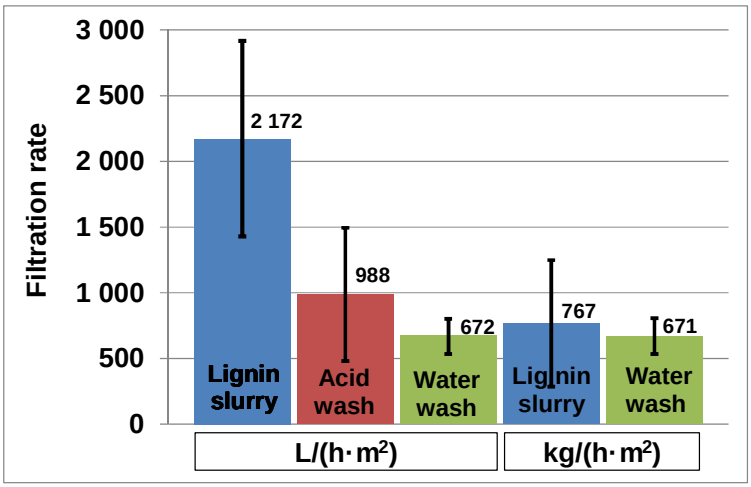

Figure 8.10 : Filtration rate of lignin slurry, acid wash and water wash at 85 °C expressed in L/(h·m^2) and kg/(h·m^2)

8.5.3.2 Purity of lignin

The quality requirements of the lignin depend on its utilisation. According to Heiskanen [45], a high quality lignin should contain less than 1.0 % ash and more preferably less than 0 .5 % for certain use. Based on preliminary tests, the washed electrolysed lignin containing ashes (Table 8.4) has an acceptable purity to make polyurethane [46]. But, the lignin could also be used for its bio-energy potential to replace fossil fuel in the lime kiln [45, 48]. In our application, the critical component to monitor is the sodium, which can cause problems of severe fouling of the walls of the lime kiln when in excess [3]. It appears, though, that if the lignin contains less than 0.3 % sodium, it could replace more than 98 % of the fossil fuel requirement [3]. A lower sodium content could be achieved by increasing the number of water wash steps or subjecting the lignin slurry to an electric field [45].

The lignin cake was washed by displacement [34, 49, 50]. The experimental cake washing method used in this work comprised one volume displacement with acid at 0.5N followed by one displacement with water. The unwashed lignin cake contained 93.4 % of lignin but a significant amount of ashes (14.7 %) which included 6.7 % sodium and 2.8 % sulphur. The washing procedure used in this study reduced the ash by 84 %, the sodium by 91 % and the sulphur by 37 % (Table 8.5). It was noted that the washed lignin cake had higher moisture content (61.5 %) than the unwashed cake (56.0 %). The moisture content can be reduced by adding a drying step after the water wash as proposed by Kouisni [2].

Given the sensitivity of the lime kiln to the sodium level in the washed lignin and according to the sodium balance provided by Uloth [3], it is estimated that the electrolysed lignin containing 0.64 % of residual sodium could replace close to 50 % of the lime kiln fossil fuel. However, it is anticipated that an additional water wash of the lignin cake would make it possible to achieve almost a complete replacement of fossil fuel as reported by Uloth [3]. Moreover, by using Öhman's novel washing method [37], higher purity lignin can be produced as well. This author recommended that the final pH of the spent acid wash should be less than 3.75 for better washing efficiency. In this experimental work the final pH was 1.7 indicating that an excess amount of acid was used.

Experiments were conducted with different types of black liquors. Once washed, however, all lignin samples from oxidised and non-oxidised softwood liquor as well as softwood and

hardwood liquors have the same appearance except that the hardwood lignin has a lighter colour (Figure 8.11).

Table 8.4 : Composition of unwashed and washed lignin recovered from electrolysed BL

Component	Electrolysed BL at pH 9.0	Unwashed lignin cake	Washed lignin cake						
			Sample #1	Sample #2	Sample #3	Mean	s	COV, %	Removal, %
Solids, %	30,4	46,8	35,7	35,8	44,0	38,5	4,763	12,4	-
Moisture, %	69,6	53,3	64,3	64,2	56,0	61,5	4,763	8,5	-
Ashes	42,8	14,7	2,50	2,30	2,19	2,33	0,157	6,7	84,1
Sodium	24,6	6,74	0,59	0,62	0,70	0,64	0,057	8,9	90,6
Total sulphur	1,02	2,77	1,71	1,72	1,81	1,75	0,055	3,2	36,9
Lignin	40,1	93,4	97,6	97,1	99,1	97,9	1,041	1,1	-

Figure 8.11 : Samples of washed lignin from oxidised softwood liquor and non-oxidised softwood liquor and hardwood liquor

8.5.4 Process mass balance

With the objective of integrating the proposed lignin recovery process to the recovery system of a kraft mill, detailed mass balances were performed (Tables 8.5 to 8.8) of the most relevant components encountered in the major steps of the proposed electrochemical lignin recovery process (Figure 8.1).

8.5.4.1 The electrolysis of black liquor

The black liquor fed to the anode compartment of the electrolytic treatment undergoes major chemical modifications [14]. The most important change is linked to the extraction of a portion of the sodium, which is converted to sodium hydroxide in the catholyte compartment of the cell. It can be observed that the sodium balances are within 4 % (Table 8.5). The concentration of sodium in the black liquor varied from 68.4 to 60.8 g/L, which corresponds to a 24 % recovery as NaOH. It is worth mentioning that every mole of sodium that crosses the membrane towards the catholyte compartment entrains 4 to 5 moles of water, thus producing a concentration effect on solids, organics and lignin. Moreover, as a result of water being transferred, the flow of treated BL is lower than the feed flow, in this case a reduction of 10 %. It was noted that the sulfate level increases through the electrolysis step due to the oxidation of sulfur compounds: sulphide becomes thiosulphate and thiosulphate is oxidised to sulphate. The potassium (K) moves along with the sodium to the catholyte compartment to make KOH with a 56 % recovery. However, it is apparent that some K (28 %) was lost between the input to the electrolysis cell and the outputs comprising the electrolysed BL and the NaOH stream. Regarding the carbonate balance, it was observed that the concentration increases through the electrolysis step. It is postulated that some organics were oxidised at the anode and converted to carbonate. No explanation for the excess of total sulfur (38 %) in the outputs has been found.

8.5.4.2 Bipolar membrane electrodialysis of Na_2SO_4

The purpose of the bipolar membrane electrodialysis (BME) of Na_2SO_4 is to provide the sulfuric acid required to wash the lignin cake. In that perspective, the caustic soda becomes a by-product. The process is operated in batch mode. The depleted sodium sulphate solution is sent back to the ClO_2 generator when 80 % conversion is achieved producing a stream of approximately 67 g/L. At that conversion rate, it is expected that the initial conductivity estimated at 157 mS/cm will be reduced to approximately 107 mS/cm corresponding to a drop of only 32 %, which does not significantly affect the cell voltage. The mass balance presented in Table 8.6 is based on the stoichiometric reaction of the sodium splitting, not on experimental chemical analyses. The dry solids and inorganics do not balance due to the conversion of water to H^+ and OH^-, which are accounted for in the products. However, it is expected that there will be some sulphate leaking through the cationic membranes contaminating the caustic soda as shown by Cloutier [44]. But

in this work, the temperature was much lower (40 vs 80 °C), thus, it is assumed that the level of sulphate will be negligible.

Table 8.5 : Mass balance of the electrolysis step

Component		Process inputs			Process outputs			Diff., %
		BL feed	Water to NaOH stream	Total	BL treated	NaOH stream	Total	
Flow, L/h		4,65	0,88	5,53	4,20	1,05	5,25	12,8
Dry solids	g/L	331	0,0		410	145		
	g/h	1 567	0,0	1 567	1 718	152	1 870	19,3
Water	g/L	821	-		748	996		
	g/h	3 820	876	4 696	3 138	1 048	4 186	9,6
Organics	g/L	181	0,0		244	0,0		
	g/h	841	0,0	841	1024	0,0	1 024	21,7
Inorganics	g/L	150	0,0		165	145		
	g/h	697	0,0	697	694	152	846	21,5
Lignin	g/L	135	0,0		159	0,0		
	g/h	628	0,0	628	666	0,0	666	6,1
Na^+	g/L	68,4	0,0		60,8	72,6		
	g/h	318	0,0	318	255	76,3	331	4,1
K^+	g/L	5,3	0,0		0,9	13,0		
	g/h	24,4	0,0	24,4	3,9	13,7	17,6	-28,0
$SO_4^=$	g/L	2,8	0,0		13,6	0,0		
	g/h	12,9	0,0	12,9	57,1	0,0	57,1	344
S_{Tot}	g/L	9,2	0,0		14,1	0,0		
	g/h	42,9	0,0	42,9	59,3	0,0	59,3	38,2
$CO_3^=$	g/L	17,7	0,0		25,5	0,0		
	g/h	82,5	0,0	82,5	107	0,0	107	29,5

8.5.4.3 Coagulation, filtration and lignin cake washing

Partial characterization and mass balances of coagulation, slurry filtration steps, acid and water washings were gathered (Table 8.7) with the characterization of the lignin cake. The chemical analyses of the acid wash and the fresh water used and the water wash filtrate are not shown because they were not performed. Their respective flows were: 1.55, 2,10 and 2.04 L/min. Therefore, no overall mass balances could be completed for those steps which were not essential to determine the impact of the process on the recovery system. However, detailed characterizations of the mixture of lignin slurry, acid and water filtrates were performed which stream will be returned to the black liquor circuit. The lignin cake was partially characterized as well.

Table 8.6 : Mass balance of bipolar membrane electrodialysis (BME)

Component		Process inputs			Process outputs				Diff., %
		Na_2SO_4 feed[1]	Water feed	Total	Na_2SO_4 after BME	H_2SO_4 after BME	NaOH after BME	Total	
Flow, L/h		0,17	2,27	2,44	0,15	1,59	0,68	2,42	-0,7
Dry solids	g/L	335	0	335	66,9	24,5	47,2	-	-
	g/h	56,6	0,0	56,6	10,2	39,1	31,9	81,1	43,4
Water	g/L	925	-	-	989	990	1001	-	-
	g/h	156	2 270	2 426	150	1 578	676	2 405	-0,9
Inorganics	g/L	335	0,0	335		-	47,2	-	-
	g/h	56,6	0,0	56,6		-	31,9	31,9	-43,7
Na^+	g/L	94,4	0,0	94,4		-	27,1	-	-
	g/h	18,3	0,0	18,3		-	18,3	18,3	0,0
$SO_4^=$	g/L	226	0,0	226		24,0	-	-	-
	g/h	38,3	0,0	38,3		38,3	-	38,3	0,0
S_{Tot}	g/L	75,4	0,0	75,4		8,0	-	-	-
	g/h	12,8	0,0	12,8		12,8	-	12,8	0,0

The flow rate at the exit of the coagulation tank is equivalent to the flow from the electrolysis. The Na_2SO_4 was added as a solid in the actual experiment without water. In practice, the salt will be added as a solution, as it comes out of the ClO_2 generator at a concentration of 335 g/L, which will dilute the lignin slurry, but will not increase the amount of water returned to the BL since it is already sent back as make-up. The volume of lignin slurry filtrate collected is about 75 % of the volume of the slurry, the rest remained in the lignin cake. On the other hand, the flows of acid and water filtrate are very close (97 %) to the acid and water flowing in.

The final pH of the water wash filtrate was low (1.7) indicating that an excess of acid was used in the acid wash step. The total flow of the mixture returning to the weak BL is estimated at 6.73 L/h containing 254 g/L of solids, including 18.5 g/L of soluble lignin, 65.7 g/L of sodium and 26.7 g/L of total sulfur and organics other than lignin. The level of carbonate in that mixture stream was not detectable. It is assumed that the carbonate that was present in the lignin slurry filtrate was released from the solution when mixed with the acid filtrate and the slightly acidic water filtrate. This indicates that an excess amount of acid was used in the acid wash step.

8.5.4.4 Global mass balance

The mass balances closure varied between -14.6 % for the dry solids indicating a deficit to an 11.6 % excess for the total sulphur (Table 8.8). No global balance could be performed on potassium due to a lack of reliable data from analysis. For this experiment, 12.8 g of K coming from the chip are fed to the electrolysis cell with the black liquor. According to the chemical analysis, 8.3 g are recovered in the caustic soda stream and only 1.9 g are present in the electrolysed black liquor stream. Therefore, 20 % of the K coming into the system is not accounted for in the process outputs comprising the caustic soda and the returned filtrates. It should be mentioned that K is not an important component in this process. On the other hand, the sodium, a critical component, balances at 8 % which is satisfactory given the numerous steps. Despite the evaporation, the water balance closes at 5 %.

