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THE ROLE OF ANTHRAQUINONE IN NEUTRAL SULPHITE PULPING OF WOOD CHIPS

Master's thesis for the degree of Master of Science in Technology
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Tiivistelmä

Tämän diplomityön tavoitteena on kirjallisuutta apuna käyttäen selvittää syitä antrakinonin (AQ) mahdolliselle karsinogeenisuudelle, sekä kokeellisesti todentaa AQ:n uusi mahdollinen toimintamekanismi neutraalisulfiittikeitossa. Todentamisessa käytetään apuna kuutta erilaisen redox-potentiaalin omaavaa kinonia, joita altistetaan pelkistäville keitto-olosuhteille. Ajatus uuden toimintamekanismin taustalla on selvittää ovatko matalamman redox-potentiaalin omaavat lisäaineet parempia antioksidantteja ja siten tehokkaampia keittokemikaaleja. Lisäksi työssä käydään lyhyesti läpi kirjallisuudessa esiintyviä antrakinonin reaktiomekanismeja, sekä tarkastellaan AQ:n ja polysulfidin (PS) välistä synergiaa.

Keittokokeet suoritettiin kahdessa osassa. Ensin selvitettiin kokeissa käytettävien kinoneiden kykyä pelkistyä natriumsulfiitin vaikutuksesta ja toisessa osassa tutkittiin kyseisten kinoneiden vaikutusta puuhakkeeseen neutraaleissa keitto-olosuhteissa. Liuenneen ligniinin pitoisuus, ligniinin molekyylimassajakauma, sekä loppu-pH mitattiin suodoksista. Lisäksi kappaluku ja kokonaissaanto mitattiin saaduista massoista.

Tulosten mukaan on selkeää näyttöä siitä, että AQ poistaa ligniiniä kaikkein tehokkaimmin. Vaikka matalampi redox-potentiaali näyttäisi viittaavan parempaan delignifiointiasteeseen, asia ei ole yksiselitteinen. Verrattaessa lisäaineettomiin referenssikeittoihin, AQ oli kinoneista ainoa joka vaikutti merkittävästi puuhakkeen delignifiointiasteeseen. Tämä saattaa viitata siihen, etteivät muut lisäaineet välttämättä toimi katalyytinomaisesti annetuissa olosuhteissa, eivätkä siten pysty tehokkaaseen ligniinin poistoon. Vaihtoehtoisesti pelkistyneet kinonimuodot saattavat olla kykenemättömiä pilkkomaan ligniiniä yhtä tehokkaasti kuin antrahydrokinoni (AHQ), tai sitten niiden pelkistyneet muodot eivät yksinkertaisesti ole yhtä stabiileja kuin AHQ.

Viimeisimpien tutkimusten mukaan antrakinonin käyttö sellun keitossa voidaan nähdä hyvin kyseenalaisena. Kuitenkin on yhä epävarmaa miksi AQ aiheuttaa syöpää testieläimissä ja millaisia ovat ihmisille haitalliset annosmäärät. Joka tapauksessa, tämän tutkimuksen perusteella voidaan todeta että ymmärrys antrakinonia kohtaan on hieman lisääntynyt, vaikkakaan ei ratkaisevasti. Näyttää siis siltä, että AQ:n toimintamekanismin selvittäminen vaatii lisätutkimuksia.

Avainsanat

Antioksidantti, antrakinoni, AQ, delignifiointi, hapettuminen, karsinogeenisuus, ligniini, lisäaine, pelkistyminen, polysulfidi, PS, reaktiomekanismi, redox-potentiaali, synergia, toimintamekanismi

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Abstract

The aim of this thesis was to investigate the carcinogenic potential of anthraquinone (AQ) and verify the new proposed working mechanism of AQ in neutral sulphite pulping by using six different quinones with varying redox potentials. The idea behind the new working mechanism was to investigate whether additives with lower redox potential could be better antioxidants and thus more effective pulping chemicals. In addition, the much discussed AQ reaction mechanisms as well as the synergism of polysulfide (PS) and AQ will be covered.

The cooking trials were performed in two stages. First it was examined how well the different quinones are reduced by the influence of sodium sulphite, and in the second stage it was investigated how efficient the different quinones were in neutral pulping of wood chips. The dissolved lignin content (DLC), molecular weight distribution (MWD) of lignin and final pH were determined from the filtrates. In addition, kappa number and total yield were measured from the cooked pulps.

According to the results, there is clear evidence that AQ has the highest delignification rate of the trials. Although it seems that lower redox potential equals better delignification, it is not undoubtedly like that. In comparison to reference cooks, AQ was the only quinone which showed notable effect on the delignification rate. This might mean that the other additives used in the experiments could not work as pulping catalysts in given conditions and thus are unable to degrade lignin effectively. Alternative explanation could be that the reduced forms of quinones are just unable to degrade lignin as efficiently as anthrahydroquinone (AHQ), or simply they are not as stable as AHQ.

Regarding the latest research, the utilization of AQ in pulping can be seen very questionable. However, it is still uncertain why it induces tumors in test animals, and what are harmful amounts to humans. Altogether based on the results of this study the understanding towards AQ is slightly increased, yet remaining unclear. In other words, it seems that the investigation of the working mechanism of AQ requires further exploration.

Keywords

Additive, anthraquinone, antioxidant, AQ, carcinogenicity, delignification, lignin, oxidation, polysulfide, PS, reaction mechanism, redox potential, reduction, synergism, working mechanism

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This work is at its end, but as has been said:

"*In every end, there is also a beginning*" –Libba Bray

Espoo, 2nd of November 2015

Sakari Vuorinen

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ABBREVIATIONS

AQ	Anthraquinone
AHQ	Antrahydroquinone
AMS	Anthraquinone-2-sulfonic acid
BfR	The Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung)
DLC	Dissolved Lignin Content
DMC	Dry Matter Content
EA	Effective Alkali
EFSA	European Food Safety Authority
HPLC	High-Performance Liquid Chromatography
IARC	International Agency for Research on Cancer
MWD	Molecular Weight Distribution
MRL	Maximum Residue Level
NCASI	National Council for Air and Stream Improvement
NCI	National Cancer Institute
NTP	National Toxicology Program
OECD	Organization for Economic Cooperation and Development
PAH	Polycyclic Aromatic Hydrocarbons
PS	Polysulfide
REDOX	Portmanteau of Reduction and Oxidation
SEC	Size-Exclusion Chromatography
SET	Single-Electron Transfer
UNECE	United Nations Economic Commission for Europe
QM	Quinone Methide

1 INTRODUCTION

The sustainability revolution (a.k.a sustainalization) has begun, meaning that the global economy and nations are more willing to be in harmony with nature. The World's population is still growing and societies are more interested of the surrounding environment they are living in. This guides the governments to support so-called "green technology", in order to provide a better future for our offspring. (Burns 2012; Lecain 2014).

Therefore demand for renewable products and technology is increasing all the time. Because of this growing demand, vast amounts of extra biomass have to be acquired. Thus, instead of cutting more trees and plants, industry must operate in a sustainable way. This moves the focus towards superior processes, which are able to supply higher yields, while lowering the environmental impacts and keeping the quality factors of the end products on a satisfied level. The pulping industry is constantly looking for a various ways to respond this growing demand of biomass, and process economics play a major role in the development. The governing endeavor to maximize pulp yields and production efficiency have led the industry to a position where companies are trying to assimilate the chemistry of pulping additives. Thus, by understanding the working mechanisms of powerful additives might help scientists to develop additives with desirable properties in future. (Kocurek et al. 1989; Hart & Rudie 2014).

However it is difficult to investigate all the impacts pulping additives cause for the process and for the end products. The influence of an additive to the quality of the end product and to the process itself has to be studied carefully. It is extremely challenging to discover an additive, what meets all the necessary requirements. In order to reach commercial stage, the additive must be effective, environmentally friendly, inexpensive, easily available, and safe to use. Additionally qualitative factors of the end product cannot deteriorate as a consequence of the additive. (Blain 1993).

Because of the prevailing conditions around the industry, effective pulping additives have to be examined, and their working mechanisms have to be wholly assimilated. This study focuses on one specific and effective pulping additive called anthraquinone (AQ). Due to the uncertainty around AQ, its potential as a possible carcinogen is studied. After this the focus moves to AQ's role in polysulfide cooking and later on towards the possible working mechanism of AQ. The experimental part of this work deals with AQ and six different quinones, which have been used to determine the possible working mechanism behind this powerful pulping additive.

LITERATURE PART

2 CHARACTERISTICS OF ANTHRAQUINONE

Anthraquinones are a functionally diverse group of chemicals. However, there are certain subgroups that are more common than the others. Actually, it has been discovered that 9,10-anthraquinones are one of the largest group of natural quinones in the world (Thomson 1971). The most common type of anthraquinone used by the pulping industry is called 9,10-dioxoanthracene, also known as 9,10-anthracenedione, anthradione, 9,10-anthraquinone, 9,10-dihydro-9,10-dioxoanthracene or simply anthraquinone (AQ) (Figure 1).

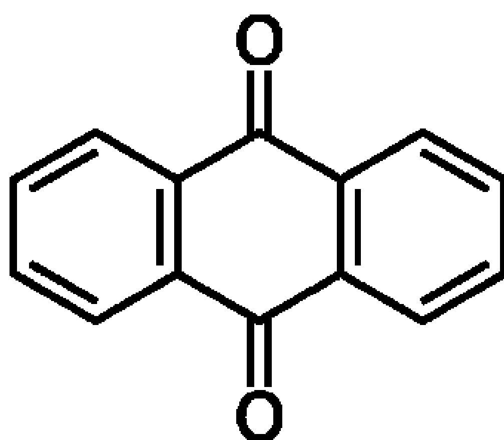

Figure 1. Anthraquinone (NTP, 2005).

2.1 Chemical and physical properties

Chemically anthraquinones are aromatic and organic anthracene derivatives with 9,10-dioxoanthracene skeleton (Chien et al. 2014). Furthermore, AQ molecule contain two ketone groups thus making it a diketone. The chemical formula of anthraquinone is $C_{14}H_8O_2$ and its molecular weight is 208.22 g/mol. (NTP 2005; IARC 2012).

Physically AQ is a crystalline powder with a golden yellow color. It is insoluble in water and acetone, slightly soluble in ether, moderately soluble in ethanol and totally soluble in alcohol, toluene and hot benzene. AQ's boiling point is 377°C and flash point is 185°C (NTP 2005). In addition it has been reported that various anthraquinones have shown different degree of lipophilic nature (Andersson et al. 1999; Leu et al. 2008).

2.2 Benefits of using AQ

There are multiple reasons why anthraquinones are considered to be so good chemicals for different applications. In fact, both natural and synthetic anthraquinones have provided numerous possibilities for various promising

applications (Sendelbach 1989). They have been utilized as an intermediate in the dye and pigment manufacture, a catalyst in the isomerization of vegetable oils, a bird repellant on growing crops, and as an additive in the pulping processes. (NTP 2005; Meister 1987).

