

5-2003

# Relationship between Alkaline Pulp Yield and the Mass Fraction and Degree of Polymerization of Cellulose in Pulp

Mehmet Sefik Tunc

Follow this and additional works at: <http://digitalcommons.library.umaine.edu/etd>

 Part of the [Chemical Engineering Commons](#), and the [Organic Chemistry Commons](#)

---

## Recommended Citation

Tunc, Mehmet Sefik, "Relationship between Alkaline Pulp Yield and the Mass Fraction and Degree of Polymerization of Cellulose in Pulp" (2003). *Electronic Theses and Dissertations*. 237.  
<http://digitalcommons.library.umaine.edu/etd/237>

This Open-Access Thesis is brought to you for free and open access by DigitalCommons@UMaine. It has been accepted for inclusion in Electronic Theses and Dissertations by an authorized administrator of DigitalCommons@UMaine.

**RELATIONSHIP BETWEEN ALKALINE PULP YIELD AND THE MASS  
FRACTION AND DEGREE OF POLYMERIZATION OF CELLULOSE IN PULP**

By

Mehmet Sefik Tunc

B.S. Ankara University, 1996

A THESIS

Submitted in Partial Fulfillment of the

Requirements for the Degree of

Master of Science

(in Chemical Engineering)

The Graduate School

The University of Maine

May, 2003

Advisory Committee:

Adriaan R.P. van Heiningen, Ober Chair and Professor of Chemical Engineering

Joseph M. Genco, Professor of Chemical Engineering

David J. Neivandt, Professor of Chemical Engineering

Haixuan Zou, Post Doctoral Research Engineer

## LIBRARY RIGHTS STATEMENT

In presenting this thesis in partial fulfillment of the requirements for an advanced degree at The University of Maine, I agree that the Library shall make it freely available for inspection. I further agree that permission for "fair use" copying of this thesis for scholarly purposes may be granted by the Librarian. It is understood that any copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Signature: M. Sefik Cunn

Date: 04/21/2003

# **RELATIONSHIP BETWEEN ALKALINE PULP YIELD AND THE MASS FRACTION AND DEGREE OF POLYMERIZATION OF CELLULOSE IN PULP**

By Mehmet Sefik Tunc

Thesis Advisor: Dr. Andriaan R.P. van Heiningen

An Abstract of the Thesis Presented  
in Partial Fulfillment of the Requirements for the  
Degree of Master of Science  
(in Chemical Engineering)  
May, 2003

Wood as a raw material is generally the dominant cost factor for the production of chemical pulp. Therefore, an increase in pulp yield has a major impact on the competitiveness of a mill. In order to optimize pulp yield, for example by changing operating conditions, a mill must be able to monitor the yield accurately. However, an accurate “real-time” pulp yield measurement method is not available at the present time. Pulping yield is presently measured from the amount of pulp produced from a given quantity of wood consumed over a 3 to 6 month time frame. This method is obviously not suitable as a process optimization tool to maximize the pulp yield.

This thesis presents a yield measurement method based on a theoretical relationship between alkaline pulping yield and the mass fraction and degree of polymerization (DP) of cellulose in pulp. The relationship so-called UoM pulp yield prediction equation is derived from the cellulose mass balance and kinetics of the alkaline hydrolysis, peeling and stopping reactions of cellulose. It is validated for kraft, kraft-AQ, polysulfide and polysulfide-AQ pulping of Rock Maple, Yellow Birch, Poplar and Black Spruce.

$$\frac{1}{Y_T' G'} = \frac{1}{Y_{C,W}} + \frac{(\Delta DP)_S}{Y_{C,W}} \cdot \frac{1}{DP}$$

Kraft cooks were performed at four sulfidities, 0, 7.5, 15 and 30%, and an effective alkali (EA) charge for the hard woods of 21% (as Na<sub>2</sub>O on o.d.(oven dried) wood) and 23% for Black Spruce. Four different polysulfide cooks at elemental sulfur additions of 0, 1, 2 and 4% (based on o.d wood) to 30% sulfidity liquors were performed on all four wood species at the same H-factor and EA (Effective Alkali) charges as that of the alkaline cooks. All kraft and polysulfide cooks were also repeated the addition of 0.1 % AQ based on o.d. wood.

UoM equation contains two parameters,  $(\Delta DP)_S$  and  $Y_{C,W}$ , respectively the number of glucose units removed by secondary peeling and the cellulose mass fraction in pulp based on wood. These two parameters is not function of cooking conditions such as sulfidity but they are a function of the species used and the  $(\Delta DP)_S$  decreases with the addition of AQ.

## ACKNOWLEDGMENTS

I would like to express my deepest gratitude to my advisor Dr. Adriaan van Heiningen for his excellent and constant guidance, patience, generous support and valuable advice.

I would also like to take the opportunity to thank my other committee members Dr. Joseph M. Genco, Dr. David Neivandt and Dr. Haixuan Zou for accepting to spend their time and energy for the benefit of my thesis.

I would like to thank the Turkish Paper Foundation (SEKA) for their support. I should specially mention Dr. Yang Gao for his practical help during my experiments. I would like to thank all the graduate students as well as staff of the Chemical Engineering Department and Pilot Plant for being so nice and helpful.

I also would like to thank Charity Mitchell, Lindsay Keegan, Susan Burgess and Marybeth Allen for their help and encouragement.

I dedicate a special thank to Dana Haeger, Katharine Wormus, Tomas LeVeen and Yingfeng Shen for being close friends. I wish them all good like in their future work.

Thank you all for making those two years in Maine such an interesting experience in my life.

Finally, I would like to dedicate this thesis to my family. This work would not have been possible without the patience and everlasting support of my family whom I owe everything.

## TABLE OF CONTENTS

ACKNOWLEDGMENTS.....	ii
LIST OF TABLES.....	vii
LIST OF FIGURES.....	viii

### Chapter

1. INTRODUCTION.....	1
1.1. PULP YIELD.....	1
1.2. OBJECTIVE.....	3
2. LITERATURE REVIEW.....	4
2.1. CHEMICAL PULPING OF WOOD.....	4
2.1.1. The Kraft Process.....	4
2.1.1.1. Lignin Reactions. ....	5
2.1.1.2. Carbohydrate Reactions ....	9
2.1.1.3. Reaction Kinetics in Kraft Cooking.....	16
2.1.1.3.1. Kinetics of Lignin Reactions.....	16
2.1.1.3.2. Kinetics of Carbohydrate Reactions ....	17
2.1.2. Modified Kraft Processes.....	18
2.1.2.1. Anthraquinone Cooking ....	18
2.1.2.2. Polysulfide Cooking ....	20
2.1.2.3. Polysulfide-Anthraquinone Cooking ....	22
2.2. AVAREGE DEGRADABLE CHAIN LENGTH $\Delta DP_s$ .....	22

2.3.	PULP YIELD MEASUREMENT METHODS.....	27
2.3.1.	Direct Pulp Yield Measurement Methods.....	27
2.3.1.1.	Inventory Measurement Method .....	27
2.3.1.2.	Basket Method .....	27
2.3.2.	Indirect Pulp Yield Measurement Methods.....	28
2.3.2.1.	Yield-Kappa Number Relationship .....	28
2.3.2.2.	Mannan Method .....	29
2.3.2.3.	The Cellulose and Carbohydrate- Lignin Methods (Y <sub>cell</sub> Method).....	29
2.3.2.4.	Marcoccia Equation .....	31
3.	THEORY.....	33
3.1.	DERIVATION OF THE UNIVERSITY OF MAINE (UoM) PULP YIELD PREDICTION EQUATION.....	33
3.2.	DEGREE OF POLYMERIZATION DERIVED FROM THE PULP INTRINSIC VISCOSITY.....	36
3.3.	CALCULATION PROCEDURE OF CARBOHYDRATE CONTENT.....	36
4.	EXPERIMENTAL.....	38
4.1.	EXPERIMENTAL METHOD.....	38
4.1.1.	Kraft Cooking .....	38
4.1.2.	Kraft-AQ Cooking.....	38
4.1.3.	Polysulfide Cooking.....	39
4.1.4.	Polysulfide-AQ Cooking.....	39



4.2.	ANALYSES.....	39
4.2.1.	Kappa Number.....	39
4.2.2.	Tappi Viscosity.....	39
4.2.3.	Intrinsic Viscosity.....	39
4.2.4.	Ash.....	40
4.2.5.	Uronic Anhydride.....	40
4.2.6.	Sugar Analysis (Carbohydrate Content).....	40
4.2.7.	Extractives.....	43
4.2.8.	Total Pulp Yield.....	43
5.	RESULTS AND DISCUSSION.....	44
5.1.	ROCK MAPLE COOKING.....	44
5.1.1.	Effect of Sulfidity and Anthraquinone.....	44
5.1.2.	Effect of Polysulfide and Polysulfide-Anthraquinone.....	55
5.2.	YELLOW BIRCH, POPLAR AND BLACK SPRUCE COOKING.....	72
5.2.1.	Effect of Sulfidity and Anthraquinone.....	72
5.2.2.	Effect of Polysulfide and Polysulfide-Anthraquinone.....	83
5.3.	UoM PULP YIELD EQUATION OF ALL COOKS.....	97
5.4.	COMBINING THE YIELD EQUATION RESULTS.....	100
5.4.1.	Rock Maple.....	100
5.4.2.	Yellow Birch.....	102
5.4.3.	Poplar.....	104
5.4.4.	Black Spruce.....	106

## 5.5. APPLICATION OF U<sub>o</sub>M EQUATION TO LITERATURE

DATA.....	108
6. CONCLUSION.....	111
REFERENCES.....	113
BIOGRAPHY OF THE AUTHOR.....	119

## LIST OF TABLES

Table 3.1.	Calculation Procedure of Carbohydrate Analyses Method.....	37
Table 5.1.	$Y_{C,w}$ and $(\Delta DP)_S$ for Non-AQ and AQ Cooking of Three Hardwood and One Softwood Species.....	99
Table 5.2.	Cooking Conditions of Kraft, Kraft-AQ, PS and PSAQ Cooks of Scot Pine (Pekkala, 1986).....	109
Table 5.3.	Cooking Conditions Results of Kraft, Kraft-AQ, PS and PSAQ Cooks of Scot Pine (Pekkala, 1986).....	109

## LIST OF FIGURES

Figure 2.1.	Cleavage of $\beta$ -aryl Ether Bonds in Nonphenolic Units during Soda Pulping (Gierer, 1970).....	6
Figure 2.2.	Main Reaction of the Phenolic $\beta$ -aryl Ether Structures during Alkali (Soda) and Kraft Pulping (Gierer, 1970).....	6
Figure 2.3.	The Base-catalyzed Reaction of the Free Phenolic Phenylcoumaran Structure (1) (Gierer, 1970).....	7
Figure 2.4.	Cleavage of Methyl Aryl Ether Bonds During Kraft Pulping (Sjostrom, 1993).....	7
Figure 2.5.	Examples of Condensation Reactions during Alkali and Kraft Pulping (Gierer, 1970).....	8
Figure 2.6.	Removal of Lignin during Pine Kraft Cooks (McDonough, 1998).....	9
Figure 2.7.	Dissolution of Lignin, Glucomannan and Xylan in Kraft Pulping of Pine (Aurell and Hartler, 1965).....	10
Figure 2.8.	Yield of Carbohydrate as a Function of Lignin Yield for Different Part of Pine Wood (Virkola, 1983).....	11
Figure 2.9.	Depolymerization of Glycosidic Bonds by Alkaline Hydrolyses (Sjostrom, 1993).....	12
Figure 2.10.	Peeling Reaction Mechanism (Sjostrom, 1993) The endwise alkaline degradation (“peeling”) of 1,4- $\beta$ -D-glucan(cellulose).....	14
Figure 2.11.	Stopping Reaction (Sjostrom, 1993).....	15

Figure 2.12.	The Redox Cycle in Anthraquinone-Enhanced Kraft Pulping (Grace & Malcolm, 1989).....	19
Figure 2.13.	Effect of Anthraquinone on Mixed Southern Hardwood Soda Pulping (Waldemar, 1977).....	20
Figure 2.14.	Alkaline Degradation Mechanism of Polysaccharides (Haas, 1967).....	23
Figure 2.15.	Schematic Representation of Cellulose Degradation (Haas, 1967).....	24
Figure 2.16.	Lab Generated Pulp and Liquor Properties for Use in Calibration Curves Southern Hardwood Chips (Marcoccia, 1998).....	28
Figure 2.17.	Yield Calibration Curve, $Y_T$ versus $(^{10}\log V)/(G')^2$ (Marcoccia, 1998).....	31
Figure 3.1.	Validation of UoM Pulp Yield Prediction Equation.....	35
Figure 5.1.	Total Yield, $Y_T$ , versus Sulfidity with or without AQ addition for Rock Maple.....	45
Figure 5.2.	Kappa Number versus Sulfidity with or without AQ addition for Rock Maple.....	46
Figure 5.3.	Tappi Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking of Rock Maple.....	47
Figure 5.4.	Intrinsic Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking of Rock Maple.....	47
Figure 5.5.	Tappi Viscosity versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple.....	48
Figure 5.6.	Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple.....	49

Figure 5.7.	Lignin-free Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple.....	50
Figure 5.8.	Cellulose Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple.....	50
Figure 5.9.	Hemicellulose Yield versus Kappa Number for Kraft and Kraft-AQ of Rock Maple.....	51
Figure 5.10.	Xylan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple.....	52
Figure 5.11.	Mannan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple.....	53
Figure 5.12.	UoM Equation for Kraft and Kraft-AQ Cooking of Rock Maple.....	54
Figure 5.13.	Marcoccia Equation for Kraft and Kraft-AQ Cooking of Rock Maple.....	55
Figure 5.14.	Total Yield, $Y_T$ , versus Percentage Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple.....	56
Figure 5.15.	Kappa Number versus Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple.....	57
Figure 5.16.	Tappi Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple.....	58
Figure 5.17.	Intrinsic Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple.....	59

Figure 5.18.	Tappi Viscosity versus Kappa Number for PS and PSAQ Cooking of Rock Maple.....	60
Figure 5.19.	Total Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple.....	61
Figure 5.20.	Lignin-free Total Yield versus Kappa Number for PS and PSAQ of Rock Maple.....	62
Figure 5.21.	Cellulose Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple.....	62
Figure 5.22.	Hemicellulose Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple.....	63
Figure 5.23.	Xylan Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple.....	64
Figure 5.24.	Mannan Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple.....	65
Figure 5.25.	UoM Equation for PS and PSAQ Cooking of Rock Maple.....	66
Figure 5.26.	Marcoccia Equation for PS and PSAQ Cooking of Rock Maple.....	67
Figure 5.27.	UoM Equation for Kraft, Kraft-AQ PS and PSAQ Cooking of Rock Maple.....	68
Figure 5.28.	Xylan Mass Fraction versus 1/DP for All Cooks of Rock Maple.....	69
Figure 5.29.	Mannan Mass Fraction versus 1/DP for All Cooks of Rock Maple.....	70

Figure 5.30.	Marcoccia Equation for Kraft, Kraft-AQ, PS and PSAQ Cooking of Rock Maple.....	71
Figure 5.31.	Total Yield, $Y_T$ , versus Sulfidity with or without AQ Addition of Yellow Birch, Poplar and Black Spruce.....	73
Figure 5.32.	Kappa Number versus Sulfidity with or without AQ Addition of Yellow Birch, Poplar and Black Spruce.....	74
Figure 5.33.	Tappi Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	75
Figure 5.34.	Intrinsic Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking for Rock Maple.....	75
Figure 5.35.	Tappi Viscosity versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	76
Figure 5.36.	Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	78
Figure 5.37.	Lignin-free Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	78
Figure 5.38.	Cellulose Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	79
Figure 5.39.	Hemicellulose Yield versus Kappa Number for Kraft and Kraft-AQ of Yellow Birch, Poplar and Black Spruce.....	79
Figure 5.40.	Xylan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	80



Figure 5.41.	Mannan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	81
Figure 5.42.	UoM Equation for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce.....	82
Figure 5.43.	Marcoccia Equation for Kraft and Kraft-AQ cooking of Yellow Birch, Poplar and Black Spruce.....	83
Figure 5.44.	Total Yield, $Y_T$ , versus Percentage Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	84
Figure 5.45.	Kappa Number versus Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	85
Figure 5.46.	Tappi Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	86
Figure 5.47.	Intrinsic Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	86
Figure 5.48.	Tappi Viscosity versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	87
Figure 5.49.	Total Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	88
Figure 5.50.	Lignin-free Total Yield versus Kappa Number for PS and PSAQ of Yellow Birch, Poplar and Black Spruce.....	89
Figure 5.51.	Cellulose Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	89

Figure 5.52.	Hemicellulose Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	90
Figure 5.53.	Xylan Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	91
Figure 5.54.	Mannan Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	92
Figure 5.55.	UoM Equation for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	93
Figure 5.56.	Marcoccia Equation for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce.....	94
Figure 5.57.	Xylan Mass Fraction versus 1/DP for All Cooks of Black Spruce.....	95
Figure 5.58.	Mannan Mass Fraction versus 1/DP for All Cooks of Rock Maple.....	96
Figure 5.59.	UoM Equation for All Cooks of Rock Maple, Yellow Birch, Poplar and Spruce.....	99
Figure 5.60.	UoM Equation for All Cooks of Rock Maple.....	100
Figure 5.61.	Marcoccia Equation for All Cooks of Rock Maple.....	102
Figure 5.62.	UoM Equation for All Cooks of Yellow Birch.....	103
Figure 5.63.	Marcoccia Equation for All Cooks of Yellow Birch.....	104
Figure 5.64.	UoM Equation for All Cooks of Poplar.....	105
Figure 5.65.	Marcoccia Equation for All Cooks of Poplar.....	105
Figure 5.66.	UoM Equation for all Cooks of Black Spruce.....	106

Figure 5.67.	Marcoccia Equation for All Cooks of Black Spruce.....	107
Figure 5.68.	UoM Equation for All Cooks of Black Spruce.....	107
Figure 5.69.	Marcoccia Equation for All Cooks of Black Spruce.....	108
Figure 5.70.	UoM Equation for Kraft, Kraft-AQ, PS and PSAQ Cooking of Scot Pine.....	110

# CHAPTER 1

## INTRODUCTION

### 1.1. PULP YIELD

Since wood is the dominant cost factor for the production of chemical pulp, an increase in pulp yield has a major impact on the competitiveness of a pulp mill. However, in order to optimize pulp yield, for example by changing operating conditions, a mill must be able to monitor the yield accurately. Unfortunately, an accurate “real-time” pulp yield measurement method is not available at the present time. Traditionally, pulp yield is estimated based on wood usage and pulp sales data covering a period of 3-6 months because of the dynamic behavior of a mill operation. However, these inventory data are insensitive to yield changes occurring for brief periods, e.g., during evaluations of pulp process modifications (Easty, 1982).

There are two methods available to a pulp mill to measure the pulp yield: a direct and indirect method. The direct pulp measurement method determines the yield from direct measurements of the amount of pulp produced and the amount of wood necessary for the production. The indirect pulp yield measurement methods rely on measurements of the properties of the pulp or spent pulping liquor to determine the pulp yield using a pre-established “calibration curve”.

Direct measurement of industrial pulp yield is very difficult. For batch cooks, one can use so-called “hanging basket cooks” whereby the yield of wood chips contained in a basket is determined (MacLeod, 1987). However, this procedure requires well trained operators and scientists, and auxiliary equipment must be installed. For obvious reasons,

basket cooks can not be used for continuous digesters. In the case of continuous digesters, the yield can be determined in principle from the solids content and flow rate of the chips and pulp streams entering and leaving respectively the digester vessel. However, the imprecision of these measurements invalidates the establishment of an accurate mass flow rate balance for pulp yield purposes (van Heiningen et al., 2002)

There are several indirect pulp yield measurements methods reported in the literature. One of the indirect pulp yield measurement methods is the yield-kappa relationship. This method applies both to batch and continuous digesters. It is based on the assumption of a constant cellulose/hemicellulose/lignin relationship irrespective of cooking conditions (Easty, 1982). However, these yield-kappa number relationships generally differ between species, and may be affected by pulping conditions (McDonough, 1998). In another method (Luthe et al., 2002), use the mannan content of pulps to evaluate the yield of polysulfide and anthraquinone pulping trials. However, this technique only applies to softwoods (Easty, 1982). Another method is based on the assumption that the cellulose content based on wood remains constant during cooking. Thus by measuring the cellulose content in pulp and assuming a certain cellulose content for the original wood species (the so-called  $Y_{\text{cell}}$  value), the pulp yield can be estimated. This method by Easty (1982) is known as the  $Y_{\text{cell}}$  method. A weakness of this method is that it ignores cellulose loss during cooking by the secondary peeling reaction. Another indirect method is the determination of the pulp yield from fiber coarseness. Since there is a linear relation between coarseness and yield (Marcoccia, 1998), this method is promising. Unfortunately it is not precise due to the limited accuracy of coarseness measurements. Pulp yield can also be estimated from black liquor properties. Genco et al.

(1990) confirmed that total organic carbon (TOC) values of black liquors correlated well with pulp yields, and was a useful parameter for batch digester control. To use this method however, the pulps must have the same kappa number. Finally, Marcoccia et al. (1998) proposed that the lignin free yield was a linear function of a combined parameter containing the pulp viscosity and the cellulose content. However, this method is empirical and requires input constants (or “calibration”).

Since cellulose is a homopolymer which is subject to well known degradation kinetics during alkaline pulping, it may be possible to theoretically relate the pulp yield to cellulose yield, and obtain the later from the cellulose degradation kinetics. In the present thesis this theoretical relationship is presented and then tested for several wood species and alkaline pulping processes.

## **1.2. OBJECTIVE**

The objective of the present study is to present a theoretical relationship between pulp yield and the cellulose mass fraction and degree of polymerization of the pulp. This relationship is then tested for three hardwoods, Rock Maple, Poplar and Yellow Birch and one softwood, Black Spruce when subjected to four alkaline pulping processes, kraft, kraft-AQ, polysulfide and polysulfide-AQ.

## **CHAPTER 2**

### **LITERATURE REVIEW**

#### **2.1. CHEMICAL PULPING OF WOOD**

The main chemical components of wood are cellulose, hemicellulose, lignin and extractives. Chemical pulping of wood can be defined as removal of lignin from the middle lamella of wood in order to allow the fibers to be liberated with minimal damage. Ideally, this would be accomplished without removal of desirable fiber wall components other than lignin. There are two main stages of chemical pulping; impregnation and cooking. In the impregnation stage chips are saturated with liquor which contains chemicals. In this phase enough time must be allowed for the chemicals to diffuse equally to all parts of the chips before the delignification reactions start. During the cooking stage the delignification reactions take place with the cooking chemicals which continuously are supplied to the reaction sites by diffusion. Delignification reactions may proceed under alkaline, acidic or neutral conditions. However the dominant pulping process is the alkaline kraft process (Gullichsen, 2000)

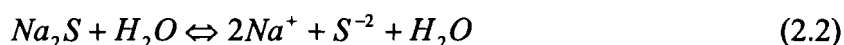
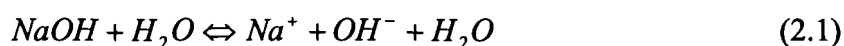
##### **2.1.1. The Kraft Process**

The kraft process is presently the most widely used cooking technology because of the following advantages:

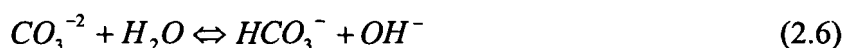
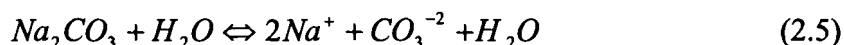
- all wood species can be used
- the process is tolerant to bark
- the pulp fibers have the highest strength

- the pulping chemicals and energy are recovered at high efficiency
- the cooking time is relatively short
- it generates valuable side-products such as tall-oil

The kraft pulping solution called white liquor is a strongly alkaline solution (pH~14) of mostly NaOH and Na<sub>2</sub>S. It also contains small amounts of Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and NaCl. The active delignification species in the kraft cooking liquor are the OH<sup>-</sup> and HS<sup>-</sup> ions formed by hydrolysis of NaOH and Na<sub>2</sub>S by the following equilibria:



In addition, the following equilibria play a role in the cooking liquor.



#### 2.1.1.1. Lignin Reactions

Although the delignification reactions of the alkaline kraft process are not exactly known, it is generally agreed that cleavage of the nonphenolic β-aryl ether bonds are mainly responsible for the solubilization of lignin. The presence of hydrogen sulfide ions significantly affects the delignification due to their strong nucleophilicity in comparison with hydroxyl ions (Sjostrom, 1993). Both hydroxyl and hydrogen sulfide ions promote the cleavage of ether linkages (Sjostrom, 1993).



Delignification occurs by reactions with the following lignin structures:

Etherified Phenolic Structures Containing  $\beta$ -Aryl Ether Bonds. The  $\beta$ -aryl ether linkage in p-phenolic structures is cleaved by hydroxide and hydro sulfide ions according to the mechanisms shown in Figures 2.1 and 2.2.

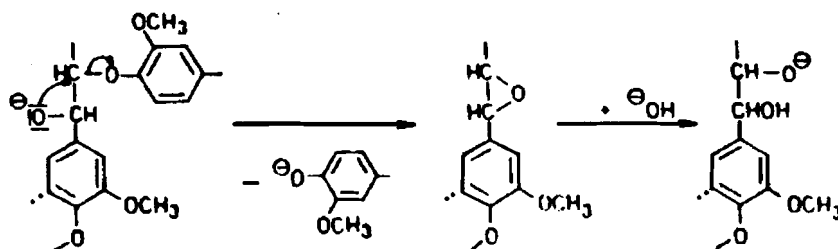


Figure 2.1. Cleavage of  $\beta$ -aryl Ether Bonds in Nonphenolic Units during Soda Pulping (Gierer, 1970)

Free Phenolic Structures Containing  $\beta$ -Aryl Ether Bonds

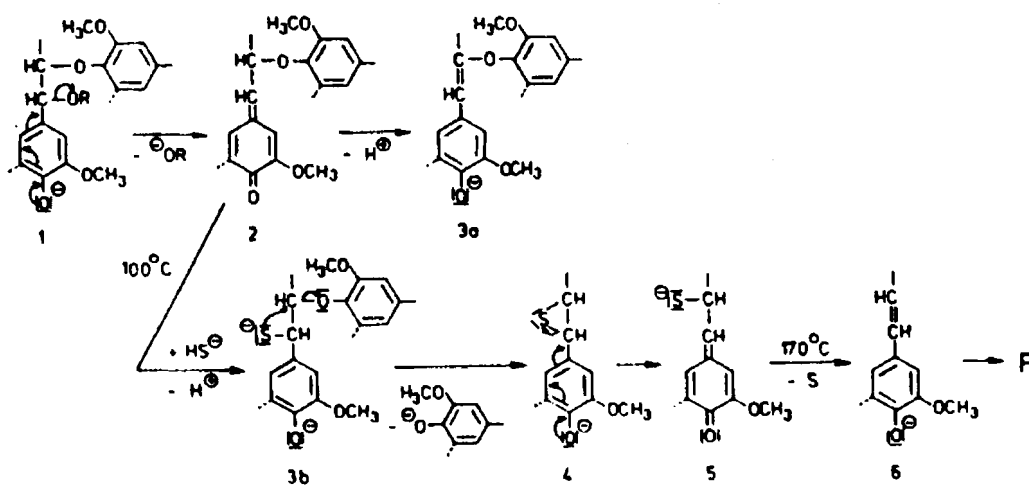


Figure 2.2. Main Reaction of the Phenolic  $\beta$ -aryl Ether Structures during Alkali (Soda) and Kraft Pulping (Gierer, 1970)  
 $R=H$ , alkyl or aryl group  
 Formation of quinone methide intermediate (2)  
 Styryl aryl ether structure (3a)  
 A thirane structure (4)  
 Polymeric product (P)

Structure Containing  $\alpha$ -Ether Bonds. The  $\alpha$ -ether bond in phenolic phenylcoumaran and pinoresinol structures (Figure 2.3) is rapidly cleaved by hydroxide ions (Sjostrom, 1993).

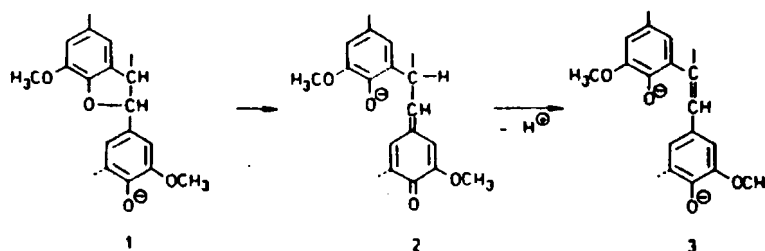


Figure 2.3. The Base-catalyzed Reaction of the Free Phenolic Phenylcoumaran Structure (1) (Gierer, 1970)  
A quinone methide intermediate (2),  
A stilbene structure (3)

Methoxyl Groups. The methyl aryl ether bond is cleaved according to the mechanism in Figure 2.4.

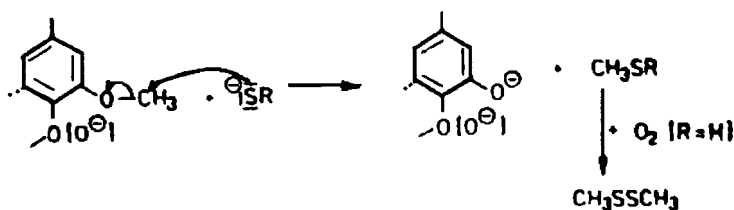


Figure 2.4. Cleavage of Methyl Aryl Ether Bonds During Kraft Pulping (Sjostrom, 1993)  
Methyl Mercaptan (CH<sub>3</sub>SH)  
Dimethyl Disulfide (CH<sub>3</sub>SSCH<sub>3</sub>)  
Methyl Group (R=H)

Condensation Reactions. Several condensation reactions are known to occur in alkaline pulping. Some examples of condensation reactions are shown in Figure 2.5.

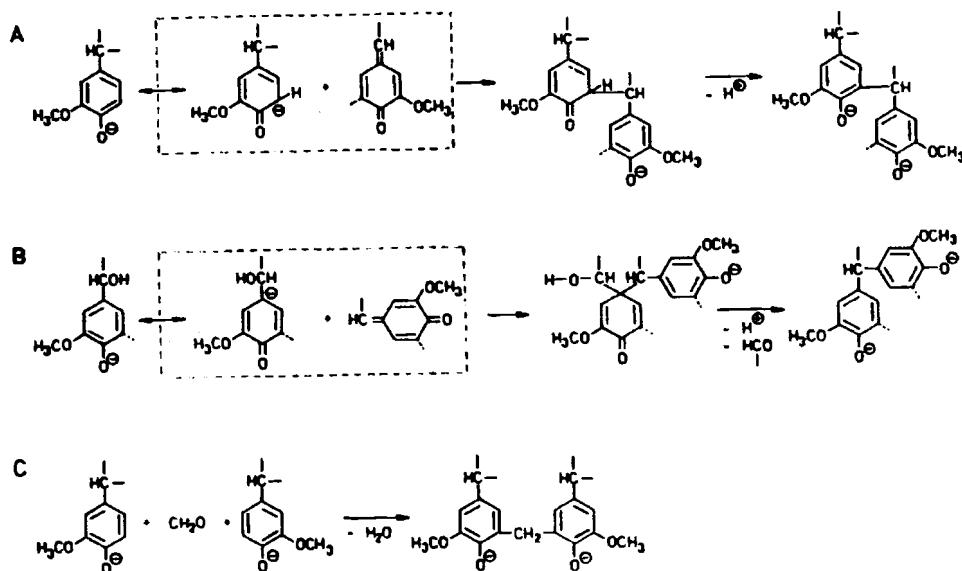


Figure 2.5. Examples of Condensation Reactions during Alkali and Kraft Pulping (Gierer, 1970)

The delignification process can be divided in three phases; initial, bulk and residual delignification. Initial delignification occurs during the impregnation phase. About 20 % of the total amount of lignin is dissolved in this stage. Another 70% of lignin is removed during bulk delignification when the cooking temperature is raised above 140°C. The rate of bulk delignification depends on the alkali and hydrosulfide concentration and the temperature in the digester. The final residual delignification proceeds very slowly.

Figure 2.6. shows the removal of lignin during kraft cooking of pine.

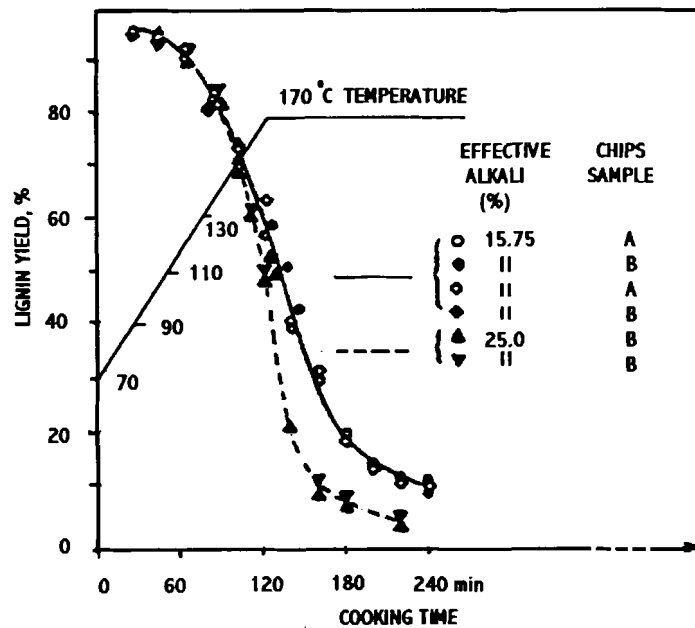


Figure 2.6. Removal of Lignin during Pine Kraft Cooks (McDonough, 1998)

#### 2.1.1.2. Carbohydrate Reactions

During kraft pulping not only delignification reactions occur but carbohydrate degradation also take place. Carbohydrate degradation is not wanted because it results in pulp yield and fiber strength loss during the pulping process. Carbohydrate degradation has been studied by many researchers (Grace et al., 1989). The principal carbohydrate reactions of alkali pulping are alkaline hydrolysis of acetyl groups, random cleavage of glycosidic bonds and the so-called peeling and stopping reactions. Beside these chemical reactions, physical dissolution and re-precipitation of the carbohydrates are also important.

Dissolution of Hemicelluloses. It is reported that a large fraction of the glucomannans dissolve between 100 °C and 130°C, However, xylan only dissolves at higher temperatures. Figure 2.7 illustrates the dissolution of the main wood compounds during kraft pulp of pine as a function of cooking time and temperature. Figure 2.8 shows the carbohydrate yield against lignin yield for pine.

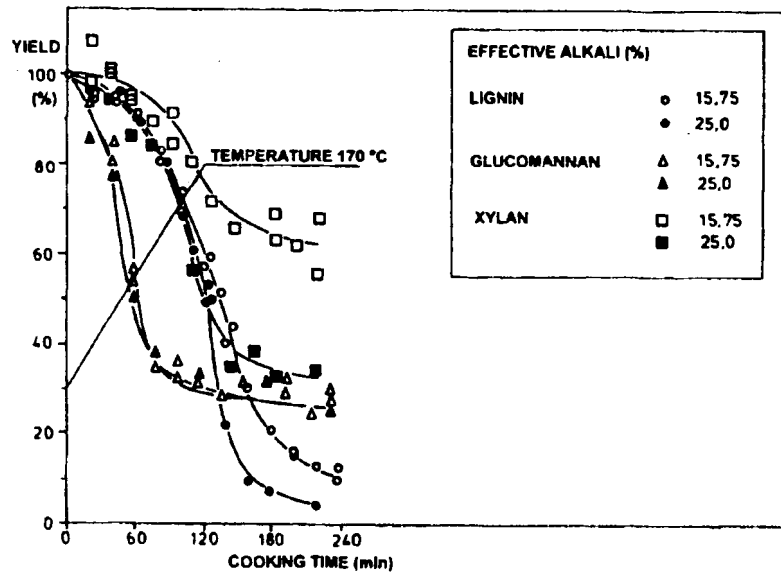


Figure 2.7. Dissolution of Lignin, Glucomannan and Xylan in Kraft Pulping of Pine (Aurell and Hartler, 1965)

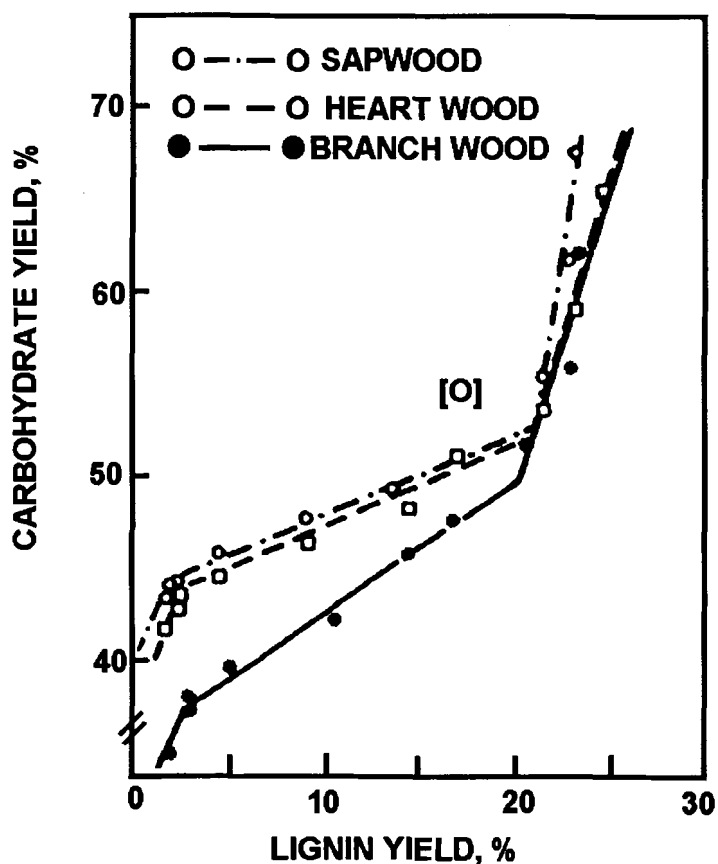


Figure 2.8. Yield of Carbohydrate as a Function of Lignin Yield for Different Part of Pine Wood (Virkola, 1983)

Cleavage of Glycosidic Bonds by Alkaline Hydrolyses. Polysaccharides in the wood are subject to chain cleavage by alkaline hydrolysis at high temperature. This lowers the polysaccharide chain length. McDonough (1998) reported that shortening of the chain length is indirectly related to yield loss because new reducing end groups are created so that depolymerization by peeling can occur anew. The cleavage of glycosidic bonds by alkaline hydrolysis is relatively slow. A suggested mechanism for the hydrolysis reaction is illustrated in Figure 2.9.