The total sulfur, which includes sulphide and thiosulphate components, sulfate and the organic sulfur tied to lignin, is all accounted for at a 4.6 % difference. The total sulfur balance is critical and indicates that the process returns the same amount to the recovery system within 5 %. It was noted that the Na/S ratio in the liquor returned to the recovery system was half the ratio of the black liquor fed to electrolysis. The sodium sulfate needed in the coagulation and electro-dialysis increases the sulfur in the process but when integrated to the recovery system the ratio will be re-established since it was derived from it. It is important, however, to note that the process creates a net loss of sodium and sulfur leaving with the lignin product. Usually, in a kraft mill, there is an excess of salt produced by the ClO_2 generator that could be used to compensate for these losses at no additional cost.

Table 8.7 : Mass balance of the coagulation, filtration, acid and water washing steps and the washed lignin cake

Component		COAGULATION		LIGNIN SLURRY FILTRATION	ACID WASH	Lignin, acid and water wash filtrates mix	Washed lignin
		Na_2SO_4 feed (1)	Lignin Slurry	Filtrate	Acid stream		
Flow, L/h		0,0	4,20	3,15	1,59	6,73	-
Dry solids	g/L	0,0	530	-	24,5	254	-
	g/h	503	2 222	-	39,1	1 207	445
Water	g/L	925	748	-	990	908	-
	g/h	0,0	3 138	-	1 578	6 113	711
Organics	g/L	0,0	244	-	0,0	69,7	-
	g/h	0,0	1 024	-	0,0	470	423
Inorganics	g/L	0,0	530	166	24,5	185	-
	g/h	503	2 222	522	39,1	1 242	10,4
Lignin	g/L	0,0	159	73	0,0	18,5	-
	g/h	0,0	666	230	0,0	124	436
Na^+	g/L	94,4	99,7	99,7	0,0	65,7	-
	g/h	163,1	418	314	0,0	442	2,8
K^+	g/L	0,11	0,93	0,93	0,0	-	-
	g/h	0,0	3,92	2,94	0,0	-	-
$SO_4^=$	g/L	0,0	94,7	94,7	24,0	-	-
	g/h	340	397	298	38,3	-	-
S_{Tot}	g/L	0,0	41,2	41,2	8,0	26,9	-
	g/h	113,4	173	130	12,8	181	7,8
$CO_3^=$	g/L	0,0	25,5	25,5	0,0	0,0	-
	g/h	0,0	107	80,2	0,0	0,0	-

(1) Chemical analyses of a typical ClO_2 generator effluent from a Québec mill

Table 8.8 : Mass balance of lignin recovery process from electrolysed black liquor at pH 9.0

Component	Process inputs								Process outputs					Difference, %
	Black liquor	Water to EL	Na_2SO_4 to coagulation	Na_2SO_4 to BME	Water to ED	Acid wash	Water wash	Total	NaOH stream EL	NaOH stream BME	Filtrate and washings	Lignin product	Total	
Dry solids	1 567	0,0	503	56,6	0,0	0,0	0,0	2 127	132,8	31,9	1 207	445	1 817	-14,6
Water	3 820	876	0,0	156	2 270	0,0	1 020	8 142	1 048	676	6 113	711	8 548	5,0
Organics	841	0,0	0,0	0,0	0,0	0,0	0,0	841	0,0	0,0	470	436	906	7,7
Inorganics	697	0,0	503	56,6	0,0	0,0	0,0	1 257	0,0	0,0	1 242	10,4	1 253	-0,3
Lignin	628	0,0	0,0	0,0	0,0	0,0	0,0	628	0,0	0,0	124	436	560	-10,7
Na^+	318	0,0	163,1	18,3	0,0	0,0	0,0	500	76,3	18,3	442	2,84	540	8,0
K^+	24,4	0,0	0,0	0,0	0,0	0,0	0,0	24,4	13,7	0,0	-	-	-	-
$SO_4^=$	12,9	0,0	347	38,3	0,0	0,0	0,0	399	0,0	0,0	-	-	-	-
S_{Tot}	42,9	0,0	113	12,8	0,0	0,0	0,0	169,1	0,0	0,0	181	7,78	189	11,6
$CO_3^=$	82,5	0,0	0,0	0,0	0,0	0,0	0,0	82,5	0,0	0,0	0,00	-	0,0	-100

8.5.4.5 Process requirements and products

The electrolytic production of lignin from black liquor relies only on electric energy from an external source and requires sodium sulfate from an internal source (Table 8.9). The amount of black liquor solids needed per unit weight of lignin produced is 3.6 g/g of lignin. The sodium sulfate requirement for coagulation and electro dialysis, which is provided by salt by-products and available in the mill, adds up to 1.18 g/g of lignin. Water is needed for the production of sulfuric acid in the electro-dialysis step, for caustic soda in the electrolysis and electro-dialysis steps, and finally for washing the lignin cake. The total quantity of water is estimated at 18.6 g/g of lignin. The acid requirement for lignin cake washing, which is provided by salt splitting amounts to 0.09 g/g of lignin in agreement with Uloth's findings (0.1 g/g lignin) when using waste acid containing residual sodium sulfate [3]. Finally, under the prevailing experimental conditions herein, the electrolysis and electro-dialysis processes consumed 1.48 Wh/g of lignin. Lower energy consumption could be achieved by increasing the temperature, lowering current density and reducing the concentration of the chemicals produced (H_2SO_4 and NaOH) [16].

Table 8.9 : Process requirements and products

Component		per g of lignin
Input	BLS, g/g	3,594
	Water from BL and to EL, g/g	18,67
	Na_2SO_4, g/g	1,284
Output	NaOH produced, g/g	0,378
	H_2SO_4 produced and used, g/g	0,090
	Hydrogen produced, g/g	0,008
	Oxygen produced, g/g	0,061
Energy	Electricity (EL+BME), Wh/g NaOH	3,561
	Electricity (EL+BME), Wh/g lignin	0,791

8.6 Conclusion and discussion

It has been demonstrated in this study that the technical feasibility of the proposed electrochemical approach to extract lignin from black liquor providing acceptable lignin product purity for a kraft bio-refinery. The technology is based essentially on the judicious use of electricity alone, without resorting to purchased chemicals from external sources. It has been shown experimentally that the process does not disturb the Na/S balance of the recovery system because it produces its own chemicals, H_2SO_4 and NaOH, from Na_2SO_4 salt splitting for washing lignin and pH adjustment, respectively. This option is in agreement with the circular economy concept. Moreover, it generates no additional effluent, which supports the sustainable development strategy.

During the present investigation, the effect of various operating parameters on the filtration rates were determined namely for the lignin slurry, the acid and water washes. The efficiency of lignin the cake washing was also reported. The different steps of the entire flowsheet were detailed and complemented by a mass balance of the major components. These data are required for the integration of the proposed lignin process to the chemical recovery system of a kraft mill which will be the object of future work.

The experimental results showed that the lignin filtration rate is relatively low (64 kg/(h·m^2), but adding Na_2SO_4 (120 g/L) during the coagulation step improves the rate by 7.5 times. A longer coagulation time (4-5 h) yields a better filtration rate forming bigger flocs and favours a higher solid content of the lignin cake using less energy in the drying step.

Based on the liquid filtration performance, the lignin slurry filters faster (2 170 L/(h·m^2)) than the acid (988 L/(h·m^2)) and water ((672 L/(h·m^2)). Nevertheless, when considering the rate of kg of solids recovered instead of the liquid filtrate, the lignin slurry and water wash have a similar filtering performance (671 vs 767 kg/(h·m^2)). These results are in agreement with the results reported with the LignoForce CO_2 process.

Electrolytic treatment of the black liquor accompanied by the addition of Na_2SO_4 in the coagulation step delivers a better filtration rate than CO_2 processing. The additional oxidation occurring at the anode seems to be more efficient than the chemical oxidation with oxygen to improve the filtration rate. Based on preliminary tests, the purity of the washed electrolysed

lignin is acceptable to the chemical industry, such as polyurethane making. On the other hand, given the sensitivity of the lime kiln to sodium, it is estimated that the electrolysed lignin containing 0.64 % of residual sodium could replace close to 50 % of the lime kiln fossil fuel. However, it can be expected that one additional water wash of the lignin cake would achieve a lower sodium level allowing for an almost total replacement of fossil fuel.

The electrolytic production of lignin from black liquor relies only on electric energy from an external source and requires sodium sulfate from an internal source. The requirements in g/g of lignin are as follows: 3.6 g of BLS, 1.18 g of of Na_2SO_4 and 18.6 g of water. The acid requirement for lignin cake washing, which is provided by salt splitting, amounts to 0.09 g/g of lignin. In addition to the acid, the process makes 0.47 g of NaOH per g of lignin produced. Finally, under the prevailing experimental conditions herein, the electrolysis and electro-dialysis processes consumed 1.48 Wh/g of lignin. It is worth mentioning that the process creates a net loss of sodium and sulfur leaving with the lignin product. The excess salt usually produced by the ClO_2 generator could compensate for this loss.

The next step in the development of the electrochemical technology proposed herein to produce lignin will be the simulation of the process integration to a kraft mill based on the complete mass balance of the major components developed in this work taking into account the impact on energy balance and existing mill equipment bottlenecks.

8.7 References

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CHAPITRE 9 ARTICLE 5: ELECTROLYTIC PROCESSING OF KRAFT BLACK LIQUOR USING THE FM-21 COMMERCIAL CELL

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The technical feasibility of the electrolytic treatment of black liquor from a kraft mill was demonstrated using the commercial FM-21 membrane cell that was originally developed for the chlor-alkali industry. The electrolytic treatment involves simultaneous desalkalinisation of 30 % solids black liquor at the anode and co-production of NaOH at the cathode. The cell was operated for a total of 38 hours during which the impact of current density (from 1.5 to 3.9 kA/m^2), NaOH strength (5.4 to 9.5 %) and temperature (62 to 71 °C) were investigated. The current density had the greatest impact on process performance. The best productivity achieved in terms of black liquor treatment was 171 L of BL /(h·m^2) while running at 3.9 kA/m^2 and about 70 °C. Under these conditions, the cell was producing 6.0 kg of NaOH/(h·m^2) at 5 % NaOH strength and energy consumption was 4 030 kWh/t NaOH. The results were compared to experiments performed with a laboratory cell. It is recommended to backwash the anode compartment on a regular basis with diluted caustic soda to prevent long term fouling of the anode and membrane.

9.1 Introduction

In the context of sustainable development and implementation of biorefineries in the pulp and paper industry, an efficient electrochemical process has been developed to precipitate lignin from black liquor (BL) [1-3] as an alternative to the conventional chemical approach using carbon dioxide, such as LignoBoost [4] and Lignoforce [5]), or sulfuric acid [6-8] as acidifying agents. The proposed technology relies on the judicious utilisation of electricity from a renewable source to reduce the pH of black liquor to the point of precipitating lignin while producing valuable NaOH for a kraft mill.

The technical feasibility of the process was previously demonstrated on a laboratory scale [3] and the effect of the basic electrochemical cell operating parameters on the performance of the electrolysis of kraft pulping black liquor was reported [91]. The fundamental electrochemistry occurring at the anode was described as a desalkalinization reaction where the hydroxyl ions were neutralized to water therefore reducing the BL pH. Oxygen was produced at the anode and partially consumed to oxidize sulfur compounds. Investigation of the mass transfer mechanism through the membrane [10] led to the conclusion that the process should be operated with the black liquor at basic pH, preferably higher than 9.0. The electrolytic treatment of BL was optimized [11] in terms of energy consumption. Finally, a study related to the precipitation of lignin from electrolyzed BL showed that the filterability of lignin was found to be excellent and superior to the CO_2 lignin [12]. The washed lignin product was found to be acceptable as a partial replacement of fossil fuel in the lime kiln according to Uloth's findings [6].

The electrolytic treatment of a high organic content feed, such as black liquor, is quite unusual in the chemical industry, especially when micelles of colloidal particles could be formed within the cell during processing. However, the challenge resides in designing the anode compartment to facilitate the exit of particulates, which would otherwise settle and severely foul it. Many electrochemical cells, including the FM-21, were designed for the production of chlorine and caustic soda from sodium chloride solution or hydrogen from an alkaline solution.

This study has demonstrated the technical feasibility of the electrolytic treatment of BL using the FM-21 commercial cell and evaluated its performance. It explored the effect of current density, temperature and concentration of caustic soda on cell performance characterized by current efficiency, energy consumption, specific NaOH and black liquor productivities per unit area.