Although bird repelling is far away from the pulping industry, there are plenty of reasons to utilize AQ in the pulping processes as well. Higher pulp yield, bottleneck elimination and chemical savings are big motives, but the benefits AQ may provide for the pulp mills are even greater. The benefits that AQ could provide in the pulp mills are listed in Figure 2. (Sturgeoff & Pitl 1994; Greer et al. 2004).

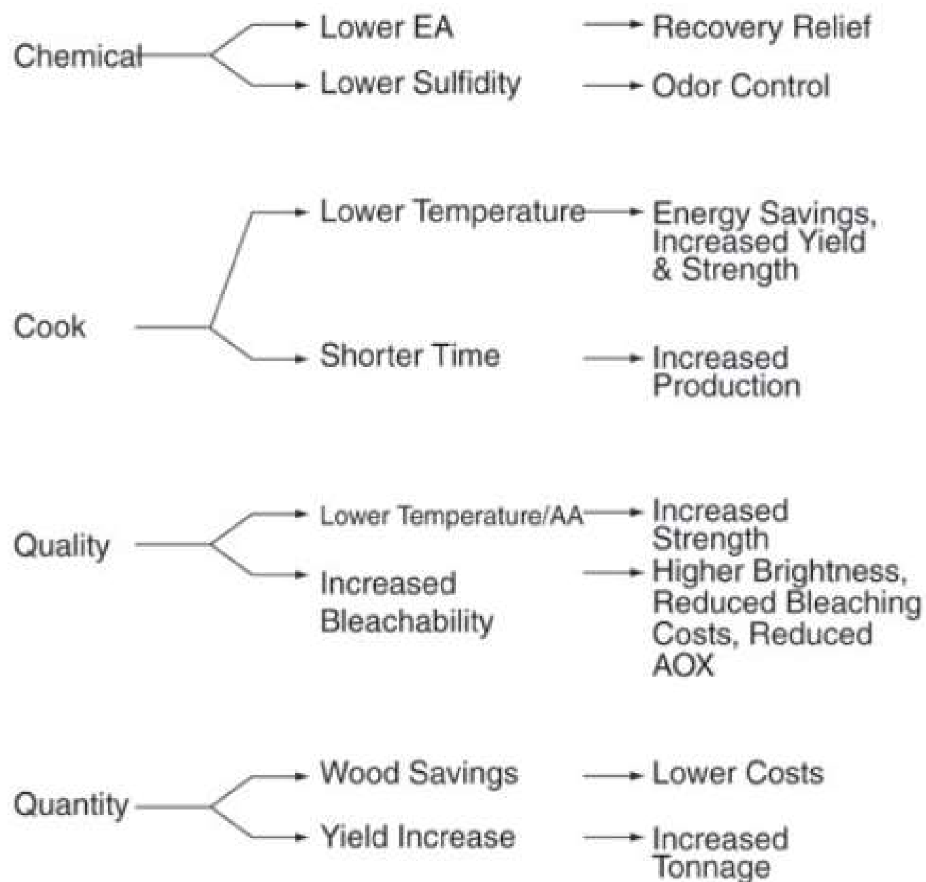

Figure 2. Benefits of using AQ in the pulp mill (Greer et al. 2004)

3 CARCINOGENICITY

Although there are many advantages for using AQ in pulping, there have been lots of controversy whether AQ is carcinogenic to humans or not. Regarding to the reports of the Federal Institute of Risk Assessment (BfR), the European Food Safety Authority (EFSA), and the International Agency for Research on Cancer (IARC), anthraquinone have been seen as a possible carcinogen for humans when eaten (BfR 2013). In order to support or oppose this claim, literature have been carefully examined.

3.1 Background on possible carcinogenicity to humans

In 2005, National Toxicology Program's (NTP) report revealed that based on the results of two year animal experiments, anthraquinone caused cancer in the liver, kidneys or urinary bladder of the used test animals. Based on the results, test groups who received the highest dose of AQ, had the highest rates of tumors as well (Table 1). (NTP 2005).

A few years after the study of NTP, National Council for Air and Stream Improvement (NCASI) found the potential for AQ transfer from unbleached linerboard to food products. According to the studies of NCASI, accumulated AQ residues in cellulose could transfer from pizza box into the pizza crust. The mean migration of AQ from the linerboard into the pizza crust was found to be as much as 196.1 ng, indicating 3.6 ±1.05 % of the total AQ contained in the linerboard. This discovery led for the supplemental investigations of AQ's carcinogenic risks to humans. (Louch 2008; IARC 2012).

In 2012, IARC evaluated the AQ's risks to humans, while EFSA reasoned opinion on the maximum residue level (MRL) for AQ. However, outcomes of these studies were incomplete. Regarding on the strong proof for the carcinogenicity of AQ in animal experiments, IARC could not prove AQ's carcinogenic potential to humans. (NTP 2005; IARC 2012). Simultaneously EFSA decided that because of the lack of information regarding toxicology and metabolism of mammals, as well as uncertain analytical methods for defining AQ residues, it cannot recommend any verified methods for AQ residue measurements. EFSA was also unable to ensure whether the default MRL of 0.01 mg AQ per kg of food is adequate for the consumers. (EFSA 2012).

Anyhow, due to alarming results based on the animal experiments, EFSA prompted BfR to reassess the use of AQ in the pulp intended for the food contact products. After reassessment, BfR decided to change its recommendation concerning the use of AQ, which is why the chemical is

now classified as a possible health hazard and thus should not be used in the manufacture of paper or board intended for food contact. (BfR 2013).

Table 1. Summary of the 2-year carcinogenesis studies of AQ (NTP 2005).

	Male B6C3F1 Mice	Female B6C3F1 Mice
Concentrations in feed	0, 833, 2,500, or 7,500 ppm	0, 833, 2,500, or 7,500 ppm
Body weights	7,500 ppm group less than control group	7,500 ppm group slightly less than control group
Survival rates	45/50, 41/50, 43/50, 23/50	35/50, 42/50, 35/50, 42/49
Nonneoplastic effects	Liver: centrilobular, hypertrophy (24/50, 34/50, 41/50, 33/49); degeneration, fatty, focal (0/50, 7/50, 6/50, 0/49); hepatocyte, erythrophagocytosis (1/50, 9/50, 13/50, 6/49); eosinophilic focus (14/50, 17/50, 24/50, 20/49); focal necrosis (2/50, 3/50, 3/50, 8/49) Urinary Bladder: intracytoplasmic inclusion body (0/50, 46/49, 46/49, 42/45) Thyroid Gland: follicular cell hyperplasia (7/50, 10/50, 15/49, 21/46) Spleen: hematopoietic cell proliferation (12/50, 14/50, 12/49, 30/42) Kidney: pigmentation (0/50, 2/50, 2/50, 18/47)	Liver: centrilobular hypertrophy (1/49, 27/50, 22/50, 39/49); degeneration, fatty, focal (2/49, 3/50, 1/50, 9/49); eosinophilic focus (6/49, 15/50, 11/50, 22/49) Urinary Bladder: intracytoplasmic inclusion body (0/44, 40/48, 43/46, 46/48) Spleen: hematopoietic cell proliferation (9/45, 17/49, 17/48, 26/48)
Neoplastic effects	Liver: hepatocellular adenoma (21/50, 32/50, 38/50, 41/49); hepatocellular carcinoma (8/50, 13/50, 17/50, 21/49); hepatoblastoma (1/50, 6/50, 11/50, 37/49); hepatocellular adenoma, hepatocellular carcinoma, or hepatoblastoma (26/50, 35/50, 43/50, 48/49)	Liver: hepatocellular adenoma (6/49, 28/50, 27/50, 40/49); hepatocellular carcinoma (2/49, 3/50, 8/50, 8/49); hepatocellular adenoma or carcinoma (6/49, 30/50, 30/50, 41/49)
Equivocal findings	Thyroid Gland: follicular cell adenoma (0/50, 0/50, 2/49, 2/46)	Thyroid Gland: follicular cell adenoma (1/45, 1/48, 2/48, 2/48); follicular cell carcinoma (0/45, 0/48, 0/48, 2/48); follicular cell adenoma or carcinoma (1/45, 1/48, 2/48, 4/48)
Decreased incidences	None	None
Level of evidence of carcinogenic activity	Clear evidence	Clear evidence

3.2 Determination of carcinogenic potential to humans

3.2.1 Definition of carcinogen

The term carcinogen refers to a chemical agent or compound which cause or increase the probability of acquiring a cancer (UNECE 2011). There are different kind of carcinogens which are classified depending on their mode of action, such as genotoxic and nongenotoxic carcinogens. The difference between these two types is that genotoxic carcinogens cause DNA damage directly, whereas nongenotoxic carcinogens enhance development of tumors by influencing on signal transduction, cell proliferation or gene expression. (OECD 2007). According to the animal studies of Maurici et al., it was concluded that the most potent mutagens are found to be carcinogenic as well (Maurici et al. 2005). However, not all mutagens are carcinogens neither all carcinogens are mutagens (Zeiger et al. 1988; NTP 2005). Additionally, substances that have carcinogenic potential to animals are considered carcinogenic to humans as well until there is enough evidence to show otherwise (UNECE 2011).

3.2.2 Classification of carcinogens

The IARC classifies carcinogens into a five different groups based on the strength of the evidence. As can be seen in Table 2: Group 1 agents are known human carcinogens, Group 2A agents are probable human carcinogens, Group 2B agents are possible human carcinogens, Group 3 agents are non-classifiable and Group 4 agents are probably not human carcinogens. (IARC 2015).

Table 2. Classification of human carcinogens (IARC 2015).

Group 1	*Carcinogenic to humans*	116 agents
Group 2A	*Probably carcinogenic to humans*	73
Group 2B	*Possibly carcinogenic to humans*	287
Group 3	*Not classifiable as to its carcinogenicity to humans*	503
Group 4	*Probably not carcinogenic to humans*	1

According to the IARC's list of classifications anthracene is classified in the group 3 and anthraquinone in the group 2B (Table 3). The meaning of this classification (2B) is that there is an inadequate evidence of AQ's carcinogenic potential to humans, but at the same time, clear evidence of carcinogenicity in experimental animals. (IARC 2015).

Table 3. Anthracene and AQ classification (IARC 2015).

CAS No	Agent	Group	Volume	Year
000120-12-7	Anthracene	3	92, Sup 7	2010
000084-65-1	Anthraquinone	2B	101	2013

The definition of the group 3 is also interesting. The term “Non-classifiable” should not be confused to non-carcinogenic. It only means that further research is needed, especially if the certain chemical is used frequently or if it has widespread applications in the industry. (IARC 2015).