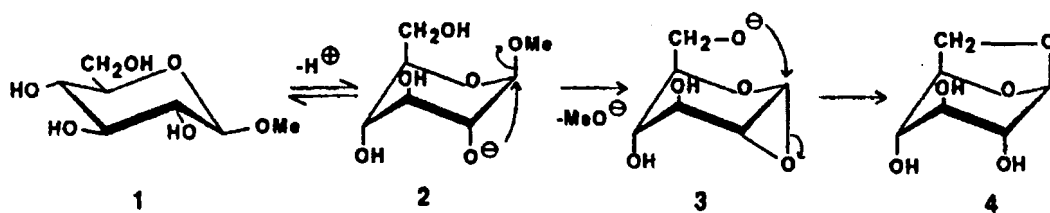


Figure 2.9. Depolymerization of Glycosidic Bonds by Alkaline Hydrolyses (Sjostrom, 1993)

It shows the base-catalyzed hydrolysis of methyl β-D-glucopyranoside(1). The reaction starts with inversion of the ring conformation. The ionized hydroxyl group at C-2 then attacks C-1 and the trans-oriented methoxyl group is eliminated. The resulting 1,2-anhydro-α-D-glucopyranose(3) is decomposed to different products directly or via 1,6-anhydro- β-D-glucophyranose ( levelglucosan)(4)

**Peeling and Stopping Reactions.** During alkaline pulping, monosaccharides and end groups in polysaccharides are converted to various carboxylic acids. These reactions are called peeling reactions. Cellulose and most hemicelluloses are degraded by peeling reactions. Figure 2.10 depicts this endwise degradation reaction mechanism. Both cellulose and hemicelluloses have a reducing end and non-reducing end group at the two opposite sides of the chain. In the peeling reaction, the reducing end group is removed as a low molecular weight carboxyl-containing compound (glucoisosaccharinic acid) and the adjacent group is converted to a new reducing end group which is again vulnerable to the peeling reaction. This reaction is also known as the primary peeling reaction. Since the result of alkaline hydrolysis of glycosidic bonds is the formation of a new reducing end group, these new reducing end groups are also vulnerable to the same peeling reaction. This reaction is also called the secondary peeling reaction. These peeling reactions continue stepwise until a so called stopping reaction takes place. The stopping

reactions converts the reducing end group to an oxidized carboxyl-containing end group (metasaccharinic acid) which is alkali stable and undergoes no more peeling reaction. Figure 2.11 shows the mechanism of the stopping reaction. Hemicelluloses are degraded more extensively than cellulose because of their low degree of polymerization and amorphous structure (Sjostrom, 1993).



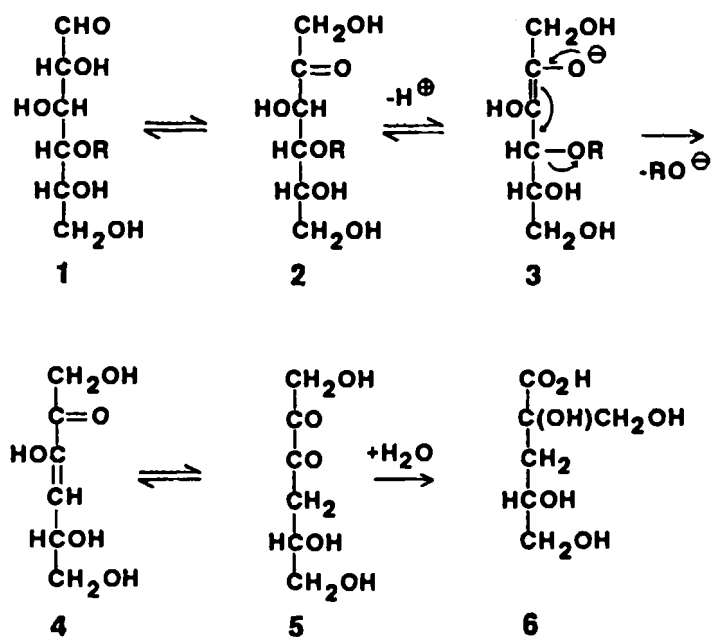


Figure 2.10. Peeling Reaction Mechanism (Sjostrom, 1993) The endwise alkaline degradation ("peeling") of 1,4-β-D-glucan(cellulose)

R=glucan(cellulose) chain occurs via the following reaction steps are:

- isomerization(1→ 2)
- enediol formation (2→ 3)
- β-alkoxyl elimination (3→ 4)
- tautomerization (4→ 5)
- benzilic acid rearrangement(5→ 6) to epimeric 3-deoxy-2-C-hydroxymethylpentonic acids (glucoisosaccharinic acid) (6)

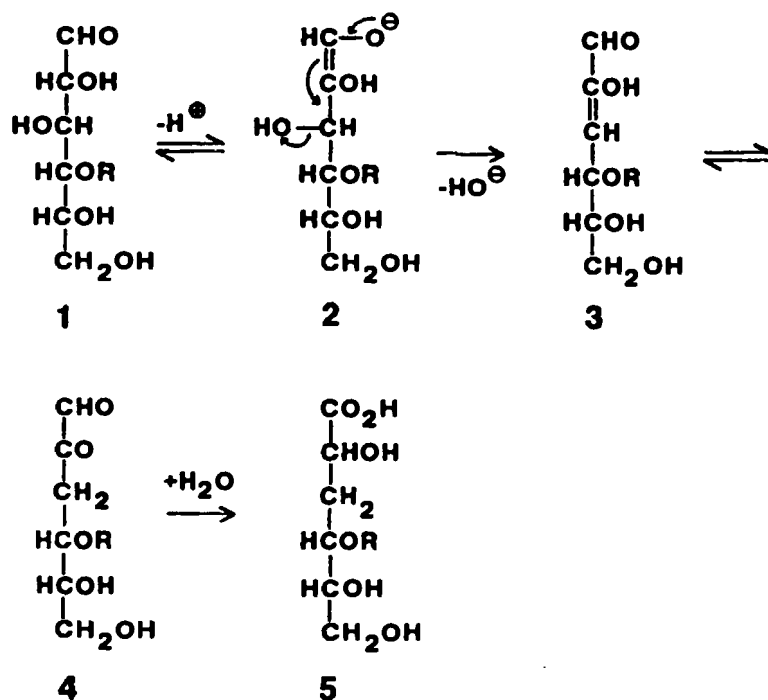


Figure 2.11. Stopping Reaction (Sjostrom, 1993)

The stopping reaction mechanism steps are:

- 1,2-Enediol formation(1→ 2)
- $\beta$ -hydroxy elimination(2→ 3)
- tautomerization(3 → 4)
- benzilic acid rearrangement(4→ 5) to epimeric 3-deoxyhexonic acid end groups (glucometasaccharinic acid)(5)

Physical Dissolution and Precipitation of Carbohydrates. Low molecular weight carbohydrates can dissolve in an alkali solution if they are easily accessible because they contain many hydrophilic hydroxyl groups. Since the degree of dissolution depends on the alkali concentration, previously dissolved some carbohydrate molecules may re-precipitate when a sufficient amount of alkali is consumed.

### 2.1.1.3. Reaction Kinetics in Kraft Cooking

#### 2.1.1.3.1. Kinetics of Lignin Reactions

The kinetics of lignin reactions were studied by many researchers. Although many kinetic models were developed, none of them are as well accepted as the H-factor model developed by Vroom (1957). In the H-factor model, the cooking temperature and time are expressed in a single parameter to describe the relative degree of delignification. The H-factor kinetic model is derived as follows:

In a homogeneous reaction system the delignification kinetics can be generally expressed as;

$$-\frac{dL}{dt} = k' [OH^-]^a [HS^-]^b L^c \quad (2.7)$$

where L is the lignin content, k' is a reaction rate constant, [OH<sup>-</sup>] is the hydroxyl ion concentration, [HS<sup>-</sup>] is the hydrosulfide ion concentration, and a, b and c are reaction orders with respect to [OH<sup>-</sup>], [HS<sup>-</sup>] and L.

If it is now assumed that the reaction order and relative rates of consumption of the cooking chemicals and lignin do not change with temperature, a relative rate of delignification may be defined as  $\frac{k_T}{k_{373}}$ , where k is the rate constant of delignification at

T(°K) and k<sub>373</sub> the rate constant at 100 °C or 373 °K. Introduction of the Arrhenius law

$$k = A \cdot e^{\frac{-E_a}{RT}} \quad (2.8)$$

where  $E_a$  : reaction activation energy

T: absolute temperature

A: constant

R: the general gas constant, 8.314 J/mol.K

$$\text{gives} \quad \frac{k_T}{k_{373}} = e^{\frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{373} \right)} \quad (2.9)$$

The H factor is now defined as

$$H = \int_0^t \frac{k_T}{k_{373}} dt \quad (2.10)$$

with t expressed in hours.

For kraft cooking it has been found that  $E_a = 32$  kcal/mol, so that the H-factor becomes

$$H = \int_0^t e^{(43.2 - 16115/T)} dt \quad (2.11)$$

#### 2.1.1.3.2. Kinetics of Carbohydrate Reactions

The kinetic of carbohydrate reactions are very complex because there are several carbohydrate compounds such as cellulose, xylans, glucomannans, each undergoing degradation reactions. The kinetics of carbohydrate reactions are studied by many researchers in the literature. The simplest approach has been to directly relate the kinetics of carbohydrate degradation to the delignification rate. Thus the carbohydrate degradation is also divided in three phases; the initial, bulk and residual phase.

Gustafson et al. (1991) related the carbohydrate degradation rate to the delignification kinetics as follows:

$$\text{Initial phase,} \quad \frac{dC}{dt} = k_{ic} \cdot [OH^-]^{p.11} \cdot \frac{dL}{dt} \quad (2.12)$$

$$\text{Bulk phase,} \quad \frac{dC}{dt} = k_{bc} \cdot \frac{dL}{dt} \quad (2.13)$$

$$\text{Residual phases,} \quad \frac{dC}{dt} = k_{rc} \cdot \frac{dL}{dt} \quad (2.14)$$

The constants,  $k_{ic}$ ,  $k_{bc}$  and  $k_{rc}$  are the rate constants during the initial, bulk and residual delignification phases for the carbohydrates.

### 2.1.2. Modified Kraft Processes

The highly alkaline and elevated temperature conditions which are found in the digester lead to yield losses in the standard kraft pulping process due to carbohydrate dissolution and degradation. The pulp yield can be increased by minimizing this dissolution and degradation of the carbohydrates. A lower temperature and average alkali concentration are characteristic of some of the modified kraft processes. These will not be discussed here. The modified processes which will be discussed here are those which rely on additives such as anthraquinone and polysulfide.

#### 2.1.2.1. Anthraquinone Cooking

In the literature it is reported that anthraquinone stabilizes carbohydrates against alkali degradation by oxidation of the reducing ends and by slowing down the peeling reaction (Gullichsen, 2000). Holton (1977) reported that anthraquinone not only increases pulp yield but also increases the delignification rate. The anthraquinone mechanism is explained in Figure 2.12 Anthraquinone (AQ) oxidizes the reducing end group of carbohydrates, thereby stabilizing the reducing end group against the alkali peeling

reaction. The generated reduced anthraquinone (AHQ) is alkali soluble and reduces lignin to a more reactive form. Thus anthraquinone functions as a redox catalyst, stabilizing the carbohydrates and activating the lignin for further degradation. The positive effect on the pulp yield of small additions of anthraquinone is seen in Figure 2.13

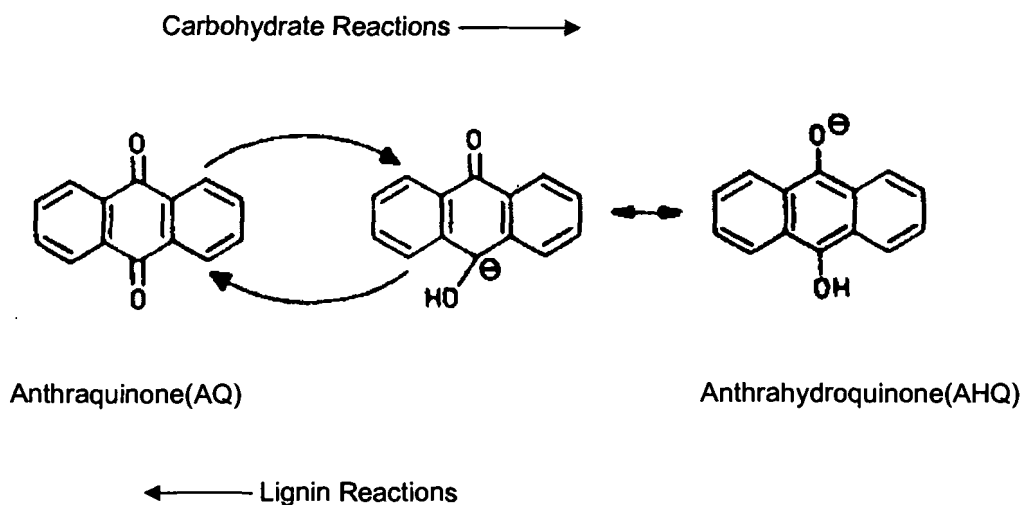


Figure 2.12. The Redox Cycle in Anthraquinone-Enhanced Kraft Pulping (Grace & Malcolm, 1989)

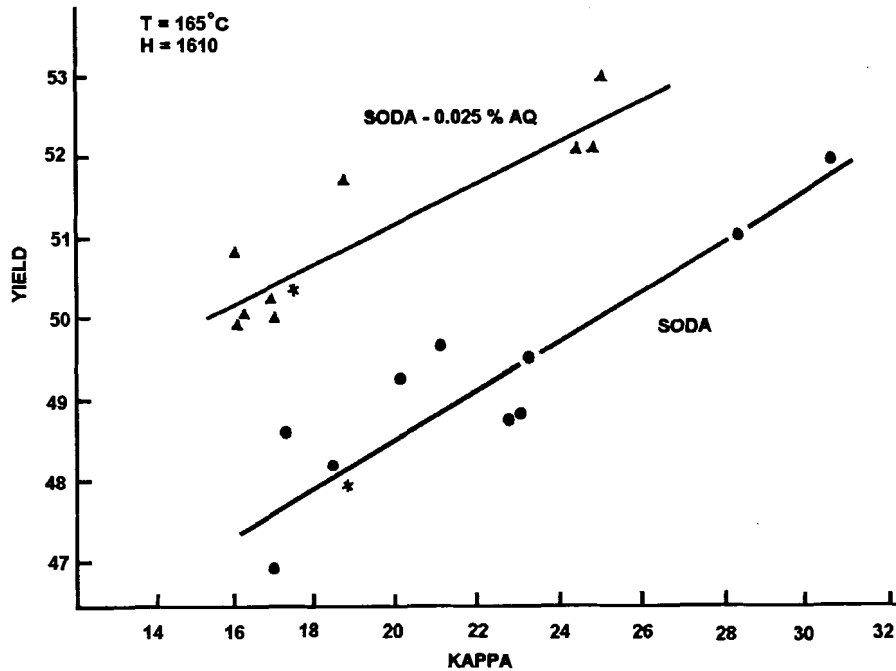
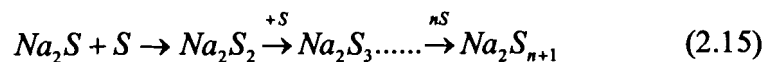


Figure 2.13. Effect of Antraquinone on Mixed Southern Hardwood Soda Pulping (Waldemar, 1977)

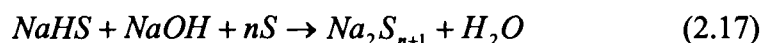
#### 2.1.2.2. Polysulfide Cooking

It is well known that the presence of polysulfide in kraft pulping increases the pulp yield by stabilizing the hemicelluloses (Gullichsen, 2000). Polysulfide also oxidizes reducing end groups of polysaccharides to alkaline stable aldonic acids, thereby reducing carbohydrate dissolution during cooking. The yield increase by using polysulfide is directly related to an increase in glucomannan content for softwoods and to xylan yield increase for hardwoods (Jiang and Lowe, 1995).

Polysulfide can be prepared by adding elemental sulfur to the white liquor leading to the following reaction:



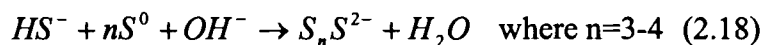
Another option is to produce polysulfide by catalytic oxidation:



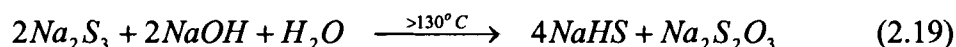
Part of the sulfide is also oxidized to thiosulfate in a side reaction.

Dorris and Uloth reported that NaOH is consumed by preparation of polysulfide when sulfur is used and by decomposition of polysulfide at high temperatures (Dorris and Uloth, 1994).

The reaction between sodium hydrosulfide and  $S_0$  is:



Polysulfide is decomposed by alkali at high temperatures according to the overall reaction:



Jiang and Lowe(1995) reported that the addition of 2-3% polysulfide (as elemental sulfur on wood) in modified cooking to 15-18 kappa number can give the same final pulp yield as in a conventional kraft cooking to 27-30 kappa number. They also found that compared to conventional cooking, polysulfide cooking gives a total bleaching yield 1-2.5% higher on wood basis. Sayner and Laundrie (1964) reported that the delignification rate of polysulfide cooking at 160 °C was about 25% faster than that of kraft. Landmark et al. (1965) also found that the pulping time of polysulfide cooking can be reduced since the delignification rate is faster.



### **2.1.2.3. Polysulfide-Anthraquinone Cooking**

The combination of polysulfide with anthraquinone cooking was studied by Li et al. (2002). They reported that the polysulfide-anthraquinone delignification rate was higher than that of kraft, anthraquinone and polysulfide cooking. They found that the rate of viscosity loss was lower for polysulfide and polysulfide-AQ comparing to kraft and anthraquinone cooking. They showed that polysulfide-AQ cooking was more selective than kraft, anthraquinone and polysulfide cooking. They also reported that although the polysulfide addition did not affect the activation energy ( $\sim 141$  kJ/mol) for delignification, anthraquinone addition to kraft and polysulfide cooking decreased the activation energy by about 10 kJ/mol. However the activation energy of carbohydrate degradation was not significantly different for kraft, anthraquinone, polysulfide or polysulfide-anthraquinone cooking. The activation energies for carbohydrate degradation were reported to range from 170 to 181 kJ/mol (Li et al., 2002).

## **2.2. AVERAGE DEGRADABLE CHAIN LENGTH $\Delta DP_n$**

During alkaline degradation of cellulose, the reducing end groups of cellulose are attacked by alkali as shown as Figure 2.14, and glucose units are removed from the cellulose molecules until stabilization reactions take place. When the reducing end group is converted to the alkali-stable m-saccharinic end group no further degradation takes place. According to the theory by Haas et al. (1967) not all reducing end groups need to be converted to metasaccharinic acid for the peeling process to stop because of the difficulty of alkali to penetrate the crystalline regions of cellulose.

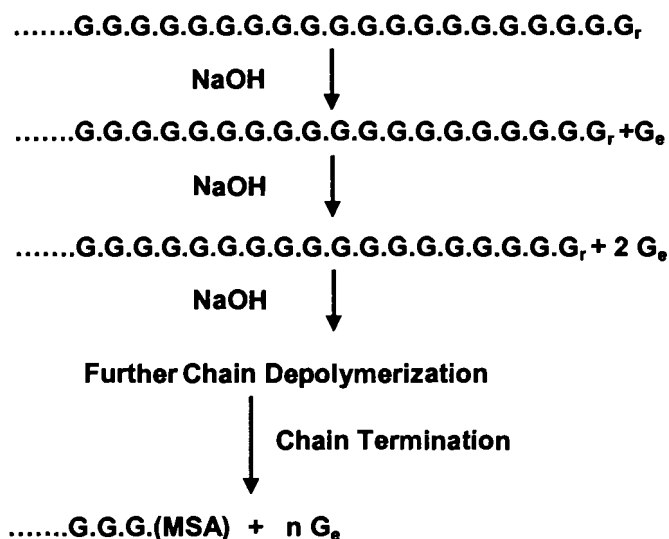


Figure 2.14. Alkaline Degradation Mechanism of Polysaccharides (Haas, 1967)

G : anhydroglucose unit;  
 G<sub>r</sub> : reducing end group;  
 G<sub>e</sub> : glucose unit eliminated by conversion to isosaccharinic acid;  
 MSA: m-saccharinic acid units.

To illustrate the cellulose degradation, Figure 2.15 A depicts the classical model of an undegraded cotton fibril. Figure 2.15 B shows the situation after acid hydrolysis to hydrocellulose with cleavage of many of the cellulose chains in the micro fibril. Finally, Figure 2.15 C shows the alkali degraded hydrocellulose with newly formed meta saccharinic acid end groups, and reducing ends at the interface between the amorphous and crystalline regions.

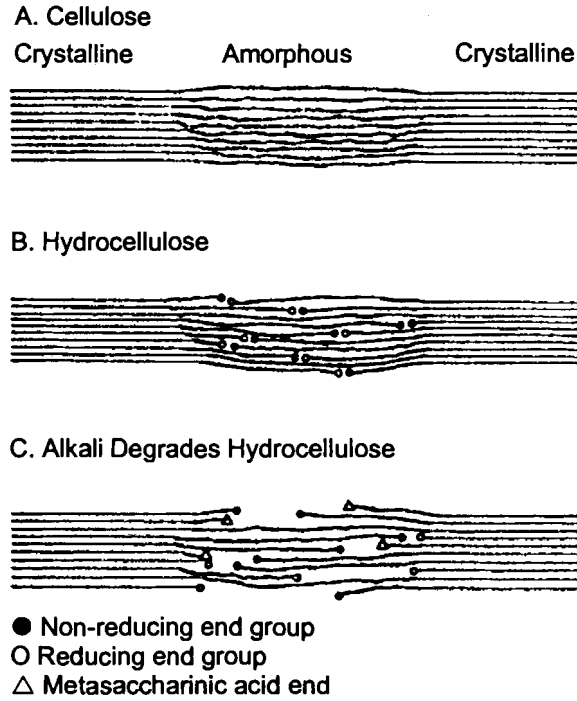


Figure 2.15. Schematic Representation of Cellulose Degradation (Haas, 1967)

Haas et al. (1967) provided the following kinetic analysis of the model shown in Figure 2.15:

The rate of glucose removed by peeling is:

$$\frac{d[G_e]}{dt} = k_1[G_r] = \frac{dA}{dt} \quad (2.20)$$

The rate of the stopping reaction is:

$$\frac{d[MSA]}{dt} = k_2[G_r] \quad (2.21)$$

The rate of the degrading cellulose chain entering the crystalline region is:

$$\frac{d[G_t]}{dt} = k_{cr}[G_r] \quad (2.22)$$

Since the rate of disappearance of  $G_r$  is equal to the sum of the two termination processes:

$$-\frac{d[G_r]}{dt} = k_2[G_r] + k_{cr}[G_r] = k_t[G_r] \quad (2.23)$$

where,

$G_e$  : mole fraction of glucose units eliminated by the propagation

$G_r$  : mole fraction of reducing end groups which are available for reaction

$G_t$  : mole fraction of reducing end groups which are not available for reaction

$A$  : weight fraction of alkali loss

$t$  : time

$MSA$  : mole fraction of metasaccharinic acid formed by termination reaction

$k_1$  : rate constant of propagation

$k_2$  : rate constant of termination by conversion to m-saccharinic acid

$k_{cr}$  : rate constant of termination caused by inaccessibility

$k_t$  : total rate constant for the chain termination

At  $t=0$ ,  $[G_r] = [G_r]_0$

Integration of equation (2.23) gives:

$$[G_r] = [G_r]_0 \cdot e^{-k_t \cdot t} \quad (2.24)$$

By inserting equation (2.24) into equation (2.20) one obtains

$$\frac{dA}{dt} = \frac{d[G_e]}{dt} = k_1[G_r]_0 \cdot e^{-k_t \cdot t} \quad (2.25)$$

At  $t=0$ ,  $A=0$ , so integration gives:

$$A = \left( \frac{k_1}{k_t} \right) \cdot [G_r]_0 \cdot (1 - e^{-k_t \cdot t}) \quad (2.26)$$

or

$$\ln \left\{ 1 - \left( \frac{k_t \cdot A}{k_1 \cdot [G_r]_0} \right) \right\} = -k_t \cdot t \quad (2.27)$$

At infinite time,

$$A_{\infty} = \left( \frac{k_1}{k_t} \right) \cdot [G_r]_0 \quad (2.28)$$

Combining equation 2.27 and 2.28 produces:

$$k_t \cdot t = \ln \left\{ \frac{A_{\infty}}{A_{\infty} - A} \right\} \quad (2.29)$$

Substituting of equation 2.24 into equation 2.21 gives:

$$\frac{d[MSA]}{dt} = k_2 [G_r]_0 \cdot e^{-k_t \cdot t} \quad (2.30)$$

At  $t = 0$ ,  $MSA = 0$

$$[MSA] = \left( \frac{k_1}{k_t} \right) \cdot [G_r]_0 \cdot (1 - e^{-k_t \cdot t}) \quad (2.31)$$

At infinite time,

$$[MSA]_{\infty} = \left( \frac{k_1}{k_t} \right) \cdot [G_r]_0 \quad (2.32)$$

Finally,

$$k_{cr} = k_t - k_2 \quad (2.33)$$

The ratio  $k_1/k_t$  equals the average degradable chain length in glucose units. For cellulose, when the termination only occurs through m-saccharinic formation,  $k_1/k_2$  would give the length of the degradable chain,  $\bar{x}_n$ . For hydrocellulose  $k_1/k_{cr}$  give the average distance  $\bar{x}_d$  of reducing end groups from the crystalline region in glucose units.  $\bar{x}_d$  is one half of the total amorphous chain length in the original cellulose because during the hydrocellulose formation, the hydrolysis of amorphous chains occurs randomly, so

$$\bar{x}_{amorphous} = 2\bar{x}_d \quad (2.34)$$

## **2.3. PULP YIELD MEASUREMENT METHODS**

Pulp yield measurement methods have been the subject of many studies. They can be classified as direct and indirect pulp yield measurement methods.

### **2.3.1. Direct Pulp Yield Measurement Methods**

#### **2.3.1.1. Inventory Measurement Method**

The inventory measurement method relies on comparison of long term wood usage and pulp production mill data. Marcoccia et al. (1998) noted that a typical time frame for generating a reasonable estimate of yield in this way is 3 to 6 months. The large time period and the inherent imprecision related to such estimates render process optimization for yield by this method a long and difficult task.

#### **2.3.1.2. Basket Method**

Pulp yield is measured directly by suspending baskets or capsules in a batch digester. By knowing the amounts of (oven dried) wood and measuring the amount of pulp generated from the wood in the baskets, the pulp yield is determined (MacLeod and Pelletier, 1987). Although it is well known that the pulping conditions are not same in all parts of the batch digester, it is assumed that the pulping conditions of the chips in the capsule are the same as that of the digester. It should be noted that the basket method only can be used in batch digester; i.e., it does not apply to continuous digesters. For this reason the basket method has limited use to determine pulp yield accurately in mill situations.

### 2.3.2. Indirect Pulp Yield Measurement Methods

#### 2.3.2.1. Yield-Kappa Number Relationship

According to the yield-kappa number relationship method, first a number of laboratory cooks must be done for the relevant wood species to develop a yield vs. kappa calibration curve. Then the mill pulp yield can be estimated using this yield-kappa calibration curve and the measured mill kappa number. It has been noted that the application of the yield-kappa method to continuous systems assumes among others that the cellulose/hemicellulose/lignin relationships remain constant (Easty and Malcolm, 1982). Depending on cooking conditions this assumption is seriously flawed, and significant differences in the yield-kappa relationship occur as was found by Marcoccia et al. (1990).

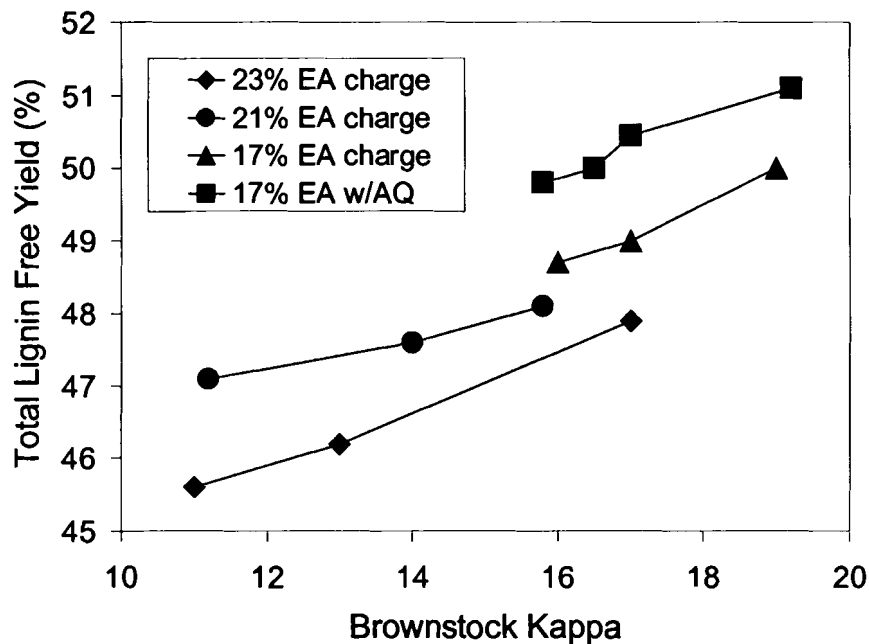


Figure 2.16. Lab Generated Pulp and Liquor Properties for Use in Calibration Curves Southern Hardwood Chips (Marcoccia, 1998)

#### 2.3.2.2. Mannan Method

The Mannan method was developed to measure the pulp yield of polysulfide and anthraquinone cooks by determining the mannan amount in the pulp. For this method laboratory cooks are required to develop a yield versus mannan calibration curve. By measurement of the mannan amount in the mill pulp and using the yield – mannan plot, the pulp yield of polysulfide and anthraquinone cooks can be estimated. However Kleppe (1980) reported that this technique could not be applied to conventional kraft cooks since in the range of interest the sugar content of pulp was essentially independent of the pulp yield. Luthe (2002) used the mannan content of softwood pulps to evaluate the yield of polysulfide and anthraquinone pulping trials. However, this technique does not apply to hardwoods.

#### 2.3.2.3. The Cellulose and Carbohydrate- Lignin Methods ( $Y_{cell}$ Method)

The  $Y_{cell}$  Method was developed by Easty and Malcolm (1982). It is based on the assumption that the cellulose yield based on wood is constant in a normal kraft pulp. Pulp yield is calculated as follow:

$$Pulp\ Yield = (Y_{cell}) \cdot \frac{(C + H + L + O)}{C} \quad (2.35)$$

where  $Y_{cell}$  = yield of cellulose (based on the o.d.(oven dried) wood), and C, H, L and O represent the weight fractions of cellulose, hemicellulose, lignin and other pulp components of pulp.

By ignoring, O, the other component, equation (2.35) can be rewritten as:

$$Pulp\ Yield = (Y_{cell}) \cdot \frac{(C + H)}{C} + (Y_{cell}) \cdot \frac{L}{C} \quad (2.36)$$



the two terms on the right hand side of equation (2.36) are:

$$\text{Carbohydrate Yield} = (Y_{\text{cell}}) \cdot \frac{(C + H)}{C}$$

$$\text{Lignin Yield} = (Y_{\text{cell}}) \cdot \frac{L}{C}$$

By defining  $Y_T'$  as the lignin-free pulp yield one obtains:

$$Y_T' = Y_{\text{cell}} \cdot \left( \frac{C + H}{C} \right) = \frac{Y_{\text{cell}}}{G'} \quad (2.37)$$

where,

$Y_T'$  = total lignin- free pulp yield on o.d. wood

$Y_{\text{cell}}$  = cellulose yield based on o.d. wood

$C$  = cellulose fraction in pulp

$H$  = hemicellulose fraction in pulp

$G'$  = lignin-free mass cellulose mass fraction of pulp

The cellulose in pulp is determined by TAPPI Test Method T249 pm-75 and the formula used for the calculation of the cellulose content is:

Cellulose in (soft wood) pulp = Glucan – Mannan/3.

Although this method is well accepted, it ignores the secondary peeling reactions by assuming a constant value for  $Y_{\text{cell}}$  during cooking. The  $Y_{\text{cell}}$  method requires laboratory cooks to determine the cellulose yield for the wood species under consideration.

#### 2.3.2.4. Marcoccia Equation.

A new indirect pulp yield measurement method was recently developed by Marcoccia et al. (1998). According to this empirical method, the total lignin-free pulp yield is uniquely related to the Tappi viscosity,  $V$  and the lignin-free mass fraction of cellulose in the pulp. The particular combination which gave the best linear correlation with the lignin-free pulp yield was  $(^{10}\log V)/(G')^2$ . An example of this correlation is shown in Figure 2.17.

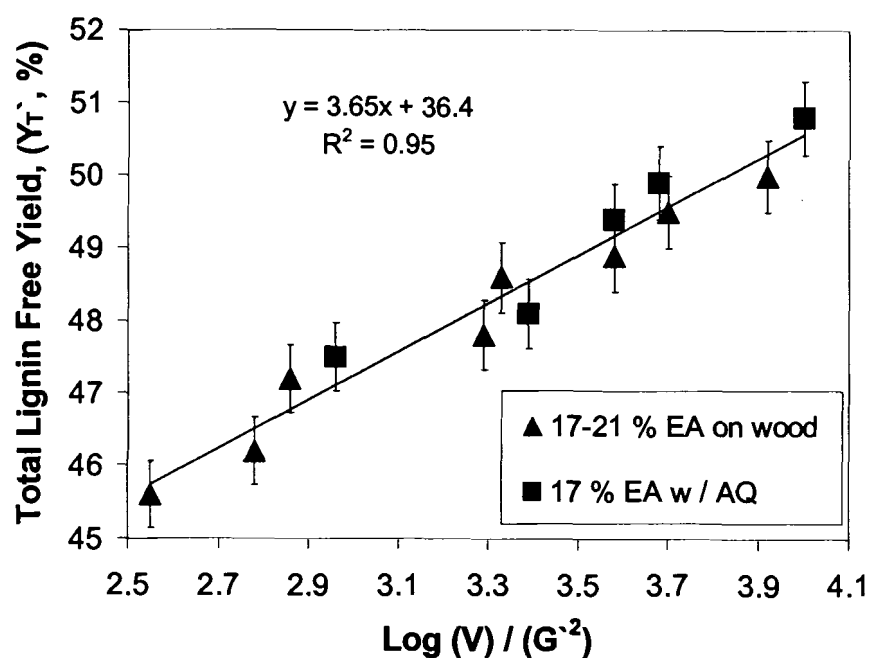


Figure 2.17. Yield Calibration Curve,  $Y_T$  versus  $(^{10}\log V)/(G')^2$  (Marcoccia, 1998)

Therefore, the empirical relation for Marcoccia's pulp yield equation is:

$$Y_T' = \frac{Y_c}{G'} = m \cdot (10 \log V) / (G')^2 + b \quad (2.38)$$

where,

$Y_c$  = cellulose yield

$G'$  = lignin-free cellulose mass fraction of pulp

$Y_T'$  = total lignin-free pulp yield on o.d. wood

$V$  = Tappi viscosity (cP.)