9.2 Specialized cell designs

9.2.1 Cell designs in the chemical industry

The appropriate design of an electrochemical cell reactor depends on the application. Filter-press-type electrolysers are one of the most important commercial electrochemical reactors comprising rectangular flow channels [13]. Their advantageous characteristics make them one of the most studied in the academic field [14]. Some of the design criteria to be considered in achieving a good performance reactor are [14-15]: (1) a uniform current density distribution that

is applicable to high densities, (2) a uniform electrode potential distribution, (3) a large specific electrode area, (4) high mass transport rates, (5) low ohmic losses, (6) applicable to multiphase systems with the ability to handle solid, liquid, or gaseous products, (7) simplicity of design and installation, (8) reliable operation with low maintenance, (9) low capital and running costs (10) and ease of scale-up.

The ElectroProd cell from ElectroCell [16] is a versatile cell design suitable for electrolysis and electrodialysis applications. It offers multiple configurations: monopolar design in 1, 2, 3 and even 4 compartment arrangements. Laboratory work reported by Cloutier et al. on the electrolytic treatment of black liquor [17-19] was performed with a laboratory version, the MP model. The BITAC® from Thyssenkrupp-Uhde with a special anode design [20] offers a modular design that provides many advantages, such as low investment costs, low energy consumption, and a long service life. Their cells can be used for chlorine and hydrogen production as well. Other manufacturers of commercial electrolytic cells have been reported by [21]; DeNora [22], Asahi Glass [23] and Asahi Kasei [24].

9.2.2 Proposed cell designs specialized for black liquor treatment

Electrochemical treatment, such as electrodialysis and electrolysis, of spent cooking liquors in the pulp and paper industry have been proposed as early as the 40's as an alternative to chemical treatment. Electrodialysis and membrane electrolysis were investigated to separate and recover various organic chemicals from sulfite spent cooking liquor [25-30] and black liquor [1-2, 31-44].

Electrolysis can be used to treat black liquor in order to precipitate lignin for various usages and also to oxidize it to value added derivatives as well. The purpose of the anodic electro-oxidation is to modify the lignin by depolymerisation [45-46] and transform it to more valuable derivatives, such as organic acids (Vanillinic acid) and anthraquinone [45, 47]. An alternative purpose of electrolytic treatment can simply be the desalkalinisation of black liquor to bring the pH down in order to precipitate lignin as proposed in this study.

A first attempt of the electrolytic treatment of black liquor was reported by Dyfverman in 1942 [48]. There are a few cell designs that have been proposed for the specific application of the electrolytic treatment of black liquor. Feeding BL to an electrolysis cell is peculiar because during the treatment lignin starts to precipitate in the form of fine colloidal particles that cause

fouling of the anode compartment. Therefore, assuring high fluidic velocity is necessary to maintain the particles in suspension thus preventing settling and, eventually, cell plugging.

The first patented concept of treating black liquor electrolytically to precipitate lignin was granted to Kennedy and Jernigan in 1959 [49]. The machine comprises a drum anode, which is soaked and rotates clockwise in the black liquor. When a current is passed through the electrolyte, ligneous material is deposited on the anode as a thin layer sprayed with water to soften up the ligneous film, which is subsequently removed with a scraper blade. There has been no commercial application of that device reported.

The electrolytic cell from Edel et al. [50] comprises an anode compartment separated from the cathode by a cationic membrane. The alkaline liquor is desalkalinized at the anode where the pH drops to the point of precipitating the lignin. Light brown foam is formed and floats at the end of the cell and the lignin product is recovered for future use. The particularity of the cell design is the floatation of the lignin product in the anodic compartment.

Herron et al. [51] developed an electrodialysis cell specifically to treat black liquor. The cell has a fluid flow design with high turbulence at the membrane surface with a continual change in flow direction created by the corrugated shape of the anode compartment. The cell design comprises a bundle of tubular anodes surrounded by two membranes creating a narrow passage for the black liquor thus enhancing flow turbulence and keeping the colloidal lignin particles in suspension. Pilot trials [52] were performed in kraft mills but no commercial installation has been reported to date.

Stiefel et al. [45] proposed a unique cell design for the treatment of black liquor with the objective of depolymerizing lignin. The purpose is not to precipitate lignin but to cleavage the lignin molecules and recover them as a value added product. The cell comprises two cylindrical anodes and a tubular ceramic nanofiltration membrane. An anionic exchange membrane is surrounding the ceramic membrane, between the cathode and the permeate containing the lignin-derived product. This design needs further development effort to reach commercialization.

Belo et al. [53] claimed to have developed a novel black liquor electrolyser that achieves lignin recovery by anodic electrodeposition. This electrolyser consists of a laboratory plate and frame of an electrochemical cell type. The principle is to be similar to Kennedy's [49] design where the precipitated lignin is deposited on the anode. A scraper is needed to remove the lignin product

from the anode. The advantage of this design is that it does not require a filtration system. But, there is no mention of how the recovered lignin is washed. It is clear that this equipment is still at the experimental laboratory stage.

9.2.3 Selecting the commercial FM-21 Cell

None of the cell designs described above have been reported to have reached commercialization for treating black liquor. The authors of the present investigation have chosen the commercial FM-21 cell because of its practicality and versatility for demonstrating the technical feasibility of the process on a larger scale. The cell was developed in the 1980's by ICI, but it is now manufactured by INOVYN, a subsidiary of INEOS [55], and is well suited for non-chlor-alkali applications. The cell is proposed for the electrolytic treatment of black liquor with the objective of taking the application from the laboratory to the next step of technology readiness, that is pre-commercialization [54].

The FM-21 electrolysis cell is mostly used in the production of chlorine, caustic soda, and hydrogen as well using an alkaline solution (KOH) as the electrolyte. It is also suitable for particular applications, such as polysilicone production and sodium hypochlorite. Therefore, this cell design appears as an excellent candidate for black liquor electrolysis. Indeed, in a previous study, it was recommended to reduce the diameter of the tubular anodes of the laboratory unit used to improve current distribution [9]. Based on that recommendation of smaller anodes, the search for the most appropriate electrolyser led to the selection of the electrode design of the FM-21 cell comprising numerous thin lantern anodes. The particularity of the electrodes used in this work is that they are stamped from a metal sheet. Both electrodes (anode and cathode) are pressed from integral sheets of pure metal, which simplifies recoating the electrodes and makes it cost effective. The effective electrode area of one monopolar cell is 0.42 m^2 (both sides of the anode). This electrolyser is therefore very compact. The individual lightweight electrodes are readily handled without the need for lifting devices allowing the electrolyser to be rebuilt or refurbished by a small crew in a short time [55]. Another key feature of the cell design other than the lantern electrodes is the elimination of external piping to the individual cell compartment by the use of a simple but effective internal manifold arrangement [21].

The FM01 laboratory unit (64 cm^2) is a scaled-down representation of the commercial FM-21 cell. Experimental results from the laboratory unit can be extrapolated to the full size cell with

confidence based on the concept of similarity for a successful scale-up as proposed by Sulaymon because of similarities in (1) geometrics, (2) kinematics, and (3) current and potential distribution [56].

The FM01 and FM-21 cells have been the object of many studies for various applications [14-15]: lignosulfonate into vanillin [57], Cerious ions oxidation [58], catecholamine derivatives [59], oxydation of cresol compounds [60], destruction oxydation of indigo textile dye [61-63], destructive oxidation of cresols, indigo textile and vinasses [64], Arsenic removal [65], reduction of ferricyanide ion to ferrocyanide ion [66], and the reduction of copper ions [67]. They were extensively characterized in terms of hydrodynamics, mixing, mass transfer, performance and scale-up [13-14, 57, 68- 81].

In addition to FM-21™, INOVYN [55] offers an easy-to-operate FM-1500™ monopolar electrolyser, based on further developments in the design of the original FM-21™ electrolyser. The FM-1500 model is a larger version containing up to 90 anodes as compared to 52 anodes in the FM-21-SP [55]. These low cost, yet extremely versatile electrolysers are used in over 45 plants worldwide with a chlorine production capacity in excess of 1 million tonnes per year. Due to its design and flexible nature the FM1500™ membrane electrolyser is ideally suited to polysilicone production and small sodium hypochlorite plants in the range of 1 to 10 tonnes per day of chlorine. It has the capacity to be skid-mounted and shipped anywhere in the world. The FM-1500™ is easy to be installed in an existing plant and, if required, has the flexibility to be expanded to cope with increased production needs. Individual electrodes and membranes can be easily and quickly removed and replaced, thereby optimizing maintenance downtime. Electrodes can be recoated without the need to replace the metal substrates.

BICHLOR™ is another electrolytic cell offered by INOVYN [55]. It is a modular electrolyser comprising a series of discrete modules consisting of anode, membrane and cathode. Any sealed individual module can be removed from the electrolyser without affecting the others. The design facilitates maintenance work on the individual modules in workshop controlled conditions, rather than in the main cell room, as required by the electrolyser filter press design. This modular design has a major influence in minimising plant down time.

The FM-1500™ and the BICHLOR™ cells are improved versions of the FM-21™ cell. It seems reasonable to eventually consider and evaluate these new cell designs as potential candidates for this application on a large scale.

9.3 Experimental methodology

9.3.1 Experimental set-up

The experimental work presented here was performed with the commercial electrolytic cell FM-21 (Figure 9.1) [82]. The cell was hydraulically connected to the same experimental set-up used in the previous studies [1-3]. Given the versatility of the installation, both streams (Black liquor and caustic soda) can be diverted from the laboratory cell to feed the larger cell. The set-up provides pH and temperature controls. Voltage and current were monitored and recorded every minute.

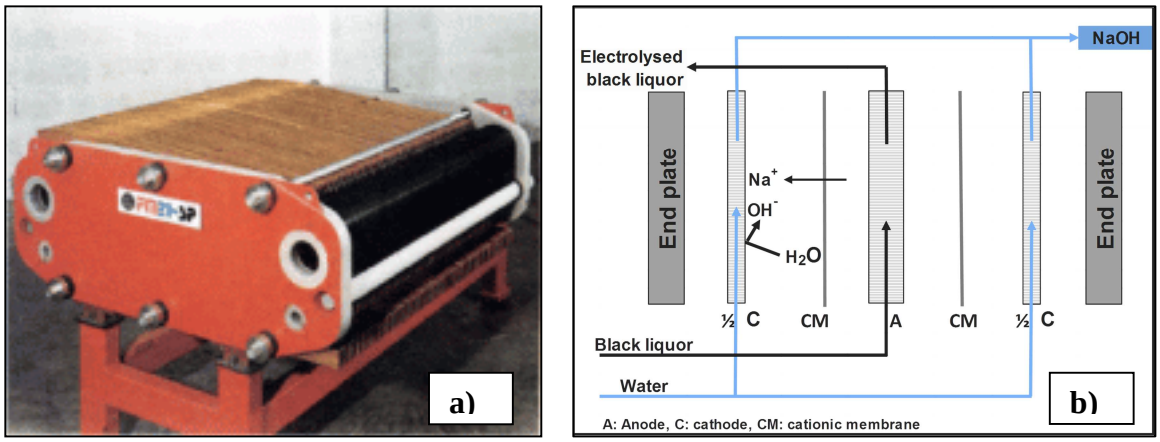

Figure 9.1 a) A full size FM-21 cell - b) Schematic of the internal cell arrangement (one anode, 2 membranes and 2 half cathodes)

The FM-21 cell was assembled with one lantern anode surrounded by two NAFION-324® membranes and two half-cathodes (Figure 9.1 b). For the purpose of illustrating the internal cell components arrangement, Figure 9.1b shows that the membranes are at a certain distance away from the anode. In reality, the cell is considered as a zero gap design meaning that the membranes are nearly sitting on the surface of the anode. The electrodes are composed of numerous (228) narrow lanterns , 2.2 mm wide, 2.2 mm thick and 210 mm long [83-Byrne] and spaced 2.2 mm apart (Figure 9.2 a). The total effective projected anode area is 0.21 m^2 per side (a total of 0.42 for both sides) and the total effective membrane (2) area is 0.42 m^2 as well (Table

9.1). The cell was electrically connected to a power supply from Rapid Power Technologies, Inc. (*M*odel 4890-23), which can deliver from 0 to 8 000 amps at 0 to 24 V.