3.2.3 Possible explanations for carcinogenicity

Studies of NTP and National Cancer Institute (NCI) compared the neoplastic findings of AQ and AQ derivatives. It was concluded that the reason for AQ’s carcinogenicity in test animals might be the parent ring system, whereas substituents determine the target organs affected and the strength of the carcinogenic response (NTP 2005; Doi et al. 2005).

According to Muños and Albores, a molecule consisting two or more fused aromatic rings is called polycyclic aromatic hydrocarbon (PAH). The International Agency for Research on Cancer (IARC) has classified some of the PAHs as carcinogenic or probably carcinogenic, but a major part of the compounds are listed in the group of indefinable chemicals. Although AQ has two oxygen units in its structure, the anthracene skeleton of AQ is a known PAH and might be the reason for a carcinogenic behavior. (Muños & Albores 2011; IARC 2015).

However, there are other possible explanations as well that could explain the carcinogenicity in test animals. One suggestion for the carcinogenic potential could be the impurities found in anthraquinone. It is discovered that AQ’s purity is approximately 99.8% and the following impurities have been found in the animal studies of NTP: 9-nitroanthracene (0.09%), anthracene (0.05%), anthrone (0.008%) and phenanthrene (0.002%) (Figure 3). (NTP 2005).

Although minor impurities exist, multiple mutagenicity assays of AQ’s contaminants have indicated that only 9-nitroanthracene has mutagenic potential (Brown and Brown 1976; IARC 1983; LaVoie and Rice 1988; NTP 2005; Pitts et al. 1982; Zeiger et al. 1988; Butterworth et al. 2001). Butterworth et al. expressed that where anthraquinone is non-mutagenic compound, 9-nitroanthracene is a bacterial mutagen and is merely responsible for the carcinogenic results in the 2-year animal studies (Butterworth et al. 2001). Regardless of the encouraging evidence of 9-

nitroanthracene mutagenicity, it has been evaluated that any nitroanthracene compound does not have carcinogenic potential to animals (NTP 2005).

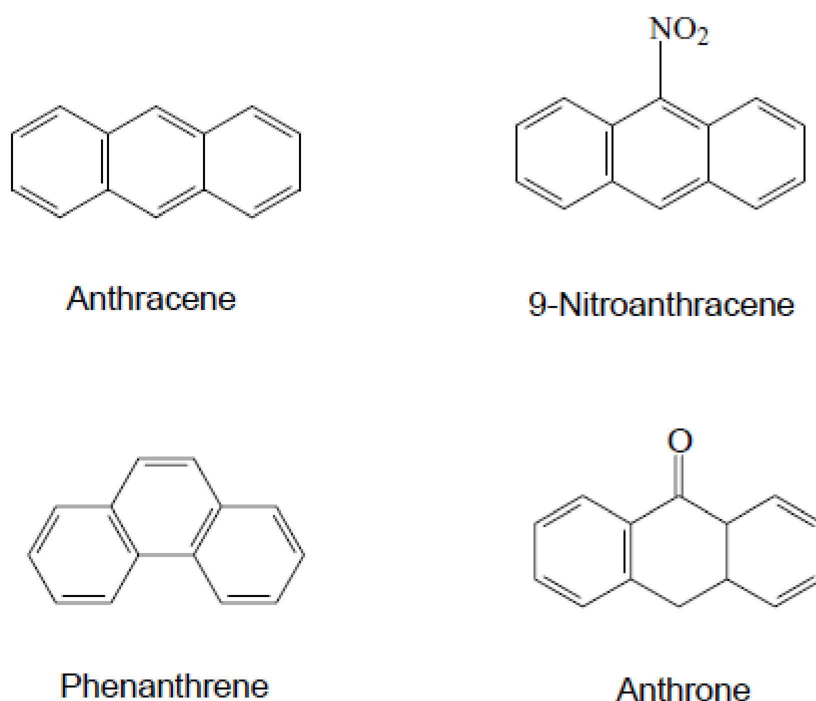

Figure 3. Structures of the impurities found in AQ (NTP 2005).

Nonetheless, probably the most promising explanation for AQ's carcinogenicity might be the carcinogenic metabolites generated in the body of mammals. In other words, AQ itself may not be carcinogenic, but when exposed on the metabolism of mammals, it transforms to harmful compounds which might be carcinogenic. For example, the major urinary metabolite of AQ, 2-hydroxyanthraquinone (Figure 4), is a bacterial mutagen, and considerably large amounts of it is formed in the system of animals. Actually when compared to 9-nitroanthracene concentration, 2-hydroxyanthraquinone is present at several-fold higher levels. (NTP 2005).

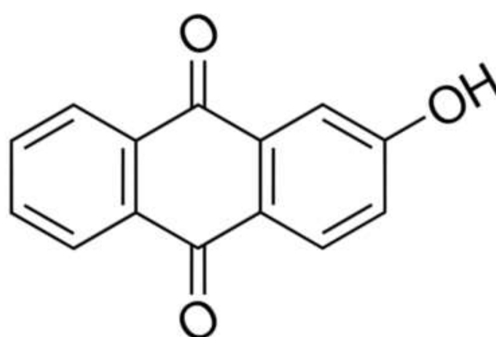

Figure 4. The chemical structure of 2-hydroxyanthraquinone (Sigma 2015).

4 THE SYNERGISM OF AQ AND POLYSULFIDE

Despite of the potential carcinogenicity of anthraquinone, it has proven its effectiveness as a dual-purpose pulping additive. Although AQ has been successfully used as such in the kraft and soda processes, it works remarkably well together with polysulfide (PS). (Holton 1977; Blain 1993; Griffin et al. 1995). AQ and PS are both diagnosed as a suitable pulping additives because of their effectiveness, inexpensiveness and adaptability with the present recovery systems. (Hägglund 1946; Kocurek et al. 1989; Li et al. 1998). Therefore the synergistic nature of these chemicals is extremely interesting.

4.1 Synergistic or not?

According to several reports, already small additions of AQ or PS provide higher carbohydrate stabilization and increased pulp yield (Kleppe & Kringstad 1963; Kleppe & Kringstad 1964; Teder 1969; Holton & Chapman 1977; Pekkala 1986). Additionally, it is observed that AQ and PS increase yield in alkaline pulping even more when used together, thus making the combined yield-enhancing effect of these chemicals greater than the sum of the yield gains they achieve separately. This phenomenon is also known as synergism. (Kleppe 1981; Pekkala 1986; Jiang 1995; Minja et al. 1998; Li et al. 1998; Sturgeoff & Bernhardt 1998; Anderson et al. 2003; Luthe & Berry 2005). Figure 5 shows the synergistic effect in contrast to the individual effects of AQ and PS in the kraft process (Li et al., 1998).

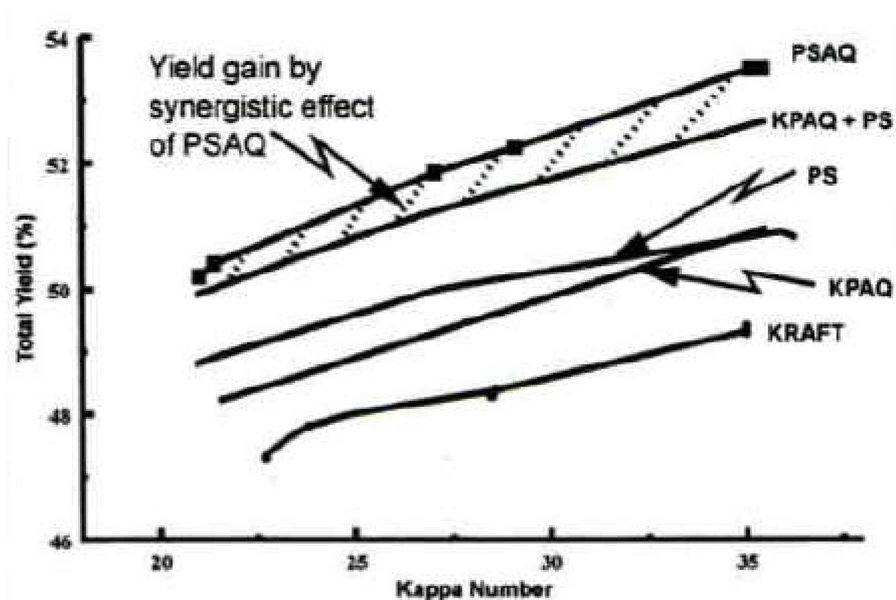

Figure 5. Synergistic effect of AQ/PS pulping, where PSAQ represents the combination of PS and AQ, and KPAQ + PS represents the sum of the individual pulping effects of PS and AQ in the kraft process (Li et al. 1998).

However, there has been some skepticism towards the synergism as well. First of all, it has been claimed that the synergistic yield gain is variable which is most probably related to a challenges in the yield determination. Therefore it is proposed that the verification of the pulp yield requires some supplementary tests. (Prasad et al. 1996). Moreover, the working mechanism behind AQ/PS reactions is unknown, so it does not necessarily mean that the yield increase is inevitably the result of the synergism (Li et al. 1998).

Nonetheless, it seems that there is clear evidence that advocates the AQ/PS synergism. The main reason for yield losses in kraft process is the degradation of the carbohydrate end groups. The degradation products of peeling reactions lead to a generation of organic acids, which further consume hydroxyl ions in the cooking liquor. Thus, the more carbohydrates are stabilized, the less organic acids are generated and the consumption of effective alkali (EA) is decreased. Hence the results of residual EA analysis illustrated in Figure 6 is analogical with the yield gain expressed in Figure 5. (Li et al. 1998).

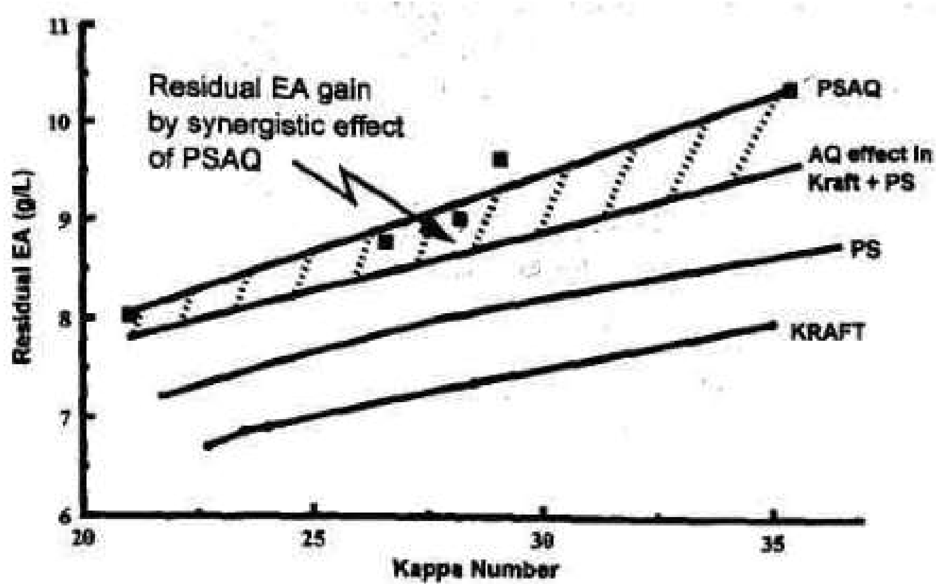

Figure 6. Synergistic effect of AQ/PS pulping on residual EA retention in black liquor (Li et al. 1998).