$m$  = empirical constant (~3.7)

$b$  = empirical constant which is species dependant

The first term on the right-hand side of equation (2.38) is related to the cellulose loss by secondary peeling. The second term,  $b$ , is mostly related to the cellulose content of wood minus the cellulose yield loss because of primary peeling.

By using the Marcoccia equation it is possible to determine the pulp yield of a mill when the Tappi viscosity and the lignin-free cellulose mass fraction of the pulp are measured. The empirical constants  $m$  and  $b$  are furnish dependent and must be established by laboratory cooks. Luthe et al. (2002) reported that the Marcocia equation is a poor yield prediction method for yield gains achieved when changing the process chemistry from kraft to polysulfide.

## CHAPTER 3

### THEORY

#### 3.1. DERIVATION OF THE UNIVERSITY OF MAINE (UoM) PULP YIELD PREDICTION EQUATION

The average degree of polymerization of the cellulose chains in wood,  $DP_0$ , decreases during pulping to a lower value,  $DP$ , due to primary and secondary peeling, but above all due to alkaline hydrolysis.

The cellulose yield of pulp,  $Y_c$  (expressed as g cellulose/g o.d. wood) is related to the cellulose mass fraction of the original wood,  $Y_{c,w}$ , as

$$Y_c = \frac{n \cdot (DP)}{n_0 \cdot (DP_0)} Y_{c,w} \quad (3.1)$$

where  $n_0$  is the number of cellulose chains in the original wood and  $n$  is the number of cellulose chains in the pulp derived by cooking this wood.

When it is assumed that the loss of degree of polymerization due to primary peeling,  $(\Delta DP)_p$ , occurs for each cellulose chain, and that the loss of degree of polymerization due to secondary peeling,  $(\Delta DP)_s$ , is constant during cooking, the following mass balance can be made:

$$n_0(DP_0) - n(DP) = n_0(\Delta DP)_p + (n - n_0)(\Delta DP)_s \quad (3.2)$$

Rearrangement of equation (3.2) gives

$$\frac{n}{n_0} = \frac{DP_0 + (\Delta DP)_s - (\Delta DP)_p}{DP + (\Delta DP)_s} \quad (3.3)$$

Insertion of (3.3) in (3.1) gives:

$$Y_c = \frac{K_1}{1 + \frac{(\Delta DP)_s}{DP}} \quad (3.4)$$

$$\text{where } K_1 = \frac{[DP_0 + (\Delta DP)_s - (\Delta DP)_p]}{DP_0} Y_{c,w} \quad (3.5)$$

Equation (3.4) can be rearranged as:

$$K_1 = Y_c + Y_c \frac{(\Delta DP)_s}{DP} \quad (3.6)$$

After dividing equation (3.6) by  $K_1 Y_c$  one obtains:

$$\frac{1}{Y_c} = \frac{1}{K_1} + \frac{1}{K_1} \frac{(\Delta DP)_s}{DP} \quad (3.7)$$

It should be noted that because  $DP_0$  is almost two order of magnitude larger than  $(\Delta DP)_s$  and  $(\Delta DP)_p$ , and because  $(\Delta DP)_s$  and  $(\Delta DP)_p$  are the same order of magnitude and these two terms have an opposite sign in equation(3.5), one can with a very small error replace equation 3.5 by

$$K_1 = Y_{c,w}$$

From a mass balance it also follows the cellulose yield of pulp,  $Y_c$ , is equal to the product of the lignin-free pulp yield based on o.d. wood,  $Y_T'$ , and lignin-free cellulose fraction in the pulp,  $G'$ , or

$$Y_c = Y_T' \cdot G' \quad (3.8)$$

By combining equation (3.8) and (3.7) and replacing  $K_1$  by  $Y_{c,w}$  the UoM Pulp Yield Prediction Equation is obtained:

$$\frac{1}{Y_T' G'} = \frac{1}{Y_{c,w}} + \frac{(\Delta DP)_s}{Y_{c,w}} \cdot \frac{1}{DP} \quad (3.9)$$

From equation (3.9) one can calculate the lignin free pulp yield,  $Y_T'$ , of a pulp sample if  $G'$  and DP of the pulp are determined by sugar analysis and viscometry respectively, while the value of  $Y_{c,w}$  and  $(\Delta DP)_s$  are determined by laboratory cooks of the wood furnish, or are known for this furnish.

The last term on the right hand side of equation (3.9) represents the cellulose loss due to secondary peeling following each chain scission by alkaline hydrolysis. If this term is neglected, equation (3.9) reduces to the so called Ycell method of Easty and Malcolm(1982) whereby  $Y_{c,w}$  is now equal to  $Y_{cell}$ , the cellulose yield based on wood. Thus the present theory can be considered an extension of the Ycell method because it takes into account the cellulose loss due to the peeling and alkaline hydrolysis during the cooking process. Another important fundamental aspect of the present analysis is that the value of  $(\Delta DP)_s$  can be obtained by plotting  $1/(Y_T' G')$  versus  $1/DP$ . If a straight line is obtained, then this fundamental value can be calculated from the slope,  $(\Delta DP)_s/Y_{c,w}$  and the y-axis intercept,  $1/Y_{c,w}$ , the inverse of the cellulose mass fraction of the original wood.

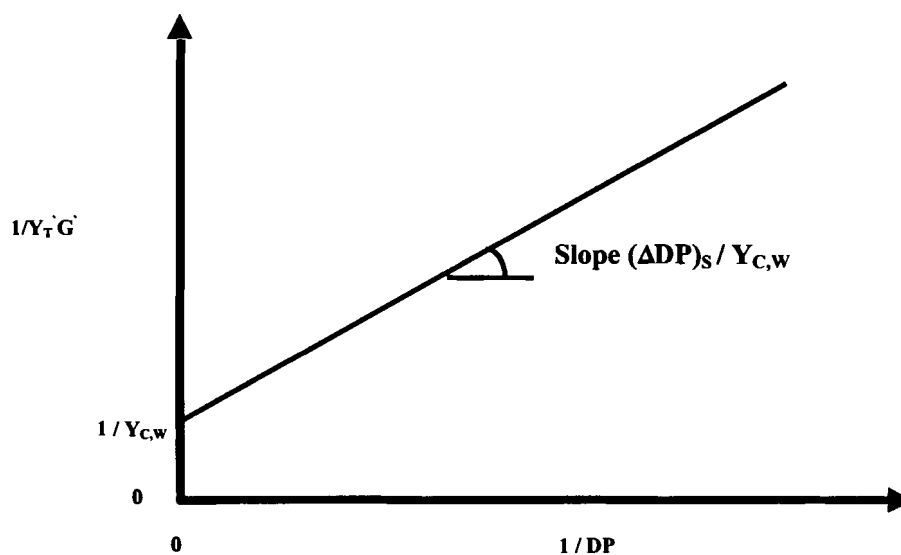


Figure 3.1. Validation of UoM Pulp Yield Prediction Equation

### 3.2. DEGREE OF POLYMERIZATION DERIVED FROM THE PULP INTRINSIC VISCOSITY

The DP of cellulose in pulp is calculated using the following relationship (da Silva Perez and van Heiningen (2002)):

$$DP = \left( \frac{(1.65[\eta] - 116H)}{G} \right)^{1.111} \quad (3.10)$$

where  $[\eta]$  is the intrinsic viscosity of the pulp in  $\text{cm}^3/\text{g}$ ,  $G$  is the mass fraction of cellulose in the (lignin containing) pulp and  $H$  is the mass fraction of the hemicelluloses in the pulp. This formula considers the actual content of celluloses in the pulp, and makes a correction for the small contribution of the hemicelluloses to the pulp intrinsic viscosity. The values of  $G$  and  $H$  are obtained from mono-sugar analysis of the hydrolysate of the pulp obtained by double hydrolysis by sulphuric acid, and making the appropriate mass corrections for the presence of glucose in glucomannan and xylan, and the presence of lignin and hexeneuronic acids. The correction for the hemicelluloses (i.e. the term  $116H$ ) is based on a DP of hemicellulose of 140. Therefore, this term is much less important than the correction for the cellulose content (i.e.  $G$ ). Therefore, the accuracy of equation (3.10) is mostly determined by the accuracy of the method to determine the cellulose content.

### 3.3. CALCULATION PROCEDURE OF CARBOHYDRATE CONTENT

The calculations which are used to estimate carbohydrate content of pulp is summarized in table 3.1.

Table 3.1.  
Calculation Procedure of Carbohydrate Analyses Method

ID	Description
1	Lignin (L)(pulp mass fraction). Determined as $0.147 \cdot \text{Kappa}$
2	Extractives(E)(pulp mass fraction)
3	Ash(A)(pulp mass fraction)
4	Pulp weight = W
5	4-O-methylglucuronic anhydride (U) (pulp mass fraction). Determined by method of Scott (1979)
6	Arabinan polymer = AR
7	Galactan polymer = GA
8	Glucan polymer = GL
9	Mannan polymer = MA
10	Xylan polymer = XY
11	Total Carbohydrate = TC
12	Total Sugar = TS
13	$\text{AR (mg)} = \text{arabinose (mg)} \cdot (132/150)$
14	$\text{GA (mg)} = \text{galactose (mg)} \cdot (162/180)$
15	$\text{GL (mg)} = \text{glucose (mg)} \cdot (162/180)$
16	$\text{MA (mg)} = \text{mannose (mg)} \cdot (162/180)$
17	$\text{XY (mg)} = \text{xylose (mg)} \cdot (132/150) + \text{U} \cdot 0.6 \cdot \text{W (mg)} \cdot (132/176)$
18	$\text{TC(mg)} = \text{AR} + \text{GA} + \text{GL} + \text{MA} + \text{XL}$
19	$\text{TS(mg)} = \text{W (mg)} \{ 1 - [\text{L} + \text{E} + \text{A} + (\text{U} \cdot 190/176)] \}$
20	Recovery (R) = Total carbohydrate / Total sugar
21	Normalized Galactan weight (mg) (NGA)= GA (mg)/R
22	Normalized Glucan weight (mg) (NGL)= GL (mg)/R
23	Normalized Xylan weight (mg) (NXL)= XL (mg)/R
24	Normalized Mannan weight (mg) = MA (mg)/R
25	Cellulose (G) (mass fraction) = $[\text{NGL} - \text{NMA} / b] / \text{W}$ For hardwood: $b = 1.6$ For softwood $b = 4.15$ (average values for Pine Black Spruce kraft pulp, based on Janson (1974))
26	Hemicellulose (H) = $(\text{TS} / \text{W}) - \text{G}$
27	Glucomannan (M) (mass fraction) = $[\text{NMA} \cdot (1+1/b) + \text{NGA}] / \text{W}$
28	Xylan (X) (mass fraction) = $\text{H} - \text{M}$



## **CHAPTER 4**

### **EXPERIMENTAL**

#### **4.1. EXPERIMENTAL METHOD**

Cooks were performed for three hard woods (Rock Maple, Poplar and Yellow Birch) and one soft wood (Black Spruce). Wood logs were debarked, and knots removed from the wood manually. The debarked logs were chipped, air-dried and screened. The fraction passing through 9/8 inch holes but retained on the screen with 5/8 inch holes was used. The air-dried and screened chips were stored in double plastic bags in the cold room. Before cooking the moisture content of the wood chips was carefully determined using a representative sample. A known weight of chips (1.5-2.0 kg o.d.) was cooked in a 10 liter rocking batch digester at a liquid to wood ratio of 4.0 l/kg. The cooks were degassed around 95-100 °C, kept at 120 °C for 50-55 minutes, and the time at cooking temperature of 170°C was adjusted depending on the H-factor. The H-factor for Rock Maple, Poplar, Yellow Birch and Black Spruce were 800, 600, 800 and 1100 hours respectively.

##### **4.1.1. Kraft Cooking**

Alkaline cooks were performed at four sulfidities, 0, 7.5, 15 and 30%, and an effective alkali (EA) charge for the hard woods of 21% (as Na<sub>2</sub>O on o.d. wood) and 23% for Black Spruce.

##### **4.1.2. Kraft-AQ Cooking**

The kraft-AQ cooks were carried out exactly as the kraft cooks except that 0.1% anthraquinone (AQ) based on o.d. wood was added to the white liquor.

#### **4.1.3. Polysulfide Cooking**

Four different polysulfide cooks at elemental sulfur additions of 0, 1, 2 and 4% (based on o.d wood) to 30% sulfidity liquors were performed on all four wood species at the same H-factor and EA charges as that of the alkaline cooks. The polysulfide liquor was prepared by dissolving elemental sulfur and Na<sub>2</sub>S in de-aired water of 60 °C while stirring for 20 minutes. Then NaOH was added.

#### **4.1.4. Polysulfide-AQ Cooking**

Polysulfide-AQ cooks were performed exactly the same as polysulfide cooks but with 0.1% anthraquinone based on o.d. wood was added to the polysulfide liquor.

### **4.2. ANALYSES**

#### **4.2.1. Kappa Number**

The kappa number is defined as the number of milliliters of 0.1 N KMnO<sub>4</sub> solution consumed per gram of moisture free pulp under standardized conditions. It shows the degree of delignification of pulp and is proportional to the lignin content of pulp. The kappa number of pulp was measured by using TAPPI standard method T236 cm-76

#### **4.2.2. Tappi Viscosity**

The TAPPI viscosity was measured according to TAPPI standard method T230 om-89.

#### **4.2.3. Intrinsic Viscosity**

The intrinsic viscosity of pulp is a measure of the degree of polymerization of the cellulose chains in pulp. The intrinsic viscosity was measured according to ASTM standard D 1795-62.

#### **4.2.4. Ash**

The ash content of pulp was determined according to TAPPI standard method T211 om-85.

#### **4.2.5. Uronic Anhydride**

The uronic anhydride content of pulp was determined using the chromophoric group analysis method developed by Scott (1979). Strong sulfuric acid was used to dehydrate the pulp. Dimethylphenol was used as a standard, and the UV absorption measurement was performed at 400 and 450 nm.

#### **4.2.6. Sugar Analysis (Carbohydrate Content)**

Sugar analyses of acid hydrolyzed pulp were performed by using the Dionex DX 500 ion chromatograph. The external standard solutions were prepared for calibration curve at the beginning of the analysis. First a stock solution was prepared. This solution was then diluted to six different concentrations to serve as calibration solutions.

##### **Preparation of the Stock Solution.**

A stock (100 ml) solution containing all of the five mono-sugars was prepared at the following approximate concentrations:

- Arabinose: 1 mg/ml or 0.10 g/100ml volumetric flask
- Galactose: 1 mg/ml or 0.10 g/100ml volumetric flask
- Glucose: 4 mg/ml or 0.40 g/100ml volumetric flask
- Xylose: 2 mg/ml or 0.20 g/100ml volumetric flask
- Mannose: 2 mg/ml or 0.20 g/100ml volumetric flask

Before weighing the mono-sugars for the stock solution, they were dried in a vacuum oven at 40°C. The final concentration was determined by weighing.

#### Preparation of the Internal Standard.

A solution (100 ml) containing approximately 50 mg/ml of fucose was prepared as an internal standard.

#### Preparation of the External Standard Solution (Calibration No.1 to No.6).

To prepare the standard solution the stock solution was diluted using the following procedure:

1. Exactly transfer 1 ml, 2 ml, 4 ml, 8 ml, 16 ml and 32 ml of stock solution into 6 numbered 50-ml volumetric flasks. The six volumetric flasks were filled separately with 40, 39, 37, 33, 25 and 9 ml of deionized water.
2. 1.5 ml 72% H<sub>2</sub>SO<sub>4</sub> and 1ml internal standard solution (fucose) were added into the flasks.
3. The solutions were hydrolyzed at 121°C for 2 hour in a pressurized (14 psig) autoclave.
4. The volumetric flasks were filled with deionized water to 50 ml volume to replenish any evaporated water.
5. The solutions were filtered through a 0.45 µm membrane.
6. About 8 ml of the filtrates were transferred into 10 ml testing vials, which were then used for HPLC analysis.

The standard solutions were kept frozen to minimize degradation by microorganism, oxygen, light and temperature.

#### Preparation of the Samples.

Before hydrolysis, about 1.5 g of extractive-free pulp was ground in a Wiley mill.

The subsequent preparation steps of the pulp meal samples are as follows:

1. 100 mg (o.d.) of sample was weighed in a test tube, and exactly 1.5 ml of 72 %  $\text{H}_2\text{SO}_4$  was added and kept for 2 hours at 30°C. During this primary hydrolysis period, the slurry was manually stirred using a stirring rod every 10-15 min.
2. 41 ml of deionized water was used to quantitatively transfer the slurry into a 50-ml volumetric flask containing 1 ml of the internal standard (fucose) solution.
3. The volumetric flasks were covered with a piece of aluminum foil.
4. The secondary hydrolysis of the solution occurred for 2 hr. at 121°C by placing the volumetric flasks inside a pressurized autoclave.
5. After the secondary hydrolysis, the volumetric flasks were filled with deionized water to a final volume of 50 ml.
6. The hydrolysate was filtered through a 0.45- $\mu\text{m}$  membrane.
7. About 8 ml of filtrate was transferred into a 10 ml testing vial and was now ready for HPLC analysis.

After these preparative steps the standard solutions and samples were analyzed by Ion Chromatography. The carbohydrate content of the samples was determined from the peak area using calibration curves obtained from the analyses of the standard solutions. The calculation procedure of the carbohydrate content was summarized in Chapter 3.

#### **4.2.7. Extractives**

The extractives were determined gravimetrically following extraction with 1,2 dichloromethane. Air dried, ground pulp samples were extracted for 5 hours with 1,2 dichloromethane using 15 minutes cycle standard soxhlet extraction via ceramic crucibles.

#### **4.2.8. Total Pulp Yield**

The cooked chips were disintegrated, washed and then screened; with the rejects retained on a slotted 0.006 inch screen and the fibers retained on a 60 mesh screen. The (o.d.) weight of the rejects was determined. The wet pulp weight was measured after increasing the dryness of the pulp to about 25-30% by centrifugation and subsequent homogenization of the entire sample in a Hobart mixer. The total yield,  $Y_T'$ , was calculated based on the average dryness of 4 pulp samples, the total wet pulp weight, the dry weight of the rejects and the dry weight of the chips used in the cook.

## CHAPTER 5

### RESULTS AND DISCUSSION

#### 5.1. ROCK MAPLE COOKING

##### 5.1.1. Effect of Sulfidity and Anthraquinone

The UoM pulp yield measurement method relates the lignin free total yield, ( $Y_T'$ ), to the degree of polymerization of cellulose, DP, and mass fraction of cellulose in pulp,  $G'$ :

$$\frac{1}{Y_T' G'} = \frac{1}{Y_{C,W}} + \frac{(\Delta DP)_s}{Y_{C,W}} \cdot \frac{1}{DP} \quad (5.1)$$

The effect on this equation of some pulping conditions, such as sulfidity and anthraquinone were investigated for Rock Maple chips. Kraft cooking was carried out at different sulfidities (0%, 7.5%, 15% and 30%) at an H-factor of 800 hr, a cooking temperature of 170°C and an effective alkali charge of 21%. Cooking at these conditions took place with and without addition of 0.1% anthraquinone on wood.

Figure 5.1 shows the effect of sulfidity on the pulping yield with and without the addition of anthraquinone (AQ). It is apparent that the total pulp yield decreases with increasing sulfidity for both kraft and kraft-AQ cooking. The main reason for this decrease is that more lignin is removed with increasing sulfidity due to the increased rate of delignification. It is also clear from Figure 5.1 that the addition of 0.1% anthraquinone (AQ) increases the total pulp yield by about 1.5% for Rock Maple at the same sulfidity.

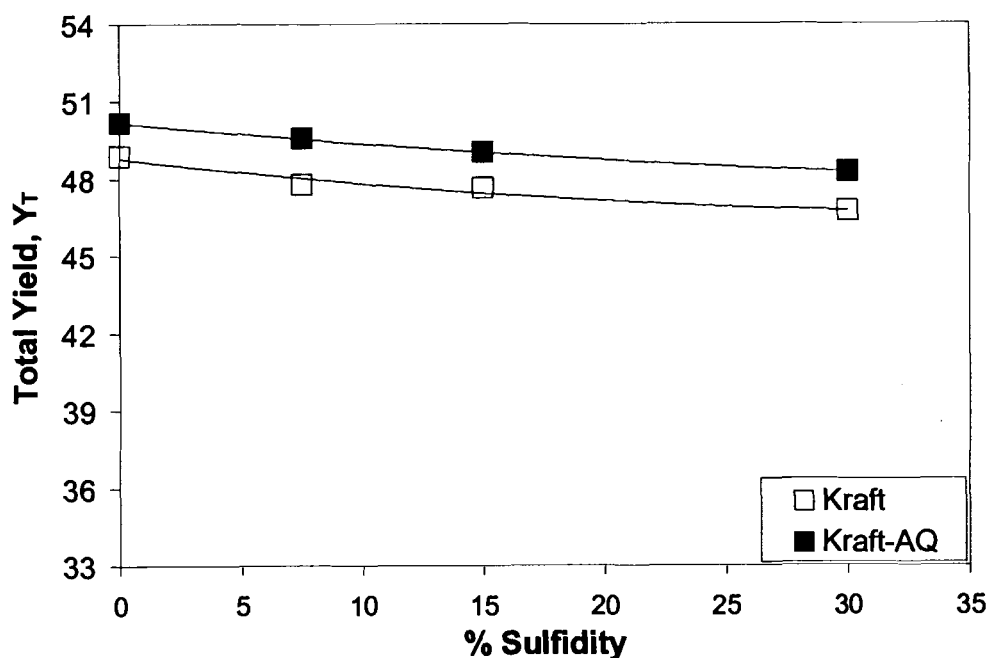


Figure 5.1. Total Yield,  $Y_T$ , versus Sulfidity with or without AQ addition for Rock Maple

The development of the kappa numbers with increasing sulfidity are plotted in Figure 5.2. It is clear from Figure 5.2 that the addition of 0.1% anthraquinone decreases the kappa number of pulp at the same sulfidity especially at the lower sulfidity levels. It is well known that AQ accelerates delignification (MacLeod, 1980). At the highest sulfidity of 30%, the decrease in kappa number due to addition of 0.1 % AQ is very small presumably because the delignification rate slows down significantly at a very low kappa number level of about 10.



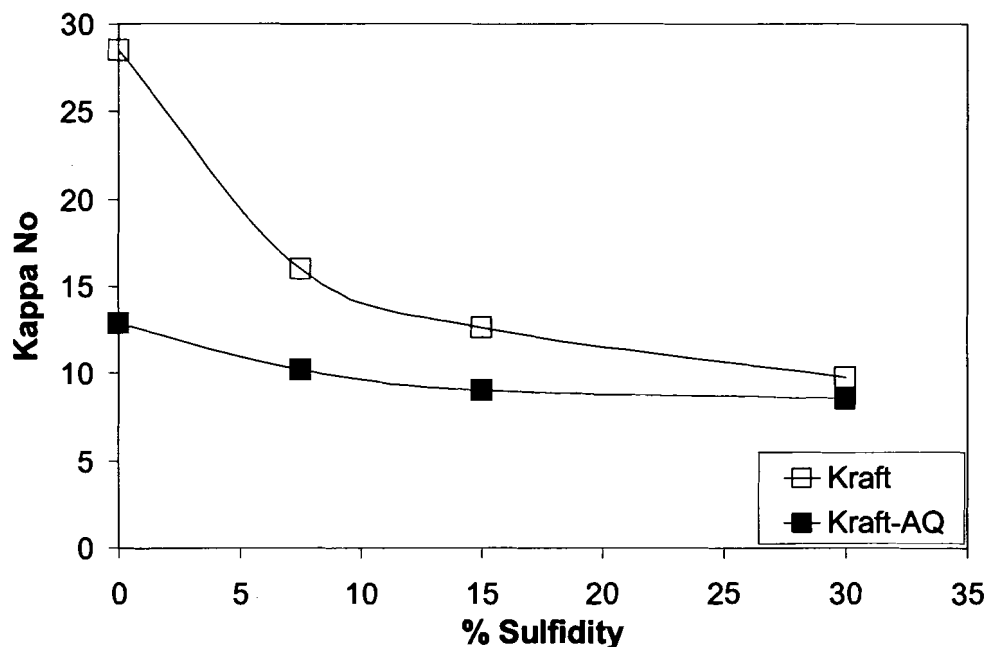


Figure 5.2. Kappa Number versus Sulfidity with or without AQ addition for Rock Maple

Figures 5.3 and 5.4 show the change in Tappi and intrinsic viscosities when increasing the sulfidity for kraft and kraft-AQ cooking. In both cases the Tappi and intrinsic viscosities decrease with increasing sulfidity, although the rate of decrease diminishes as the sulfidity increases. It has been reported (Kubes, 1983) that the cellulose degradation by alkaline hydrolysis is only affected by  $[\text{OH}^-]$  and not  $[\text{HS}^-]$  therefore we do not have any explanation for the decrease at the present time. It can also be seen from the Figures 5.3 and 5.4 that at the same sulfidity the viscosity values are mostly slightly lower for kraft-AQ cooking compared to kraft. This behavior is expected since the addition of AQ leads to a smaller alkali consumption as a consequence of the reduced cellulose degradation. The net effect is a higher alkali concentration during kraft-AQ pulping, and thus a lower pulp viscosity is expected than pulps produced without AQ at otherwise the same cooking conditions.

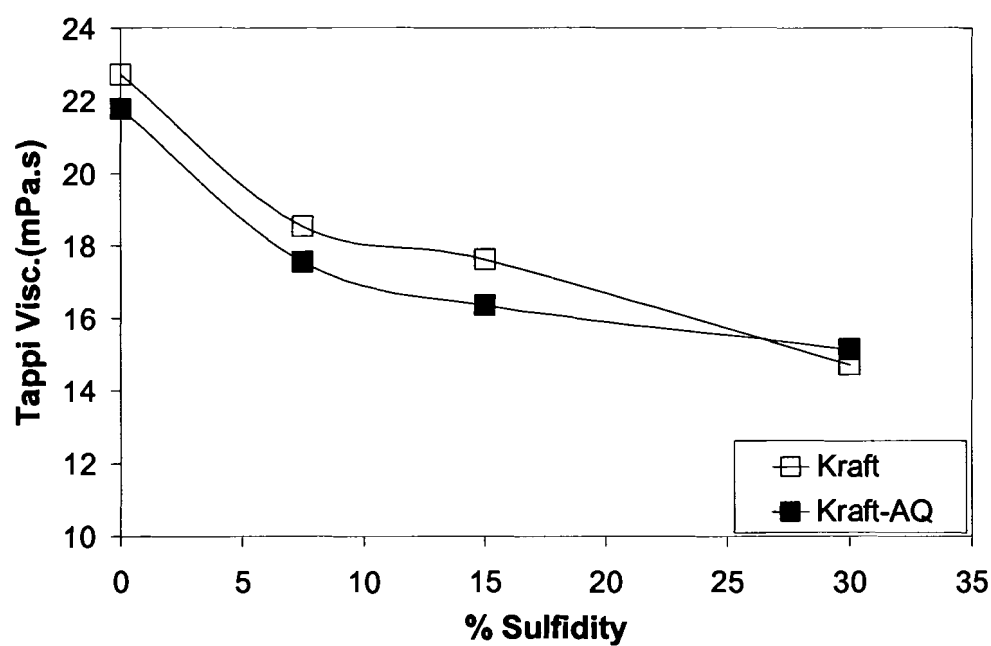


Figure 5.3. Tappi Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking of Rock Maple

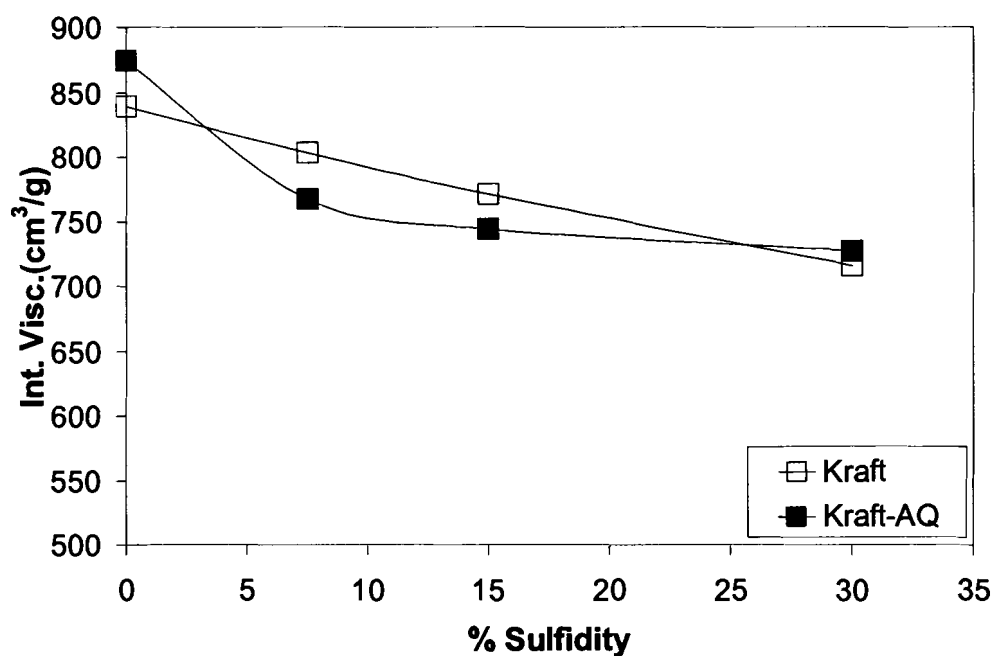


Figure 5.4. Intrinsic Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking of Rock Maple

Figure 5.5 indicates the change in Tappi viscosity with kappa number for kraft and kraft-AQ. It is apparent that the Tappi viscosity decreases with increasing delignification, and that the addition of 0.1 % AQ increases the Tappi viscosity at same kappa number, especially at higher kappa numbers.

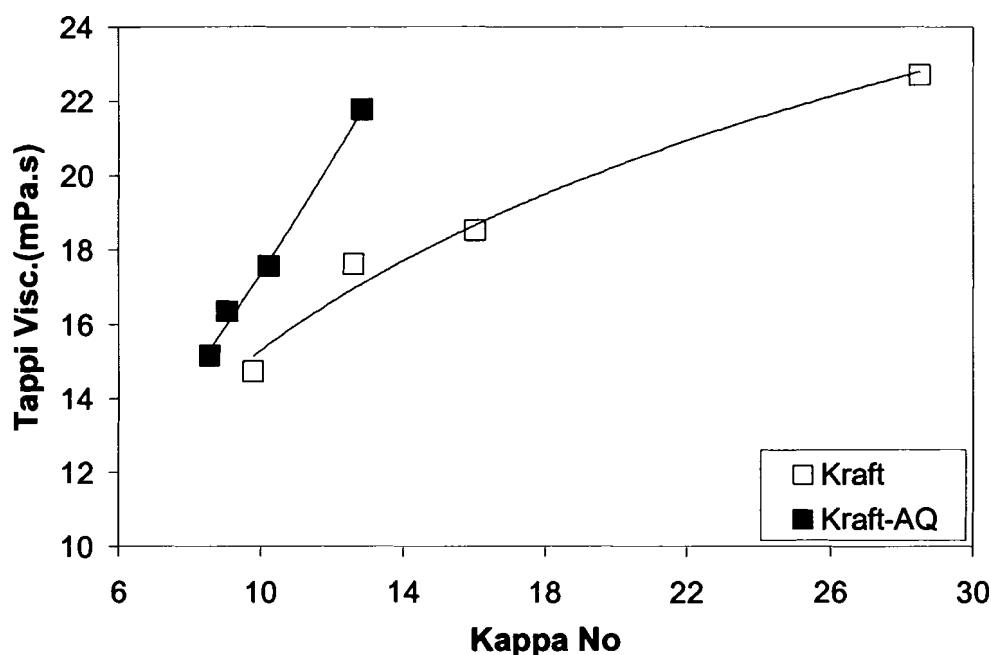


Figure 5.5. Tappi Viscosity versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple

The total pulp yield and lignin-free pulp yield are plotted against kappa number in Figures 5.6 and 5.7 respectively. It is apparent from Figure 5.6 that the total yield decreases with decreasing kappa number for both kraft and kraft-AQ cooking. The effect of lignin removal on the yield is eliminated in Figure 5.7. This graph shows that the addition of AQ leads to higher carbohydrate retention of about 1.5 % (based on wood) at kappa 13 compared to about 1 % at kappa 8. The increased carbohydrate retention with AQ addition is caused by stabilization of carbohydrate reducing ends by oxidation with AQ (Gullichsen, 2000). In order to identify the cause of the higher increase in lignin free

yield with increasing kappa number for kraft-AQ relative to kraft, the cellulose yield,  $100Y_C$  (% on o.d. wood) is plotted against kappa number in Figure 5.8. It can be seen that although the cellulose yield for kraft-AQ increases over the narrow range of kappa number, the cellulose yield increases very slightly for kraft cooking. On the other hand, it is apparent from Figure 5.9 that the hemicellulose yield  $100 Y_H$ , (% on o.d. wood), is constant for kraft and kraft-AQ cooks. Therefore the larger yield improvement with increasing kappa number for kraft-AQ cooking is the result of more cellulose retention while the hemicellulose yield is not significantly affected over the narrow range of delignification.