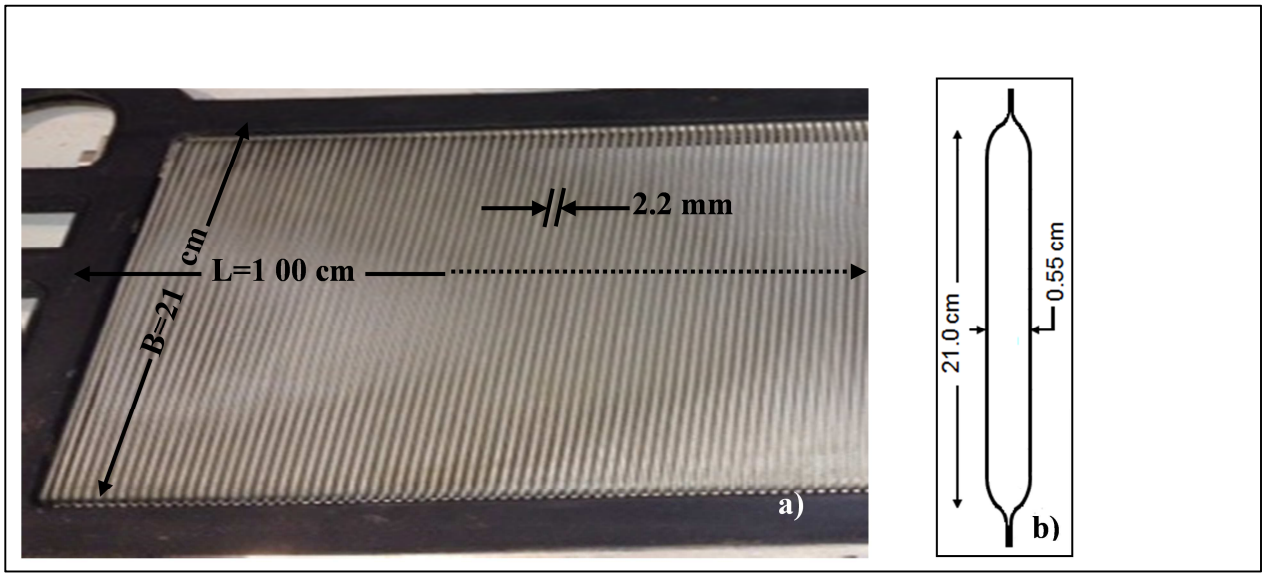

Figure 9.2 a): Section of a lantern anode b) Side view of anode

The feed ports to the anode compartment were modified to accommodate black liquor electrolysis with the potential formation of colloidal lignin particles and, to assure an evenly distributed flow and, therefore, current distribution as well. In a typical chlor-akkali plant, the internal mixing of electrolytes within the anode compartment is driven by gas lift [21]. In this application, it is assumed that most of the oxygen formed at the anode is consumed in the reaction of oxidizing sulfur compounds [9].

9.3.2 Experimental method

The experimental method used in this study was similar to the one described in our previous work [1-3]. The same experimental set-up was used but this time it was connected to the FM-21 cell rather than the ELSEP laboratory cell. The anolyte tank was filled with the minimum operable volume (50 L) of 30 % black liquor in order to shorten the time to lower the pH to the target value. As recommended by Ghatak [38], every batch of black liquor was filtered through a 400 mesh screen to remove suspended materials such as wood fibers and other particulates. The concentration of black liquor was 30 % solids and contained approximately 60 g/L of sodium and 120 g/L of lignin, which is typical of a kraft black liquor [2-3The catholyte tank initially contained 180 L of NaOH at 5.4 % strength.

Table 9.1 : Dimensions of cell components and operating conditions

No. of lanterns (lamellas) per anode side	228
Lantern width, mm	2,2
Lantern width (B), mm	210
Effective anode area per face, m^2	0,105
Total effective anode area (2 sides), m^2	0,211
Membrane width, mm	210
Membrane length (L), mm	1 000
Total membrane area, m^2	0,42
Electrode spacing (S), mm	5,5
Hydraulic diameter $d_e = 2 \cdot B \cdot S/(B+S)$, cm	1,10
Density of electrolyte, g/cm^3	1,166
Kinematic viscosity of electrolyte **(ν)**, cm^2/s	0,0116
Black liquor flow (Q), L/min	26,0
Mean fluid velocity (v), cm/s	46,9
Over all compartment voidage **(ε)**	0,80
Reynold number (Re) = $v \cdot d_e/\nu$	4 439

Initially, the pH of the black liquor was reduced from 12.5 to 9.0. Thereafter, the pH was automatically controlled at 9.0 by the addition of fresh black liquor at 30 % solids. Under that pH target, the effect of the following parameters were investigated: (1) current density, (2) NaOH strength and, (3) temperature. The current density is calculated by dividing the total current applied to the cell by the total membrane surface (0.42 m^2) as recommended by the cell manufacturer. The pumps were running at their maximum capacity to assure the highest flow velocities possible, which were 26 L/min for the black liquor and 33 L/min for the caustic soda stream, respectively. We estimated that the flow regime in the anode compartment was turbulent (Re=4 439), which is critical for the clearance of the potential colloidal lignin particles out of the

anode compartment. Black liquor and NaOH streams were fed as co-current flows into the cell. Initial and final volumes of fresh and treated liquors fed into the cell and coming out of the cell were measured for each run. Knowing the duration of the experiment, the respective flows could be computed. The cell performance was characterized by (1) the current efficiency, (2) the energy consumption, the specific NaOH and black liquor productivities.

The current efficiency is estimated from the total number of moles of NaOH produced calculated from the volume multiplied by the concentration (Titration) and divided by the number of theoretical moles that should have been produced according the number of Faradays used. The energy consumption is reported in kWh per ton of NaOH. The NaOH productivity was computed from the total amount of NaOH produced (volume x concentration) divided by the total membrane area. Black liquor productivity was estimated from the flow divided by the membrane surface area and reported in $L/(h \cdot m^2)$.

9.4 Results and discussion

The black liquor was delivered from the mill at a pH of about 12.5. Based on our previous study, it was recommended operating the electrolytic step at pH 9.0 [10]. So, the system was loaded with an initial volume of fresh black liquor and electrolysis proceeded to reduce the pH of this initial batch down to the target value of 9.0. Thereafter, the experimental program was executed at that pH.

9.4.1 Adjustment of black liquor pH

As electrolysis proceeded, the evolution of the pH of the initial batch of black liquor and temperature are shown in Figures 3 and 4, respectively. After 5 h, the targeted value of 9.0 (Figure 9.3) was attained. During that period, the conductivity of both streams increased. The chemistry occurring at the anode during the electrolytic treatment of black liquor is more accurately represented by a desalkalinization reaction than an acidification [84]. The reactions at the anode are quite different for black liquor electrolysis compared with alkaline water electrolysis. The hydroxyl ions are oxidized to water resulting in desalkalinization and electroactive organic anions are oxidized as well. This anodic reaction proceeds via a sluggish one electron charge transfer (38).

Normally, at constant temperature, the BL conductivity drops [3] because a fraction of the sodium is being extracted leaving behind a sodium depleted and less conductive BL. In this particular batch experiment, the initial temperature was 48 °C and was increased to 83 °C (Figure 9.4) thus improving conductivity. In a subsequent test performed at constant pH (9.0), the black liquor conductivity increased steadily with temperature at a rate of 1.52 (mS/cm)/°C (Figure 9.5). Moreover, the NaOH conductivity (Figure 9.3) also increased from the combination of an increase of temperature and concentration, which was initially at 5.4 % (wt) and reached 6.5 % by the end of the experiment.

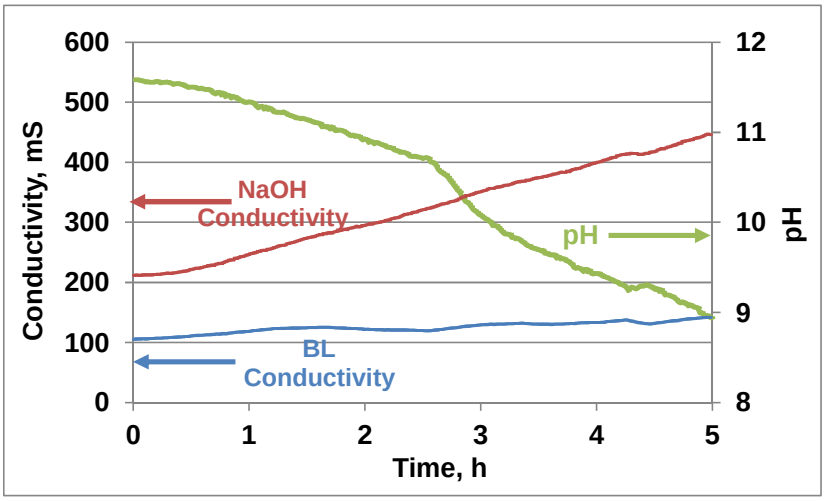

Figure 9.3 : Evolution of conductivity and pH of BL (50 L), and conductivity of the NaOH solution (180 L) during initial batch processing

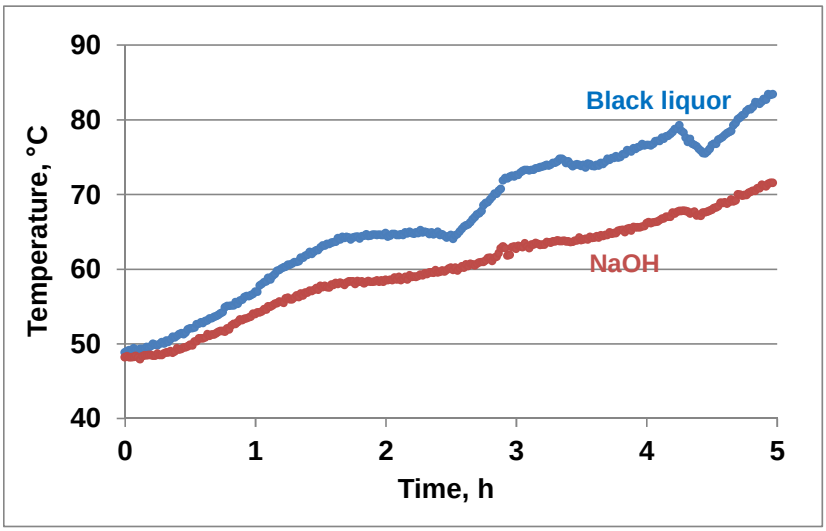

Figure 9.4 : Evolution of black liquor temperature and NaOH solution during initial batch processing

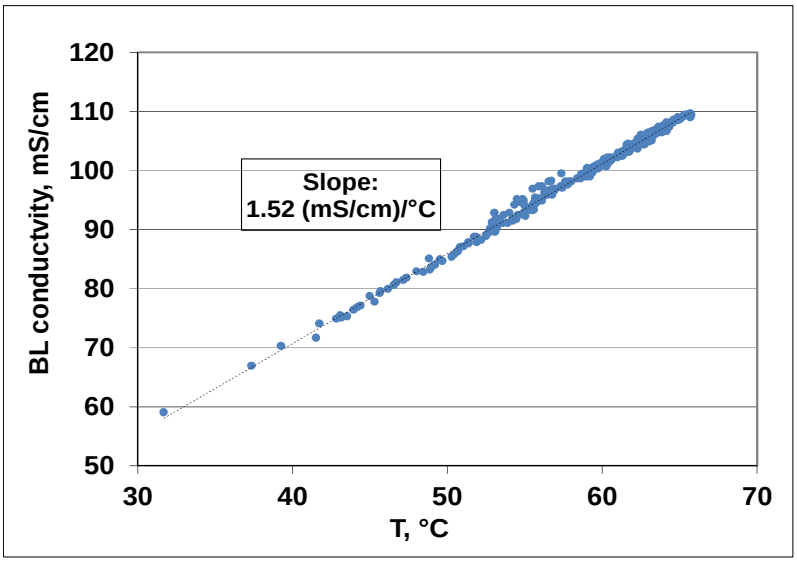

Figure 9.5 : Black liquor conductivity as a function of temperature

9.4.2 Decomposition voltage and limiting current density

The results of this study with the FM-21 cell were compared with those obtained with the laboratory ELSEP unit. The current density profile as a function of the total voltage for a 30% black liquor solution was developed for both cells at pH 9.0 while making 10 % caustic soda (Figure 9.6). We can observe that the current takes off at a lower voltage with the ELSEP cell (2.32 V) than the FM-21 (2.85 V). No explanation could be proposed other than that the BL batches were different considering that the operating conditions were similar. It was also noted that the FM-21 cell resistance was 14 % higher (1.56 Ω/m^2) than the resistance of the ELSEP cell (1.37 Ω/m^2). This situation is partially due to the thicker compartment of the FM-21 cell (5.5 mm) compared to the ELSEP cell (4.0 mm) [9].

The limiting current density is the current density at which the sodium concentration at the membrane and black liquor interface tends to zero [85]. Under that condition, the process becomes diffusion limited. At that point, the voltage-current curve starts to deviate from linear even though the voltage has increased (Figure 9.6). Based on the deviation, the limiting current density for the electrolysis of BL using the FM-21 cell was estimated to be around 3.2 kA/m^2. In

the previous work with the ELSEP laboratory cell, the current density did not exceed 2.0 kA/m^2 and the limiting current density of the process was not attained at pH 9.0.