4.2 Possible reasons for synergism

Regarding to above-mentioned evidence, it seems that the synergistic effect between AQ and PS is a real phenomenon. The synergism of AQ and PS is believed to stem from the complementary activities of each chemical. Still, the knowledge of which are the most relevant activities concerning yield improvement at a given kappa number is uncertain. (Griffin et al. 1995; Li et al. 1998; Anderson et al. 2003).

4.2.1 Higher carbohydrate stabilization

In general, addition of AQ or PS as such increase the total pulp yield in kraft cook, but the mechanisms causing the yield gain are more or less different. Where PS increases the pulp yield through intensive carbohydrate stabilization, addition of AQ has been diagnosed to cause both accelerated delignification rate and carbohydrate stabilization. (Kleppe & Kringstad 1963; Kleppe & Kringstad 1964; Sanyer & Laundrie 1964; Teder 1969; Kocurek et al. 1989). Despite of the accelerated delignification rate caused by AQ, the preservation of carbohydrates against alkaline degradation plays a vital role in the pulp yield maximization (Anderson et al. 2003). At least PS is diagnosed to oxidize the active end groups of wood polysaccharides to alkali stable aldonic acid groups under low temperature (100-120°C) and alkaline conditions (Hägglund 1946; Kleppe & Kringstad 1963; Alfredsson et al. 1963; Venemark, 1964; Teder 1969; Jiang 1994; Parthasarathy et al. 1995). This reaction mechanism is represented in Figure 7.

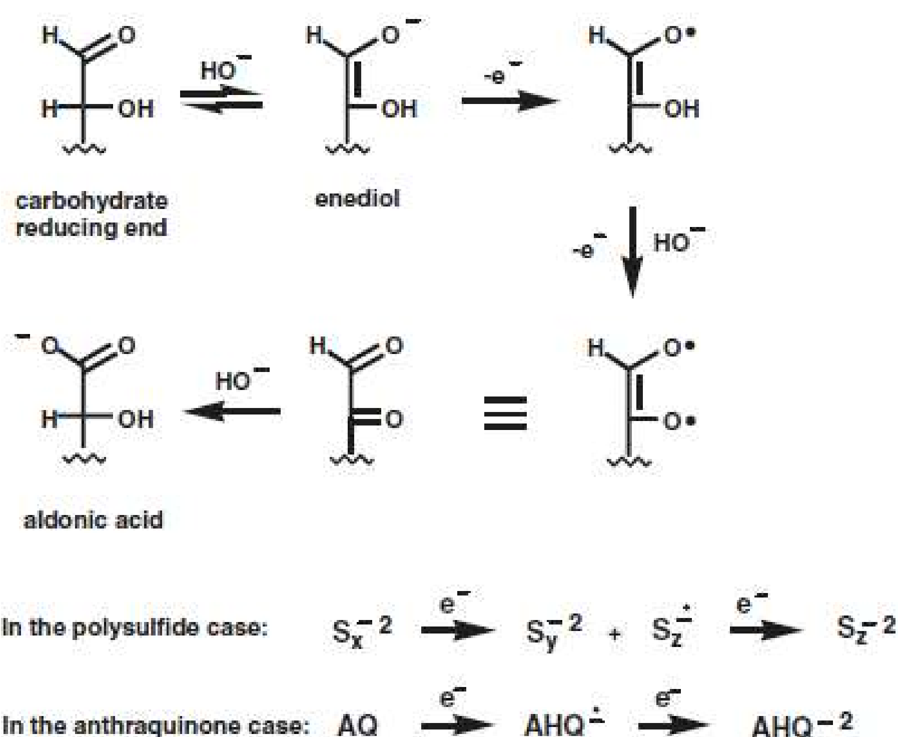

Figure 7. Proposed carbohydrate oxidation reactions of PS and AQ, where AQ is anthraquinone; AHQ^{-*} is anthrahydroquinone radical anion; AHQ^{-2} is anthrahydroquinone dianion; Sx^{-2} is polysulfide dianion and Sz^{-*} is polysulfide ion radical (Anderson et al., 2003).

Along with Figure 7, it is suggested that both AQ and PS can act as an oxidizing agent, so they are able to accept electrons from an enediol either in one step or two one-electron steps (Anderson et al., 2003). Although AQ is suggested to have similar oxidative behavior as PS, its role in the

carbohydrate preservation is considered rather marginal. This is due to its low reactivity with the insoluble wood polysaccharides. (Vuorinen 1993; Anderson et al. 2003).

Albeit higher carbohydrate stabilization seems to be the key element to increased pulp yields, it is not inevitably like that. It has been even suggested that polysulfide might aid AQ in the delignification by destroying the recalcitrant vinyl ether structures of lignin thus speeding up the cooking and shortening the time required, which further decrease the alkaline degradation of carbohydrates (Dimmel & Bovee 1993; Berthold et al. 1996; Berthold & Lindstrom 1997). Thus it seems that there are at least two possible explanations for the synergism: Either PS preserve polysaccharides more effectively due to presence of AQ, or maybe PS is able to help AQ in more effective lignin degradation. Anyhow, the relationship of PS and AQ is highly complex and the actions might go other way around as well.

4.2.2 PS as a reducing agent for AQ

In fact, it is suggested that PS could provide reductive conditions for AQ. According to this theory, the soluble PS ions should be much more effective reducing agents than insoluble polymeric polysaccharides. Theoretically, after two-electron reduction of AQ, soluble anthrahydroquinone (AHQ^{-2}) would be formed which would further fragment lignin and thus oxidize itself to soluble anthrahydroquinone ion radical (AHQ^{-*}). This form of AQ would further be reduced by PS dianion (Sx^{-2}) back to AHQ^{-2}, and generated PS ion radical (Sx^{-*}) should oxidize carbohydrates while being reduced back to its PS dianion form. (Anderson et al. 2003). The proposed reaction cycle is visualized in Figure 8.

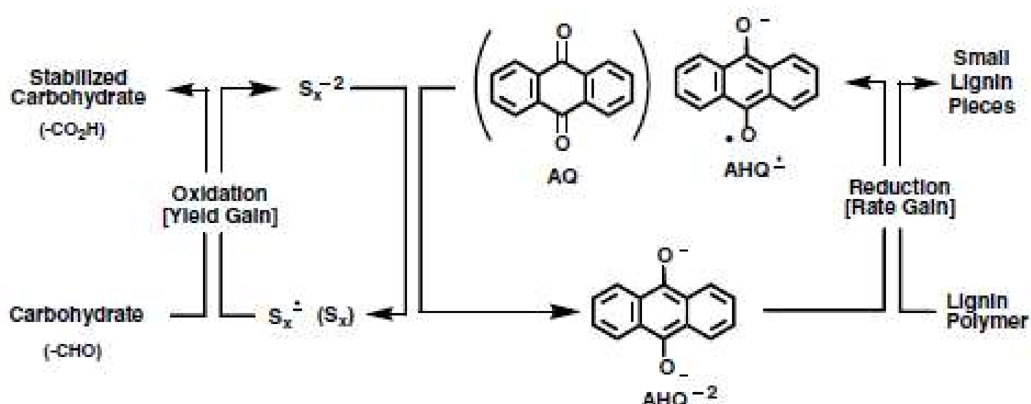

Figure 8. Proposed redox reactions of PS & AQ, where PS ion radical (Sx-*) is expected to be better electron acceptor than PS dianion (Sx-2) (Anderson et al. 2003).

To investigate whether this theory holds true, the reduction of AQ to AHQ was tested in specific laboratory conditions. According to the results, PS dianion (S_x^{-2}) was incapable to reduce AQ to AHQ in chosen conditions. Thus it seems that electron transfer between AQ and PS might not be the mechanism behind AQ/PS synergism. (Anderson et al. 2003).

4.2.3 Complementary reaction conditions of AQ/PS pulping

So, the origin of the synergistic effect might as well be resulted from the altered reaction conditions, which lead to a more effective polysaccharide preservation. Actually, the addition of AQ to a cook allows pulping processes to shorten time as well as decrease temperature, sulfidity and effective alkali (EA) consumption (Greer et al. 2004). Each of these above-mentioned factors might have a direct or indirect impact on the PS reactions during cook, which could explain the synergism.

It has already been stated that the synergism refers to a higher pulp yield, which is a natural consequence of increased carbohydrate retention. However, effective delignification of pulp requires a sufficient amount of alkali and temperature, but as alkali concentration or temperature gets higher, carbohydrate content of pulp start to decrease mainly due to polymer dissolution and polymer degradation. Because carbohydrate degradation concerns mainly on hemicelluloses in AQ/PS pulping, the synergistic yield gains are most likely a result of increased hemicellulose content of the reduced pulp. (Pekkala 1986; Kocurek et al. 1989; Jiang 1995; Luthe & Berry 2005). The principal hemicelluloses responsible for the major part of degradation are glucomannan in softwood and xylan in hardwood (Pekkala 1986; Mao & Hartler 1994). The degradation of wood products is illustrated in Figure 9.

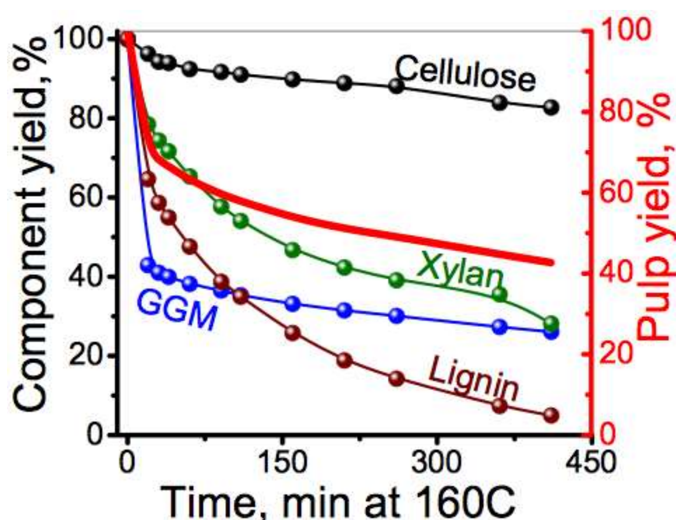

Figure 9. Relative yield of wood components. Pine-Kraft pulp; [OH-] = 0.5M; [HS-] = 0.1M; L:W 200; 160°C (Paananen et al. 2013; Paananen 2014).