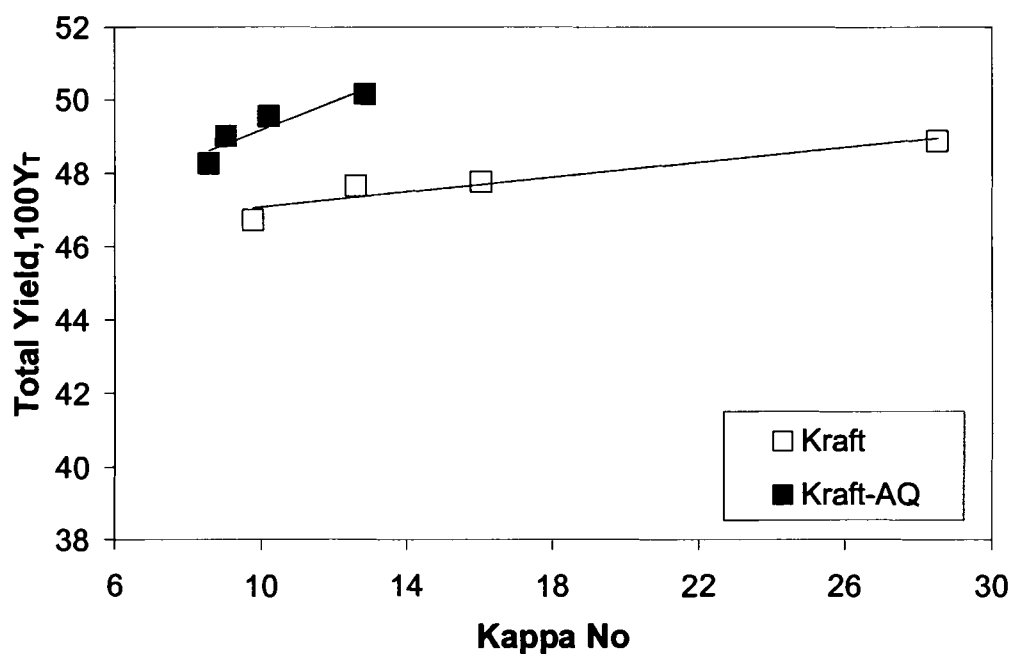


Figure 5.6. Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple

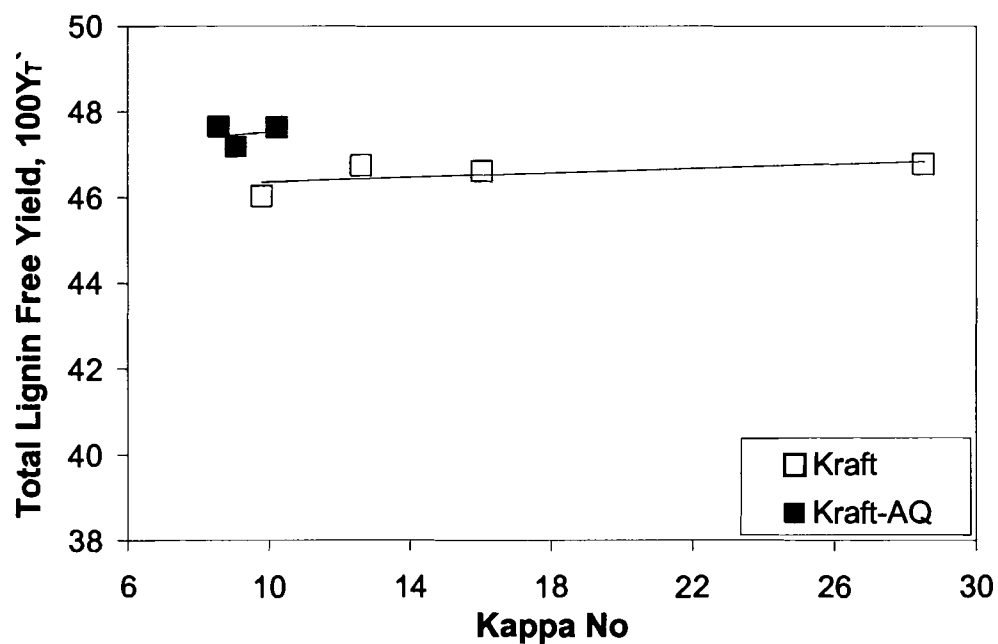


Figure 5.7. Lignin-free Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple

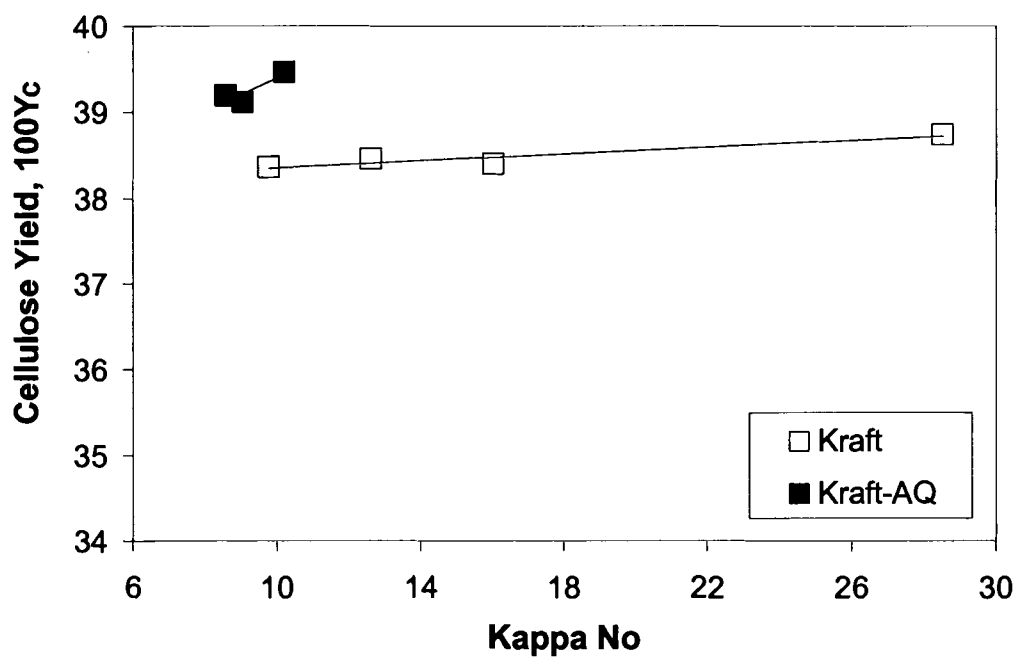


Figure 5.8. Cellulose Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple

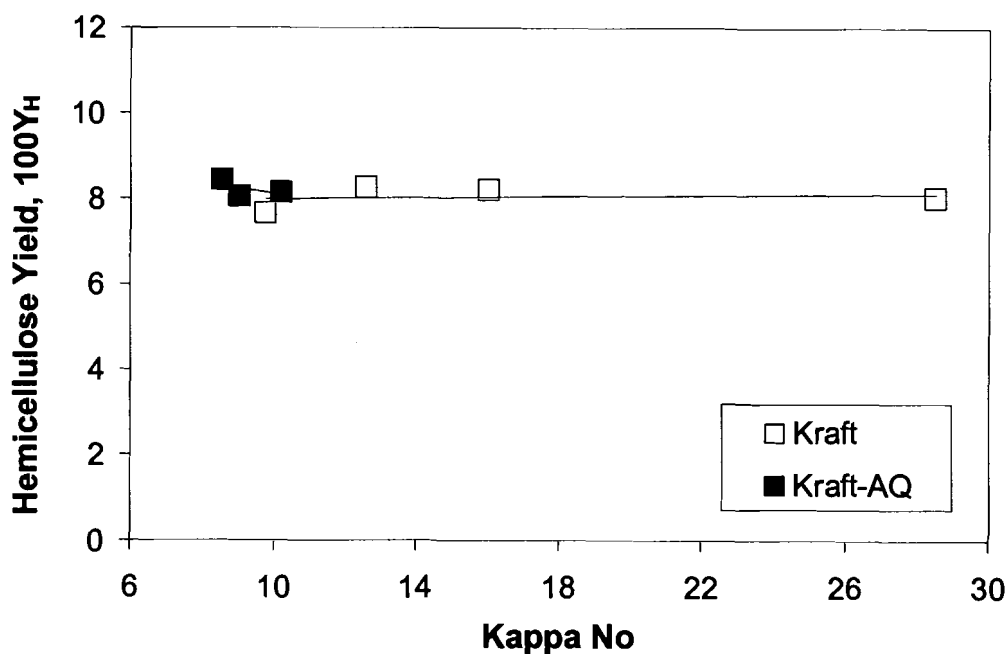


Figure 5.9. Hemicellulose Yield versus Kappa Number for Kraft and Kraft-AQ of Rock Maple

Figure 5.10 shows how the xylan yield,  $100 Y_X$  (% on o.d. wood) changes with increasing degree of sulfidity. It is apparent from Figure 5.10 that the main hardwood hemicellulose, xylan, is not affected by the degree of sulfidity, leading to different kappa numbers at the same effective alkali charges and H-factor. It can also be seen that the addition of 0.1 % AQ slightly increases the xylan retention. McDonough (1998) explained that during cooking the xylan loss occurs only by physical dissolution. Since AQ addition is expected to increase the residual effective alkali content of the cooking liquor, xylan retention is expected to be lower with AQ kraft cooking. The opposite effect seen in Figure 5.10 suggests that AQ also has a stabilizing effect on xylan by oxidation of reducing ends.

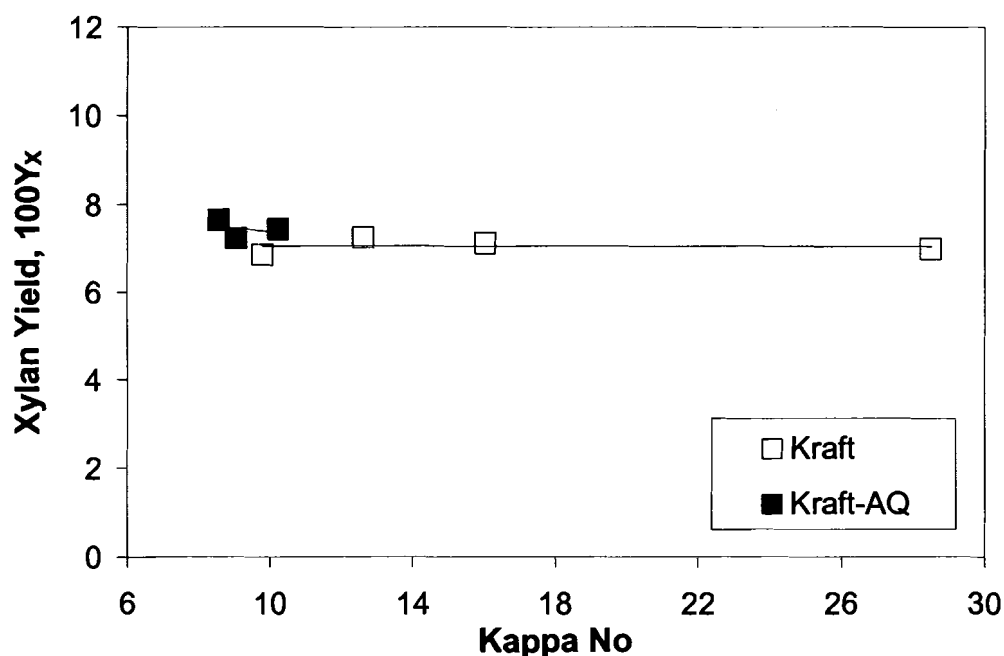


Figure 5.10. Xylan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple

Figure 5.11 depicts the mannan yield,  $100 Y_M$  (% on o.d. wood), for the different kappa number pulps obtained by varying the sulfidity. It can be seen that the mannan yield increases very slightly for kraft cooking while no significant change in mannan yield can be seen for kraft-AQ cooking over the narrow range of kappa number. In his review, McDonough mentioned that mannan is removed both by peeling and physical dissolution (McDonough, 1998). From Figure 5.11 it is seen that AQ addition decreases mannan retention in the pulp somewhat at the same kappa number, although the change appears to be within the uncertainty of the data. It should be noted that kraft pulp and kraft-AQ pulps were hydrolyzed using different conditions. The primary hydrolysis for the kraft pulps was done for 1 hour while the primary hydrolysis of the kraft-AQ pulps was extended to 2 hours.

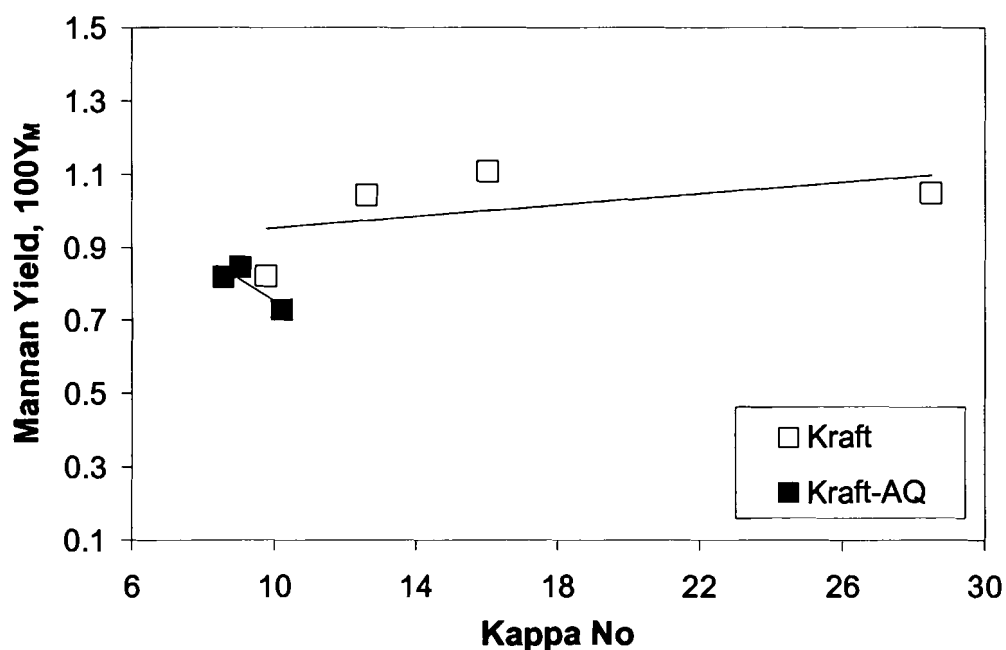


Figure 5.11. Mannan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Rock Maple

The yield data for kraft and kraft-AQ of Rock Maple are plotted in Figure 5.12 according to the UoM yield equation. It shows that two separate linear relationships are obtained for the kraft and kraft-AQ cooks. As expected based on the UoM equation,  $1/Y_T G$  increases with  $1/DP$ . Figure 5.11 also shows that  $1/Y_T G$  decreases from about 2.60 to 2.55 with the addition of 0.1% AQ, i.e. the cellulose mass fraction based on wood,  $Y_C$ , increases from 0.385 to 0.392 % due to oxidation of the reducing ends by anthraquinone.



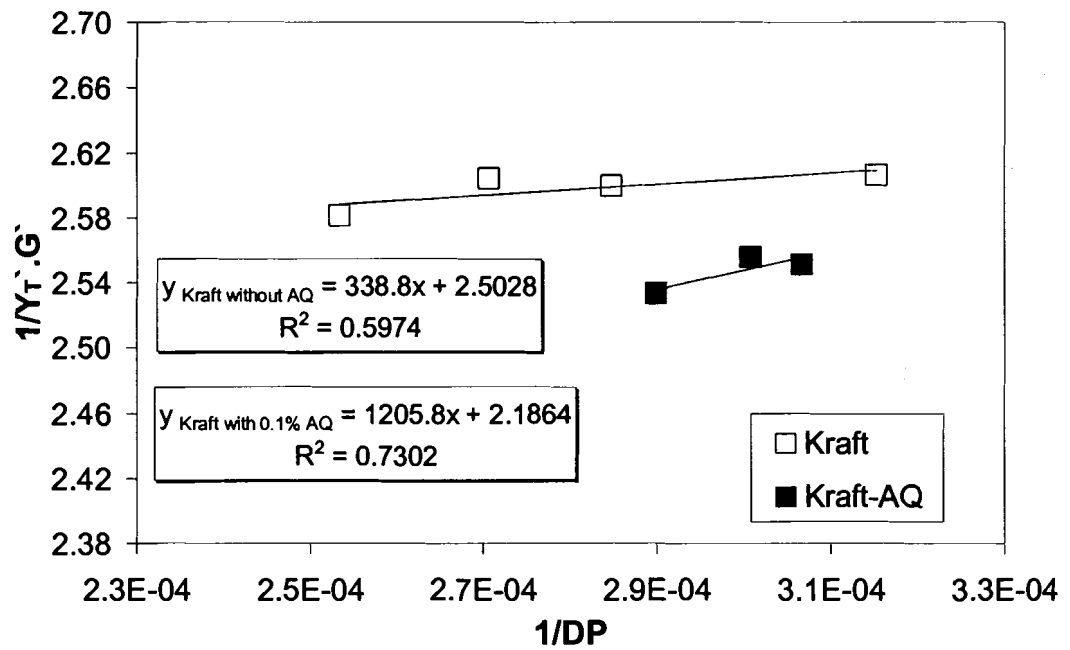


Figure 5.12. UoM Equation for Kraft and Kraft-AQ Cooking of Rock Maple

The cooking results are also plotted in Figure 5.13 according to the pulp yield prediction equation proposed by Marcoccia (Marcoccia, 1998). They show a linear increase in  $Y_T$  with increasing values of  $(\log V)/(G^2)$  as expected. However it is also seen that two different equations are needed to describe kraft and kraft-AQ cooking, as was the case for the UoM equation shown in Figure 5.12.

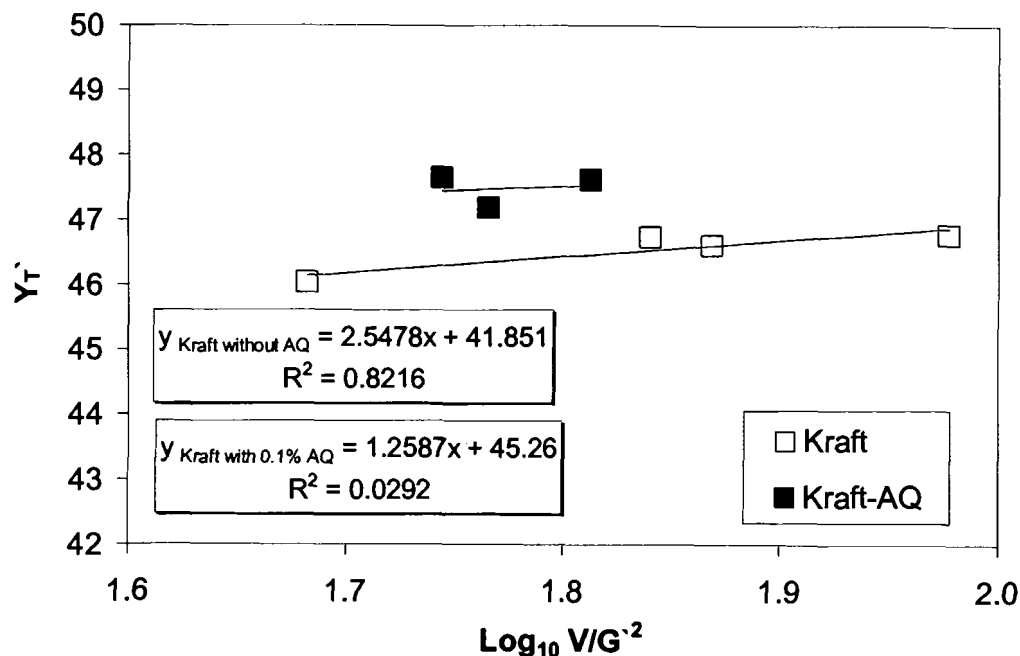


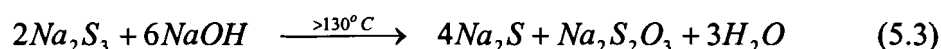
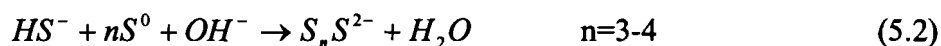
Figure 5.13. Marcoccia Equation for Kraft and Kraft-AQ Cooking of Rock Maple

### 5.1.2. Effect of Polysulfide and Polysulfide-Anthraquinone

The polysulfide (PS) and polysulfide-anthraquinone (PSAQ) cooks of Rock Maple were carried out at an H factor of 800 hr., an effective alkali of 21%, a sulfidity of 30% and a cooking temperature of 170° C. The elemental sulfur content of the polysulfide cooks was varied from 0, 1, 2 and 4%. The PSAQ cooks were performed with an addition of 0.1 % AQ on o.d. wood.

Figure 5.14 shows the total yield of Rock Maple chips for the different PS and PSAQ cooks plotted as a function of percentage elemental sulfur charge. It is apparent that both the PS and PSAQ yield increases with polysulfide (elemental S) charge. The yield increases about 1% with each 1% increase in elemental S addition for both the PS and PSAQ cooks. The increase in yield is due to oxidation of the reducing end groups of

the carbohydrates by polysulfide (Gullichsen, 2000), and due to the decrease in alkali concentration of the polysulfide cooking liquor with increasing percentage of elemental sulfur. The decrease in alkali concentration with increasing percentage of elemental sulfur in polysulfide cooking is caused by the consumption of hydroxyl ions when sulfur reacts with  $\text{Na}_2\text{S}$  to form polysulfide, and by the formation of thiosulfate from polysulfide at high temperatures (Dorris, 1994).



The lower hydroxide concentration leads to a larger retention of carbohydrates and lignin, and thus to a higher total yield.

Figure 5.14 also shows that the PSAQ yield is essentially the same as the PS yield, and that without addition of elemental S, the kraft-AQ cook gives a higher yield than kraft.

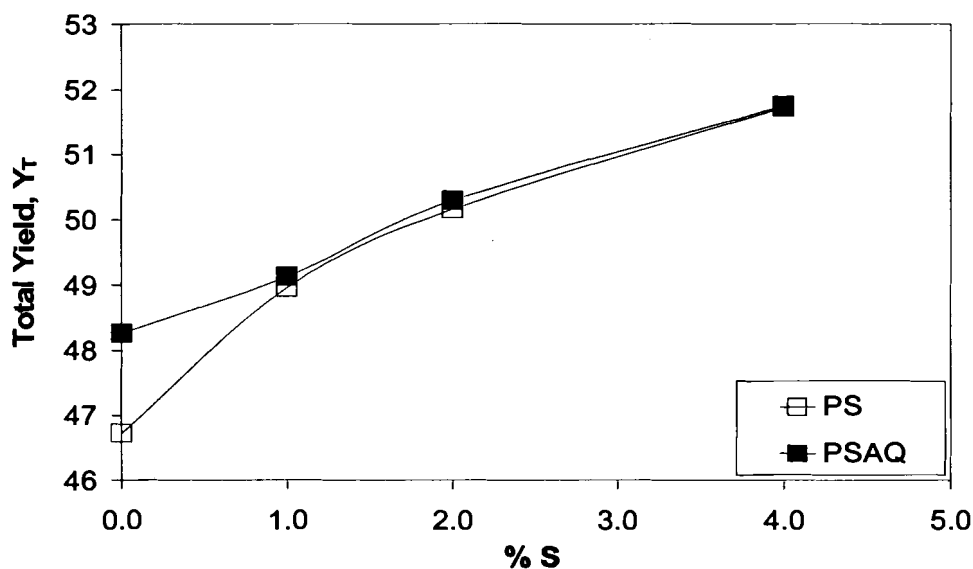


Figure 5.14. Total Yield,  $Y_T$ , versus Percentage Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple

Figure 5.15 shows that the kappa number increases with increasing polysulfide charge for both PS and PSAQ cooking. Ahlgren reported that the delignification rate was not significantly affected by changes in the polysulfide concentration (Ahlgren, 1967). Therefore the increase in kappa number most likely is caused by the decrease in initial alkali concentration with increasing elemental sulfur charge. It can also be seen that at the same elemental sulfur charge, the kappa number is higher for PS than PSAQ cooks. This is expected since 0.1 % addition of anthraquinone increases the delignification rate and thus results in a decrease in kappa number. The kappa number differences between PS and PSAQ cooks decrease with increasing polysulfide concentration (elemental S).

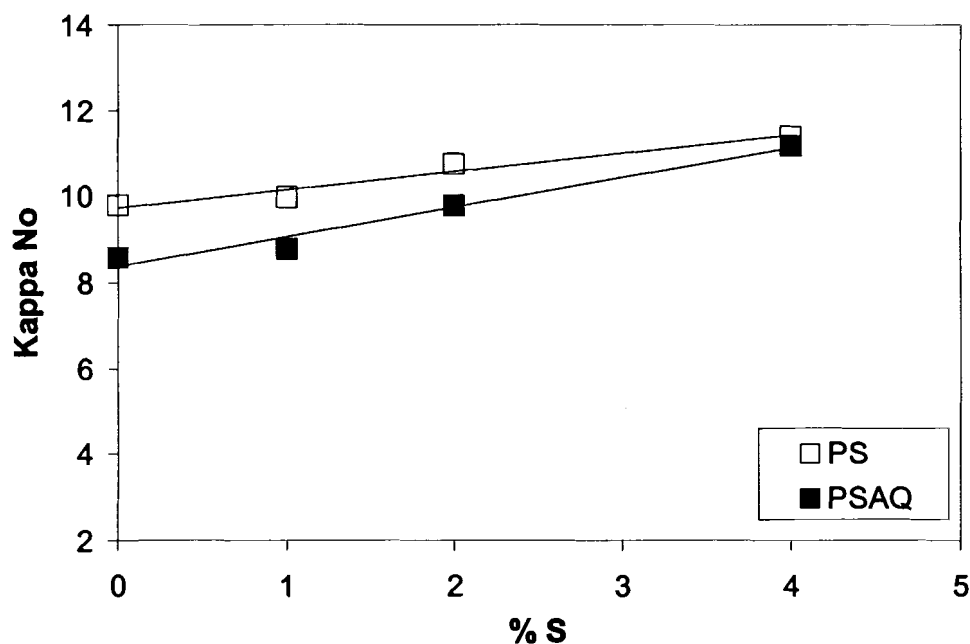


Figure 5.15. Kappa Number versus Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple

Figures 5.16 and 5.17 show the changes in intrinsic viscosity and Tappi viscosity for PS and PSAQ pulps for increasing polysulfide concentration (elemental sulfur). It is clear that the Tappi and intrinsic viscosities increase slightly with polysulfide concentration, but they are almost not affected by the anthraquinone (0.1%) addition. This is not in agreement with Li et al. (2002) who reported that the viscosity losses for PS and PSAQ pulps were lower than Kraft and Kraft-AQ.

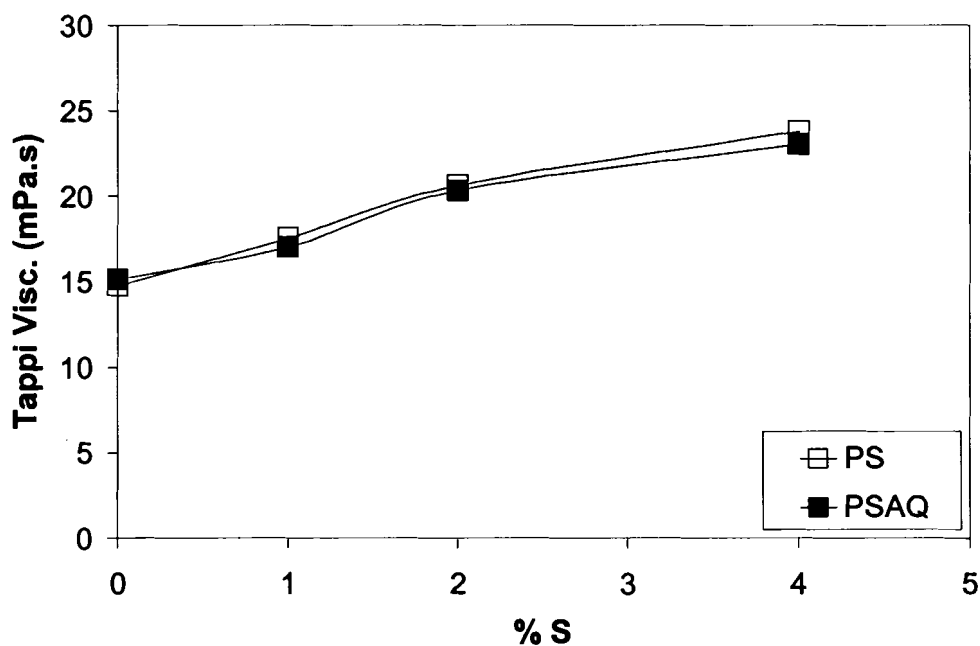


Figure 5.16. Tappi Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple

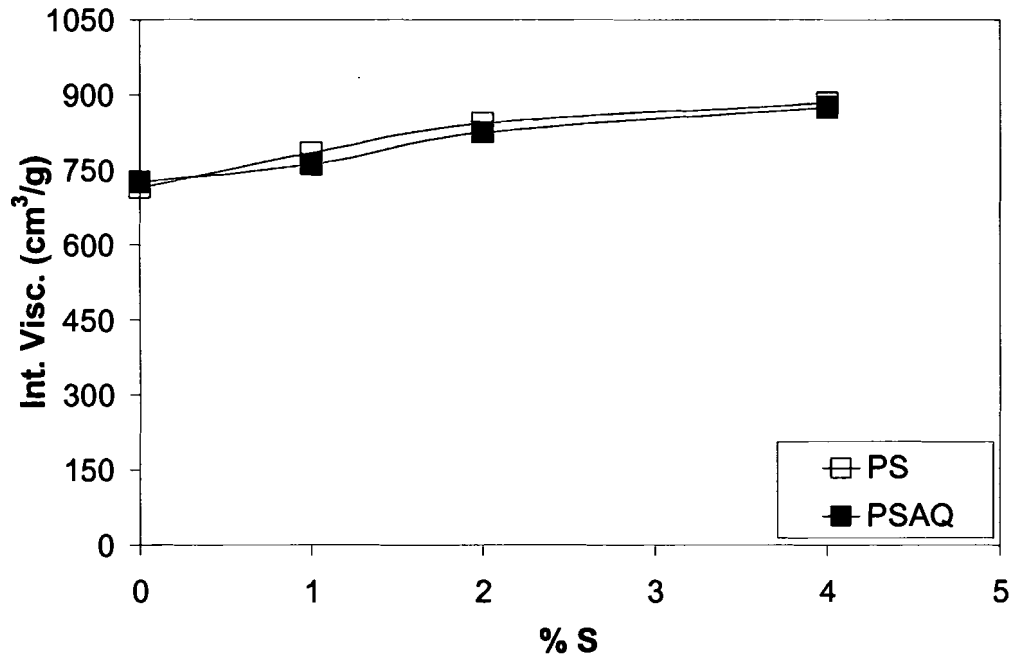


Figure 5.17. Intrinsic Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Rock Maple

Figure 5.18 displays the change in Tappi viscosity with kappa number for the PS and PSAQ pulps. As expected the Tappi viscosity decreases with increasing delignification for both pulp types. It is obvious from Figure 5.18 that the addition of 0.1 % AQ increases the Tappi viscosity at the same kappa number, especially at lower kappa numbers.

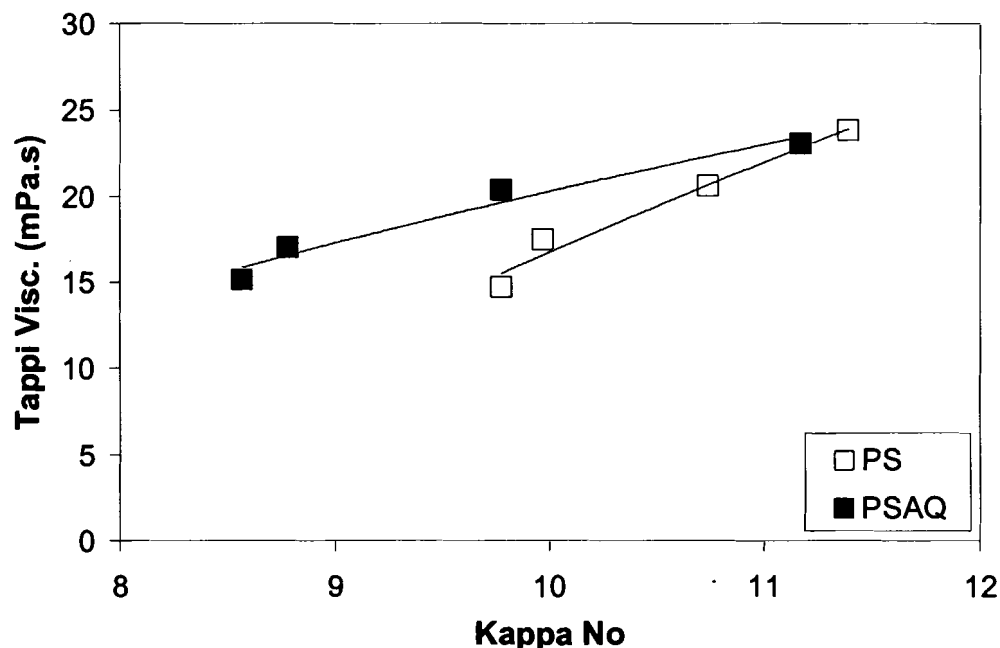


Figure 5.18. Tappi Viscosity versus Kappa Number for PS and PSAQ Cooking of Rock Maple

The total yield and total lignin free yield of the PS and PSAQ pulps are plotted against kappa number in Figures 5.19 and 5.20. It can be seen that there is a sharp increase in total yield with increasing kappa number, especially for PS pulp. The yield of PSAQ pulp is higher than that of PS pulp at the same kappa number. For a kappa number of 10, the yield increase by adding 0.1% AQ is about 2-3 %. At a kappa number of about 11 this increase is about 0.5-1.0 %. It is also obvious that lignin free total yield increases with increasing kappa number and thus with increasing elemental sulfur charge. For a kappa number of about 10, the yield increase by adding 0.1 % AQ is about 2.5-3 % while at a kappa number of about 11 this increase is about 1.5-2 %. This indicates that the effect of AQ on the yield diminishes with increasing kappa number, i.e. for pulps produced with increasing charges of elemental sulfur. Therefore, the results in Figures 5.20 and 5.15 show that the positive affect of AQ addition on both yield and

delignification diminishes at increasing elemental sulfur charges for polysulfide cooking. In order to explain this decrease, the cellulose and hemicellulose yield (on wood) of the PS and PSAQ pulps were plotted against kappa number in Figures 5.21 and 5.22. It is apparent from Figure 5.21 that the cellulose yield of the PS cooks as well as the PSAQ cooks increase with kappa number and thus with increasing elemental sulfur charge. However the results in Figure 5.21 also show that the cellulose yield increase with increasing kappa number is smaller for PSAQ pulps than PS pulps. Also, at the same kappa number the cellulose yield is higher for the PSAQ pulps by 0.5 to 1.0 %. A similar behavior is seen in Figure 5.22 for the hemicellulose yield, with a 2 % higher yield for PSAQ pulps at low kappa numbers and 1 % at the highest kappa numbers.

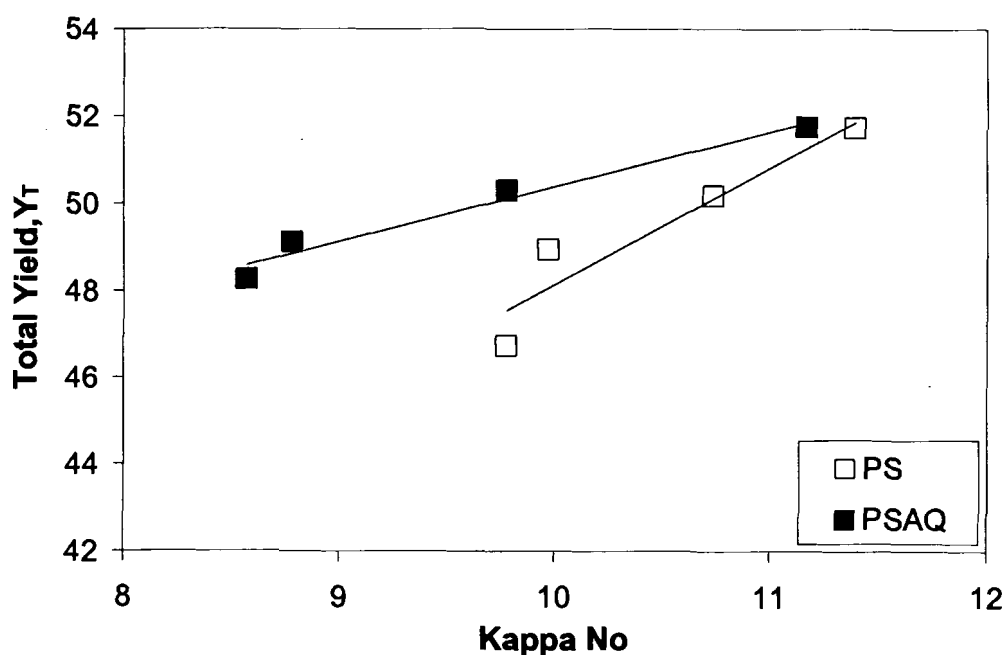


Figure 5.19. Total Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple



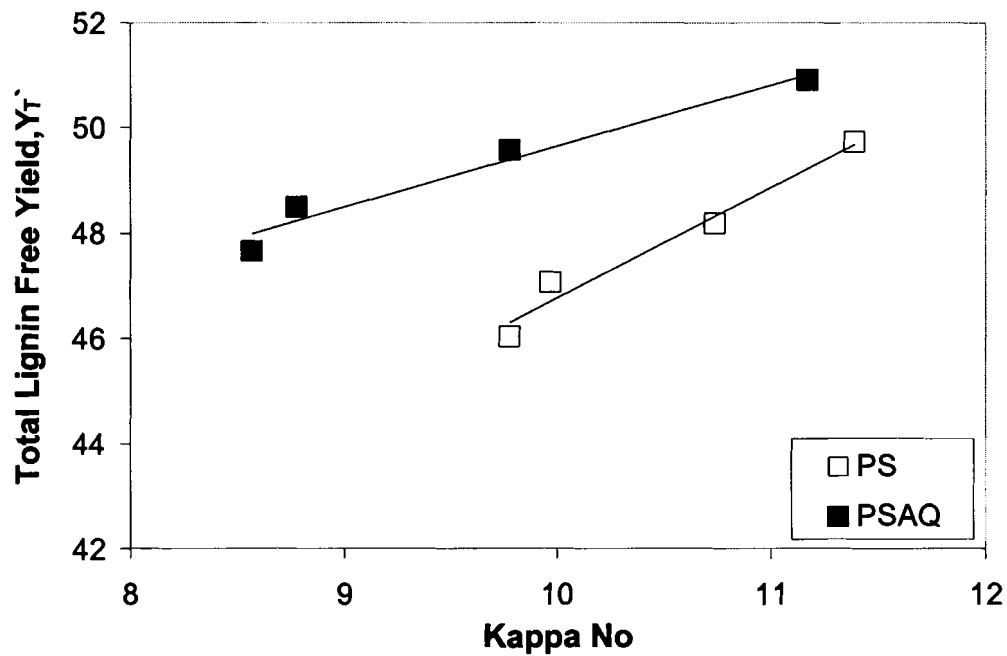


Figure 5.20. Lignin-free Total Yield versus Kappa Number for PS and PSAQ of Rock Maple

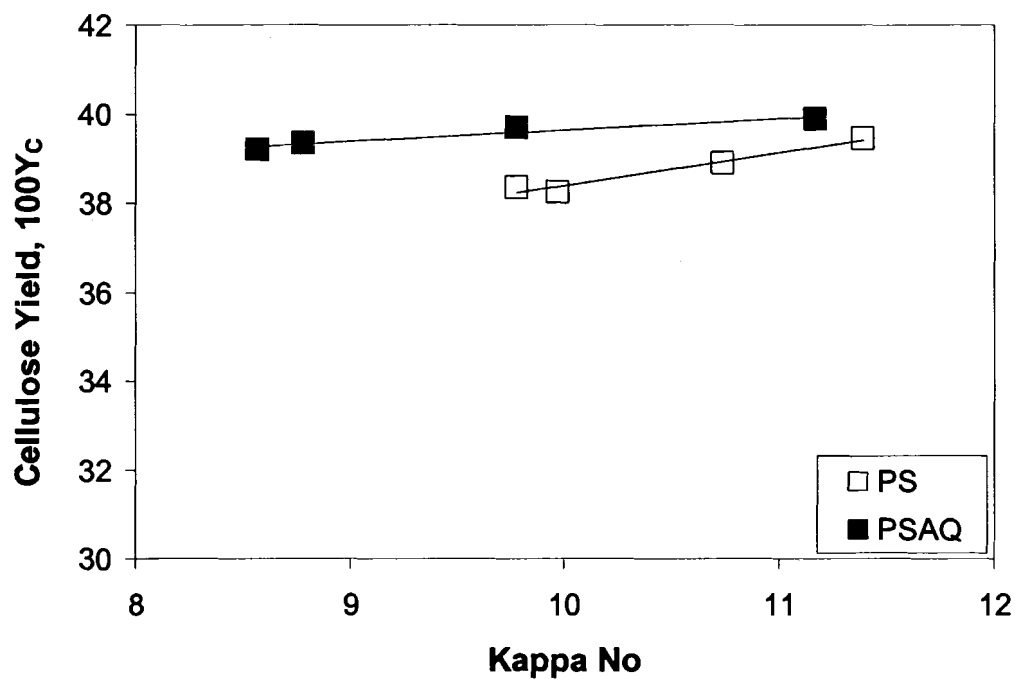


Figure 5.21. Cellulose Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple

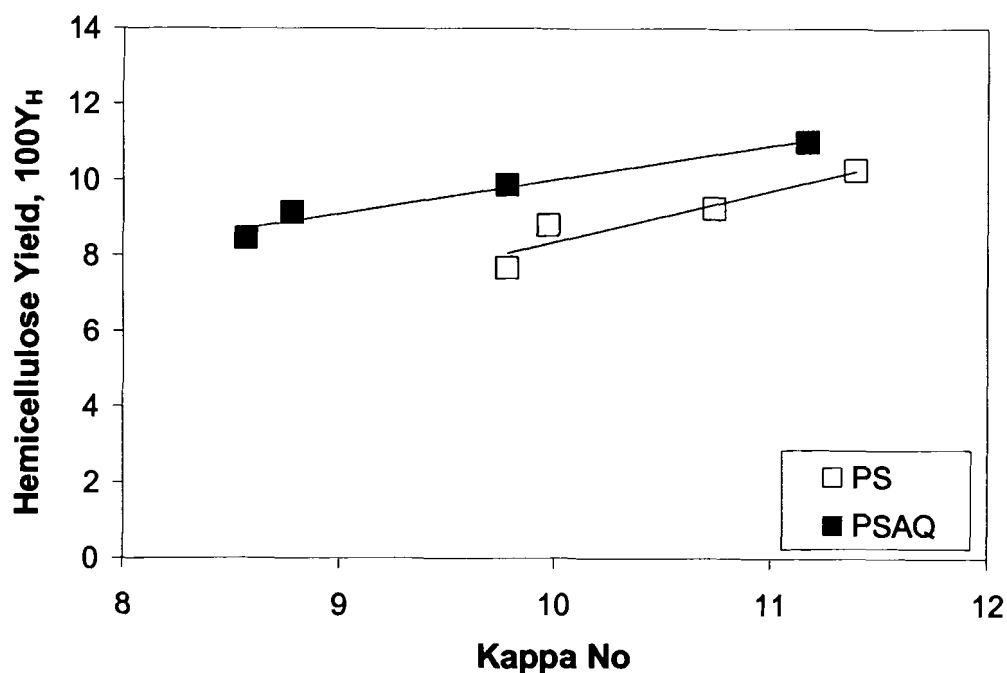


Figure 5.22. Hemicellulose Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple

Figure 5.23 shows how the xylan yield changes with increasing kappa number, and thus degree of polysulfide (elemental sulfur) for PS and PSAQ pulps. Since it is reported that xylan loss occurs only by physical dissolution (McDonough, 1998), the increase in xylan retention might be caused by the lower residual alkali concentration of the polysulfide cooking liquors. The decrease in alkali concentration with increasing percentage of elemental sulfur in polysulfide cooking is caused by the consumption of hydroxyl ions when sulfur reacts with  $\text{Na}_2\text{S}$  to form polysulfide at high temperatures (Dorris, 1994). It can also be seen that the addition of 0.1 % AQ slightly further increases the xylan retention compared to the PS cook.