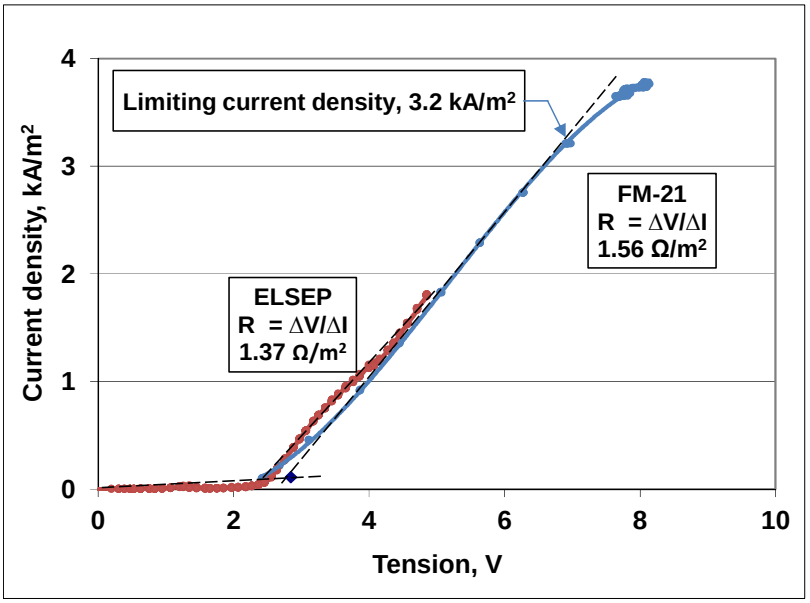

Figure 9.6 : Current density as a function of cell voltage for the ELSEP and FM-21 cells

9.4.3 Correlation matrix

A correlation matrix was computed using the software EXPLORE developed by CANMET – ENERGY [86]. The matrix (Table 9.2) shows the correlation between the most pertinent parameters of the process, dependent and independent variables, indicating how strongly two variables are related to each other. The absolute values of the correlation coefficients were divided into four categories and colour coded (Table 9.2).

As expected, the current density shows a strong correlation with voltage (0.93), energy (0.75), NaOH (0.83) and BL flow or productivity (0.96). The cell is considered as a resistance and a higher current density increases voltage and energy consumption. On the other hand, the

higher the current density, the higher the productivities and the BL flows since more work can be accomplished per unit area. Current density has a low correlation with Faraday efficiency meaning that in the range tested, it has a low impact on current efficiency.

Table 9.2 : Matrix of correlation between dependent and independent process variables

No.	Variable	1	2	3	4	5	6	7	8	9
1	Current density, kA/m^2	1,00								
2	BL temp., °C	0,25	1,00							
3	NaOH temp.,°C	-0,28	0,73	1,00						
4	NaOH, %	0,23	0,04	0,11	1,00					
5	Tension, V	0,93	0,06	-0,44	0,06	1,00				
6	Current efficiency, %	0,33	0,46	0,07	0,39	0,09	1,00			
7	kWh/t NaOH	0,75	-0,38	-0,38	-0,28	0,50	-0,79	1,00		
8	Productivity, kg NaOH/(h/m^2)	0,83	0,42	-0,13	0,35	0,65	0,79	0,28	1,00	
9	Productivity, L of BL/(h/m^2)	0,96	0,28	-0,20	0,03	0,92	0,23	0,28	0,77	1,00
NUL: 0.0 <|R|≦ ±0.3		Weak: 0.3<|R|≦0.5			Moderate:0.5<|R|≦0.7			Strong: 0.7<|R|≦1.0		

It is expected that both temperatures (BL and NaOH) would be correlated (0.73) because both streams were circulated through a common heating system. Despite a common heat exchanger, there was a difference in temperature between the two streams due to unequal heat losses because of the length of piping and size of the reservoirs, which were different for each stream. the temperature is not dependent on current density for the NaOH stream (R=-0.28) and the BL stream (R=0.25) even though the current that reached 1 600 amps provides a significant amount of power. In fact, it only accelerates the heating process allowing the temperature target to be reached faster. Temperature seems to have a relatively weak effect on current efficiency (R=0.46), energy (R= -0.38) and NaOH productivity (R=0.42) and no impact on black liquor productivity (R=0.28). The NaOH concentration also has a relatively weak effect on current efficiency (R=0.39) and NaOH productivity (R=0.35) and, no effect on BL productivity (R=0.03) within the range studied. Energy consumption is moderately correlated with the cell voltage (R=0.50), as expected.

9.4.4 The effect of current density and NaOH strength

Current density plays a major role in the performance of an electrochemical process. It drives productivity up, but negatively impacts energy consumption; the higher the current density, the better the productivity but at the expense of higher energy consumption. According to Chikhi [80], a higher current density causes a non-uniform distribution of the current density affecting cell performance. However, a higher electrolyte flow rate could compensate and make current density more uniform. In this study, flows were limited by the pump capacities, therefore that variable could not be investigated. Chikhi [80] also showed that NaOH concentration has no influence on the current density distribution. In this study, black liquor and NaOH streams were fed in a co-current flow into the cell. Operating at counter-current flow (BL and NaOH solution) can help to reduce or eliminate non-uniformities of current densities [80].

Over the experimental program, the current density was varied from 1.5 to 3.9 kA/m^2 and results compared at two caustic soda concentrations: 7.25 and 8.9 %. The impact of current density on cell voltage shows a linear relationship for both concentrations (Figure 9.7). At 7.25 % NaOH strength, increasing the current density by a factor of 2.6 increases the voltage by only 60%. A similar result occurred at 8.9 % NaOH where the voltage increased by 50%. We also observed that the cell voltage is lower at 8.9 % NaOH rather than 7.25 % partly due to a higher conductivity from the higher NaOH concentration.

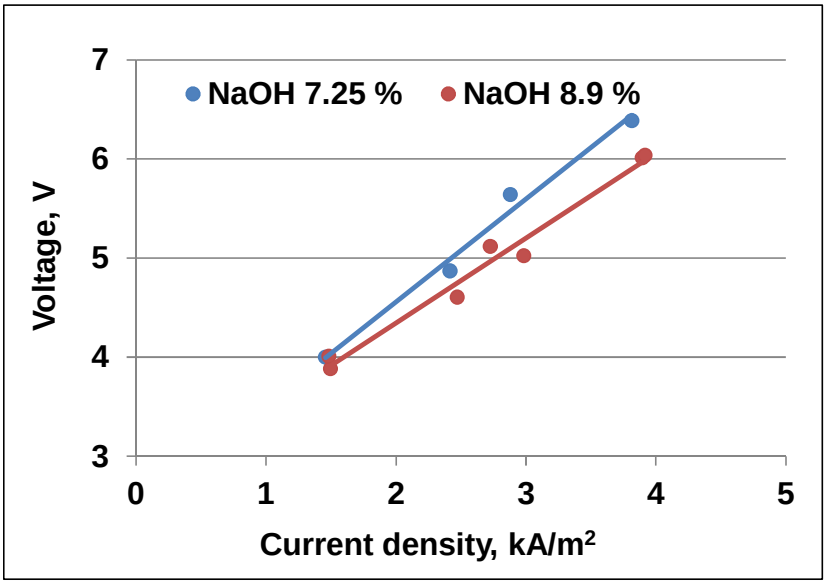

Figure 9.7 : Effect of current density and NaOH strength on cell voltage at pH 9.0 and 70°C.

The experimental results with the FM-21cell show that the current efficiency tends to increase with current density (Figure 9.8). The vertical and horizontal margins of error were computed from the error bar functionality provided by Excel software. They are based on the standard deviation of experimental measurements at a 95 % confidence interval. In previous work with the ELSEP cell, the current efficiency was decreasing [11] above 1.25 kA/m^2. It is important to note that both cell designs and particularly the anode compartmens are entirely different. The ELSEP [50-Herron] cell contains 10 tubular anodes of 2.5 cm diameter and spaced out by 2.5 cm when the FM-21 contains 228 thin lanterns spaced out by 2.2 mm. These specific configurations have an impact on process performance. The cell configuration influences current distribution and performance [80]. It was reported that the ELSEP would benefit from using smaller diameter anodes in terms of current and potential distributions well known to affect performance [85]. Based on the numerous studies reported with the FM-21 unit, it is assumed that the cell design was optimized for delivering a better performance at a higher current density.

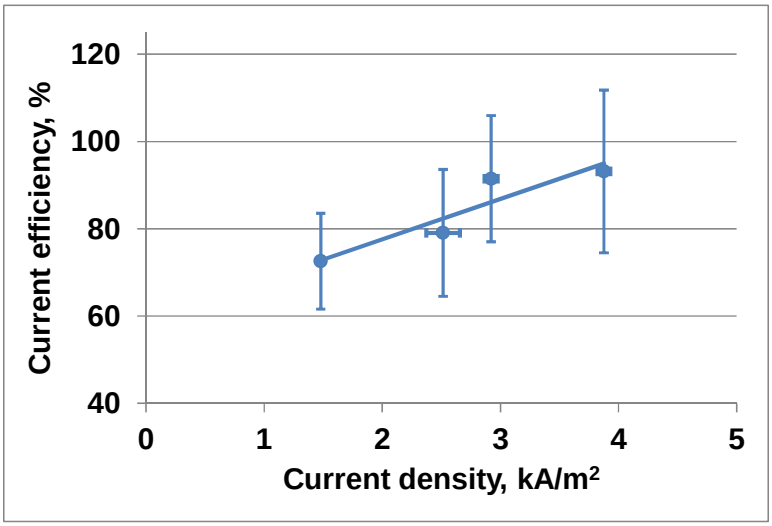

Figure 9.8 : The effect of current density on current efficency at 8.4 % NaOH

Despite the fact that the current efficiency increases with current density, the energy consumption increases (Figure 9.9) most likely due to a higher cell voltage drop that counteracts the benefit of a better current efficiency.

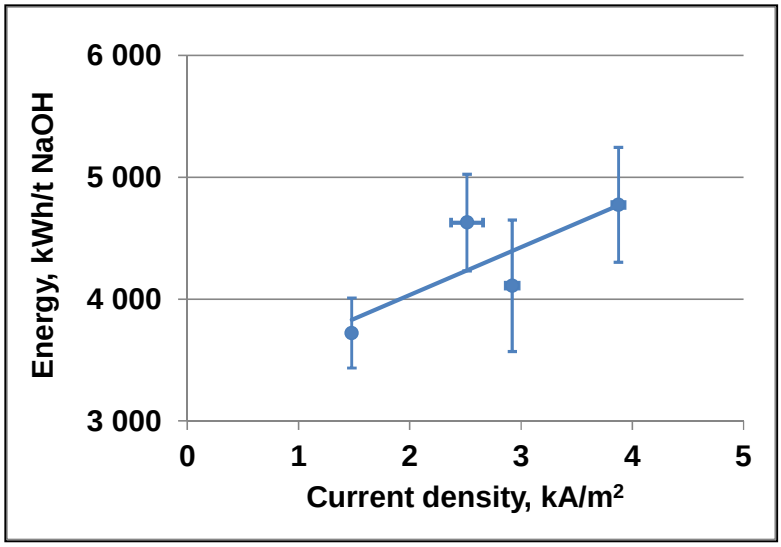

Figure 9.9 : The effect of current density on energy consumption at pH 9.0 while making 8.4 % NaOH

As expected, more black liquor can be treated at a higher current density, which is in agreement with a higher current efficiency and higher caustic soda production rate (Figure 9.10), because more current is supplied as a driving force per specific area. In terms of energy, operating at a lower current density consumes less kWh per liter of BL treated or per kg of NaOH produced, which is in agreement with our conclusion from a previous laboratory study [11].

The higher the productivity, the smaller the anode and membrane area requirements. Therefore, fewer cells are required thus reducing the capital cost required for a given installation capacity. However, the optimum operating conditions will be determined based on the most economical situation taking into account the best combination of productivity and energy consumption. The economical analysis of the proposed process was beyond the scope of this study.

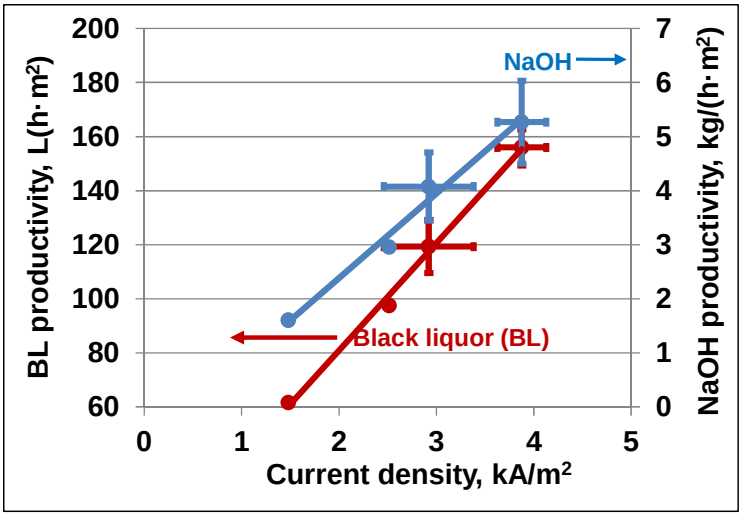

Figure 9.10 : The effect of current density on NaOH and BL productivities at pH 9.0, 70 °C while making 8.4 % NaOH

9.4.5 Effect of temperature

The effect of temperature on process performance was investigated in the range of 63 to 71 °C. The process performance will definitely be better at a higher temperature, however, it is recommended by the anode manufacturer to operate at a maximum of 70 °C to prolong life of the anode coating. Figures 9.11 shows the cell voltage as a function of BL temperature and Figure 9.12 indicates the cell voltage as a function of the temperature difference between BL and caustic soda stream under specific test conditions.