Therefore, when EA consumption is decreased due to influence of AQ and PS, the easily degradable hemicellulose is protected at the same time. It is even suggested that the reduction in EA consumption could be the main reason for higher carbohydrate stabilization and synergistic yield gains. (Li et al. 1998; Greer et al. 2004). However, the formation of new reducing end groups can also be avoided by lowering the reaction temperatures (Minja et al. 1998). Hydrolytic splitting starts to degrade polysaccharides after 150°C, so when the temperature is kept under this level, more carbohydrates are protected (Kocurek et al. 1989).

In addition to temperature and EA consumption, the effect of sulfidity should be considered in AQ/PS cook as well. In conventional kraft pulping, higher sulfidity has been found to increase pulp yield (Kleppe 1970). However, the sulfidity of orange liquor of PS cook is much lower than the sulfidity of white liquor of kraft cook (Paananen 2014). According to several sources the yield enhancing effect of AQ is greater with lower sulfidity levels (Fossum et al. 1980; Hakanen & Teder 1997; Sturgeoff & Bernhardt 1998; Knowpulp 2007). When lignin is removed faster due to accelerated delignification, the cooking time is also shorter. Shortened cooking time is a major advantage in pulping, because it shortens the time that wood polysaccharides are exposed to alkaline degradation and dissolution, which in turn protect polysaccharides and increase the pulp yield.

Interestingly the yield benefit from the synergism is notably decreased when cooked to a lower kappa numbers (Minja et al. 1998). According to studies of Jiang, this phenomenon can be seen in PS cooking as well. Addition of PS increased the yield more in higher kappa numbers and as the delignification was prolonged, more hemicelluloses were degraded. (Jiang 1994). This effect is clearly present in Figure 5.

Altogether, there are multiple variables in the cooking process, which may have direct or indirect influence on lignin degradation or carbohydrate preservation. Therefore it is very difficult to be certain whether synergism is explained through any of these considered alternatives. Nonetheless it seems that the altered reaction conditions might provide the hidden answer for AQ/PS synergism.

5 THE WORKING MECHANISM OF AQ

Anthraquinone (AQ) is an extremely effective pulping catalyst, and already small additions of this chemical inflict notable benefits for the pulp mills (Holton 1977; Pekkala 1982; Blain 1993; Greer et al. 2004; Hart & Rudie 2014). Therefore a full and detailed understanding of AQ working mechanism would possibly lead to a better and more powerful pulping catalyst. However the mechanism is relatively difficult to define. In spite of considerable amount of research work spent for comprehending the working mechanism, it is still not well understood (Dimmel et al. 1985; Hart & Rudie 2014). Although obscurity surrounds this seemingly complex mechanism of AQ, there have been several suggestions in the literature that might provide explanation for its performance.

The purpose of this chapter is to give a general view of AQ reaction mechanism, investigate the reaction mechanisms that might be responsible for lignin fragmentation, and finally propose a new working mechanism that could be a reason for improved delignification. Thus, the focus is not in the stabilization of carbohydrates, but rather in the promotion of the lignin solubilization.

5.1 Background

AQ's insolubility in water as well as poor solubility in alkaline liquor has been most probably the major reasons for its relatively late discovery as an efficient pulping additive (Holton 1977; Revenga et al. 1996). In 1972, the study of Bach and Fiehn focused on compounds that could stabilize carbohydrates in alkaline pulping of wood. As a result of this research water-soluble AQ derivative called anthraquinone-2-sulfonate (AMS) was found to effectively stabilize cellulose and increase yield in alkaline conditions. Anthraquinone itself did not seem to have notable effect on cellulose preservation why it was considered as a poor pulping catalyst under the conditions of their study. (Bach & Fiehn 1972).

Anyhow, a few years later it was discovered that AQ is more effective pulping catalyst than diagnosed in the earlier studies. This was revealed due to AQ's tendency to be reduced to anthrahydroquinone (AHQ) in suitable conditions, which would further lead to an accelerated pulping, increased pulping yield and decreased kappa number of the cooked pulp. (Holton 1977; Holton & Chapman 1977; Farrington et al. 1977). Although the all-embracing knowledge of the working mechanism of AQ is still missing, there are lots of possible mechanisms in the literature (Hart & Rudie 2014).

5.2 Redox reaction mechanisms

As already stated, the literature is full of mechanisms that could work as an explanation for the performance of AQ. Redox reaction cycle is yet one of the most cited concept at the moment. In addition to this generally accepted AQ redox cycle, two well-known redox reaction mechanisms are covered: the single-electron transfer (SET) mechanism and the adduct mechanism.

5.2.1 Redox cycle

According to several studies, there are two fundamental effects that AQ evidently provides for pulping: accelerated delignification rate and increased carbohydrate preservation (Löwendahl & Samuelson 1978; Obst et al. 1979; Dimmel 1985; Blain 1993). These two effects are believed to derive from the ability of AQ to work as a pulping catalyst between wood polysaccharides and phenolic lignin structures. The phenomenon where electrons are transferred from carbohydrates to lignin through the reduction and oxidation reactions of AQ is called redox cycle. (Fleming et al. 1979; Obst et al. 1979; Lindenfors 1980; Eckert & Amos 1982; Wright & Fullerton 1984; Dimmel 1985). The redox cycle is illustrated in Figure 10.

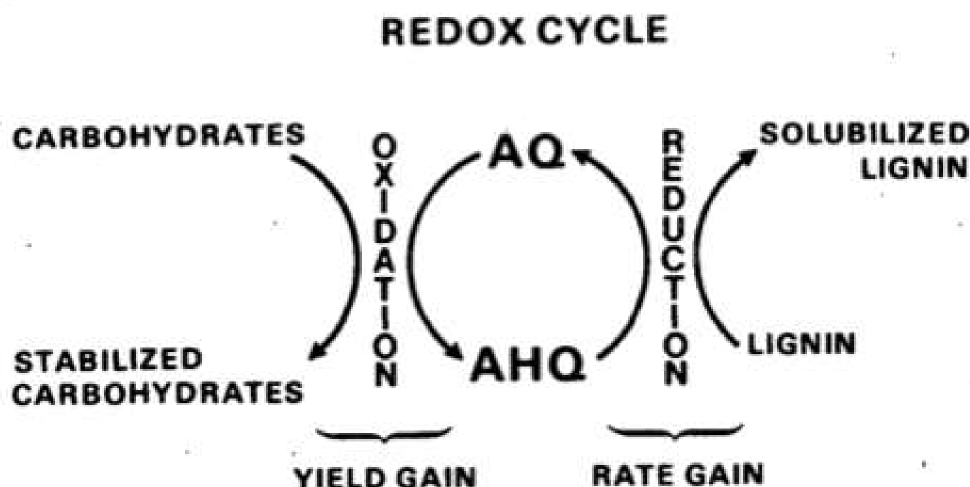

Figure 10. AQ redox cycle in alkaline pulping of wood (Dimmel 1985).

Redox cycle of AQ is a simple illustration of generally approved principle about carbohydrate preservation and accelerated delignification under the influence of AQ. In the beginning of this cycle, the peeling end groups of polysaccharides become oxidized by AQ, which is in turn reduced to anthrahydroquinone (AHQ) (Löwendahl & Samuelson 1978). This oxidation reaction is proposed to occur through the mechanism presented in Figure 7. After this, AHQ is believed to reduce and fragment lignin. Simultaneously AHQ is oxidized back to its original form (AQ) and the cycle is ready for the next round. Although redox cycle illustrates well the catalytic behavior of AQ, it does not explain in detail how the carbohydrates are preserved or

how the delignification rate is accelerated. Thus, the complex chemistry behind the phenomenon cannot be seen through the redox cycle.

In order to achieve a deeper knowledge on redox cycle, the relevant redox reaction mechanisms are examined. These mechanisms are single-electron transfer (SET) and adduct mechanism. However, before undergoing these reaction mechanisms, it must be understood that instead of what is expressed in the redox cycle earlier (Fig. 10), there are actually three different forms of AQ during pulping: the fully oxidized form of anthraquinone (AQ); the partially reduced/oxidized anthrahydroquinone radical anion (AHQ^{-*}); and the fully reduced anthrahydroquinone dianion (AHQ^{-2}) (Fig. 11) (Dimmel 1996).

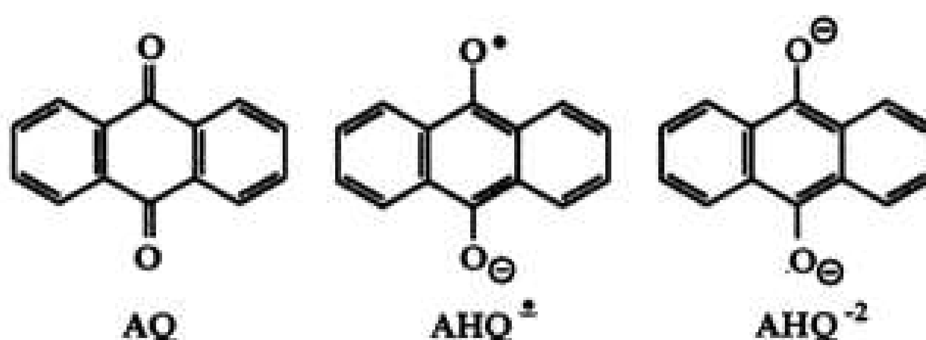

Figure 11. Three oxidation states of AQ (Dimmel 1996).

Because of the existence of AHQ radical anion, the “traditional” way of expressing the redox cycle is not that informative. Therefore the more detailed way to express redox cycle is shown in Figure 12.

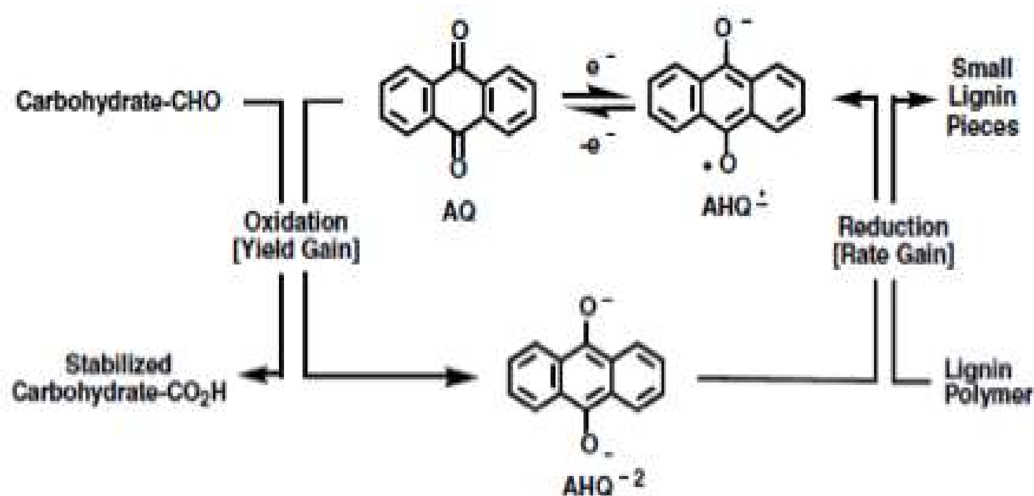

Figure 12. “Updated” version of AQ redox cycle (Anderson et al. 2003).