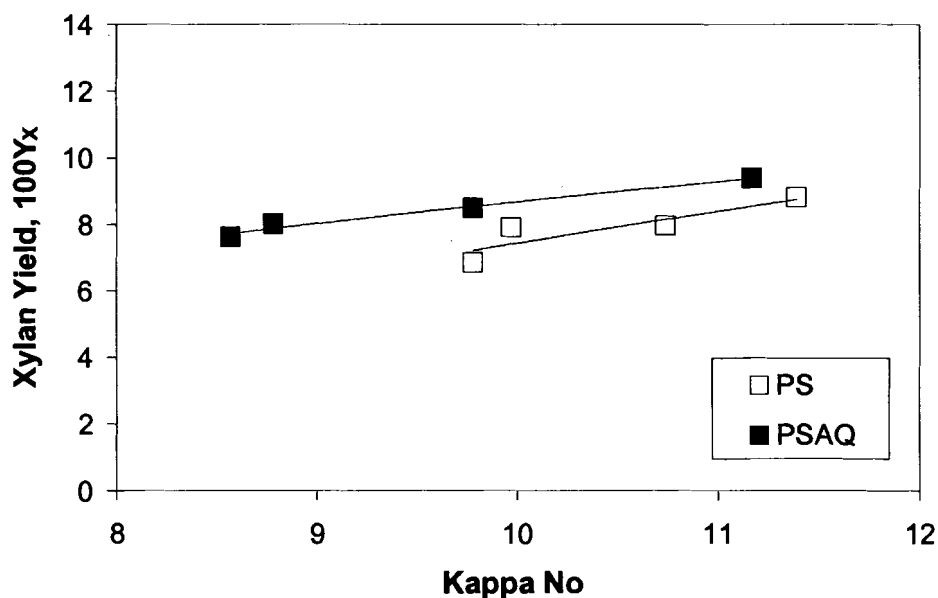


Figure 5.23. Xylan Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple

Figure 5.24 shows the mannan yield of PS and PSAQ pulps of different kappa numbers obtained by varying the polysulfide concentration. It is apparent that the mannan retention increases with increasing kappa number and thus with increasing polysulfide charge. It is reported that mannan is removed by peeling and physical dissolution during cooking (McDonough, 1998). It is also well known that polysulfide can stop the peeling reaction by oxidizing the reducing end group of carbohydrates (Gullichsen, 2000). Therefore, one of the reasons for the increase in mannan retention during PS and PSAQ cooks is the presence of polysulfide. The other reason may be the reduced alkali concentration in polysulfide liquors with increasing polysulfide (elemental sulfur) concentration as discussed earlier. It is also obvious from Figure 5.24 that the addition of 0.1 % AQ increases the mannan content at the same kappa number. It is known that AQ increases carbohydrate retention by oxidizing reducing end groups (Gullichsen, 2000).

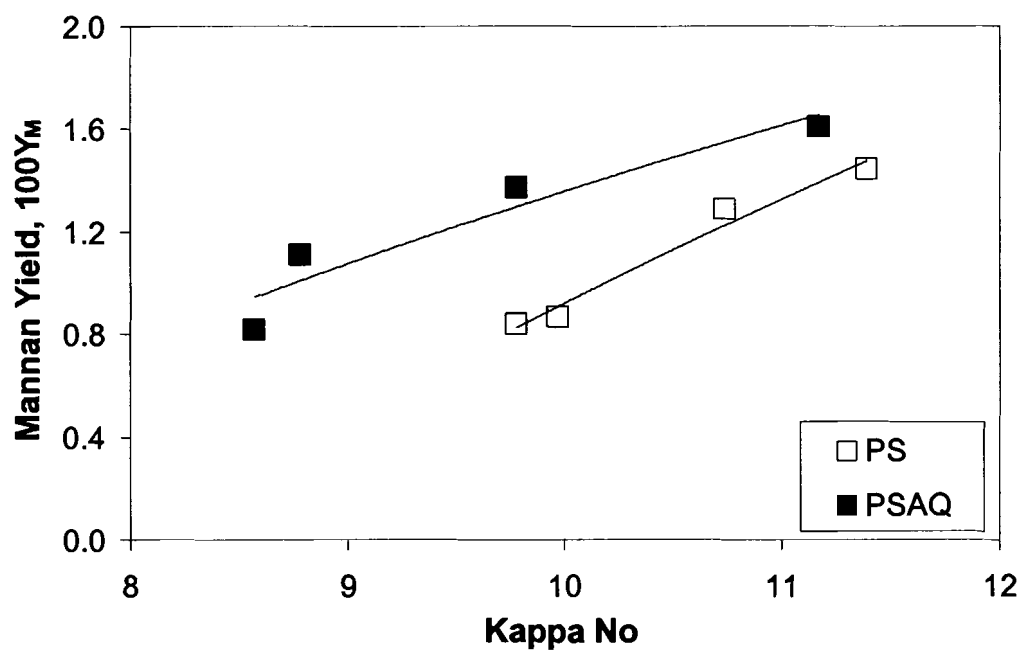


Figure 5.24. Mannan Yield versus Kappa Number for PS and PSAQ Cooking of Rock Maple

$1/Y_T \cdot G'$  was plotted against  $1/DP$  according to the UoM equation in Figure 5.25. A different linear relationship is obtained for PS and PSAQ. The explanation is that the addition of AQ leads to stabilization of cellulose throughout the cook.

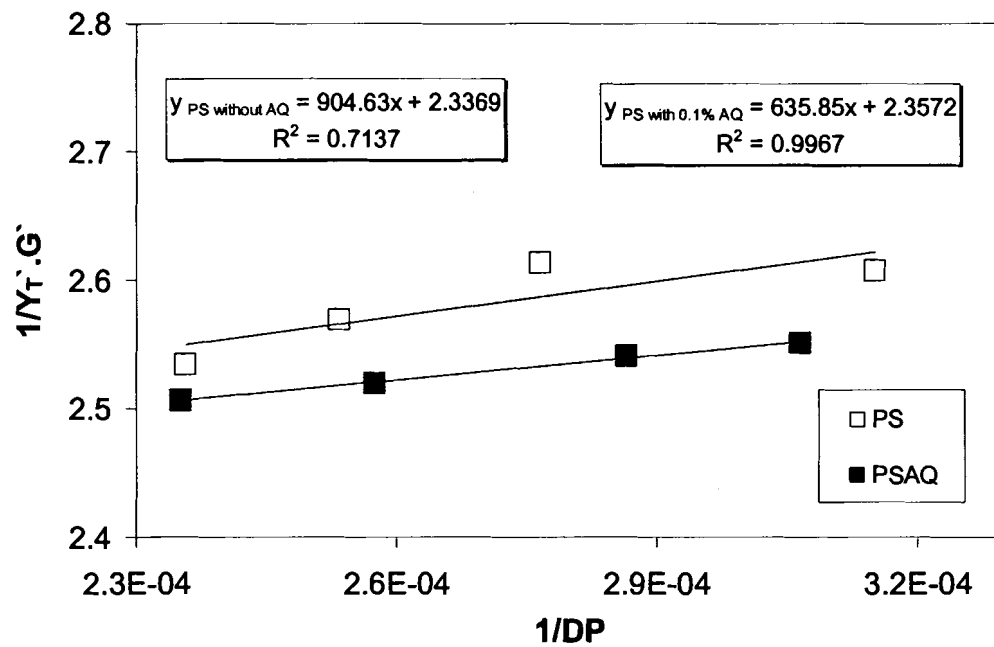


Figure 5.25. UoM Equation for PS and PSAQ Cooking of Rock Maple

The results were also plotted in Figure 5.26 according to the pulp yield prediction equation developed by Marcoccia et al. (Marcoccia, 1998). Two different linear relationships are also obtained for the PS and PSAQ pulps when using this yield prediction equation.

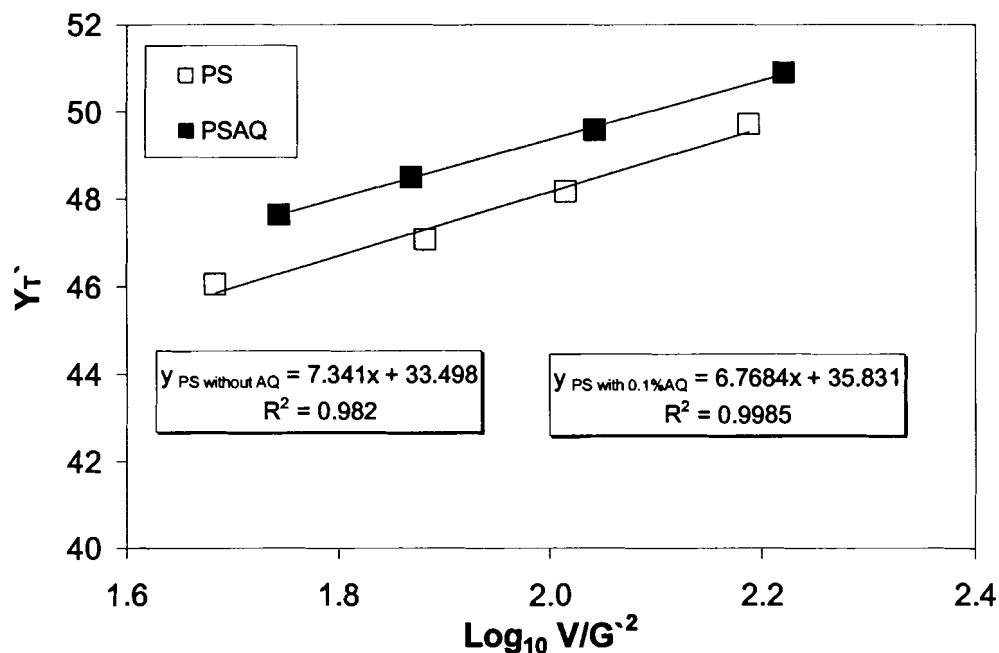


Figure 5.26. Marcoccia Equation for PS and PSAQ Cooking of Rock Maple

The UoM equation plots for kraft, kraft-AQ, PS and PSAQ cooking of Rock Maple are combined in Figure 5.27. It is apparent that the results of Kraft and PS pulps can be represented by the same correlation, while another single linear relation is adequate for Kraft-AQ and PSAQ pulps. Therefore, the UoM pulp yield prediction is not affected by changes in sulfidity or polysulfide charge, but the parameters must be adjusted when AQ is added to the cooks. Based on the results in Figure 5.27, one can conclude that the slope of the two lines are not significantly different (taking into account the scatter of the data) while the addition of AQ leads to a significant shift to lower values of  $1/Y_T'G'$ . This means that over the present range of  $1/DP$ , the addition of AQ leads to a significant increase in cellulose yield (based on o.d. wood).

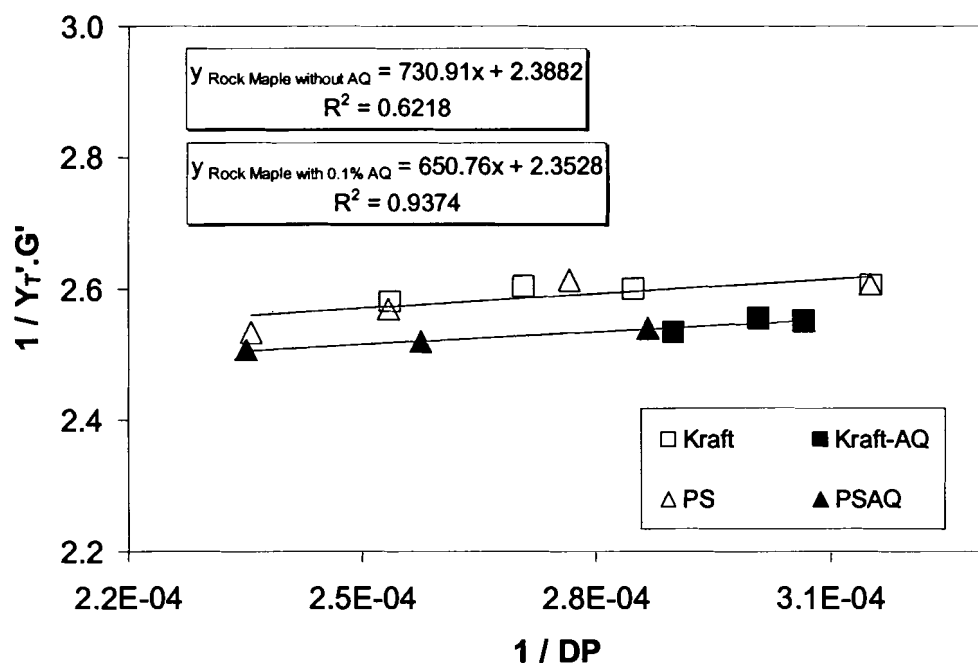


Figure 5.27. UoM Equation for Kraft, Kraft-AQ PS and PSAQ Cooking of Rock Maple

In order to better understand the mechanism of anthraquinone and polysulfide during cooking, the mass fraction of xylan and mannan in the pulp (based on o.d. wood) is plotted against  $1/DP$  for Rock Maple pulps in Figures 5.28 and 5.29.

It can be seen in Figure 5.28 that the xylan retention of kraft and kraft-AQ cooks is unchanged, while the xylan retention of PS and PSAQ cooks increases significantly with decreasing  $1/DP$  or with increasing degree of polymerization of cellulose. It also shows that the addition of 0.1% AQ leads to a small, perhaps insignificant increase in xylan retention of the PS and kraft cooks.

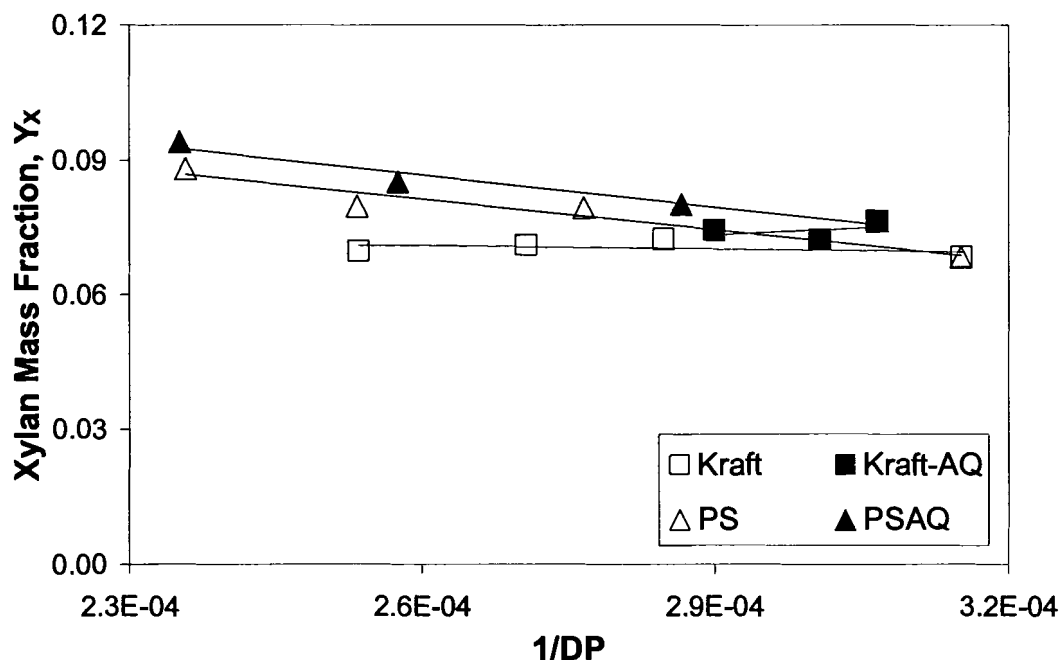


Figure 5.28. Xylan Mass Fraction versus 1/DP for All Cooks of Rock Maple

It can be seen in Figure 5.29 that the mannan retention of PS and PSAQ cooks increases significantly with increasing degree of polymerization similar to the xylan retention. The addition of 0.1% AQ appears to further increase the mannan retention of PS cooking with increasing degree of polymerization, although the effect is clearly smaller than that of polysulfide. From Figure 5.29 it is seen that 0.1 % AQ addition decreases the mannan retention compared to kraft cooking. The possible explanation for this opposite trend may be that kraft pulp and kraft-AQ pulps were hydrolyzed using different conditions. The primary hydrolysis for the kraft pulps was done for 1 hour while the primary hydrolysis of the kraft-AQ pulps was extended to 2 hours.



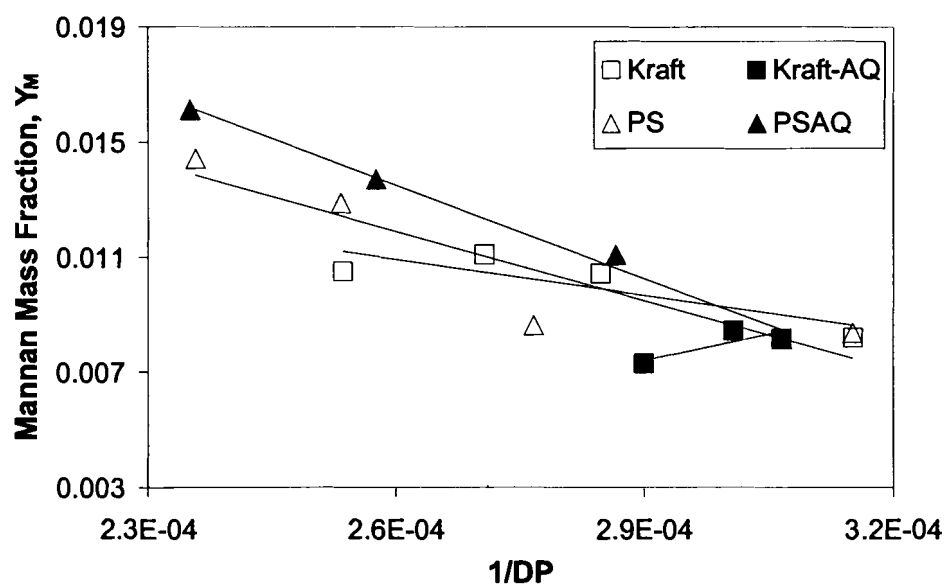


Figure 5.29. Mannan Mass Fraction versus 1/DP for All Cooks of Rock Maple

For pulps with the same value of 1/DP, the cellulose has experienced the same integrated time-temperature effect of alkaline hydrolysis, i.e. have been exposed to the same “G”-factor (Kubes et al., 1983). Therefore by comparing in Figures, 5.27, 5.28 and 5.29 at constant values of 1/DP, one may identify the effect of AQ and polysulfide separate from the effect of alkali on the three carbohydrate components, cellulose, xylan and mannan respectively. Thus the results in Figure 5.27-5.29 show that AQ increases the cellulose retention, while polysulfide does not. On the other hand, polysulfide leads to significant increases in xylan and mannan while AQ addition results in small, perhaps insignificant, increases in both xylan and mannan. Considering that there are an order of magnitude more reducing ends associated with the hemicelluloses than cellulose (due to their differences in DP) this suggests that the action of AQ is specific on cellulose, and may be related to preferential adsorption of the sparingly soluble AQ on solid cellulose rather than on the hemicelluloses.

The Kraft, Kraft-AQ, PS and PSAQ cooking results are also plotted in Figure 5.30 according to the Marcoccia equation. It is apparent that according to the Marcoccia equation there is a different linear relation obtained for each of the four different cooking processes. Thus it shows that in addition to a shift upwards in the “calibration curve” with AQ addition, the slope of the curves also increase for polysulfide cooks compared to the kraft cooks. Therefore the Marcoccia approach becomes unsuitable when predicting the yield for polysulfide (-AQ) cooks using generalized “calibration curves”.

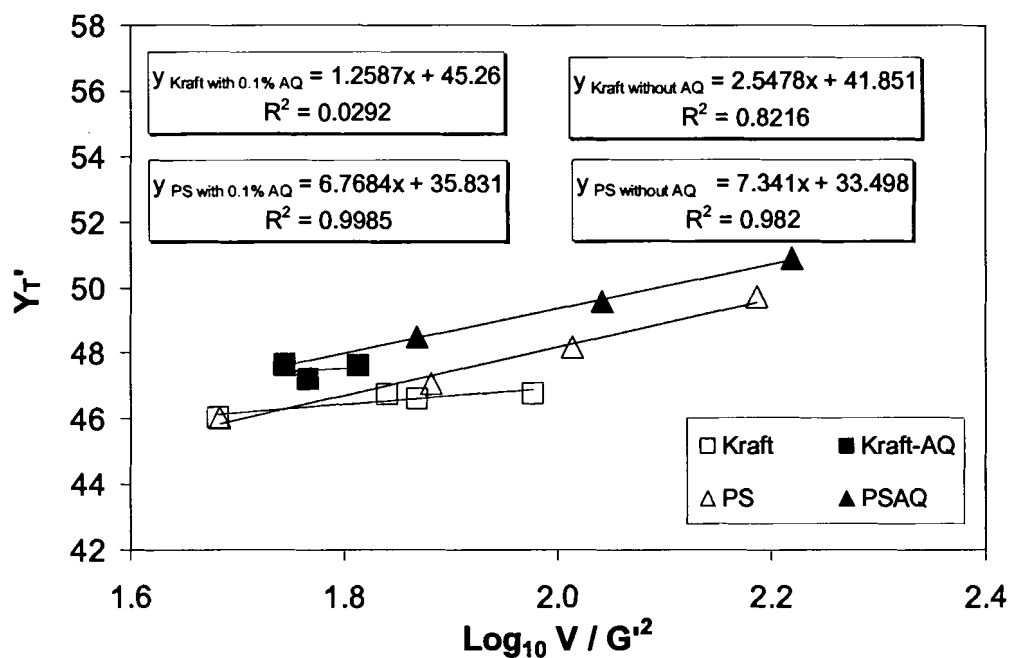


Figure 5.30. Marcoccia Equation for Kraft, Kraft-AQ, PS and PSAQ Cooking of Rock Maple

## **5.2. YELLOW BIRCH, POPLAR AND BLACK SPRUCE COOKING**

### **5.2.1. Effect of Sulfidity and Anthraquinone**

The cooking results of two hard woods, Yellow Birch and Black Spruce, and one softwood, Black Spruce, are discussed together in this section. As mentioned before, kraft cooking was carried out at different sulfidities (0%, 7.5%, 15% and 30%), and at three different H-factors of 600, 800 and 2000 hrs for Poplar, Yellow Birch and Black Spruce respectively. The cooking temperature was 170°C, and the effective alkali charge 21% for Yellow Birch and Poplar but 24% for Black Spruce. Cooking at these conditions was carried out with and without addition of 0.1% anthraquinone.

Figure 5.31 shows the effect of sulfidity on the pulping yield with and without the addition of anthraquinone (AQ) for Yellow Birch, Poplar and Black Spruce pulps. It is apparent that the total pulp yield decreases with increasing sulfidity for both kraft and kraft-AQ cooking. The main reason for this decrease is that more lignin is removed with increasing sulfidity due to the increased rate of delignification. It is also clear from Figure 5.31 that the addition of 0.1% anthraquinone (AQ) increases the total pulp yield by about 0.5-1.0 % for Yellow Birch, 1.5-2 % for Poplar and 0.2-0.6 % for Black Spruce at the same sulfidity. It should be noted (as will be shown later) that these increases are likely influenced by the fact that kappa numbers of Yellow Birch and Black Spruce are very low for a hardwood and softwood respectively.

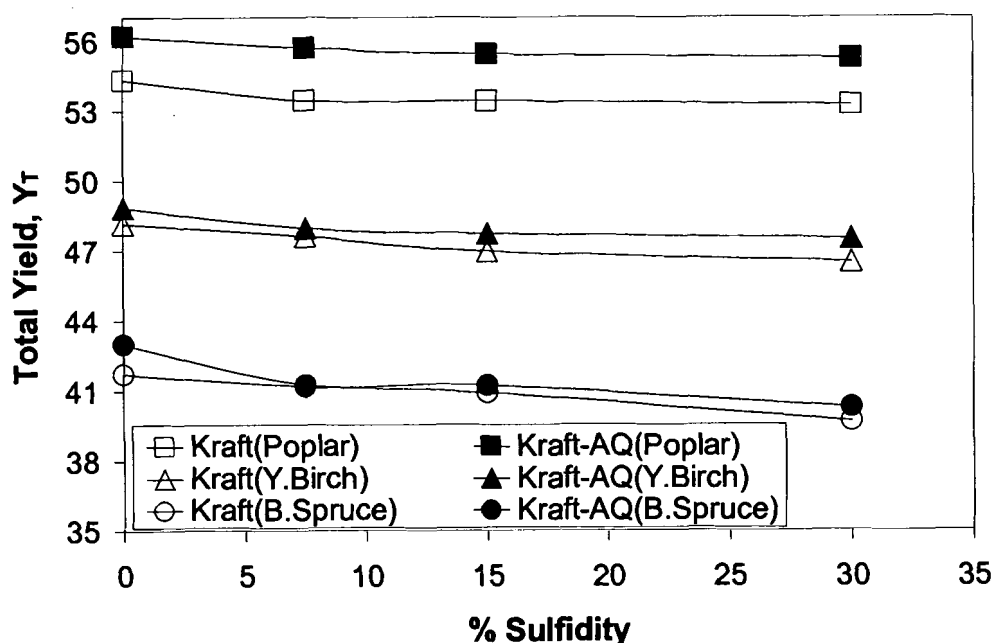


Figure 5.31. Total Yield,  $Y_T$ , versus Sulfidity with or without AQ Addition of Yellow Birch, Poplar and Black Spruce

Figure 5.32 displays the development of the kappa numbers with increasing sulfidity for Yellow Birch, Poplar and Black Spruce pulps. It is obvious from Figure 5.32 that the addition of 0.1% anthraquinone decreases the kappa number of pulp at the same sulfidity especially at the lower sulfidity levels for all wood species. It is well known that AQ accelerates delignification (MacLeod, 1980). At the highest sulfidity of 30% the decrease in kappa number due to the addition of 0.1 % AQ is very small presumably due to the same reason as discussed for Rock Maple that the delignification rate slows down significantly at these very low kappa numbers.

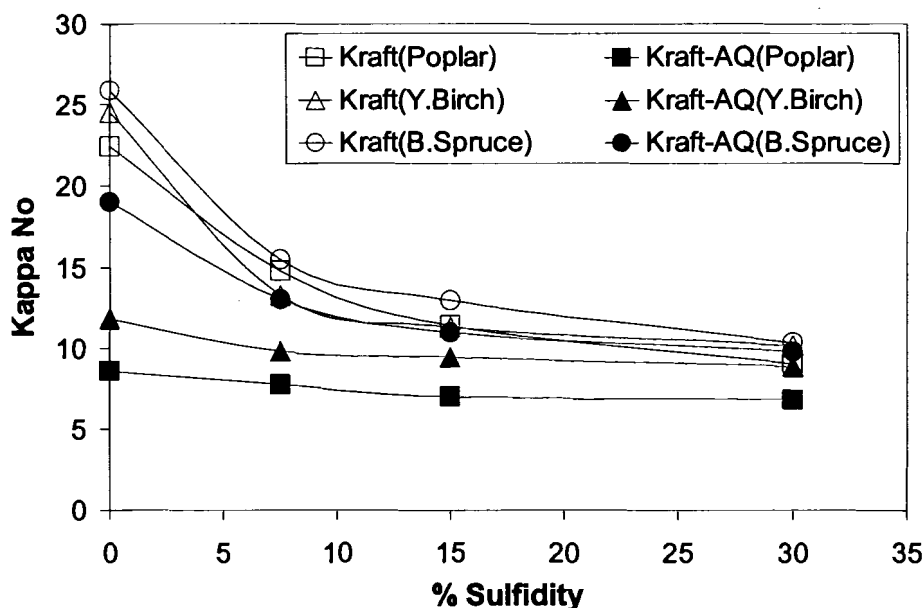


Figure 5.32. Kappa Number versus Sulfidity with or without AQ Addition of Yellow Birch, Poplar and Black Spruce

Figures 5.33 and 5.34 show the change in pulp Tappi and intrinsic viscosities when increasing the sulfidity for kraft and kraft-AQ cooking of Yellow Birch, Poplar and Black Spruce. For both hardwoods, Yellow Birch and Poplar, the Tappi and intrinsic viscosities decrease with increasing sulfidity, although the rate of decrease diminishes as the sulfidity increases. It can also be seen from Figures 5.33 and 5.34 that for Poplar at the same sulfidity the viscosity values are lower for kraft-AQ cooking compared to kraft. For Yellow Birch there is no general trend with sulfidity, except that the viscosity is significantly higher for the soda than soda-AQ pulp. It is obvious from Figures 5.33 and 5.34 that the Tappi and intrinsic viscosities does not significantly change with increasing sulfidity for Black Spruce. Presumably this is related to the fact that all these softwood pulps are severely overcooked, and that the viscosities might have reached a “floor level” which is obtained when most of the cellulose chains in the amorphous cellulose have been broken by alkaline hydrolysis.

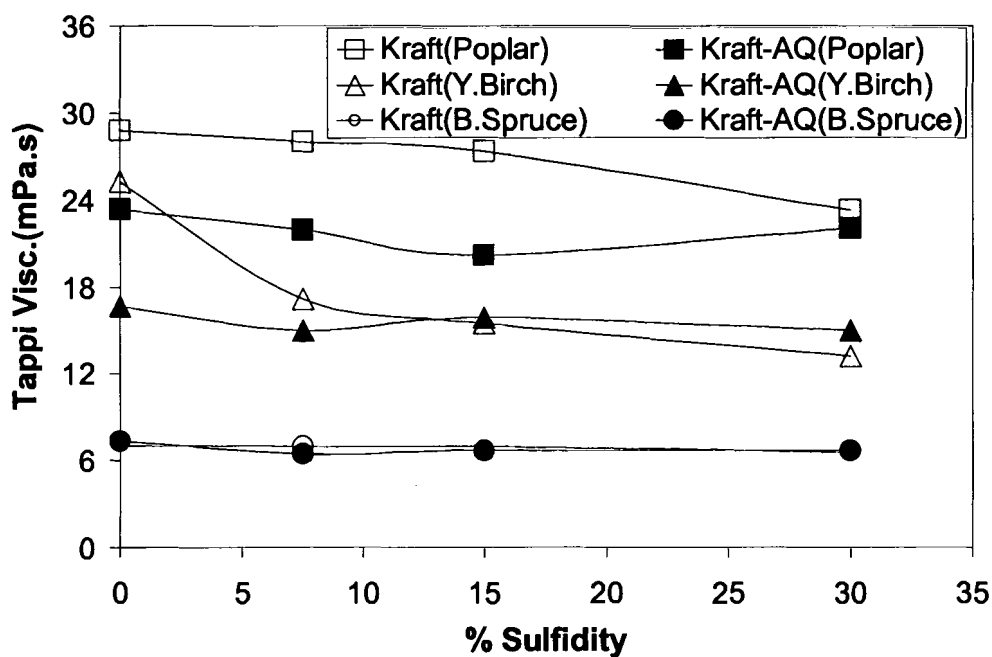


Figure 5.33. Tappi Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

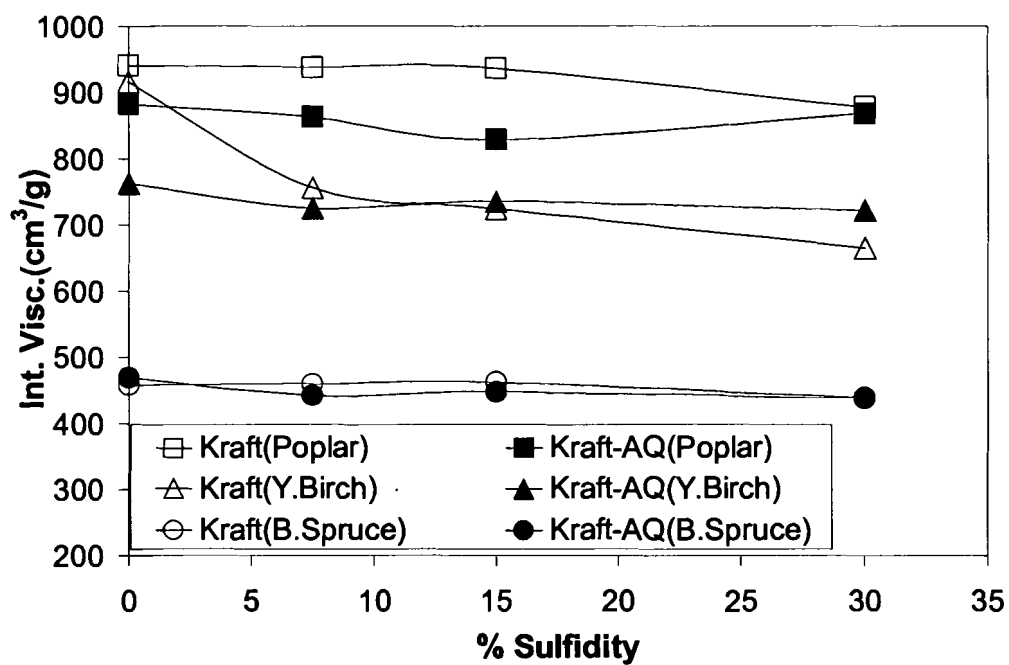


Figure 5.34. Intrinsic Viscosity versus Sulfidity for Kraft and Kraft-AQ Cooking for Rock Maple

Figure 5.35 presents the change in Tappi viscosity with changing kappa number for the kraft and kraft-AQ cooks of Yellow Birch, Poplar and Black Spruce. As expected the Tappi viscosity decreases with increasing delignification both Yellow Birch and Poplar. However the Tappi viscosity is not changing significantly with increasing delignification for Black Spruce, presumably because the “floor level” of viscosity was reached for all these pulps. The addition of 0.1 % AQ increases the Tappi viscosity slightly at the same kappa number for Yellow Birch, but no affect is seen for Poplar and Black Spruce.