The cell voltage (Figure 9.11) dropped when the temperature was increased from 63 to almost 70 °C regardless of the the current density and NaOH strength. The main reason for the cell voltage reduction is the higher conductivities of the solutions (black liquor and NaOH) at higher temperatures. However, above 70 °C, the results show an increase in voltage, which seems to be contradictory. Indeed, a previous study [11] at laboratory scale had shown a progressive voltage reduction when temperature was increased from 60 °C to slightly above 83 °C. The only explanation for a higher voltage above 70 °C is cumulative fouling of the anode compartment over the experimental program caused by lignin precipitation, especially at lower temperatures, that might have increased the cell resistance thus overriding the benefit of a higher temeprature. A temperature difference between the anolyte and the catholyte (Figure 9.12) was experienced. That situation could have benefited the process performance, but unfortunately it was not

possible to confirm that benefit of running the catholyte (NaOH) at a higher temperature than the anolyte as proposed by Lipsztajn et al. [87].

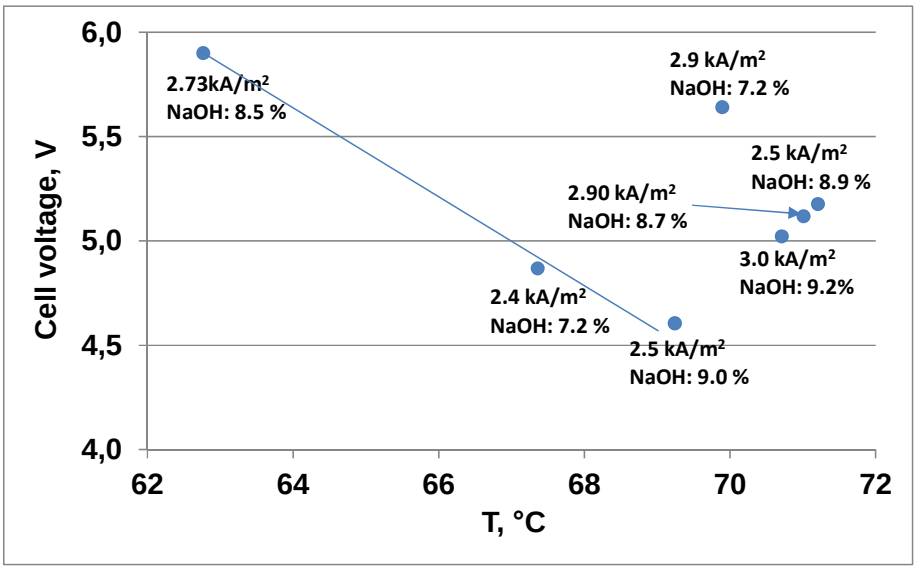

Figure 9.11 : The effect of temperature on cell voltage at pH 9.0

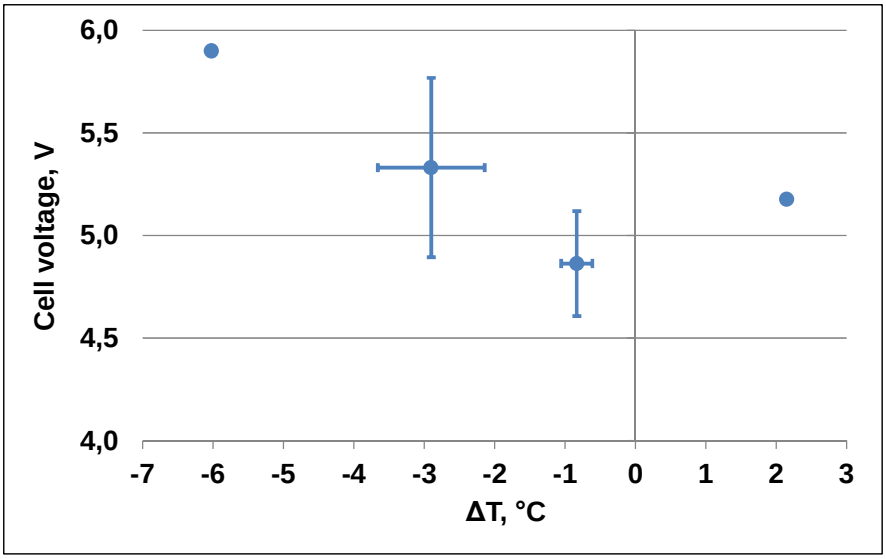

Figure 9.12 : Cell voltage as a function of a temperature differential between

the anolyte (pH 9.0) and the catholyte (8.4 % NaOH) at 2.7 kA/m^2

As shown in the correlation matrix (Table 9.2), the correlation coefficient between temperature and current efficiency is weak (R=0.46). In fact, no conclusion can be drawn on the effect of temperature on current efficiency in the range of NaOH strength tested (Figure 9.13). A large

variation from 65 % to above 100 % was observed at similar operating conditions, which makes it impossible to quantify with statistical significance the effect of temperature in the range studied based on the limited number of repeats performed. Much more repeats would have been required. In an earlier study, it was shown that current efficiency was improving with temperature, especially at higher caustic soda (10.2 %) [11].

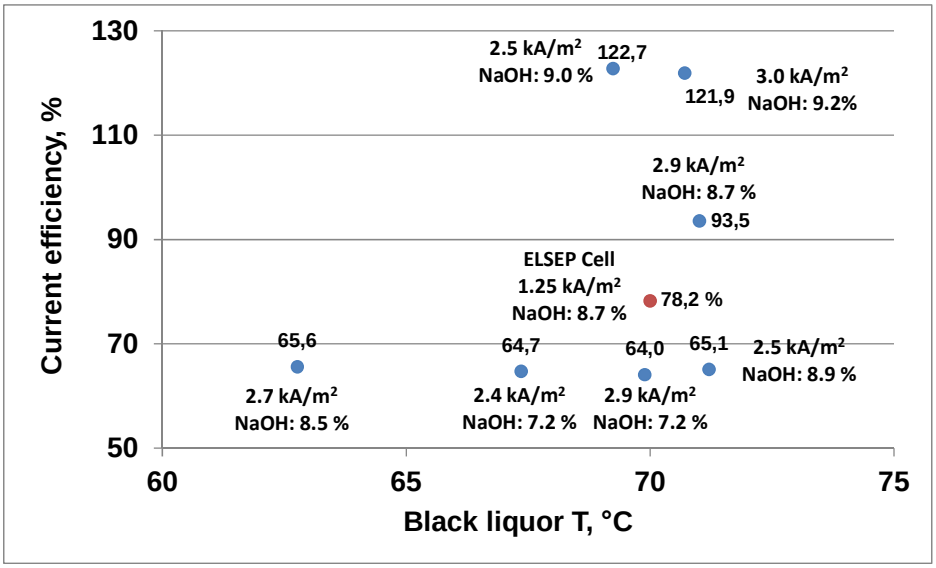

Figure 9.13 : Current efficiency as a function of BL temperature at pH 9.0

Regarding the effect of temperature on energy consumption, Figure 9.14 shows a higher energy consumption at a lower temperature and is especially elevated at 63 °C (6 200 kWh/t NaOH). Firstly, at a lower temperature the conductivities of both streams are lower contributing to a higher cell voltage. Secondly, it is important to mention that at a lower temperature the solubility of lignin is reduced and the possible precipitation of lignin might have caused fouling of the anode compartment therefore contributing to the increase in cell voltage and energy consumption. As the temperature increases, it is likely expected that some of the precipitated lignin have redissolved in the liquor thereby reducing compartment resistance combined with better conduction for the solutions.

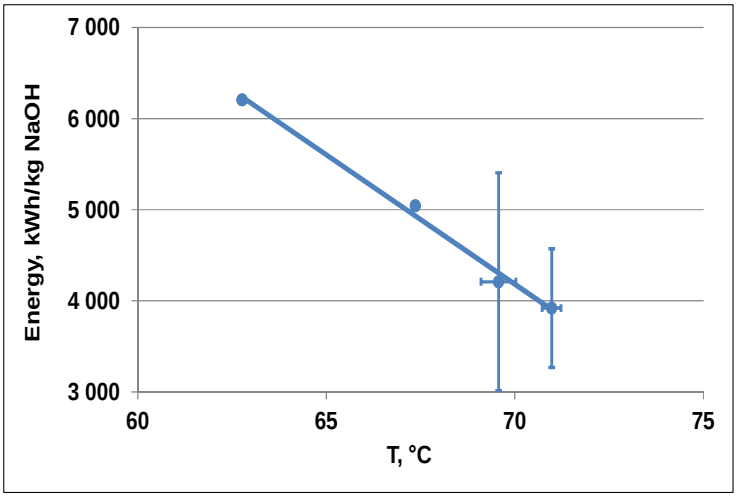

Figure 9.14 : Energy consumption as a function of BL temperature (pH 9.0), 2.7 kA/m^2 while making 8.4 % NaOH

Despite the fact that it was not possible to reach a conclusion on the effect of temperature on current efficiency, the effect on productivity performance was significant with correlation coefficients of 0.83 and 0.96 for NaOH and black liquor productivities, respectively. Both productivities increased with temperature (Figure 9.15), which is in agreement with previous work [11]. There is a net productivity benefit by operating at 70 °C in comparison to the low 60's. It is, however, valuable to mention that running at lower temperature will extend the coating of the anode and reduce operating costs.

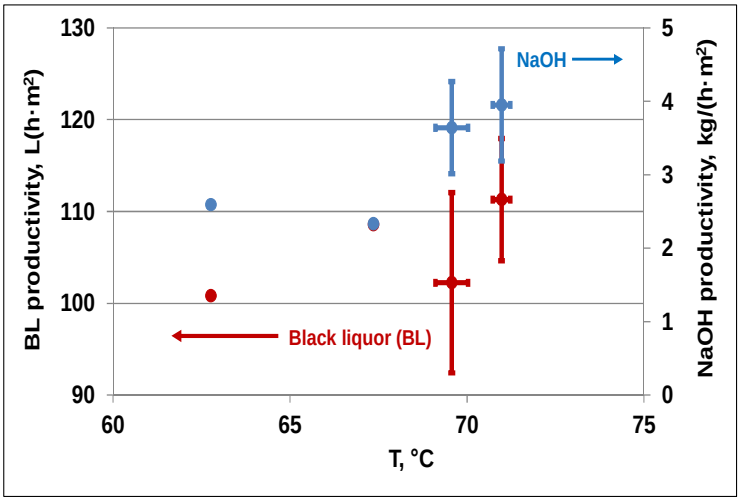

Figure 9.15 : Process productivity as a function of BL temperature (pH 9.0), 2.7 kA/m^2, 8.4 % NaOH

9.5 Conclusions and discussions

This study demonstrated the technical feasibility of the electrolytic treatment of 30 % solids black liquor from a kraft mill using the commercial FM-21 cell. The FM-21cell, although developed initially for the chlor-alkali industry, has the advantage of being versatile and commercially available.

Firstly, a batch of black liquor was electrolyzed to reduce pH from 12.5 to 9.0 at which lignin will precipitate. Then, the cell was operated in a feed and bleed mode to study the impact of (1) current density from 1.5 to 3.9 kA/m^2, (2) NaOH strength from 5.4 to 9.5 % and (3) temperature from 62 to 71 °C. The best productivity achieved in terms of black flow treated was 171 L/(h·m^2) while running at 3.9 kA/m^2 and about 70 °C. At these conditions, the cell was producing 6.0 kg of NaOH/(h·m^2) at 5 % strength and the energy consumption was estimated at 4 030 kWh/t NaOH.

The experimental results with the FM-21 cell were compared satisfactorily with those obtained with the ELSEP laboratory cell. The limiting current density with the FM-21 cell was determined to be 3.2 kA/m^2 when operating at pH 9.0 and 70 °C. At pH 9.0, the resistance of the FM-21 (1.56 Ω/m^2) is approximately 14 % higher due in part to thicker compartment channels (0.55 cm) compared to the ELSEP (0.4 cm). The limiting current density could be increased by increasing both flows, the black liquor and caustic soda stream.