According to Figure 12, both AQ and AHQ radical anion are capable of oxidizing the reducing end groups of carbohydrates either by single-electron or two-electron transfers thus forming the AHQ (dianion). On the other hand,

AHQ is reducing lignin either by one electron or by two electrons resulting in lignin fragmentation. (Dimmel 1985 & 1996, Anderson et al. 2003).

5.2.2 Adduct mechanism

Adduct mechanism was introduced some years before SET mechanism, and was in fact considered as the generally accepted reaction mechanism for AHQ. Unlike in SET mechanism, the adduct mechanism comprises bond formation between AHQ and quinone methides (QMs) of lignin followed by lignin fragmentation. (Obst et al. 1979; Gierer et al. 1979; Dimmel 1985). The mechanism is illustrated below (Figure 13).

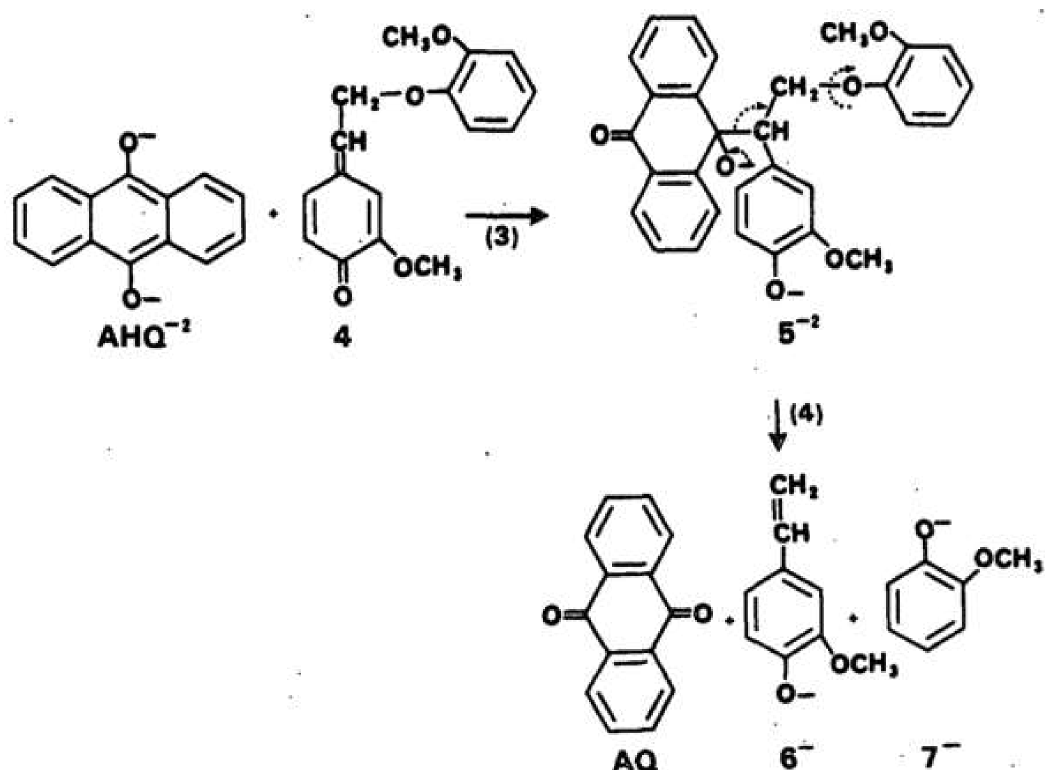

Figure 13. Proposed adduct reaction mechanism (Dimmel 1985).

In this mechanism nucleophilic additive, like AHQ, is added to lignin QM in order to generate an adduct (3). The mechanism proposes that C-10 carbon of AHQ forms a bond with the C-α carbon of the QM. The generated addition product is further heated up in alkaline conditions, resulting in β-aryl ether fragmentation, where AQ is regenerated and two phenolate ions are formed (4). (Fleming et al. 1978; Obst et al. 1979; Gierer et al. 1979; Landucci 1980; Dimmel 1985). However, one of the revealed weaknesses of this mechanism is the tendency of AHQ/QM adduct to be reversible (Dimmel & Shepard 1982).

5.2.3 Single-electron transfer mechanism

SET is a mechanism that involves a transfer of a single electron between anthrahydroquinone and QM of lignin. Along with many studies, single electron is proposed to transfer from AHQ to QM of lignin thus engendering QM radical, which further result in β-aryl ether fragmentation. (Dimmel 1985 & 1996; Dimmel et al. 1985). This prevalent delignification mechanism is shown in Figure 14.

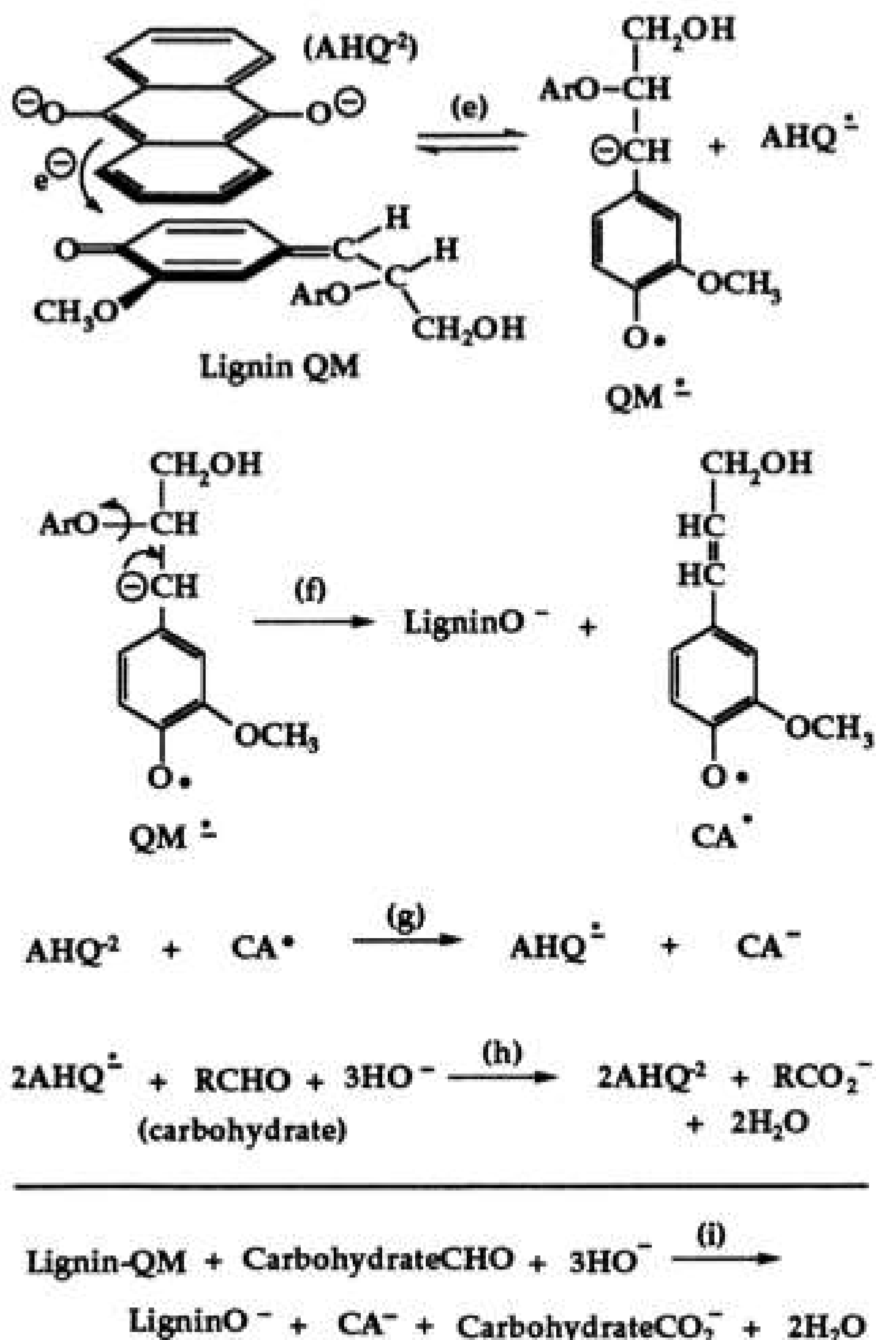

Figure 14. Proposed SET reaction mechanism, where CA = Coniferyl alcohol (Dimmel 1996).

As shown in Figure 14, the reaction scheme starts with an electron donation of AHQ to a QM of lignin (e). This results in QM breakage, thus forming QM radical anion and AHQ radical anion. QM radical anion is further fragmented through β-aryl ether fragmentation to a lignin ion and a coniferyl alcohol radical (CA*) (f). After this, CA* is reacting with another AHQ dianion to generate a second AHQ radical anion (g). Reaction (h) then demonstrates how AHQ radical anions are converted back to AHQ dianions by oxidizing the reducing end groups of carbohydrates to aldonic acid groups. The last reaction (i) reflects the sum of all the reactions. Hence, SET mechanism provides a possible indication how electrons might be transferred between carbohydrates and lignin, thus leading to carbohydrate stabilization and lignin fragmentation. (Dimmel 1996).

Although each of these proposed reaction mechanisms (adduct and SET) could work as a functional reaction mechanism for AHQ, there have been more or less inconsistencies with the experimental data (Hart & Rudie 2014). Therefore it seems that the only generally accepted phenomenon in the redox chemistry of AQ pulping is - redox cycle.

5.3 The proposed new working mechanism

So, as the redox reaction mechanisms cannot fully explain the effect of AHQ during pulping, there must be something else. Model compound studies suggest that there are at least two ways how AHQ could promote delignification: promotion of lignin fragmentation and prevention of lignin condensation (Obst et al. 1979; Gierer et al. 1979; Landucci 1980; Dimmel et al. 1981; Brunow & Poppius 1982; Dimmel 1985). Where the above-mentioned redox reaction mechanisms explain the former effect, the proposed working mechanism in this study focuses on the latter phenomenon.