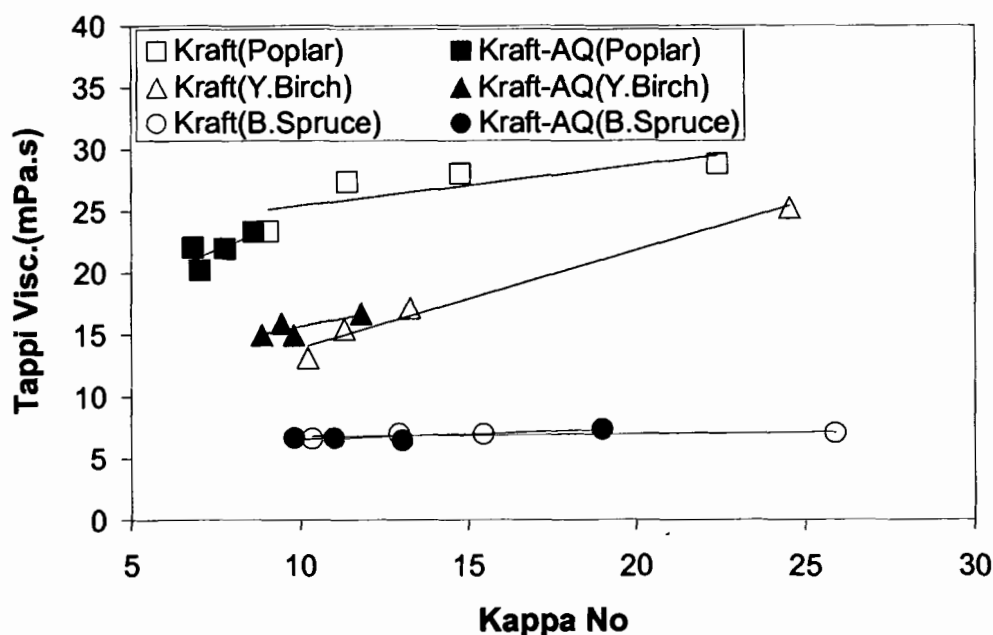


Figure 5.35. Tappi Viscosity versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

The total pulp yield and lignin-free pulp yield are plotted against kappa number in Figures 5.36 and 5.37 respectively. It is apparent from Figure 5.36 that the total yield decreases with decreasing kappa number for both kraft and kraft-AQ cooking for all three pulps. The effect of lignin removal on the yield is eliminated in Figure 5.37. These results show that the addition of 0.1 % AQ leads to higher carbohydrate retention for Yellow Birch and Poplar. For Black Spruce the difference becomes negligible at the extremely low kappa numbers.

In order to identify the cause of the higher increase in lignin free yield with increasing kappa number in Figure 5.37 for kraft-AQ relative to kraft, the cellulose yield (on o.d. wood) is plotted against kappa number in Figure 5.38. It can be seen that the cellulose yield increases for both kraft and kraft-AQ. On the other hand, it is apparent from Figure 5.39 that the hemicellulose yield is constant for kraft cooking, while the hemicellulose yield increases significantly with increasing kappa number only for kraft-AQ pulping of Black Spruce. Therefore the larger yield improvement with increasing kappa number for kraft-AQ cooking is mostly the result of more cellulose retention.



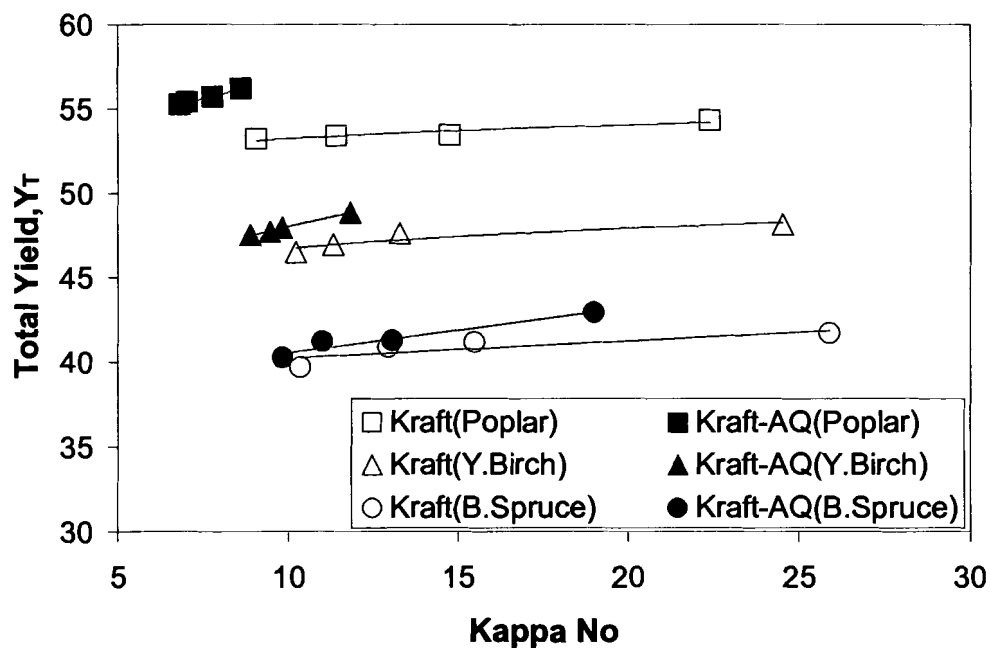


Figure 5.36. Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

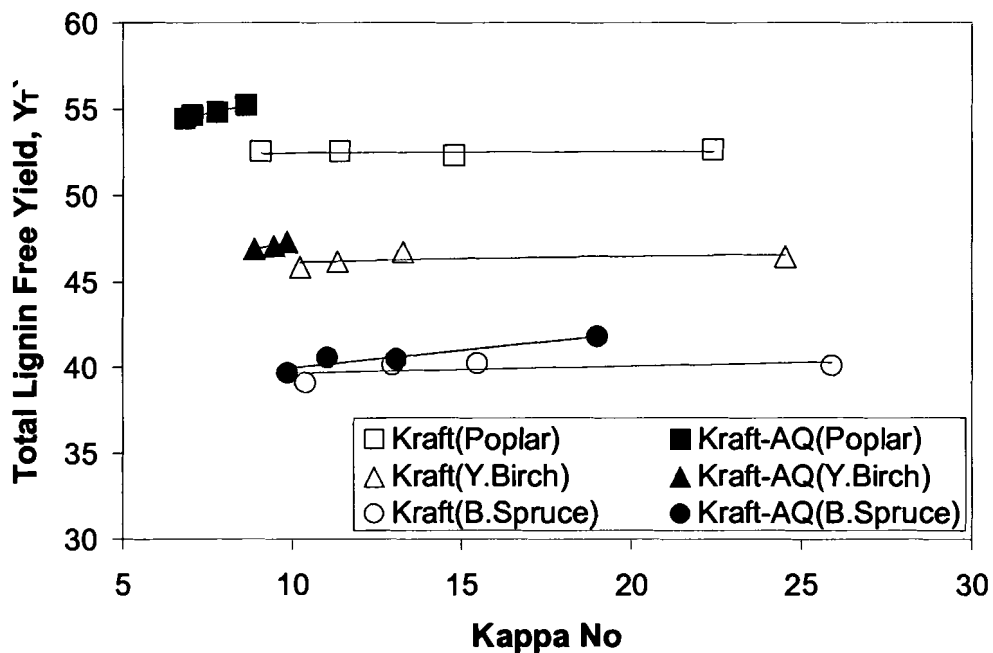


Figure 5.37. Lignin-free Total Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

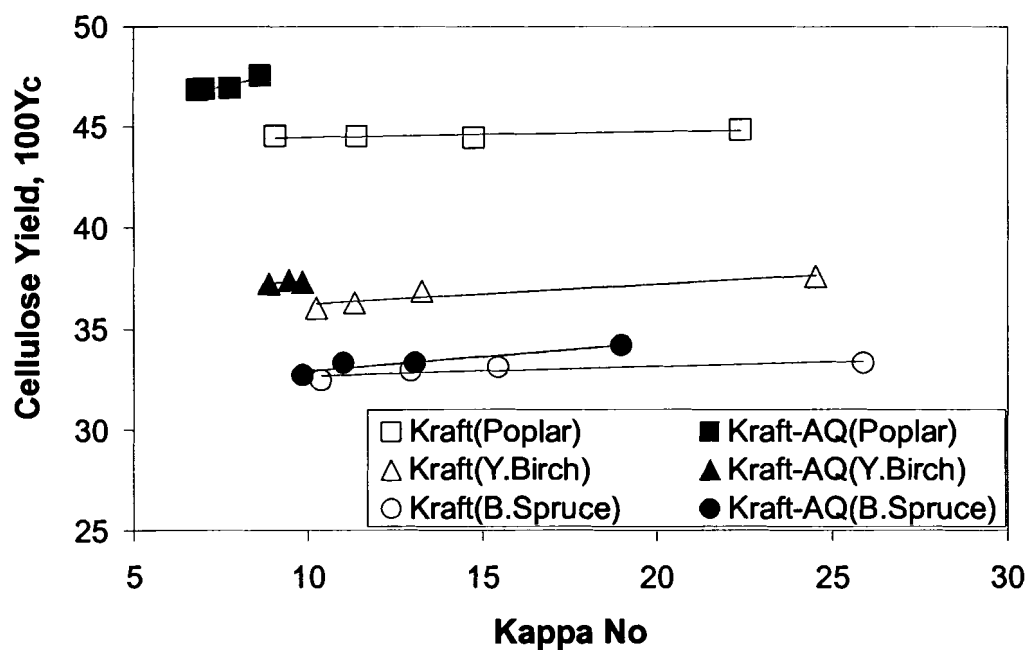


Figure 5.38. Cellulose Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

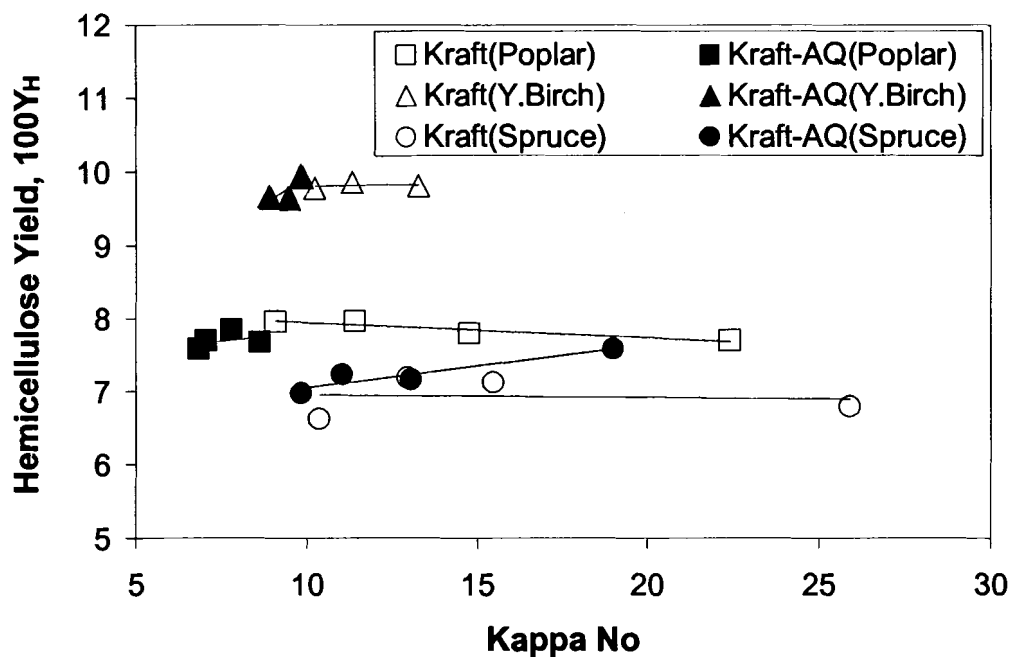


Figure 5.39. Hemicellulose yield versus Kappa Number for Kraft and Kraft-AQ of Yellow Birch, Poplar and Black Spruce

Figure 5.40 shows how the xylan yield with increasing degree of sulfidity for the Yellow Birch, Poplar and Black Spruce pulps. It can be seen that the xylan retention is not affected by the degree of sulfidity, leading to different kappa numbers for all three pulp samples. It can also be seen that the addition of 0.1 % AQ does not affect the xylan retention in agreement with literature (McDonough, 1998).

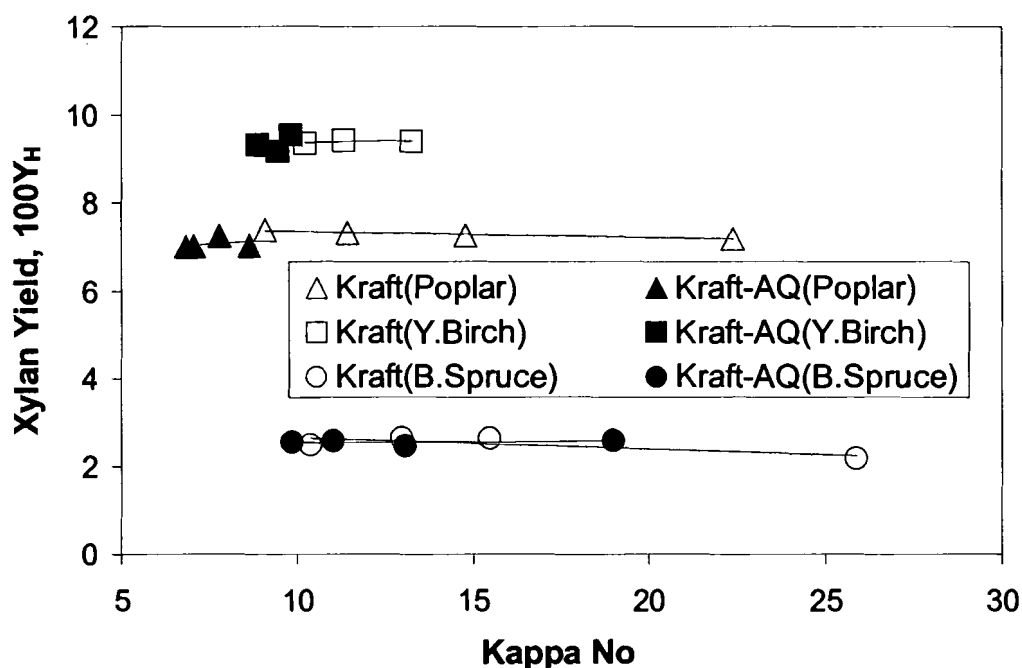


Figure 5.40. Xylan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

Figure 5.41 depicts the mannan yield at the different kappa pulps obtained by varying the sulfidity. It can be seen that the mannan yield (on o.d. wood) is less than 1% and is not affected by sulfidity or the addition of AQ for the two hardwood species, Yellow Birch and Poplar. The mannan yield of Black Spruce pulp increases with kappa number for kraft and kraft-AQ cooking. Also the addition of 0.1 % AQ increases the mannan yield of Black Spruce.

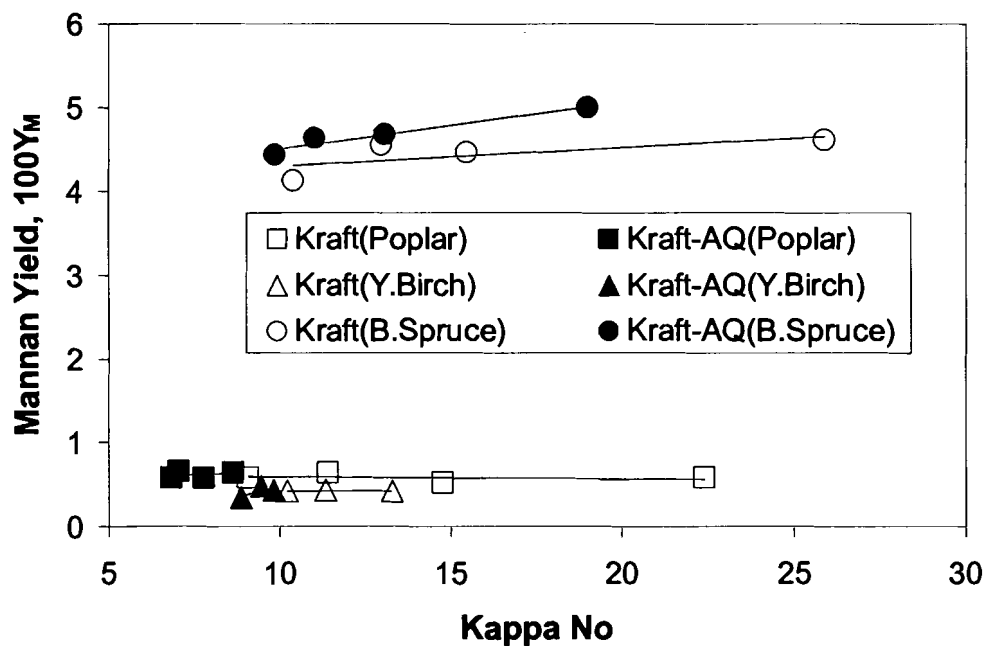


Figure 5.41. Mannan Yield versus Kappa Number for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

The yield data for kraft and kraft-AQ of Yellow Birch, Poplar and Black Spruce are plotted in Figure 5.42 according to the UoM yield equation. It shows that different linear relationships are again obtained for kraft and kraft-AQ pulping for all three pulps. However, it is also clear that the range of  $1/DP$  values for all series of cooks is rather small, except for kraft cooking of Yellow Birch.

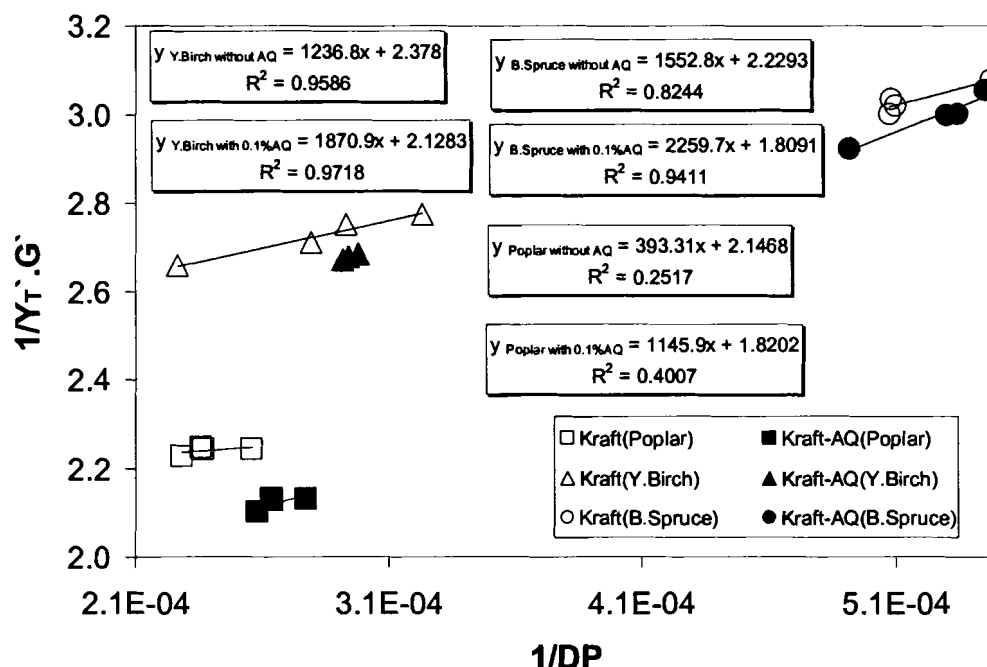


Figure 5.42. UoM Equation for Kraft and Kraft-AQ Cooking of Yellow Birch, Poplar and Black Spruce

The Marcoccia (Marcoccia, 1998) plots of the yield results for Yellow Birch, Poplar and Black Spruce are shown in Figure 5.43. They all show a linear increase in  $Y_T$  with increasing values of  $(\log V)/(G^2)$  as expected. However, except for the kraft pulps of Yellow Birch, the range of  $(\log V)/(G^2)$  is too small in all cases to give significant value to these correlations. The low values of both  $Y_T$  and  $(\log V)/(G^2)$  for Black Spruce are again indicative of the fact that these pulps are overcooked and highly degraded.

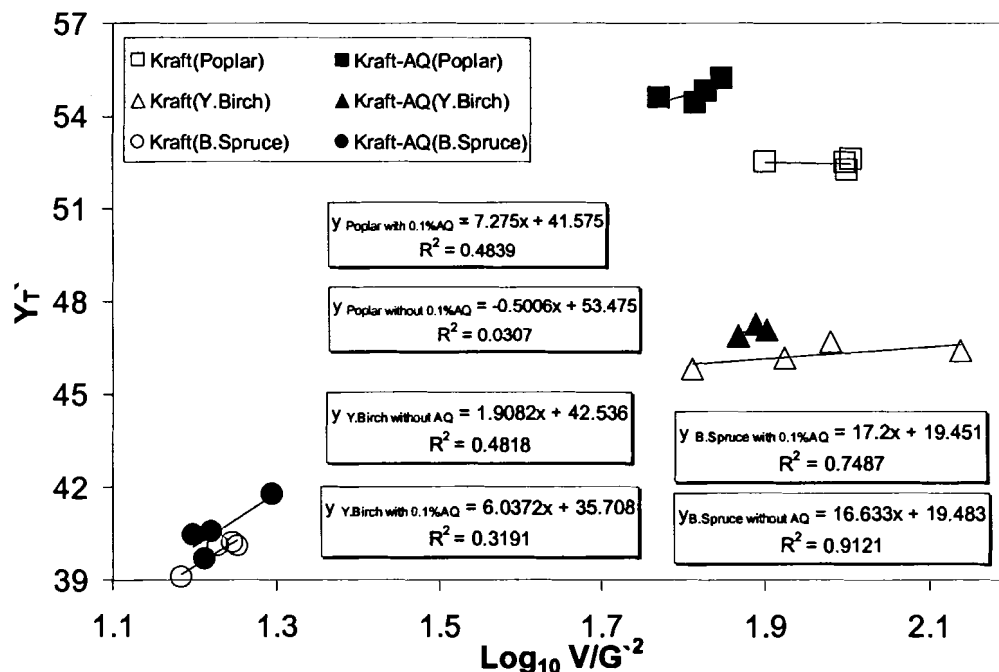


Figure 5.43. Marcoccia Equation for Kraft and Kraft-AQ cooking of Yellow Birch, Poplar and Black Spruce

### 5.2.2. Effect of Polysulfide and Polysulfide-Anthraquinone

The effect of polysulfide cooking and polysulfide anthraquinone cooking of Yellow Birch, Poplar and Black Spruce was also investigated. The polysulfide (PS) and polysulfide-anthraquinone (PSAQ) cooks were carried out at a H-factor of 600, 800 and 2000 hrs. for Poplar, Yellow Birch and Black Spruce respectively. The effective alkali was 21% for Yellow Birch and Poplar, and 24% for Black Spruce. In all cases the sulfidity was 30% and the cooking temperature 170° C. The elemental sulfur content of the polysulfide cooks was varied from 0 to 4%. PSAQ cooks were performed at the same conditions with an addition of 0.1 % AQ on o.d. wood.

Figure 5.44 shows the total yield of Yellow Birch, Poplar and Black Spruce chips for the different PS and PSAQ cooks plotted as a function of percentage elemental sulfur addition. It can be seen that for both the PS and PSAQ cooks, the yield increases linearly

with polysulfide (elemental S) addition. The yield increases 1.0-1.5% with each 1% increase in elemental S addition. The increase in yield is due to oxidation of the reducing end groups of the carbohydrates by polysulfide (Gullichsen, 2000) and the decrease in alkali concentration of the polysulfide cooking liquor with increasing percentage of elemental sulfur as discussed earlier for Rock Maple. Figure 5.44 also shows that the PSAQ yield is higher than the PS yield at the same elemental S charges.

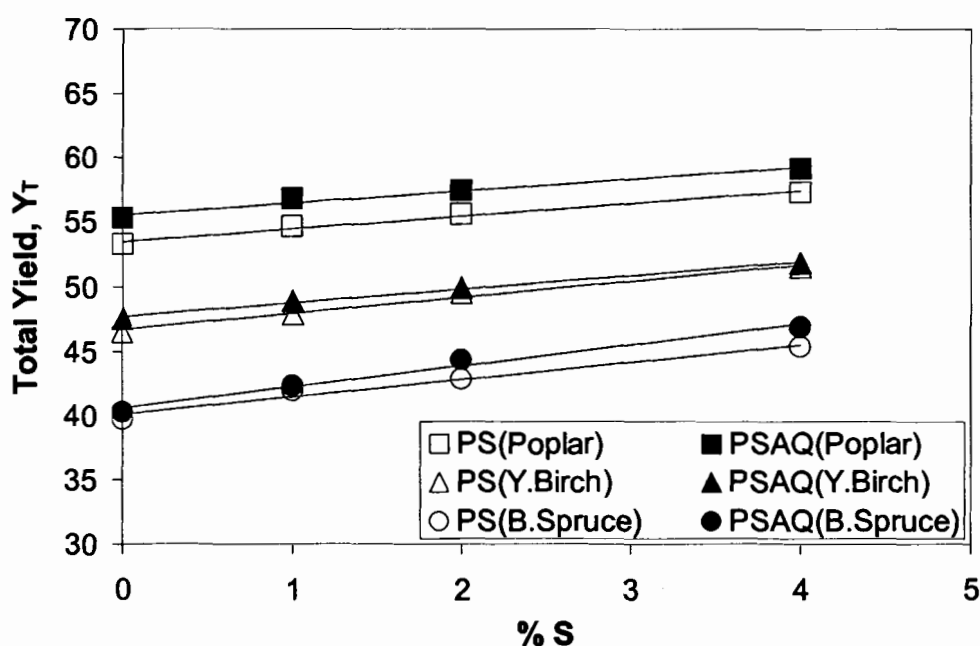


Figure 5.44. Total Yield,  $Y_T$ , versus Percentage Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

Figure 5.45 shows that the kappa number generally increases slightly with increasing polysulfide charge for both PS and PSAQ cooking of Yellow Birch, Poplar and Black Spruce. The increase in kappa number most likely is caused by the decrease in alkali concentration with increasing elemental sulfur charge. It can also be seen that at the same elemental sulfur charge, the kappa number is higher for PS than PSAQ cooks. This is expected since 0.1 % addition of anthraquinone increases the delignification rate and

thus results in a decrease in kappa number. The kappa number differences between PS and PSAQ cooks of Yellow Birch and Poplar decrease with increasing percentage elemental sulfur while the kappa number differences between PS and PSAQ cooks of Black Spruce increases with increasing polysulfide concentration (elemental S).

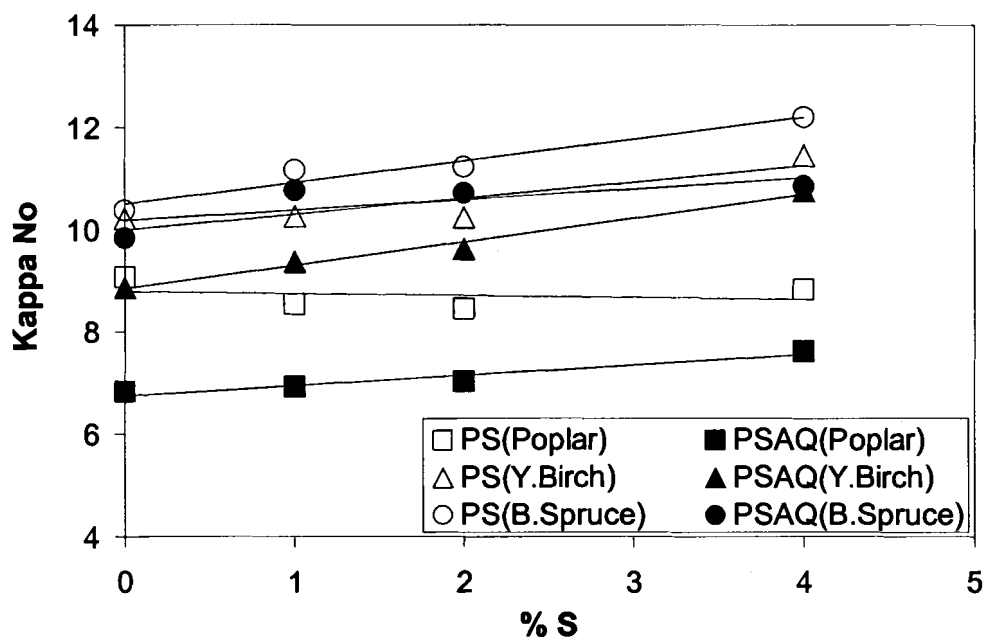


Figure 5.45. Kappa Number versus Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

Figures 5.46 and 5.47 show the changes in intrinsic viscosity and Tappi viscosity for PS and PSAQ pulps of Yellow Birch, Poplar and Black Spruce for increasing polysulfide concentration (elemental sulfur). It is clear that for both the PS and PSAQ pulps the Tappi and intrinsic viscosities increase with polysulfide concentration. The effect of anthraquinone addition on the viscosity is positive for Yellow Birch and Black Spruce, but slightly negative for Poplar.



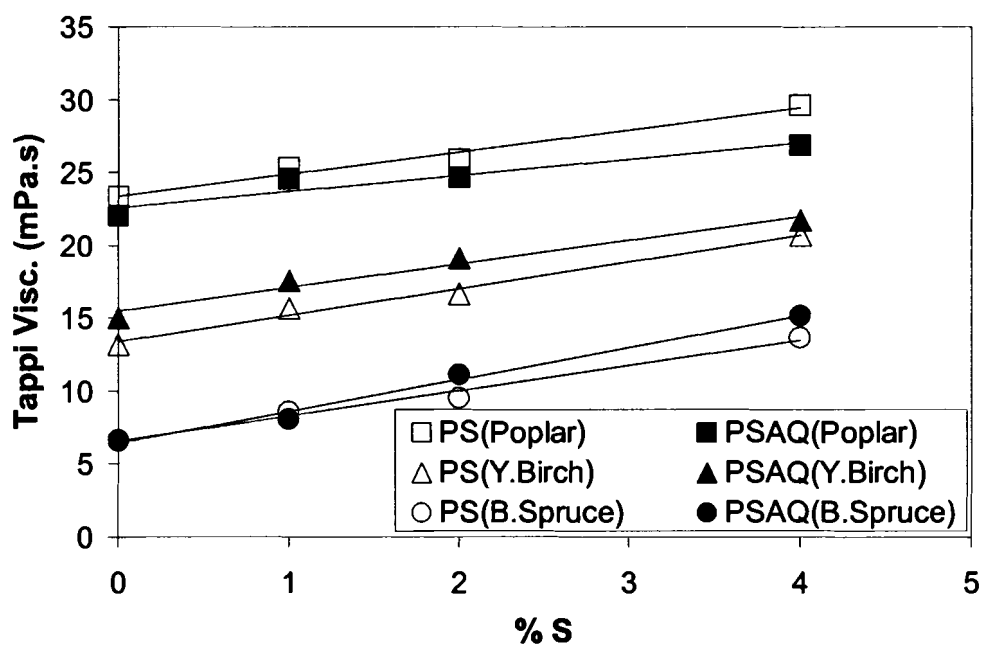


Figure 5.46. Tappi Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

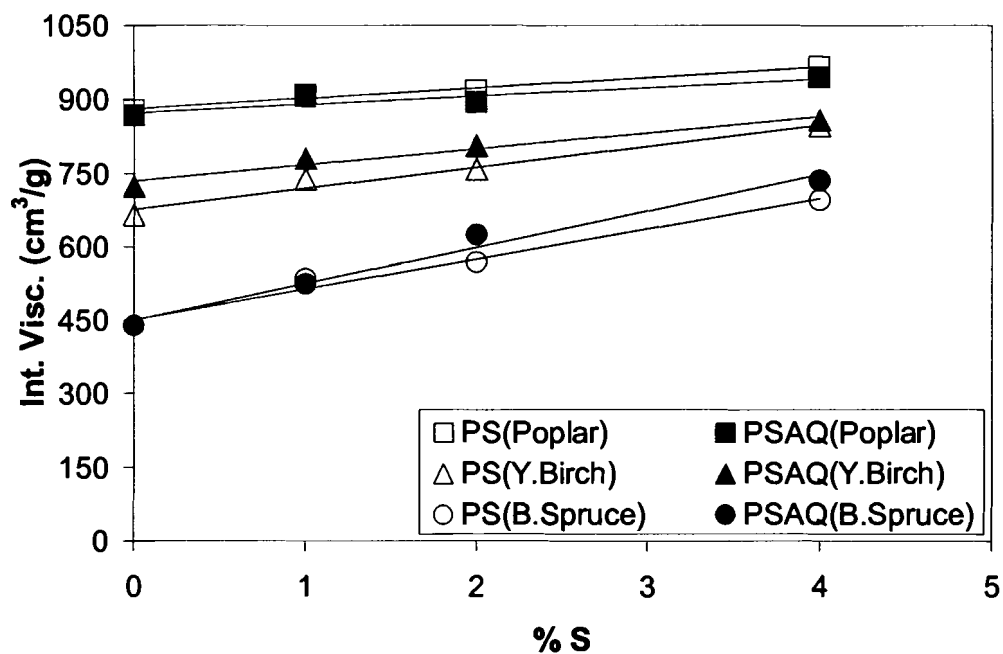


Figure 5.47. Intrinsic Viscosity versus Elemental Sulfur Charge for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

Figure 5.48 shows the change in Tappi viscosity with kappa number for PS and PSAQ of Yellow Birch, Poplar and Black Spruce. As expected the Tappi viscosity increases with kappa number and the addition of 0.1 % AQ.

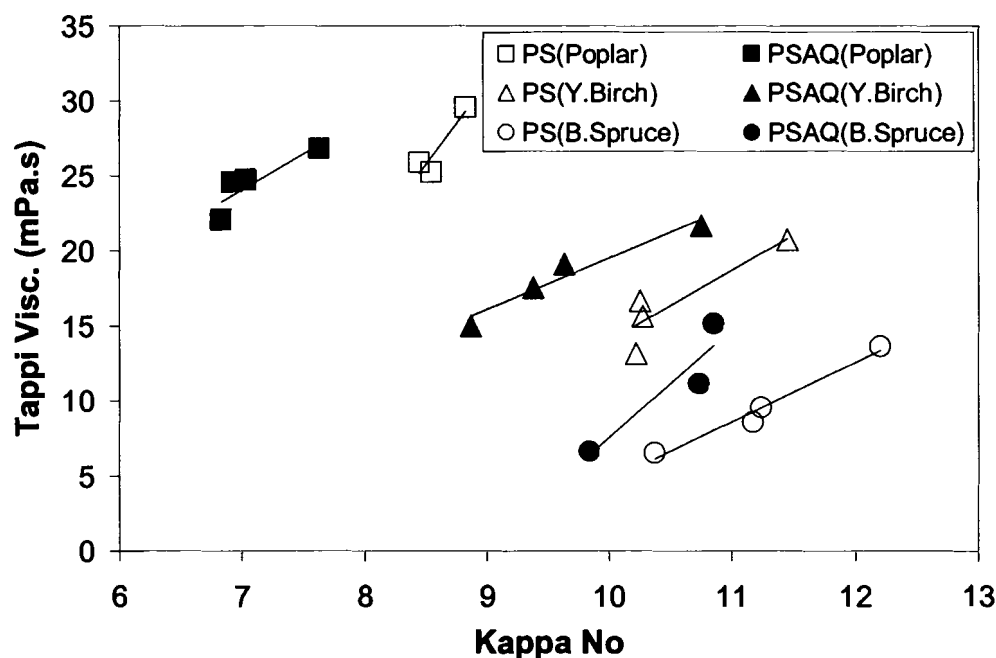


Figure 5.48. Tappi Viscosity versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

The total yield and total lignin free yield of the PS and PSAQ pulps of Yellow Birch, Poplar and Black Spruce are plotted against kappa number in Figures 5.49 and 5.50. It can be seen that there is an increase in total yield with increasing kappa number for all three species. Also the yield of PSAQ pulp is higher than that of PS pulp at the same kappa number. For a kappa number of 10.5, the yield increase by adding 0.1% AQ is about 2.5-3 % for Yellow Birch and 3-4 % for Black Spruce. Similarly the lignin free total yield increases with increasing kappa number and thus increasing elemental sulfur addition.