During the experimental program, the cell was operated for a total of 38 hours with interruption at the end of the day. The demonstration was a successful experience deriving from the minor modification of the feed ports of the anolyte compartment. However, given the harsh conditions of black liquor and the potential of lignin precipitation and fouling of the anode, it is recommended to perform backwashing of the anode compartment on a regular basis with the caustic soda produced which can be diluted down to pH 11.0 in order to minimise the quantity used. At that pH, the precipitated lignin will dissolve restoring cell performance and preventing severe long-term fouling of the anode compartment.

It can conclude that the tests performed with the FM-21 cell made it possible to advance the technology to the point of pre-commercialization. Therefore, it is recommended that the FM-21 cell be used for the electrolysis of black liquor to precipitate lignin in a kraft mill taking into

account the minor modification of the anode compartment. However, the FM-1500 and the BICHLOR models from the same company, which are improved versions of the FM-21, should be considered as candidates as well. The FM-1500 offers a larger capacity than the FM-21 and the BICHLOR has the advantage of having modular compartments that can be removed from the electrolysers without affecting the others.

9.6 References

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CHAPITRE 10 DISCUSSION GÉNÉRALE

La production de pâte de plusieurs usines kraft est limitée par la capacité de la chaudière de récupération et/ou l'atelier de caustification due à une surcharge thermique et chimique respectivement. De plus, l'industrie des pâtes et papiers s'intéresse à développer de nouveaux marchés basés sur la production de produits à valeur ajoutée tel que la lignine dont la valeur actuelle est strictement énergétique pour remplacer les combustibles fossiles. L'extraction de lignine représente une opportunité unique pour améliorer la situation financière d'une installation existante. Extraire la lignine est actuellement la pratique la plus courante et la plus efficace pour désengorger la chaudière de récupération en réduisant la charge thermique. Tel que décrit dans cette thèse, la lignine peut être extraite basée sur une approche chimique mais cette technologie possède plusieurs limitations dont plusieurs peuvent être éliminées par une approche électrochimique.

En effet, la récupératin de lignine peut aussi être effectuée de façon électrochimique en utilisant l'électricité de façon judicieuse offrant de nombreux avantages au point de vue environnental et énergétique. À date, aucune étude n'a été effectuée permettant de fournir les données nécessaires pour le design et l'intégration judicieuse en usine de la technologie d'électrolyse de la liqueur noire. Cette présente étude porte sur le développement d'un procédé électrolytique comme moyen électrochimique de produire de la lignine à partir de la liqueur noire d'une usine de pâte kraft.

Les articles 1 et 2 ont couvert l'aspect des réactions chimiques qui prennent place lors de l'électrolyse de la liqueur noire et des phénomènes de transfert de masse à travers la membrane alors que l'article 3 a consisté à l'optimisation des conditions d'opération du procédé électrolytique à l'échelle de laboratoire. L'article 4 comprend la récupération de la lignine de la liqueur électrolysée incluant les étapes de coagulation, de précipitation, de filtration et de lavage de la lignine électrolysée. Finalement, l'article 5 confirme la faisabilité technique du procédé d'électrolyse de la liqueur noire à l'échelle commerciale. La présente discussion examine de façon générale, les principaux résultats, les limitations, les connections entre les différentes sections et les avantages de la technologie proposée ainsi que les prochaines étapes pour l'intégration en usine.

Dans l'article 1, l'analyse des résultats des essais expérimentaux ont permis de conclure que le diamètre des anodes de la cellule devraient être nettement inférieur à 1.0 cm afin d'uniformiser la

distribution de courant le long de la cellule. Cette observation a conduit à la recommendation de d'effectuer des essais avec la cellule électrolytique commerciale FM-21 qui est équipée d'anodes de type lanterne de 2.2 mm. De plus, il a été démontré que les sulfures présents dans la liqueur noire étaient oxydés par l'oxygène produit à l'anode. Cet effet est bénéfique convertissant ceux-ci en un produit plus stable (Thiosulfate) évitant la génération de sulfure d'hydrogène toxique lors du lavage acide de la lignine. D'autre part, l'étude de la distribution du voltage selon les composantes individuelles de la cellule d'électrolyse a conduit à la recommendation d'améliorer la conductivité de la liqueur noire en ajoutant du sulfate de sodium afin de réduire la consommation d'énergie.

L'article 2 démontre clairement que l'électrolyse de la liqueur noire ne devrait pas être effectuée à un pH acide. Il est fortement souhaitable de maintenir le pH alcalin pour protéger la membrane contre la précipitation de métaux divalents afin de prolonger sa durée de vie. Il a été démontré que si le pH est maintenu à 9.0, environ 30 % du sodium doit être extrait de la liqueur noire. Ce sodium est converti en soude caustique allégeant la charge au système de caustification dont la capacité est parfois limitée.

L'article 3 qui a consisté à l'optimisation de l'électrolyse de la liqueur noire, confirme que d'effectuer l'électrolyse de la liqueur noire à un pH alcalin (9.0) tel que recommendé antérieurement est aussi très favorable du point de vue énergétique. À ce pH, la consommation d'énergie est minimale. L'efficacité du procédé est indépendante de la source de liqueur qu'elle provienne de bois résineux ou de bois feuillu, qu'elle soit oxydée ou pas rendant le procédé plus versatile. L'addition de sulfate de sodium tel que recommendé est bénénifique pour la performance du procédé tant du point de vue productivité et de la consommation d'énergie.

L'article 4 démontre clairement que l'approche électrolytique (pH 9.0) offre un taux de récupération de lignine (68 %) semblable aux approches chimiques utilisant l'acide sulfurique et le CO_2. De plus, il a été démontré que la technologie proposée n'affecte pas le rapport Na/S des liqueurs de l'usine. L'addition de sulfate est bénéfique non seulement à l'étape d'électrolyse mais aussi pour l'étape de coagulation. En effet, le taux de filtration augmente par un facteur de 7.5 lorsque que 120 g/L de sulfate de sodium est ajouté à la liqueur. Un temps de coagulation de 4-5 h est bénéfique. L'addition de sulfate avec un temps de coagualtion prolongé donne un taux de filtration nettement supérieur à celui de la technologie de CO_2. Il est prévu que plus de 90 %

du combustible fossil du four à chaux peut être remplacé par de la lignine qui a été soumise à deux étapes de lavage. La récupération de la lignine par filtration est proposée par rapport à d'autres techniques de séparation dû à la familiarité de cette opération dans les usines kraft.

L'article 5 confirme la performance du procédé utilisant la cellule commerciale FM-21 développée pour l'industrie du chlor-alcali. La cellule doit être opérée à une densité de courant inférieure à 3.2 kA/m^2 et une température de 70 ºC pour maximiser la durée de vie des anodes.

Du point de vue environnemental, ce procédé réduit considérablement les rejets aux effluents d'un atelier de lignine par rapport à l'approche chimique en accord avec les critères du développement durable. De plus, les produits chimiques requis au lavage de la lignine sont produits sur place à partir du sulfate de sodium.

Au point de transfert technologique, il est primordial d'effectuer des bilans massique et énergétique de l'intégration dans une usine typique et de considérer de contrôler le procédé à l'aide de sondes de conductivité plutôt que de pH, ces premières étant plus robustes et résistantes dans un milieu agressif comme la liqueur noire.

L'économique du procédé repose sur une augmentation de production de pâte et sur la valeur accordée à la lignine. Dans cette étude, la valeur de la lignine est principalement basée sa valeur calorifique pour remplacer le combustible fossil du four à chaux. Cependant, cette lignine peut être utilisée comme matière première pour l'industrie chimique telle que la fabrication de polyuréthane ou autres produits chimiques. Il est impératif de positionner cette nouvelle technologie par rapport à l'approche chimique conventionnelle utilisant le CO_2 tant du point de vue économique que du point de vue opérationnel.

CHAPITRE 11 CONCLUSION ET RECOMMANDATIONS

11.1 Conclusion

L'initiative de bioraffinage fait partie de la feuille de route pour capturer les avantages naturels de l'industrie des pâtes et papiers du Canada. Cette industrie est constamment à la recherche de nouvelles sources de revenus visant en autres la production de bioproduits à valeur ajoutée dont la lignine. L'approche électrochimique de récupération de lignine considérée comme de seconde génération par rapport à l'approche chimique utilisant du CO_2 et de l'acide sulfurique s'inscrit dans le contexte du développement durable favorisant la production de produits chimiques localement minimisant l'empreinte environnementale. Le traitement électrolytique de la liqueur noire pour la production de lignine offre des opportunités uniques, d'abord pour l'industrie du bioraffinage en émergence et pour l'amélioration des usines de pâtes kraft existantes dont l'augmentation de production de pâte et la récupération de soude caustique. Cette approche de traitement électrolytique de la liqueur noire ne nécessite aucun agent acidifiant de source externe et ne génère aucun effluent additionnel. La technologie peut fournir de la lignine et de la soude caustique à une bioraffinerie basé sur l'utilisation judicieuse de l'électricité pour réduire le pH de la liqueur noire au point de précipitation de la lignine tout en produisant de la soude caustique. L'acide sulfurique nécessaire au lavage de la lignine provient du sulfate de sodium déjà présent dans l'usine et soumis à une étape d'électrodialyse à membranes bipolaires. Cette étape permet de recycler les eaux de lavage sans affecter le rapport de la teneur en sodium et soufre de la liqueur de cuisson.

Cette étude a démontré la faisabilité technique et la robustesse de l'application de la technologie d'électrolyse au traitement de la liqueur noire de l'échelle de laboratoire jusqu'à à la mise à l'échelle utilisant avec succès la cellule électrolytique commerciale FM-21 fabriquée par INEOS.

D'abord, les réactions fondamentales d'électrochimie lors du traitement de la liqueur noire ont été élucidées à l'aide de la cellule de laboratoire. La membrane agit comme milieu sélectif pour les ions sodium qui se déplacent de la liqueur noire dans le compartiment anodique vers le compartiment cathodique sous l'influence du champ électrique pour y former de la soude caustique. Les principales réactions comprennent la décomposition de l'eau et l'oxydation

avancée des composés sulfureux à l'anode et la conversion du carbonate de sodium en bicarbonate et éventuellement en dioxyde de carbone selon le pH final du traitement.

Il a été démontré par modélisation que la densité de courant dans la cellule de laboratoire équipée d'anodes tubulaires le long de la cellule présentant un profil sinusoïdal et pouvait être améliorée. On a observé un maximum de densité de courant vis-à-vis de la partie de la surface de l'anode tout près de la membrane et un minimum dans les sections entre les anodes. Dans le but de d'uniformiser la densité de courant en diminuant cette oscillation, il est proposé de réduire le diamètre des anodes permettant alors de mettre plus d'anodes offrant ainsi plus de surface de réaction par unité de longueur.

L'analyse de la contribution des différentes composantes de la cellule a révélé que la réaction de décomposition comptait pour 48 % du voltage total suivie de la surtension des électrodes à 21 %. La perte ohmique des électrolytes (liqueur noire et soude caustique) et des membranes est estimée à 25.6%, 20.1% and 5.5 % respectivement. La consommation énergétique du procédé bénéficierait grandement de matériaux d'électrode offrant une meilleure surtension et d'une conductivité bonifiée de la liqueur noire.

Les phénomènes de transport de masse lors du traitement électrolytique de la liqueur noire ont été élucidés. La membrane agit comme milieu sélectif pour les ions sodium qui se déplacent de la liqueur noire dans le compartiment anodique vers le compartiment cathodique sous l'influence du champ électrique pour y former de la soude caustique. Une solution analytique simplifiée de l'équation de Nernst-Planck a été appliquée pour développer le profil de la concentration des ions Na^+, H^+ ainsi que le profil du pH à travers la membrane. La concentration des ions Na^+ dans la membrane se maintient au même niveau que dans la liqueur noire sur presque toute l'épaisseur de la membrane. Et puis, elle s'ajuste en fin de course au niveau de la concentration de sodium dans la soude caustique, qu'elle soit plus élevée ou plus faible que celle dans la liqueur noire. Le profil du pH affiche une forme semblable. Lorsque le pH de la liqueur noire traitée est légèrement acide (pH 6.0), la membrane opère dans un état acide sur presque toute la profondeur dans la membrane. A l'approche de la surface en contact avec la soude caustique, le pH devient neutre. Cette situation peut être critique car les ions divalents en solution pourraient précipiter et endommager la membrane. Il est alors fortement recommandé de maintenir la liqueur noire alcaline en gardant le pH au-dessus de 8.0-9.0.

Lors du traitement électrolytique de la liqueur noire à pH 9.0, correspondant au point désiré de précipitation de la lignine, le taux d'extraction du sodium a été d'environ 30 %. Celui-ci dépend évidemment de l'alcalinité de la liqueur noire, plus elle contient de sels alcalins, plus il faut extraire de sodium pour atteindre la cible de pH.