5.3.1 Condensation reactions of lignin

In order to comprehend the inhibition of lignin condensation, there must be a certain understanding of the condensation reactions of lignin. The tendency of fragmented lignin particles to react with each other lead to a formation of new type of bonding, resulting in condensed high molecular weight lignin (Sarkanen & Ludwig 1971; Casey & Bryce 1980). The condensed lignin clusters are further proposed to form alkali-stable linkages thus being more recalcitrant to solubilization than the native lignin (Gierer 1970; Casey & Bryce 1980).

According to Chakar & Ragauskas, the lignin nucleophiles (e.g. carbanions from phenolic structures) are competing with hydrogen sulfide and sodium hydroxide anions for quinone methide intermediates. This competitive

addition of nucleophiles is found to be reversible, and the outcome will depend on the nucleophilicity of compounds, as well as the ability of the addition product to undergo a rapid, irreversible reaction. (Chakar & Ragauskas 2004). The proposed condensation of the QM intermediates is exemplified in Figure 15.

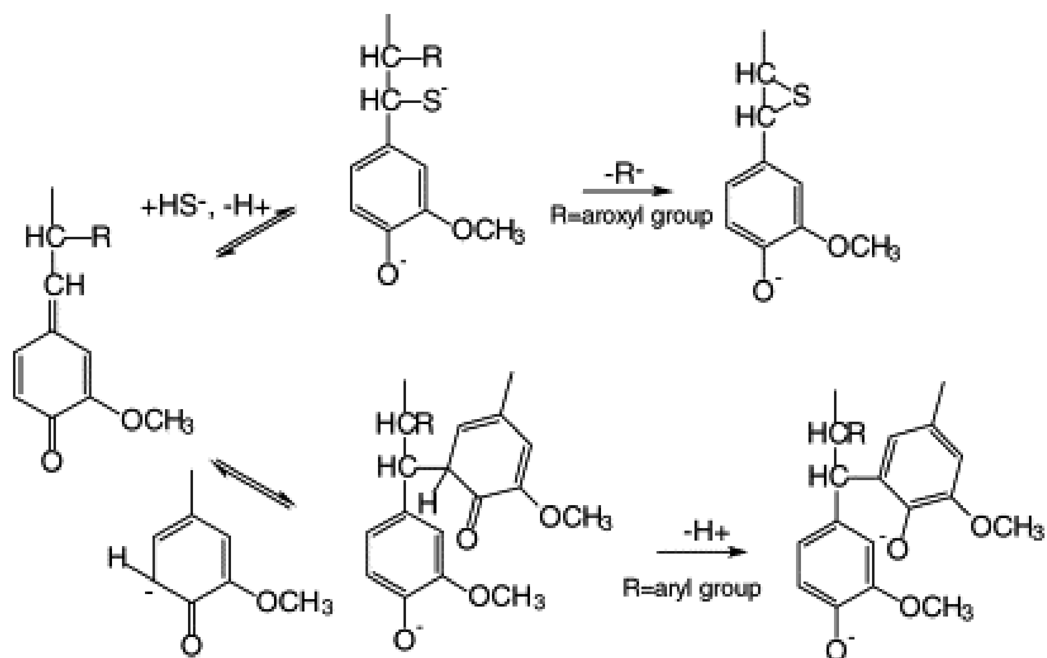

Figure 15. Competitive addition of internal and external nucleophiles to QM intermediates, where OAr is aroxyl group and Ar is aryl (Gierer 1970; Chakar & Ragauskas 2004).

In this figure, the QM intermediate work as an acceptor and phenolate ion as a nucleophile. The condensation reaction is suggested to proceed via Michael addition, where the formation of an addition product is followed by a fast, irreversible proton abstraction and subsequent rearomatization. (Chakar & Ragauskas 2004). However, it is discovered that the QM intermediates are not the only type of acceptors in the cook. The study of Gierer and Lindberg proposes that formaldehyde is diagnosed to function as an acceptor as well (Gierer & Lindberg 1979).

5.3.2 Antioxidant mechanism

The working mechanism proposed in this study suggests that AHQ, a strong nucleophile and antioxidant, could inhibit the lignin coupling reactions formed in situ and thereby result in a smaller molecular weight of the dissolved lignin (Hanhikoski 2013). Although lignin itself is diagnosed as a natural antioxidant, there are plenty of free radicals originated from the fragmentation reactions of lignin (Lu et al. 1998; Dizhbite et al. 2004; Dimmel 1996). The free radicals are found to assist oxidative coupling reactions of

lignin, which is undesirable in effective delignification of wood (Ralph et al. 2004).

Along with the work of Sies, antioxidant is any substance that prevents the oxidation of other substances. This is vital, because the oxidation reactions are capable of producing free radicals. Free radicals are further able to inflict chain reactions, where an unpaired electron is transferred from a compound to another. This effect is also known as “radicals generate radicals phenomenon”. Anyhow, the mission of antioxidants is to cease these chain reactions by neutralizing the free radicals via electron donation (Fig. 16). (Sies 1997).

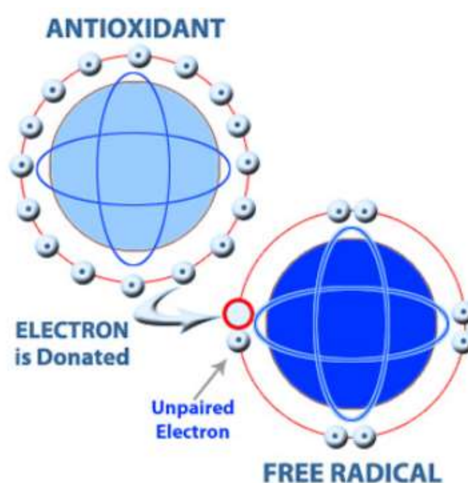

Figure 16. Antioxidant neutralizing a free radical (Defares 2015).

Thus, antioxidants are reducing free radicals while simultaneously being oxidized themselves. Therefore powerful reducing agents are considered as great antioxidants as well. (Sies 1997).

5.3.3 Redox potential

Redox potential (E°) or reduction/oxidation potential, is a concept that shows the tendency of a chemical species to receive electrons. In redox reactions, there are always two half-reactions present: a reduction half-reaction and an oxidation half-reaction. These two reactions occur together, because without electron donor there would not be any electrons to receive. Therefore in the situation of two different species the species with a higher redox potential tend to be reduced by oxidizing the other. (Boyer 2002; McMurry & Fay 2004).

The reason why different species have divergent redox potentials originate from the structures of the species. The amount of electrons orbiting the nucleus of an atom, as well as the distance of electrons from the nucleus define the tendency of that atom to attract electrons. Thus, some nuclei of

atoms pull electrons so strongly, that they are capable to attract additional electrons into their orbitals. Hence, as this attracting potential of atom gets higher, so does its redox potential. (Boyer 2002).

There are multiple ways to measure redox potential by switching the conditions or reference electrode used. Anyhow, a common way to measure redox potential is to use standard conditions and a standard hydrogen electrode (SHE). The method is called standard reduction potential and all the standard potentials are measured at 1 atm, 298 K and with 1 M solutions. It has been generally verified that hydrogen has zero redox potential, so the redox potentials of other compounds are actually determined in relation to the potential of hydrogen. In other words, the reduction potential of chemical species is in fact a potential difference between hydrogen and measured species. This difference is measured with voltmeter so the electron transfer is expressed in volts (V). (McMurry & Fay 2004). Table 4 shows the standard reduction potentials for various chemical species in decreasing order.

Table 4. Standard reduction potentials for various half-reactions (McMurry & Fay 2004).

	Reduction Half-Reaction		E° (V)	
Stronger oxidizing agent	$F_2(g) + 2e^-$	$\longrightarrow 2F^-(aq)$	2.87	Weaker reducing agent
	$H_2O_2(aq) + 2H^+(aq) + 2e^-$	$\longrightarrow 2H_2O(l)$	1.78	
	$MnO_4^-(aq) + 8H^+(aq) + 5e^-$	$\longrightarrow Mn^{2+}(aq) + 4H_2O(l)$	1.51	
	$Cl_2(g) + 2e^-$	$\longrightarrow 2Cl^-(aq)$	1.36	
	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^-$	$\longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.33	
	$O_2(g) + 4H^+(aq) + 4e^-$	$\longrightarrow 2H_2O(l)$	1.23	
	$Br_2(l) + 2e^-$	$\longrightarrow 2Br^-(aq)$	1.09	
	$Ag^+(aq) + e^-$	$\longrightarrow Ag(s)$	0.80	
	$Fe^{3+}(aq) + e^-$	$\longrightarrow Fe^{2+}(aq)$	0.77	
	$O_2(g) + 2H^+(aq) + 2e^-$	$\longrightarrow H_2O_2(aq)$	0.70	
	$I_2(s) + 2e^-$	$\longrightarrow 2I^-(aq)$	0.54	
	$O_2(g) + 2H_2O(l) + 4e^-$	$\longrightarrow 4OH^-(aq)$	0.40	
	$Cu^{2+}(aq) + 2e^-$	$\longrightarrow Cu(s)$	0.34	
	$Sn^{4+}(aq) + 2e^-$	$\longrightarrow Sn^{2+}(aq)$	0.15	
	$2H^+(aq) + 2e^-$	$\longrightarrow H_2(g)$	0	
	$Pb^{2+}(aq) + 2e^-$	$\longrightarrow Pb(s)$	−0.13	
	$Ni^{2+}(aq) + 2e^-$	$\longrightarrow Ni(s)$	−0.26	
	$Cd^{2+}(aq) + 2e^-$	$\longrightarrow Cd(s)$	−0.40	
	$Fe^{2+}(aq) + 2e^-$	$\longrightarrow Fe(s)$	−0.45	
	$Zn^{2+}(aq) + 2e^-$	$\longrightarrow Zn(s)$	−0.76	
	$2H_2O(l) + 2e^-$	$\longrightarrow H_2(g) + 2OH^-(aq)$	−0.83	
	$Al^{3+}(aq) + 3e^-$	$\longrightarrow Al(s)$	−1.66	
	$Mg^{2+}(aq) + 2e^-$	$\longrightarrow Mg(s)$	−2.37	
	$Na^+(aq) + e^-$	$\longrightarrow Na(s)$	−2.71	
Weaker oxidizing agent	$Li^+(aq) + e^-$	$\longrightarrow Li(s)$	−3.04	Stronger reducing agent

EXPERIMENTAL PART

6 MATERIALS AND METHODS

The objective of the experimental part was to study the working mechanism of AQ by using AQ, and six different quinones with varying redox potentials. The aim was to experimentally investigate whether the effective delignification of AQ cooks is partly based on to the antioxidant mechanism. The experiment included three central steps: preparation, procedure and analyses of the experiment.