The cellulose and hemicellulose yield (on wood) of the PS and PSAQ pulps are plotted against kappa number in Figures 5.51 and 5.52. It is apparent from Figure 5.51 that the cellulose yield of the PS cooks as well as the PSAQ cooks of all three wood species increases with kappa number and thus with increasing elemental sulfur charge. The results in Figure 5.52 show that the hemicellulose yield increases strongly with kappa number, and thus with increasing polysulfide addition.

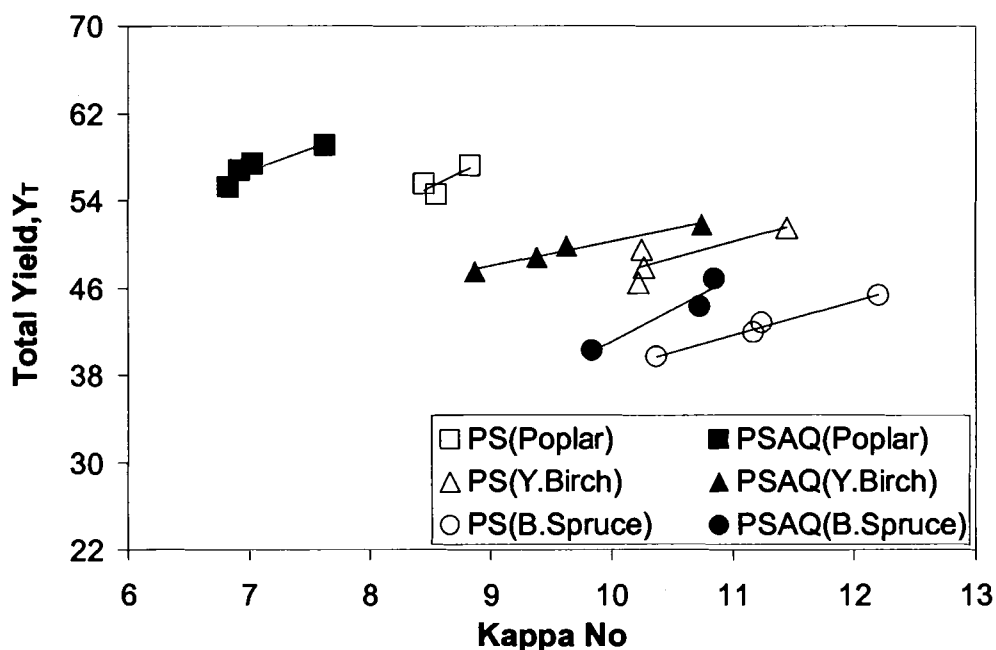


Figure 5.49. Total Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

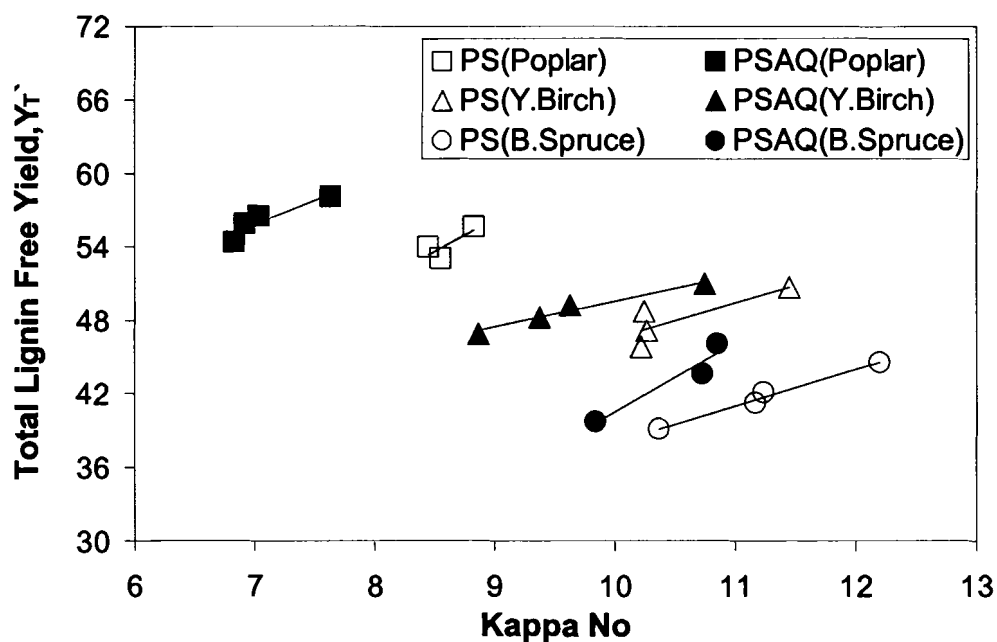


Figure 5.50. Lignin-free Total Yield versus Kappa Number for PS and PSAQ of Yellow Birch, Poplar and Black Spruce

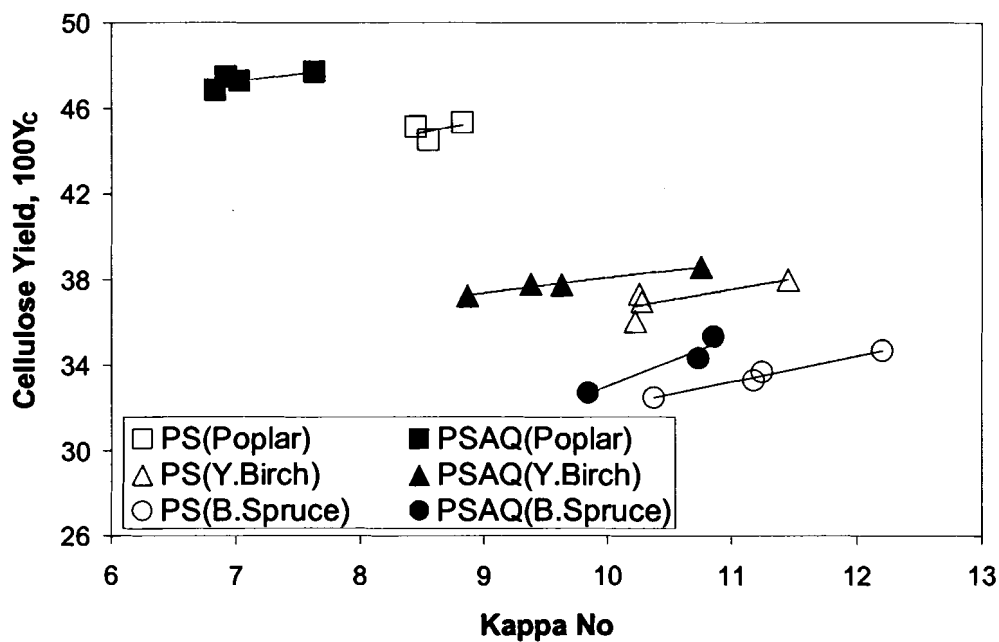


Figure 5.51. Cellulose Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

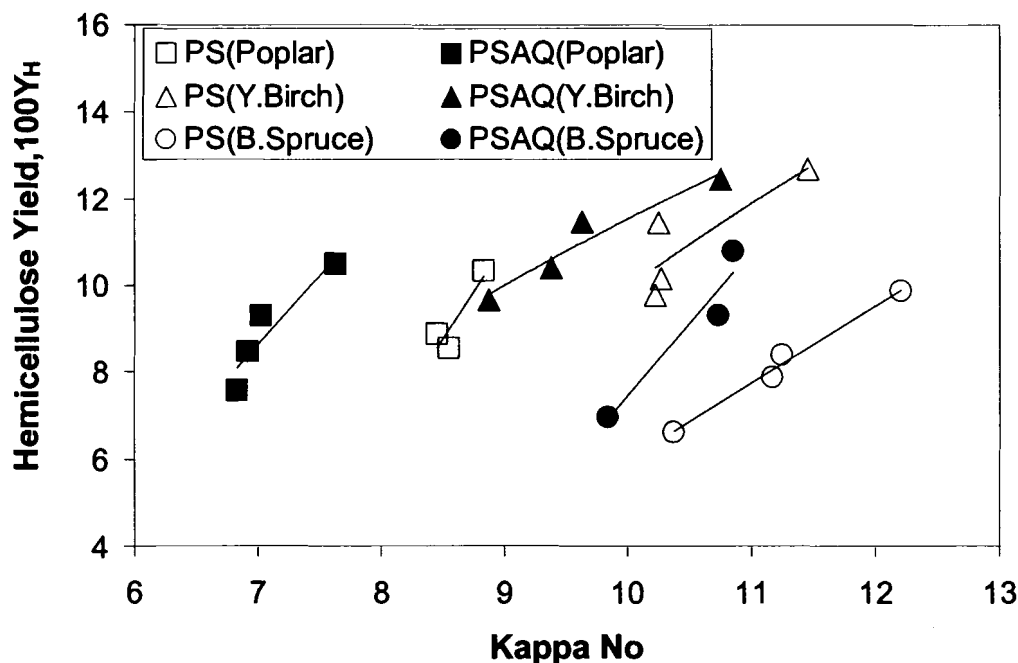


Figure 5.52. Hemicellulose Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

Figure 5.53 shows that the xylan yield increases with increasing kappa number, and thus degree of polysulfide (elemental sulfur) charge for PS and PSAQ pulps of Yellow Birch, Poplar and Black Spruce. Since it has been reported that xylan removal during cooking is caused by physical dissolution, the increase in xylan retention is most probably because of the lower alkali concentration of higher concentration polysulfide cooking liquors. It can also be seen that the addition of 0.1 % AQ further increases the xylan retention of all three pulps during the PSAQ cooking.

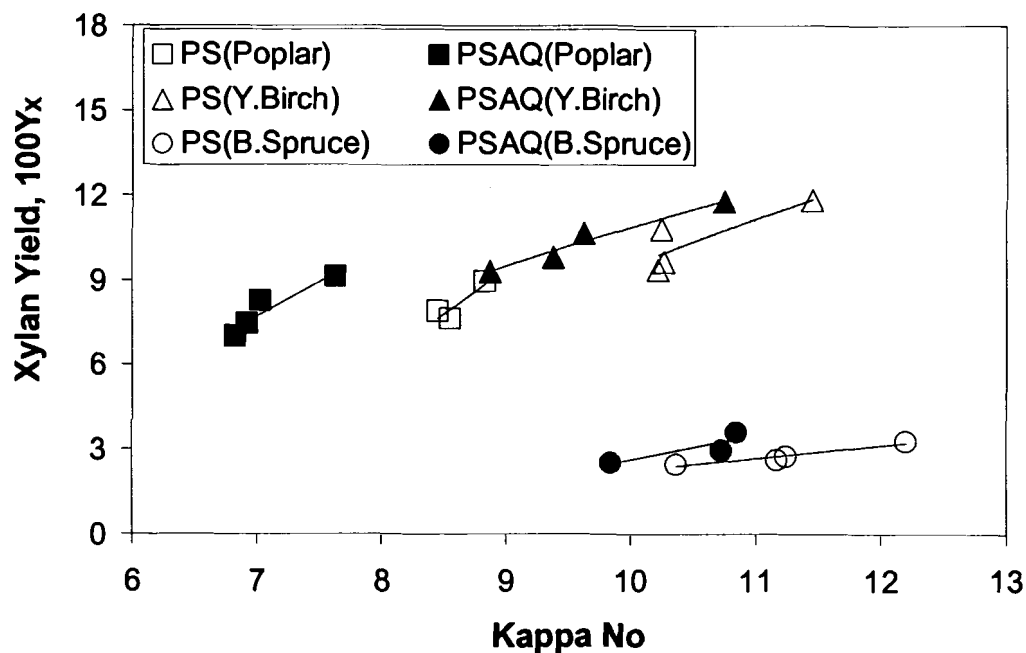


Figure 5.53. Xylan Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

Figure 5.54 shows the mannan yield of PS and PSAQ pulps of Yellow Birch, Poplar and Black Black Spruce at the different kappa numbers obtained by varying the polysulfide concentration. The mannan retention also increases with increasing kappa number or polysulfide charge. The increase is especially pronounced for the soft wood Black Spruce. This suggests that the increased mannan retention is caused both by effect of the oxidation of its reducing ends by polysulfide, as well as the lower alkali concentration at higher polysulfide charges. Also for mannan the 0.1% AQ addition further increases its retention during PSAQ cooking.

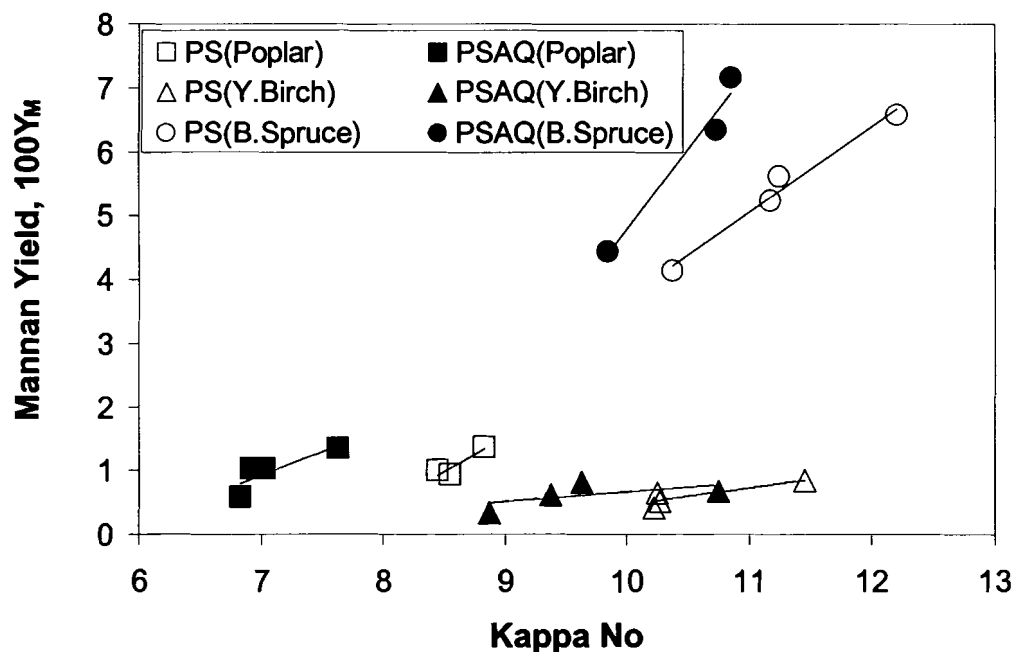


Figure 5.54. Mannan Yield versus Kappa Number for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

$1/Y_T \cdot G$  was plotted against  $1/DP$  according to the UoM equation in Figure 5.55 for PS and PSAQ cooking of Yellow Birch, Poplar and Black Spruce. For both PS and PSAQ a linear relationship is obtained for all three pulps. However the correlations are different for PS and PSAQ cooking. The explanation is that the addition of AQ leads to less peeling and thus more cellulose retention. Anthraquinone can oxidize reducing end groups of cellulose and reduce the peeling reactions (Gullichsen, 2000).

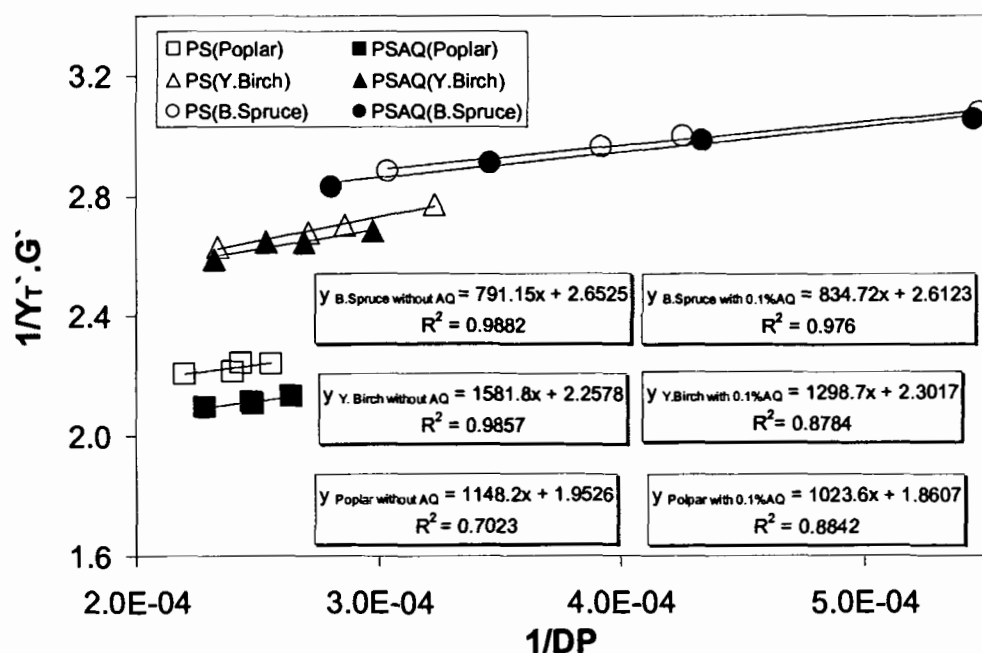


Figure 5.55. UoM Equation for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

The same cooking data are also plotted according to the pulp yield prediction equation which is developed by Marcoccia et al. (Marcoccia, 1998) in Figure 5.56. Excellent linear relationships are also obtained using this equation for the PS and PSAQ pulps.



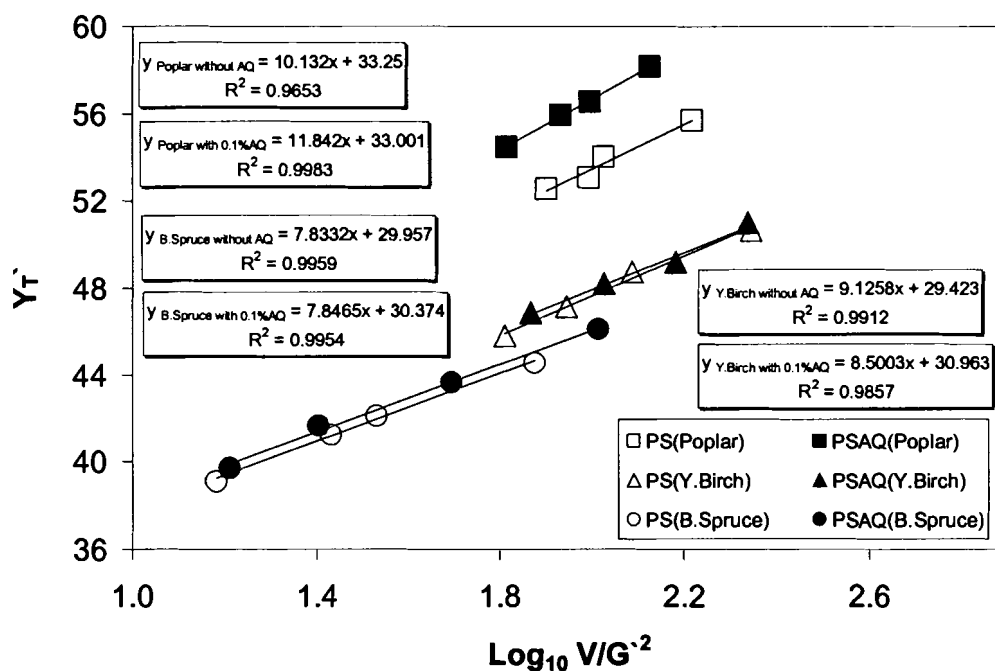


Figure 5.56. Marcoccia Equation for PS and PSAQ Cooking of Yellow Birch, Poplar and Black Spruce

To further investigate the mechanism of AQ and PS, the mass fraction of xylan and mannan in the pulp (based on o.d. wood),  $Y_X$  and  $Y_M$  respectively is plotted against  $1/DP$  in Figures 5.57 and 5.58 for the softwood species studied, Black Spruce. The mechanism for a hardwood was discussed earlier for Rock Maple.

It can be seen from Figure 5.57 that while the xylan retention of kraft and kraft-AQ cooking is not affected by the DP of cellulose, the retention of xylan increases for PS and PSAQ cooking with increasing degree of polymerization. It can also be seen that the addition of 0.1% AQ does not significantly increase the retention of xylan at the same value of  $1/DP$  for kraft and PS cooks.

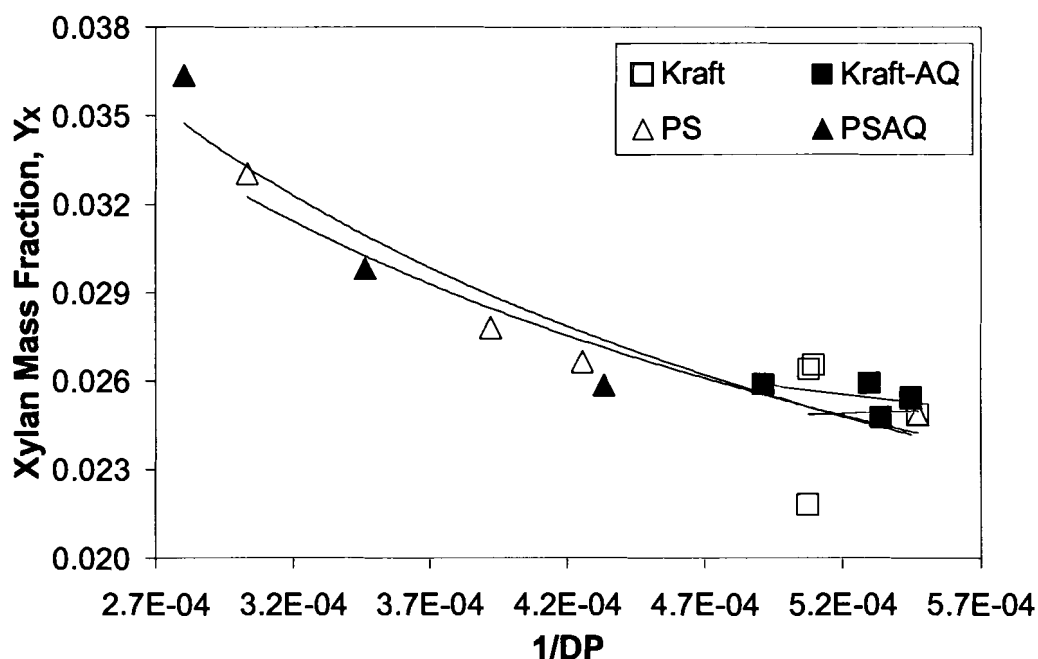


Figure 5.57. Xylan Mass Fraction versus 1/DP for All Cooks of Black Spruce

It is obvious from Figure 5.58 that the mannan retention of all cooks, Kraft, Kraft-AQ, PS and PSAQ cooks decreases linearly with increasing values of 1/DP. The addition of 0.1% AQ further increases the mannan yield by about 0.3% at same degree of polymerization for all cooks. Thus contrary to xylan which is not stabilized by AQ (see Figure 5.57), more mannan is retained by AQ, as found earlier by Aurell and Hartler (1965). The same linear slopes for all 4 cooking processes in Figure 5.58 suggest that the removal of mannan is directly linked to the cellulose degradation.

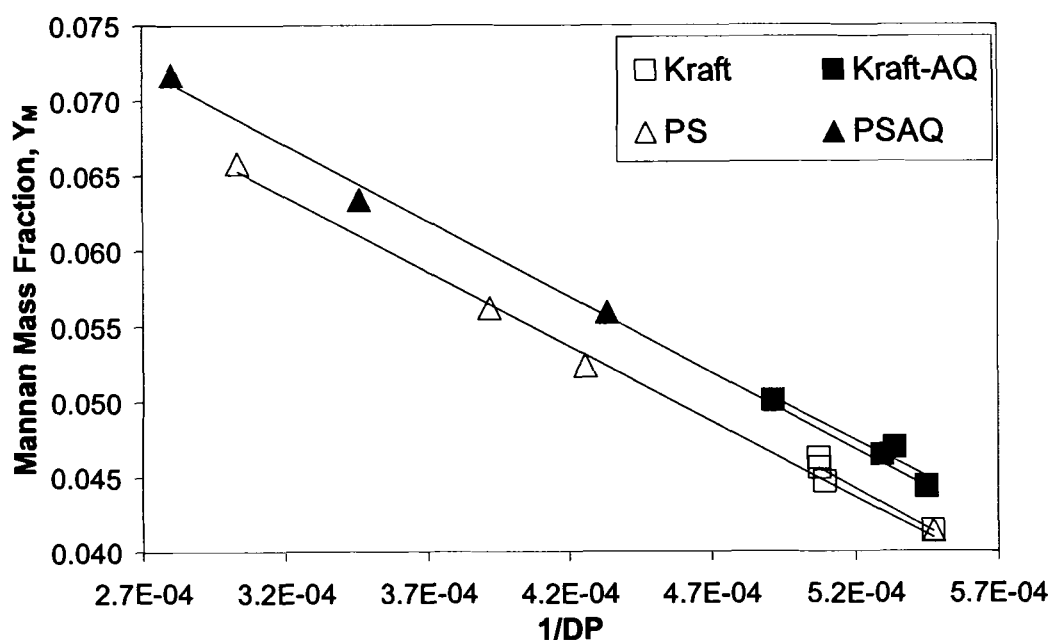


Figure 5.58. Mannan Mass Fraction versus 1/DP for All Cooks of Rock Maple

Thus, the results in Figure 5.56 to 5.58 for Black Spruce, and the equivalent Figures 5.27 to 5.29 for Rock Maple in combination suggest that polysulfide increases the xylan and mannan retention while AQ increases the cellulose and mannan retention. The finding that both addition have an effect on the mannan may be related to the fact that mannan and cellulose are (physically/ chemically) linked inside the fiber wall.

### 5.3. UoM PULP YIELD EQUATION OF ALL COOKS

The Yield results for Kraft, Kraft-AQ, PS and PSAQ cooking of the three hardwoods, Rock Maple, Yellow Birch and Poplar, and one soft wood, Black Spruce, are plotted according to the UoM equation in Figure 5.59. It is apparent that the results of kraft and PS pulps can be represented by the same correlation, while another single linear relation is adequate for Kraft-AQ and PSAQ pulps for each of the four wood species with a reasonable  $R^2$  for each single relationship. Therefore the UoM pulp yield prediction equation can be used to predict to pulp yield of kraft and PS cooking regardless of the polysulfide addition.

The UoM equation can be used to calculate cellulose yield of wood,  $Y_{C,w}$  and the number of cellulose units removed by secondary peeling reaction,  $(\Delta DP)_s$ . The values of  $Y_{C,w}$  and  $(\Delta DP)_s$ , for non-AQ and AQ cooking of all species are summarized in Table 5.1. It can be seen from Table 5.1 that the  $(\Delta DP)_s$  values for all wood species are different for non-AQ and AQ cooking.

The values for  $(\Delta DP)_s$  are significantly larger than the values reported for cotton of 65 at 170 °C (Franzon and Samuelson, 1957) and 68 over the entire temperature range of 60 to 190 °C (Lai and Sarkanen, 1967). However, both reference studies rely on nitrated cellulose as their reference material for the DP determination. Evans and Wallis (1989) have since shown that cellulose degradation by nitration leads to an under prediction of the DP of cotton by a factor of about 2.3. This raises the literature values of  $(\Delta DP)_s$  to 150-160 for cotton, close to the  $(\Delta DP)_s$  of 182 found in our previous study (van Heiningen et al, 2002) when applying the present technique to alkaline cooks of cotton. However, these values of  $(\Delta DP)_s$  for cotton are still a factor 2-4 lower than the

present results for wood. A possible explanation for the difference may be that the degradable chain length,  $(\Delta DP)_s$  is determined by the size of the amorphous regions, i.e. the peeling reaction is mostly terminated by physical inaccessibility of the crystalline regions rather than the stopping reaction (Haas et al. 1967). This implies that the average size of the amorphous regions in wood is larger than that in cotton. This is not unreasonable since the crystallinity of wood cellulose is smaller than that of cotton (Fengel and Wegener, 1984).

The values of  $Y_{C,w}$  of the four wood species and the cellulose mass fraction reported in the literature (Timell, 1969; Cote et al., 1966) for these four species are also listed in Table 2. It can be seen that the differences between  $Y_{C,w}$  and the literature values of the cellulose mass fraction of the three hardwood species are small, providing further confidence in the present yield measurement method. The value of  $Y_{C,w}$  for Black Spruce is significantly lower than the literature value, 0.372 versus 0.411.

Generally the value of  $(\Delta DP)_s$  is somewhat lower for the AQ cooks compared to the non-AQ cooks. This implies that cellulose is stabilized by AQ both during heat-up and during the cooking process. The values of  $Y_{C,w}$  for non-AQ and AQ cooks are quite different for Poplar. This might be due to a systematic error.

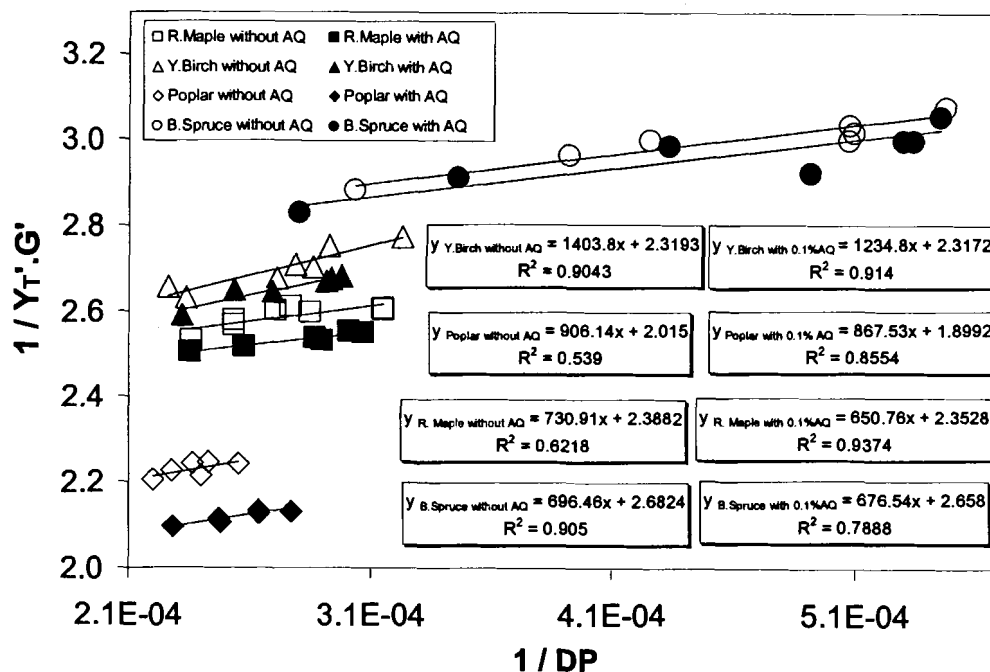


Figure 5.59. UoM Equation for All Cooks of Rock Maple, Yellow Birch, Poplar and Spruce

Table 5.1.  
 $Y_{C,w}$  and  $(\Delta DP)_s$  for Non-AQ and AQ Cooking of Three Hardwood and One Softwood Species

Species	Rock Maple		Yellow Birch		Poplar		Black Spruce	
	$Y_{C,w}$	$(\Delta DP)_s$	$Y_{C,w}$	$(\Delta DP)_s$	$Y_{C,w}$	$(\Delta DP)_s$	$Y_{C,w}$	$(\Delta DP)_s$
Kraft and PS	0.412	306	0.431	605	0.492	412	0.372	260
Kraft-AQ and PSAQ	0.425	277	0.431	533	0.525	442	0.376	254
Wood Cellulose Mass Fraction (literature)	0.402		0.426		0.510		0.411	

## 5.4. COMBINING THE YIELD EQUATION RESULTS

### 5.4.1 Rock Maple

The presented yield results for Kraft, Kraft-AQ, PS and PSAQ cooking of Rock Maple are combined in a graph together with those obtained by Gao et al. (2003) for Kraft cooking of Rock Maple at different temperatures (160, 170 °C) and a wide range of H-factors( 200-2000 hrs)

Figures 5.60 and 5.61 show all these cooking results of Rock Maple using the UoM and Marcoccia pulp yield prediction equations respectively.

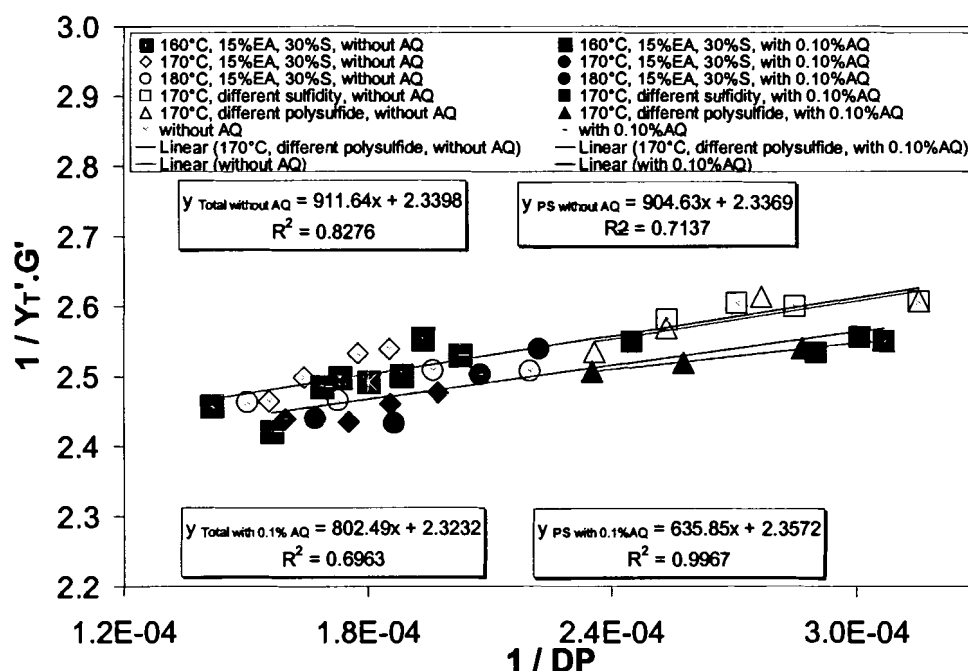


Figure 5.60. UoM Equation for All Cooks of Rock Maple

Figure 5.60 shows that all the data are reasonably well represented by two linear equations, one for all the cooks without AQ, and one for cooks with AQ addition. It can also be seen that there is no significant difference between the relationship for just the PS cooks and those of all other cooks without AQ addition. The same is true for PSAQ

cooks and all kraft cooks with AQ addition. Thus the results in Figure 5.60 show that the yield results of Rock Maple are well represented by two separate linear relationships, one for cooks with AQ addition and one for non-AQ cooks, when plotted accordingly to the UoM Yield Prediction Equation. These two equations are valid irrespective of the cooking temperature, H-factor, polysulfide charge, sulfidity or effective alkali charge.

For non-AQ cooking the equation is

$$\frac{1}{Y_r' G'} = 912 \left( \frac{1}{DP} \right) + 2.3398 \quad (5.4)$$

while for cooks with AQ addition the equation is

$$\frac{1}{Y_r' G'} = 803 \left( \frac{1}{DP} \right) + 2.3232 \quad (5.5)$$

From equations 5.4 and 5.5 it follows that  $Y_{C,w}$  is equal to 0.427 and 0.430 for non-AQ and AQ cooks respectively, i.e. the addition of AQ has no significant effect on  $Y_{C,w}$ . The values of  $(\Delta DP)_S$  can now be calculated as  $912 \cdot 0.427 = 389$  and  $803 \cdot 0.430 = 324$ . In other words the two UoM Yield Prediction Equations for Rock Maple implies that the number of glucose units peeled after alkaline hydrolysis until the sequential process is terminated by the stopping reaction is less for AQ pulping (324) than non-AQ cooking (389) AQ cooking respectively of Rock Maple.

When the results of the combined studies are plotted in Figure 5.61 according the Marcoccia Equation, one can see that 4 separate linear correlations are needed to represent the yield data kraft, kraft-AQ, PS and PSAQ cooking. This clearly shows that the Marcoccia equation is less general than the UoM Equation approach to represent pulp yield data.