Le traitement électrolytique de la liqueur noire a été soumis à un programme d'optimisation des principales conditions d'opération utilisant différents types de liqueur. Les résultats ont été soumis à une analyse statistique pour déterminer l'effet significatif ou pas de certains paramètres sur la performance du procédé.

La densité de courant est la deuxième plus importante variable après le pH affectant la performance du procédé en termes de consommation d'énergie et, de productivité de soude caustique et de lignine par unité de surface. Selon les essais en laboratoire et dans la plage de densité de courant investiguée, il est recommandé d'opérer à la densité de courant maximale testée soit 1.89 kA/m^2 ou supérieure avec production de soude caustique à 10% de concentration. D'ailleurs, sous ces conditions expérimentales, il ne semble pas y avoir de gain à opérer à une plus basse concentration.

En regard de la performance énergétique, il est recommandé d'opérer à pH 9.0 pour minimiser la consommation d'électricité par tonne de lignine récupérée. De plus, en maintenant le pH de la liqueur noire alcalin, la membrane opère entièrement dans un état alcalin éliminant alors le potentiel de précipitation de cations divalents protégeant ainsi la membrane et assurant une durée de vie prolongée. Étant donné les bénéfices de performance très limités d'opérer à 80 °C versus 70 °C, il est recommandé de suivre l'avis du le manufacturier d'anodes d'opérer à 70 °C contribuant à prolonger leur durée de vie.

Il a été démontré que sous les conditions testées, il n'y a pas de différence significative dans la performance du procédé lors du traitement de la liqueur noire de bois résineux et de feuillus et entre la liqueur noire oxydée et non oxydée malgré des différences significatives dans la composition et la concentration de certains composés majeurs.

De façon inattendue, le nombre d'anodes dans la cellule de laboratoire qui a variée de 4 à 10 a dévoilé un impact statistiquement significatif sur l'efficacité de courant, et ce résultat a été confirmé par une analyse de variance. La seule explication plausible pourrait être l'influence de cette variable sur la distribution de courant de la cellule affectant l'efficacité de courant.

L'addition de sulfate de sodium à la liqueur noire et que l'on retrouve en abondance dans une usine kraft améliore la performance globale du procédé : une meilleure productivité et une réduction de la consommation d'énergie ce qui aura pour effet de diminuer le nombre de cellules requises et conséquemment de réduire le coût en immobilisations et les coûts d'opération.

La filtrabilité représente un défi important dans le design d'un atelier de production de lignine. Cette étude a démontré la faisabilité technique de filtrer la lignine électrolysée avec succès et de la laver pour obtenir un produit de qualité acceptable pour une bioraffinerie.

Les résultats expérimentaux ont montré que le taux de filtration de la lignine est relativement faible (64 kg/(h·m^2), mais que l'addition de Na_2SO_4 (120 g/L) dans l'étape de coagulation accroît la filtration par un facteur d'au moins 7.5. Un temps de coagulation prolongé (4-5 h) améliore le taux de filtration suite à la formation de gros flocs et, produit un gâteau de lignine avec une plus haute teneur en solides réduisant ainsi l'énergie requise au séchage. Des taux de filtration de (670 et de 770 kg de lignine/(h·m^2)) ont été obtenus pour la suspension de lignine et de lavage, respectivement. Ces valeurs sont nettement supérieures aux taux de filtration du procédé de précipitation de la lignine au CO_2. Le traitement électrolytique bénéfice de la super-oxydation de la liqueur noire à l'anode bonifiée par l'addition de sel, deux techniques connues pour améliorer la filtrabilité.

Le procédé électrolytique offre un taux de récupération de lignine semblable à celui aux options chimiques utilisant le CO_2 ou l'acide sulfurique, soit près de 70%. Basée sur les résultats préliminaires, la pureté de la lignine lavée est suffisante pour fournir la matière première à l'industrie chimique entre autres la production de polyuréthane. D'autre part, étant donné la sensibilité du four à chaux au sodium, la lignine électrolysée soumise à une seule étape de lavage et contenant 0.64 % de sodium pourrait remplacer environ 50 % du combustible fossile. Cependant, il est estimé qu'une étape additionnelle de lavage permettrait de réduire suffisamment la teneur en sodium permettant de substituer presque 100 % du combustible fossile. La consommation d'électricité comprenant l'étape d'électrolyse et d'électrodialyse est estimée à 1.48 Wh/g de lignine, nettement inférieure à son pouvoir calorifique supérieur (7.0-7.5 Wh/g) offrant un bilan énergétique positif.

Suite à l'investigation et l'optimisation de l'étape d'électrolyse à l'échelle laboratoire, des essais ont été effectués avec la cellule FM-21 pour traiter la liqueur noire contenant 30 % de solides afin

de comparer sa performance avec la cellule de laboratoire. La cellule FM-21, bien qu'elle ait été développée initialement pour l'industrie du chlor-alkali, offre l'avantage d'être versatile et disponible commercialement.

Les essais d'électrolyse ont été effectués en opérant la cellule en mode d'alimentation et de purge continue (Feed and bleed). La densité de courant limite du procédé avec cette cellule se situe à environ 3.2 kA/m^2. La meilleure performance de productivité en termes de débit de liqueur noire traitée a été de 171 L/(h·m^2) basée sur la surface de membranes. Cette productivité a été obtenue à une densité de courant de 3.9 kA/m^2 légèrement au dessus de la densité de courant limite. Sous ces conditions, la cellule produisait 6.0 kg de NaOH/(h·m^2) à 5 % de concentration. L'énergie consommée a été estimée à 4 030 kWh/t NaOH. Les résultats obtenus avec cette cellule commerciale ont été comparés de manière satisfaisante avec la cellule de laboratoire bien que sa résistance électrique soit 14 % supérieure dû en partie aux compartiments anodiques et cathodiques plus épais. La limite de courant pourrait être haussée en augmentant les débits de liqueur noire et de soude caustique dans leur compartiment respectif.

La démonstration du traitement électrolytique de la liqueur noire a été effectuée avec succès grâce à une modification mineure du système de distribution de la liqueur à l'entrée du compartiment anodique. Les résultats encourageants ont permis de faire avancer la technologie proposée du niveau de laboratoire au niveau de pré-commercialisation. Il est alors recommandé d'utiliser la cellule FM-21 pour traiter la liqueur noire pour la précipitation de la lignine en considérant la modification mineure apportée au design.

11.2 Contribution de cette recherche

Les principales contributions de cette recherche se résument ainsi :

- Élucidation des principales réactions fondamentales qui se produisent lors de l'électrolyse de la liqueur noire.
- Analyse détaillée de la contribution des différentes composantes au voltage total de la cellule avec recommandation pour amélioration.
- Application du modèle simplifié de l'équation de Nernst-Planck pour déterminer le profil des ions et du pH à travers la membrane menant à la recommandation de maintenir la liqueur noire à un pH alcalin.

- Optimisation du traitement électrolytique de la liqueur noire et détermination des meilleures conditions d'opération.
- Amélioration de la filtrabilité de la lignine par rapport aux options chimiques.
- Identification du mode de filtration de la lignine et détermination de l'épaisseur maximale du gâteau pour une meilleure filtrabilité.
- Détermination du pH optimal (9.0) de l'électrolyse pour la consommation minimale d'énergie par tonne de lignine récupérée.
- Avancement du niveau de maturité technologique au stade de pré-commercialisation en démontrant avec succès la faisabilité technique de l'électrolyse de la liqueur noire utilisant la cellule commerciale FM-21.
- Démontration très claire des bénéfices de l'option électrolytique par rapport à l'approche chimique.
- Démontration de certains aspects du développement durable de la technologie proposée.

11.3 Recommandations

Bien que cette étude ait couvert en détails les conditions d'opération des principales étapes de la technologie, l'impact de son intégration dans une usine de mise en pâte kraft nécessite une étude approfondie comprenant les bilans massique et énergétique. De plus, une analyse économique permettra de positionner ce procédé parmi les autres options de production de lignine à partir de de la liqueur noire.

11.3.1 Aspect opérationnel de la technologie

Les résultats des essais avec la cellule de laboratoire ont permis de conclure qu'il serait bénéfique de réduire le diamètre des anodes. Cette conclusion a conduit à recommander la cellule FM-21 équipée d'électrodes formées de fines lamelles appelées "lanternes". Dans cette étude, la cellule a été opérée pendant un nombre total de 38 h. Il est essentiel d'effectuer des essais prolongés dans une étude de démonstration en usine pour confirmer l'opérabilité en continu amenant ainsi la technologie au stade commercial. Cette démonstration pourrait inclure le développement d'une méthode de nettoyage du compartiment anodique par un lavage à la soude caustique diluée soit 0.1 N correspondant à un pH de 11.0 qui a le pouvoir de solubiliser la lignine. Un nettoyage à la soude caustique est une pratique courante pour toute technologie membranaire.

Il est recommandé d'opérer l'étape d'électrolyse à un pH alcalin, de préférence 9.0, d'abord pour minimiser l'énergie électrique consommée par tonne de lignine récupérée et puis pour prévenir la précipitation dans la membrane d'ions divalents qui sont présents dans la liqueur. Cette valeur de pH pourrait varier selon les caractéristiques de la liqueur noire spécifique à chaque usine.

Les unités d'électrolyse de la liqueur noire et d'électrodialyse à membranes bipolaire du sulfate de sodium produisent de la soude caustique plutôt diluée (5-10%). Il est de pratique courante dans une usine de diluer la soude caustique concentrée (50 %) livrée à l'usine avec de l'eau pour accommoder les besoins de l'usine dont la concentration varie de 5 à 10 %. Il est donc recommandé d'utiliser la soude caustique à faible concentration en remplacement de l'eau permettant d'améliorer le bilan d'eau.

Tous les essais de filtration ont été effectués avec un montage expérimental équipé d'une pompe à vide. Il est recommandé de considérer un système à pression tel qu'utilisé pour l'option chimique LignoForce™ connu pour opérer à des pressions plus élevées et capable de livrer de meilleurs taux de filtration. Cependant, il faut s'assurer de ne pas dépasser la pression qui pourrait rendre le gâteau compressible.

Il est essentiel d'effectuer des tests de durabilité des anodes en laboratoire. Celles utilisées lors de cette étude étaient composées d'une base de titane recouverte d'oxyde d'iridium. Ces matériaux sont très dispendieux et une durée de vie prolongée favorise la rentabilité du procédé.

11.3.2 Bilan massique

La technologie a été développée avec la perspective de développement durable et l'objectif de recycler les eaux de lavage de la lignine sans affecter le bilan Na/S. Il est recommandé de développer un modèle de simulation de l'intégration de la technologie dans une usine kraft afin de déterminer le bilan massique détaillé des composantes majeures de liqueurs noire et de cuisson (Solides, eau, sodium et soufre) à l'aide de logiciels tels que CHEMCAD, ASPEN ou autres et d'identifier le potentiel d'engorgement des unités de production et celles du système de récupération spécifique qui sont spécifiques à chaque usine.

11.3.3 Bilan énergétique

Il est attendu que l'approche électrochimique consomme plus d'électricité que l'approche chimique. Malgré tout, il semble possible que le bilan énergétique global de l'usine soit positif

avec l'intégration d'un atelier de production de lignine. Sous certaines conditions d'opération, la consommation d'électricité par tonne de lignine récupérée est nettement inférieure son pouvoir calorifique supérieur. De plus, selon la littérature, il semble possible de rétablir le bilan énergétique en brûlant la lignine dans des unités de combustion autres que la chaudière de récupération (chaudière à biomasse) afin d'obtenir un meilleur rendement thermique. Donc, il serait primordial d'intégrer l'aspect énergétique dans le modèle de simulation mentionné ci-haut afin de déterminer les besoins additionnels d'énergie de source externe à l'usine, si nécessaire.

11.3.4 Aspect économique

L'aspect économique de l'intégration d'un atelier de production de lignine est déterminant pour l'implantation commerciale. La valeur accordée à la lignine repose sur le prix du marché ou sa valeur énergétique. Une analyse de sensibilité pourrait comprendre entre autres les variables principales suivantes :

(1) le coût en immobilisation,

(2) la valeur de la lignine

(3) la valeur d'une tonne additionnelle de pâte, si une augmentation de production de pâte est considérée,

(4) le coût de l'électricité,

(5) la densité de courant de l'étape d'électrolyse, paramètre crucial d'un procédé électrochimique

(6) le prix des produits chimiques (acide sulfurique et soude caustique)

(7) la durée de vie des électrodes et des membranes.

Une analyse économique comparative permettrait de positionner la technologie électrolytique par rapport aux autres options de production de lignine.

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