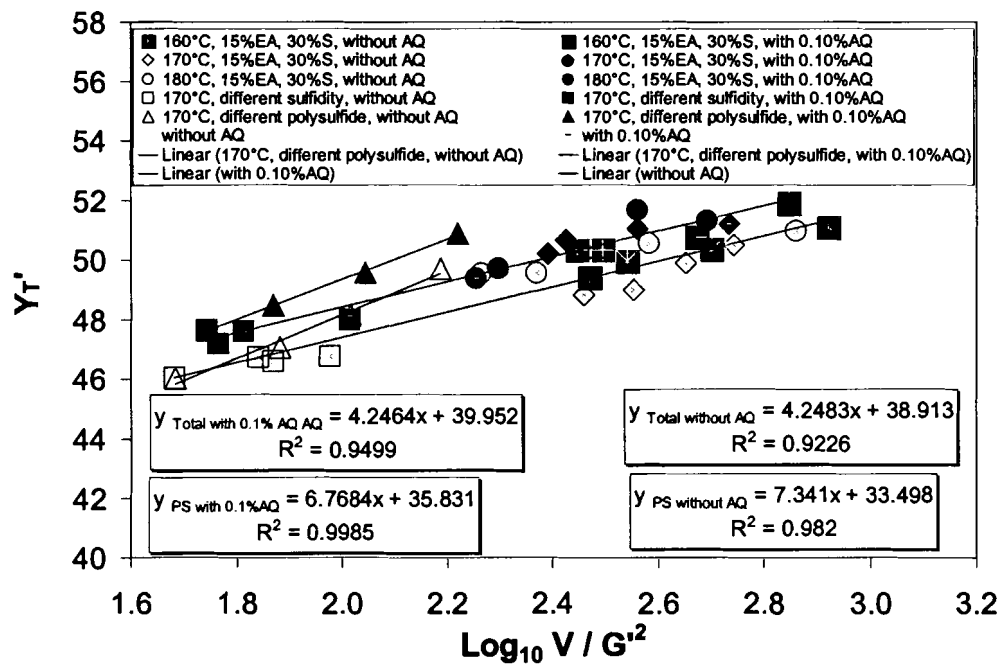


Figure 5.61. Marcoccia Equation for All Cooks of Rock Maple

#### 5.4.2. Yellow Birch

Figures 5.62 and 5.63 show the yield results for kraft, kraft-AQ, PS and PSAQ cooking of Yellow Birch plotted according to the UoM and Marcoccia pulp yield prediction equations. It is again obvious from these two figures that UoM pulp yield prediction equation is more general than the Marcoccia pulp yield prediction equation, since the PS and PSAQ pulp yield data are also well represented by correlation for the non-AQ and AQ cooks.

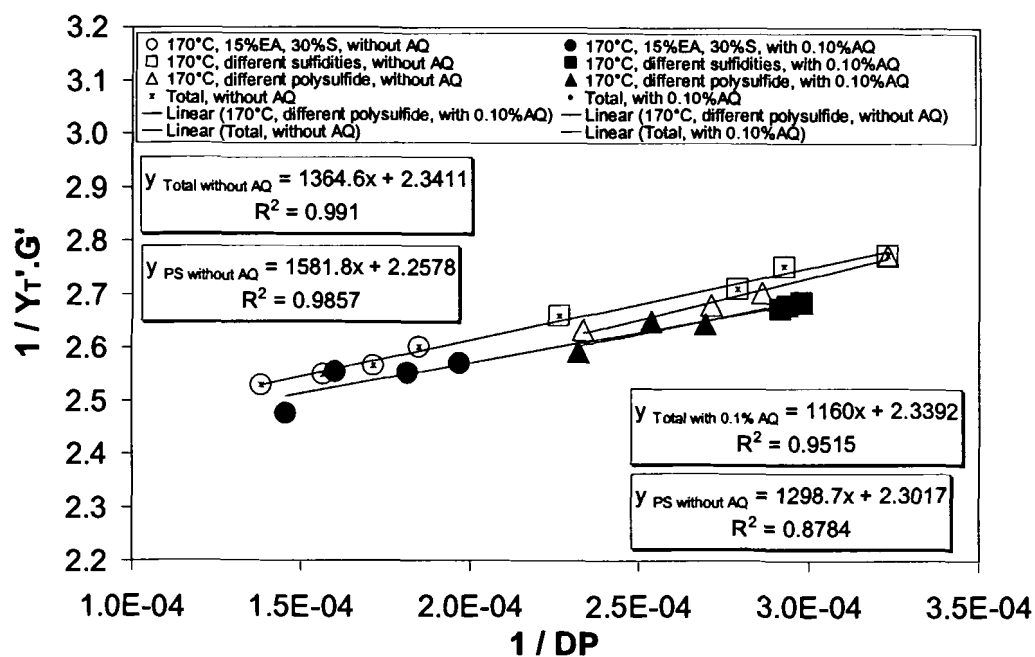


Figure 5.62. UoM Equation for All Cooks of Yellow Birch

The  $Y_{C,W}$  for the both non-AQ and AQ cooks can be correlated from these correlations as 0.427. Using the values one can determine  $(\Delta DP)_s$  for non-AQ and AQ cooking of Yellow Birch as 583 and 495. These values are higher than those found for Rock Maple. This might be related to a difference in the size of the amorphous regions of cellulose of these two species.

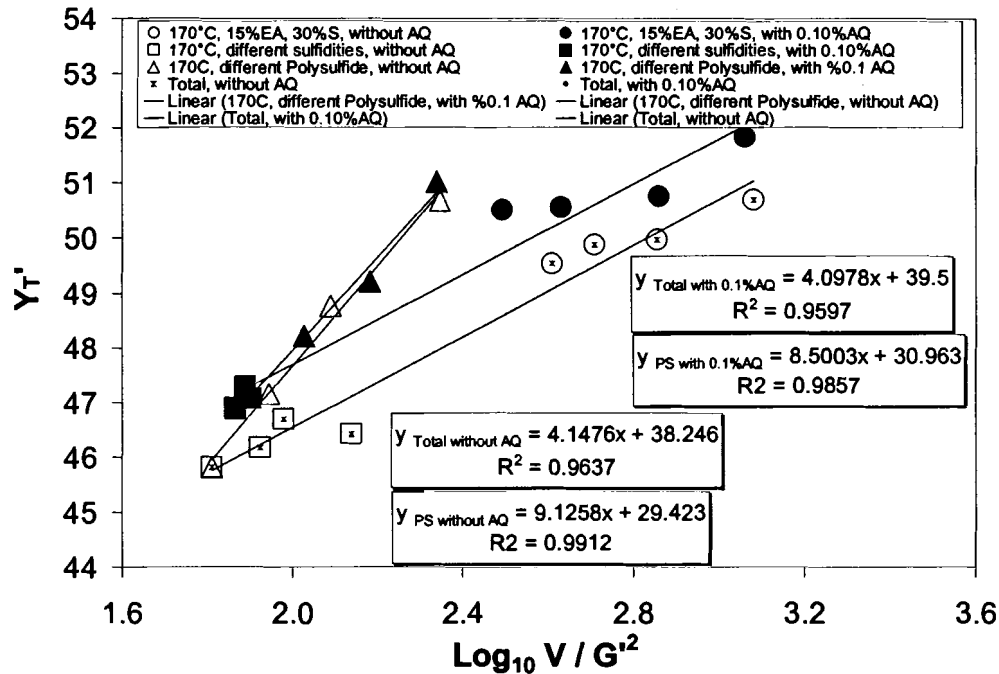


Figure 5.63. Marcoccia Equation for All Cooks of Yellow Birch

#### 5.4.3. Poplar

Figures 5.64 and 5.65 show the pulp yield results for all the cooks of Poplar according to the UoM and Marcoccia pulp yield prediction equations. It is again obvious from these two figures that UoM pulp yield prediction equation is more general in representing the data than the Marcoccia pulp yield prediction equation. However it should also be noted that in Figure 5.64 the data for AQ cooking do not fall on the same correlation as that of the PSAQ cooks. At this time we do not have a good explanation for this behavior, but a systematic experimental error is suspected. Further research is under way to resolve this discrepancy. For the non-AQ cooks, the values of  $Y_{C,w}$  and  $(\Delta DP)_s$  are determined to be 0.488 and 387. As expected, the values for  $Y_{C,w}$  of Poplar is significantly larger than that of Rock Maple and Yellow Birch of 0.427 for non-AQ cooks.

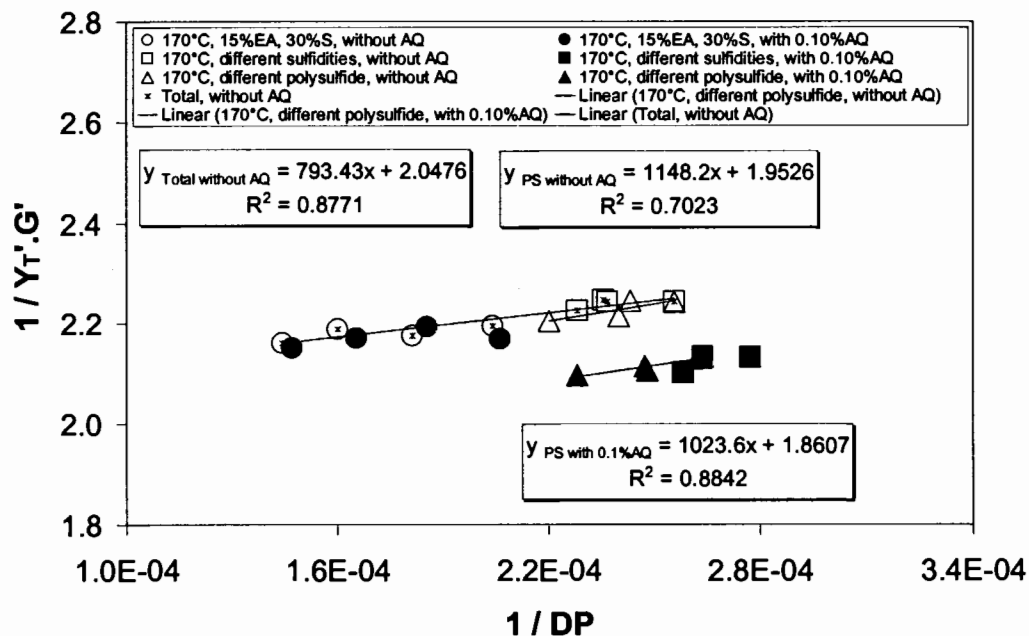


Figure 5.64. UoM Equation for All Cooks of Poplar

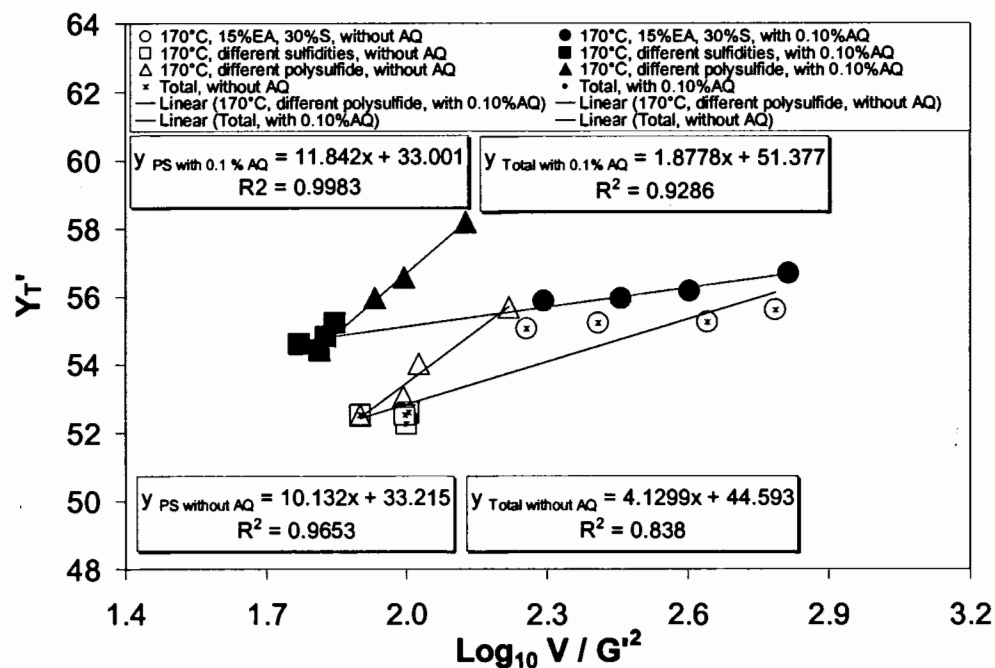


Figure 5.65. Marcoccia Equation for All Cooks of Poplar

#### 5.4.4. Black Spruce

Figures 5.66 and 5.67 show the total cooking results of the softwood, Black Spruce, plotted according to the UoM and Marcoccia pulp yield prediction equations respectively. It can be seen that for non-AQ and AQ cooks two non-linear relationships are obtained. For Black Spruce the range of  $1/DP$  is very wide and value of  $1/DP$  larger than  $3 \times 10^{-4}$  are not of practical interest. For this reason, the results are plotted in Figures 5.68 and 5.69 using only cooking results with  $1/DP$  less than  $1 \times 10^{-4}$ . It is apparent from these two figures that UoM pulp yield prediction equation as well as Marcoccia pulp yield prediction equation gives a good linear correlation in the area of interest. For Black Spruce we do not have enough results for PS and PSAQ in the area of interest to compare affect of PS and PSAQ cooking to these two pulp yield prediction equations.

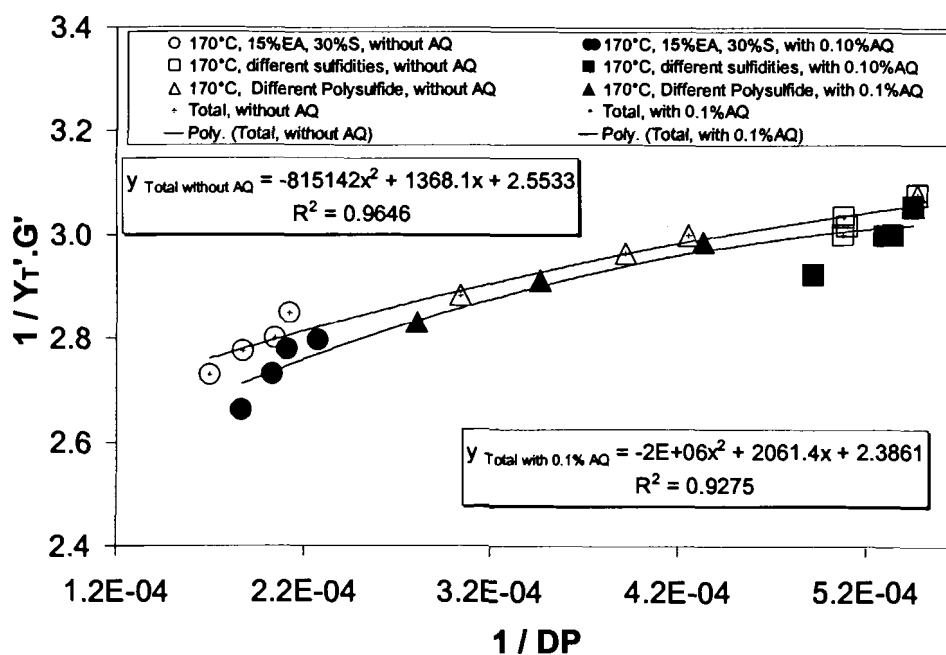


Figure 5.66. UoM Equation for All Cooks of Black Spruce

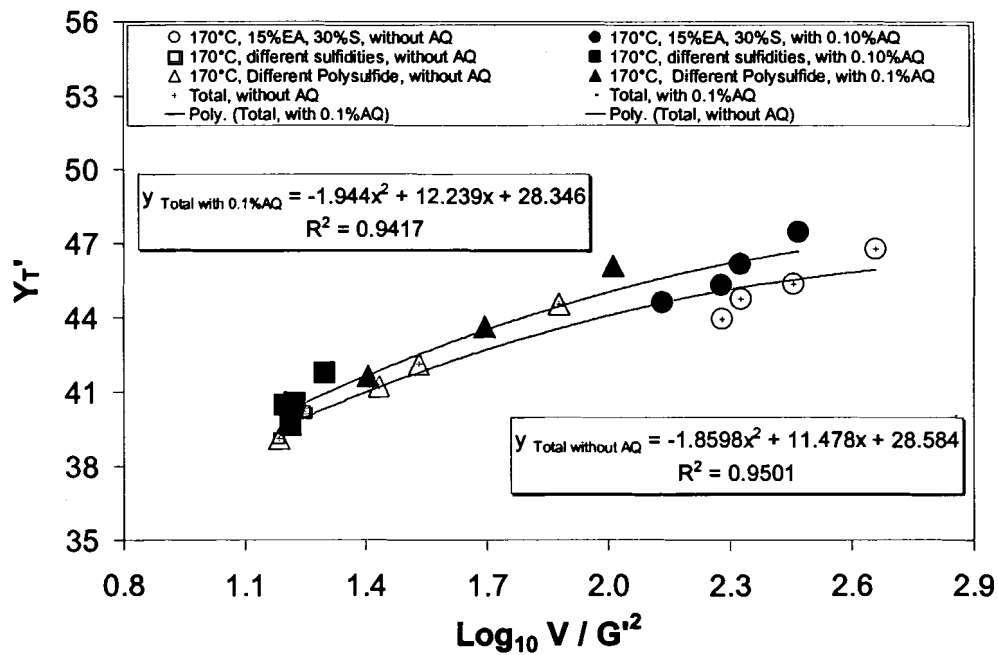


Figure 5.67. Marcoccia Equation for All Cooks of Black Spruce

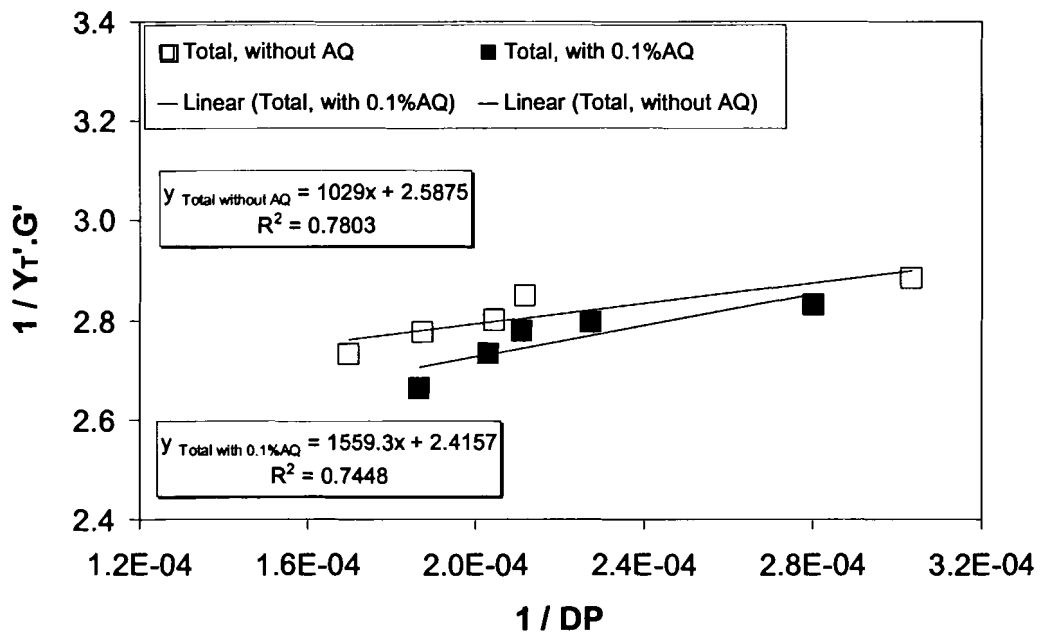


Figure 5.68. UoM Equation for All Cooks of Black Spruce

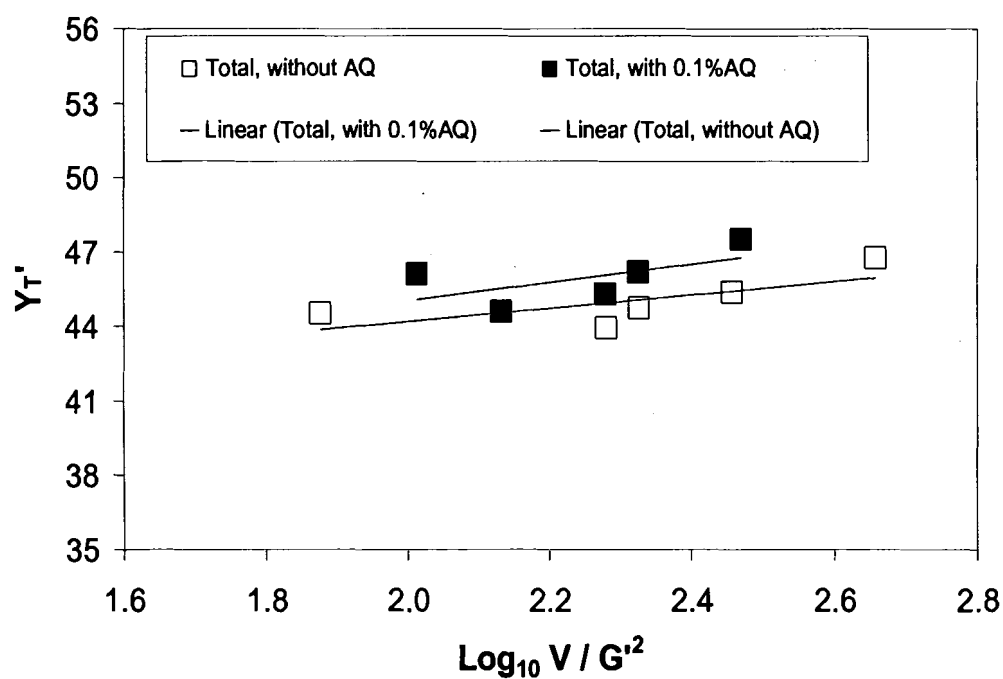


Figure 5.69. Marcoccia Equation for All Cooks of Black Spruce

## 5.5. APPLICATION OF UoM EQUATION TO LITERATURE DATA

In this section the UoM Equation is applied to literature data available on cooking of Scot Pine (Pekkala, 1986). Tables 5.2 and 5.3 show the cooking condition and results for kraft, kraft-AQ, PS and PSAQ cooks of Scot pine at different H-factors.

Table 5.2.  
Cooking Conditions of Kraft, Kraft-AQ, PS and PSAQ  
Cooks of Scot Pine (Pekkala, 1986)

Pulp	H-factor	EA(mol/kg wood)	Sulfidity(%)	PS (g/kg)	AQ (g/kg)	Kappa No
Kraft	877	5.5	30	0	0	38.0
Kraft	2045	5.5	30	0	0	20.1
Kraft	3445	5.5	30	0	0	14.8
Kraft-AQ	644	5.5	30	0	1	36.9
Kraft-AQ	1111	5.5	30	0	1	23.1
PS	1111	5.5	12	13	0	33.7
PS	2045	5.5	12	13	0	21.8
PS	3445	5.5	12	13	0	16.6
PSAQ	877	5.5	12	13	1	34.6
PSAQ	1345	5.5	12	13	1	22.6
PSAQ	3445	5.5	12	13	1	13.8
PSAQ(2)	644	5.5	23	20	1	32.2
PSAQ(2)	3445	5.5	23	20	1	14.5

Table 5.3.  
Cooking Conditions Results of Kraft, Kraft-AQ, PS and PSAQ  
Cooks of Scot Pine ( Pekkala, 1986)

Pulp	Yield,%	Mannnan,%	Xylan, %	Cellulose,%	Int Visc. (dm <sup>3</sup> /kg)
Kraft	46.6	9.7	7.9	76.5	1110
Kraft	42.4	8.1	8.8	79.9	870
Kraft	40.4	7.6	8.6	81.4	670
Kraft-AQ	47.0	9.5	7.7	77.1	1070
Kraft-AQ	43.2	8.5	8.2	79.7	900
PS	47.9	12.5	7.8	74.6	1030
PS	45.4	11.7	8.4	76.5	880
PS	42.5	10.6	8.3	78.6	740
PSAQ	49.1	13.9	7.8	72.9	1030
PSAQ	46.4	12.9	7.8	75.7	860
PSAQ	42.8	11.0	7.4	79.4	660
PSAQ(2)	49.5	14.2	7.5	73.4	1070
PSAQ(2)	44.0	11.5	8.3	78.0	790



The results in Table 5.3 are plotted according to the UoM pulp yield prediction equation in Figure 5.70. As expected, two separate linear correlations are obtained for cooking with or without AQ, irrespective of the H-factor or whether polysulfide is used. Using the UoM pulp yield prediction equation, the  $Y_{c,w}$  value for non-AQ and AQ cooks is calculated as 0.385, and the  $(\Delta DP)_s$  values of the non-AQ and AQ cooks are 187 and 161 respectively. Cote et al. (1966) reported that the  $Y_{c,w}$  of Scot Pine is 0.403.

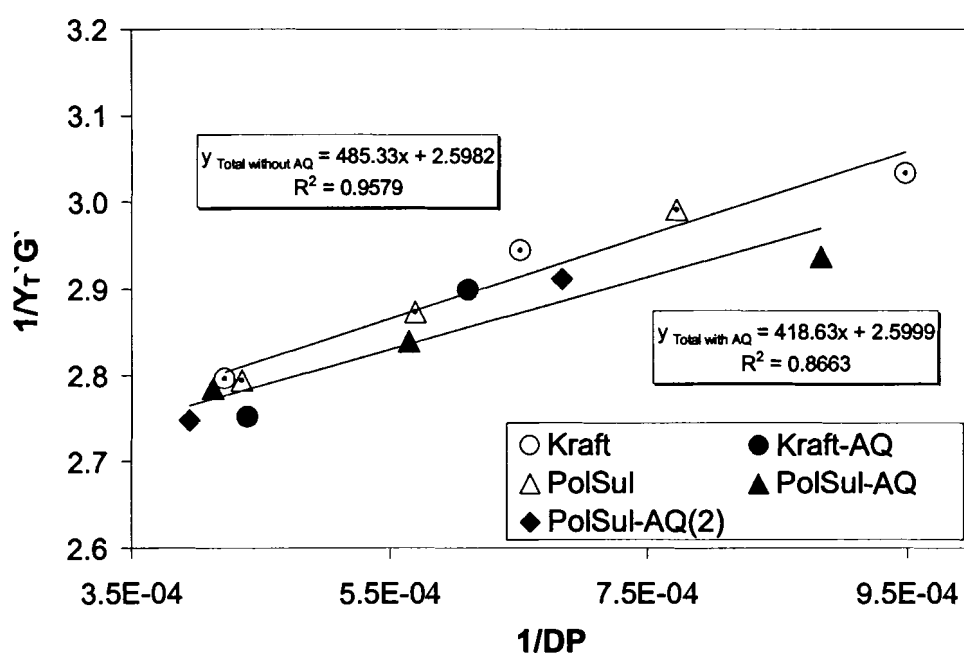


Figure 5.70. UoM Equation for Kraft, Kraft-AQ, PS and PSAQ Cooking of Scot Pine

## CHAPTER 6

### CONCLUSION

The cooking results show that the cellulose retention of kraft, kraft-AQ, PS and PSAQ increases with increasing kappa number (decreasing delignification). Although hemicellulose retention of PS and PSAQ cooks increases with increasing kappa number, that of kraft and Kraft-AQ is constant over the present range of kappa numbers. Therefore the yield improvement with increasing kappa number for kraft and kraft-AQ is due to cellulose retention, while the yield improvement for PS and PSAQ is the result of cellulose as well as hemicellulose retention. The cooking results also show that the addition of AQ leads to an increased retention of cellulose and mannan at the same degree of cellulose degradation, while polysulfide produces a significant increase in xylan and glucomannan retention. This suggests that the detailed mechanism of carbohydrate stabilization is different for AQ and polysulfide.

A fundamental relationship between alkaline pulping yield and the mass fraction and degree of polymerization (DP) of cellulose in pulp has been derived. The equation is validated for kraft, kraft-AQ, PS and PSAQ cooking of three hardwoods, Rock Maple, Yellow Birch and Poplar, and one softwood, Black Spruce.

$$\frac{1}{Y_T' G'} = \frac{1}{Y_{C,W}} + \frac{(\Delta DP)_s}{Y_{C,W}} \cdot \frac{1}{DP}$$

This so-called UoM equation contains two parameters,  $(\Delta DP)_S$  and  $Y_{C,w}$ , respectively the number of glucose units removed by secondary peeling and the cellulose mass fraction in pulp based on wood. These two parameters are a function of the species used. Also,  $(\Delta DP)_S$  decreases when AQ is added to the cooks. However the two parameters are not a function of all other cooking parameters such as sulfidity, alkalinity, temperature, H-factor and polysulfide addition. The value of  $(\Delta DP)_S$  for the different species may be related to the size of the amorphous regions of cellulose in the species.

The validity of Marcoccia pulp yield prediction equation was also investigated for kraft, kraft-AQ, PS and PSAQ cooks of the three hardwoods and single softwood. Four separate linear correlations are needed to represent the data for each cooking process and each wood species. Thus the Marcoccia equation is affected by both AQ and PS addition. Therefore the UoM pulp yield prediction equation is more general than the Marcoccia pulp yield prediction equation.

## REFERENCES

**Ahlgren, P., Teder, A.,** "Delignification Rate in Polysulfide Pulping," *Svensk Papperstidning* 70(4): 135-143 (1967)

**Aurell, R., Hartler, N.,** "Kraft pulping of pine. Part 1.," *Svensk Papperstidning* 68(3): 59-68 (1965)

**Cote, W.A. Jr., Simson, B.W., and Timell, T.E.,** "Chemical Composition of Wood and Bark from Normal and Compression Regions of Fifteen Species of Gymnosperms," *Svensk Papperstidning* 69(17): 547-558 (1966)

**Da Silva Perez, D., van Heiningen, A.R.P.,** "Determination of cellulose degree of polymerization in chemical pulps by viscosimetry," 7<sup>th</sup> *EWLP* Conference, Turku, Finland 393-396 (2002)

**Dorris, G.M., Uloth, V.C.,** "Analysis of Oxidized White Liquors. Part II: Potentiometric Titrations for the Determination of Polysulphides and Sulphoxy Anions," *J. of Pulp and Paper Science* 20(9): 242-248 (1994)

**Easty, D.B., Malcolm, E.W.,** "Estimation of Pulp Yield in Continuous Digesters from Carbohydrate and Lignin Determinations," *Tappi Journal* 65(12): 78-80 (1982)

**Fengel, D., Wegener, G.,** "Wood; Chemistry, Ultrastructure, Reactions," Walter de Gruyter and Co., Berlin (1984)

**Genco, J.M., Busayasakul, N., Medhora, H.K., and Robbins, W.,** "Hemicellulose Retention During Kraft Pulping," Tappi Journal 73(4): 223-233 (1990)

**Gierer, J.,** "The reaction of lignin during pulping. A description and comparison of conventional pulping processes," Svensk Papperstidning 73: 571-596 (1970)

**Grace, T.M., Malcolm, E.W.,** "Pulp and Paper Manufacture," volume 5 "Alkaline Pulping," Published by the Technology Section Canadian Pulp & Paper Association, A3rd Eddition, TAPPI/CPPA, Atlanta/Montreal (1989)

**Gullichsen, J., Fogetlbolm, C.J.,** "Chemical Pulping," Finnish Paper Engineers' Association and TAPPI, Jyvaskyla, Finland (2000)

**Gustafson, R., McKean, W., and Pu,Q.S.,** Appita 44(6) (1991)

**Haas, D.W., Hrutfiord, B.F., and Sarkanen, K.V.,** "Kinetic Study on the Alkaline Degradation of Cotton Hydrocellulose," J. of Applied Polymer Science 11: 587-600 (1967)

**Holton, H.H., Chapman, F.L.,** "Kraft Pulping with Anthraquinone," Tappi Journal 60(11): 121-125 (1977)

**Jiang, J.E., Lowe, R.W.,** "Extended Modified Cooking of Southern Pine with Polysulfide- Effect on Elemental-Chlorine-Free Bleaching," J. of Pulp and Paper Science 21(3): 76-80 (1995)

**Kleppe, P.J.,** "A mill trail with addition of a small amount of AQ to kraft and polysulfide pulping," Paper presented at EUCEPA Symposium on the Delignification Method of the Future, Helsinki, Finland, June 1980

**Kubes, G.J., Fleming, B.I., MacLeod, J.M., Bolker, H.I., and Werthemann, D.P.,** "Viscosities of Unbleached Alkaline Pulps. II The G- Factor," J. of Wood Chemistry and Technology 3(3): 313-333 (1983)

**Lai, Y-Z, Sarkanen, K.V.,** "Kinetics of alkaline hydrolysis of glycosidic bonds in cotton cellulose," Cellulose Chemistry and Technology 1: 517-527(1967)

**Landmark, P.A., Kleppe, P.J., and Johnsen, K.,** "Cooking Liquor Oxidation and Improved Cooking Technique in Polysulfide Pulping," Tappi Journal 48(5): 56A-58A (1965)

**Li, Z., Li, J., and Kubes, G.J.,** “Kinetics of Delignification and Cellulose Degradation During Kraft Pulping with Polysulfide and Anthraquinone,” *J. of Pulp and Paper Science* 28(7): 234-239 (2002)

**Luthe, C., Berry, R., Radiotis, T., and Nadeau, L.,** “Measuring Softwood Yield Gain at Kraft Pulp Mills,” *Paprican Research Report 1582*, Quebec, Canada, March 2002

**MacLeod, J.M., Fleming, B.J., Kubes, G.J., and Bolker, H.I.,** “The Strength of Kraft-AQ and Soda-AQ Pulps,” *Tappi Journal* 63(1): 57-60 (1980)

**MacLeod, J.M., Pelletier, L.J.,** “Basket cases: Kraft pulps inside digesters,” *Tappi Journal* 70(11): 47-53 (1987)

**Marcoccia, B.S., Stormberg, B., and Prough, J.R.,** “Achieving Major Increases in Hardwood Yield with Lo-Aolids Cooking: A study in Progress,” 1998 Breaking the Pulp Yield Barrier Symposium, 17-18, Atlanta, Tappi

**McDonough, T.J.,** “Kraft Pulp Yield Basics,” 1998 Breaking the Pulp Yield Barrier Symposium, 17-18, Atlanta, Tappi

**Pekkala, O.,** “Prolonged kraft cooking modified by anthraquinone and polysulfide,” *Paperi ja Tra* 68(5): 385-400 (1986)

**Sayner, N., Laundrie, J.F.,** "Factors Affecting Yield Increase and Fiber Quality in Polysulfide Pulping of Loblolly Pine, other Softwoods, and Red Oak," Tappi Journal 47(10): 640-652 (1964)

**Scott, R.W.,** Anal. Chem. 51: 936 (1979)

**Sjostrom, E.,** "Wood Chemistry Fundamentals and Applications," Academic Press, 2<sup>nd</sup> Ed., San Diego, USA (1993)

**Timell, T.E.,** "The Chemical Composition of Tension Wood," Svensk Papperstidning 72: 173-181 (1969)

**Van Heiningen, A.R.P., Gao, Y. and Da Silva Perez, D.,** "Reduction of Alkaline Pulp Yield from the Mass Fraction and Degree of Polymerization of Cellulose," 7<sup>th</sup> EWLP Conference, Turku, Finland, 63-68 (2002)

**Virkola, N.E.,** "Pauumassan valmistus. Suomen Paperi-insinöörien yhdistyksen oppi-ja kasikirja," Toinen uudistettu painos (1983)

**Waldemar, J., Suomen, P.,** Paperi-insinöörien yhdistyksen oppi-ja kasikirja I, Toinen uudistettu painos (1997)



**Wroom, K.E., "The 'H' Factor: A Means of Expressing Cooking Times and Temperatures as a Single Variable," Pulp and Paper Mag. Can. 58(3): 228-231 (1957)**

## **BIOGRAPHY OF THE AUTHOR**

Mehmet Sefik was born in Siirt, Turkey on September 1, 1973. He was raised in the fourth largest city of Turkey, Adana, until 1992. Four years later he graduated with a Bachelor of Science degree from the Chemical Engineering Department of Ankara University in June 1996. Upon graduating, Mehmet enrolled in Ankara University Graduate School where he pursued his Master of Science in Chemical Engineering.

When in the spring of 2001 Mehmet was awarded a full scholarship from the Turkish Pulp and Paper Foundation to continue his studies in the United States, he enthusiastically accepted such an opportunity to do so. He attended the Chemical Engineering Department at the University of Maine in the spring of 2001 with the hope of obtaining a Master of Science degree.

Mehmet Sefik is a candidate for the Master of Science degree in Chemical Engineering from The University of Maine in May, 2003.