6.1 Preparation of the tests

The wood chips used in the trials were Ø 3 mm sieved air-dried Finnish Scots pine (*Pinus sylvestris L.*) chips as showed in Figure 17. Selected chips were initially stored in the freezer at -20°C, so before using the chips in the experiments, they were defrosted and air-dried two weeks in the room temperature. After two weeks the dry matter content (DMC) of the chips was determined with the SCAN-CM 39:94 and they were placed into the closed plastic bag in order to prevent changes in the DMC.

Figure 17. Air-dried pine pin chips in the plastic bag.

In order to perform the trials, along with the homogenous wood material, the following chemicals were acquired: purified anhydrous sodium sulphite (Na_2SO_3) for cooking, as well as AQ and six different quinones with varying redox potentials for additives. Redox potentials, CAS numbers and molar masses of the used additives are presented in Table 5, while Figure 18 expresses the structures of each quinone. The quinones illustrated in these experiments were purchased from Sigma-Aldrich and Tokyo Chemical Industry Co.

Table 5. Redox potentials (E°), CAS numbers and the molar masses of the additives used in the trials (Sigma 2015; TCI 2015; Evans et al. 1978; Conant & Fieser 1924).

Additive	E° (V)	CAS #	Molar mass (g/mol)
Anthraquinone (AQ)	0.155	84-65-1	208.22
AQ-2-sulfonic acid	0.187	131-08-8	310.25
AQ-1-sulfonic acid	0.195	128-56-3	310.26
AQ-2-carboxylic acid	0.213	117-78-2	252.22
AQ-1,5-disulfonic acid	0.239	853-35-0	412.29
2-hydroxy-1,4-naphthoquinone	0.360	83-72-7	174.15
2,5-dihydroxy-1,4-benzoquinone	0.441	615-94-1	140.09

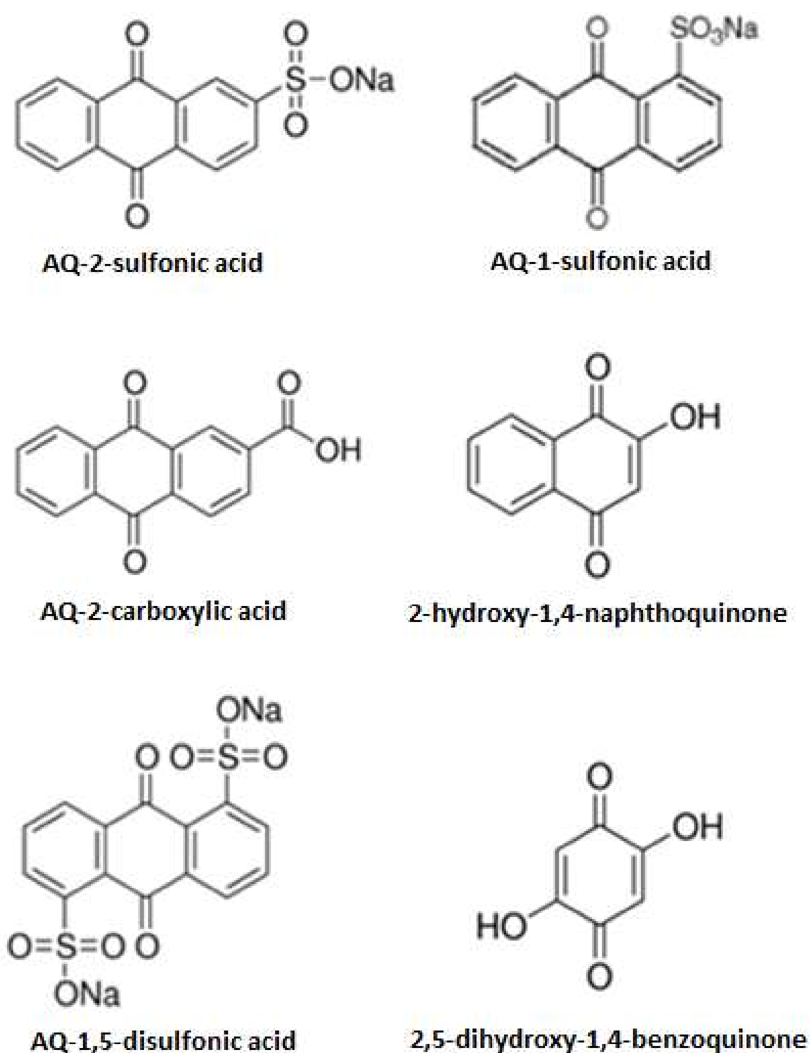

Figure 18. Structures of the different quinones used in this study (Sigma 2015; TCI 2015).

6.2 Cooking procedure

The cooking procedure was performed in two stages. The first stage of the procedure included the demonstration of the required conditions for the additives, whereas the second stage focused on whether the research hypothesis could be possible. Instead of using white liquor, Na_2SO_3 was used as a cooking chemical due to its simpler chemistry.

6.2.1 Stage 1: Demonstrating the reduction of additives

In order to examine whether additives could be reduced, 25 grams of anhydrous sodium sulphite and 200 ml of deionized water were mixed in 250 ml Erlenmeyer flask. After the dissolution of sodium sulphite 0.75 ml 4N H_2SO_4 was added to solution for adjusting the pH for the desirable level (pH 8). A small addition (0.05 grams) of chosen additive was then added in the solution and it was mixed with the magnet stirrer and heated up to 95°C by Heidolph cooking plate (Figure 19).

Figure 19. Heating and mixing the reaction solution.

The reduction of the additives was monitored through color change in the solution. The approximate time for reaching the stabile color transition stage was also measured. This stage was important in order to indicate that the reduction of an additive takes place and that the antioxidant effect could work in principle.

6.2.2 Stage 2: Cooking wood chips with additives

The second stage of the cooking procedure was performed in the neutral and reductive cooking conditions as defined in the stage 1. Additionally, air-dried Scots pine chips were added in order to find out whether antioxidant effect has part in the delignification of AQ.

First, wood chips and additive dosages were measured in six (1 litre) autoclaves. The cooking liquor was then prepared by mixing solid sodium sulphite crystals and deionized water in a big plastic carafe. The solution was blended with the glass stick and after dissolution, pH was adjusted to 8 by 4N H_2SO_4. The exact amount of cooking liquor was measured to each autoclave, after they were closed and pressurized to 5 bars with nitrogen gas. (Figure 20).

Figure 20. Six nitrogen pressured autoclaves.

After pressurization all six autoclaves were placed to (Muru) air bath digester as presented in Figure 21. The cooking temperature inside the autoclaves was first increased from 20°C to 80°C in 30 minutes and from 80°C to 170°C in 60 minutes after it was maintained at 120 min for first, 180 min for second and 240 min for third batch. This kind of relatively slow heating procedure was necessary for cooking chemicals due to the neutral conditions prevailing inside the autoclaves. Adequate impregnation of wood chips was required in order to get homogeneous pulp and simultaneously to minimize amount of rejects generated during cooking.

Figure 21. “Muru” air bath digester.

When cooking was completed, the autoclaves were cooled down approximately 15 min at the bucket full of cold water. The autoclaves were thereafter opened one at a time and cooking liquor was poured to a graduated cylinder as presented in Figure 22.

Figure 22. Cooled autoclaves (left) and poured filtrate (right).

The filtrate was then measured with Schott pH meter and poured into small bottles for further analyses. Bottles were filled as full as possible before closing in order to protect the filtrate from unwanted reactions with oxygen. In addition, the bottles were stored in the dark refrigerator to minimize any changes that temperature or light emission could cause for the samples before carrying out the filtrate analyses. The excess filtrates were stored in the freezer.

The dirty pulp was then moved from autoclave to a filtering bag and washed two times with 2.5 litre deionized water as shown in Figure 23. The washing was performed by dipping the dirty pulp approximately 15 minutes in the three litre carafe, after the pulp was rewashed (~15 min) in another carafe.

Figure 23. After the first wash (left) and the second wash (right).

The washing was finished by soaking the pulp overnight (~16 h) in the 10 litre bucket with 5 litres deionized water. The soaked pulp was then treated with a "British" pulp-grinding machine (30 seconds at 2800 r/min) (Fig. 24).

Figure 24. Soaked pulp (left) and the pulp-grinding machine (right).

After grinding the defibrillated pulp was drained with a suction filter, weighed and stored at air proof plastic bag for further analyses. Later on the pulps were diagnosed as too "chip like" material, so they were further disintegrated by Noram disintegrator (10 000 rounds ~ 3 min) and screened

by “Serlachius” laboratory screener (~ 25 min), which allowed only smaller than 0.35 mm fibres to get through the filter. After this the pulp was dried by laboratory centrifuge, homogenized by hands, and placed to a closed plastic bags. Figure 25 shows the difference of one pulp sample before and after the further screening.

Figure 25. Pulp before (left) and after further screening (right).

The general cooking conditions and chemical charges used in the experiments are illustrated in Table 6. More detailed cooking parameters are presented in Appendix 4.

Table 6. General cooking parameters.

A.d. pine chips (g)	51.83
DMC of the chips (%)	96.47
O.d. pine chips (g)	50.00
Na_2SO_3 charge (% on o.d. wood)	50
Additive charge (% on o.d. wood)	0.1
Initial pH	8
Pressure (bars)	5
L:W (L/kg o.d. wood)	4:1
Cooking temperature (°C)	170
Heat-up from 20°C to 80°C (min)	30
Heat-up from 80°C to 170°C (min)	60
- Cooking time 1 (min)	120
- Cooking time 2 (min)	180
- Cooking time 3 (min)	240

6.3 Analyses

The main objective of the analyses was to diagnose whether research hypothesis holds true. In other words, was there any evidence for the antioxidant mechanism? Thus each pulp and filtrate sample were analyzed with couple fundamental analyses. The reduction of each additive was also examined in order to determine whether sodium sulphite could provide appropriate conditions for additive reduction or not.

6.3.1 Stage 1: Reduction analysis

Reduction of each additive was diagnosed by simply monitoring the color transition visually against white paper sheet, while boiling the reaction solution in 250 ml Erlenmeyer flask. The color of each solution was documented right after the addition of additive as well as after the stabilization of the color transition. Due to reaction conditions of this experiment the expected color for reduced quinone was red. The color differences of each additive are listed in Appendix 2.

6.3.2 Stage 2: Pulp and filtrate analyses

After preparation of the pulp samples, the following analyses were made for the pulp: pulp yield and kappa number. In addition, the reject content and the total yield were measured for the cooked chips. Total yield, reject content, and pulp yield (i.e. accept) were determined gravimetrically, whereas kappa number was determined according to SCAN-C 1:00.

Analyses made for cooking liquors included the determinations of final pH and dissolved lignin content (DLC). Additionally the molecular weight distribution (MWD) of dissolved lignin was done for chosen samples. Final pH was simply measured from the filtrates by calibrated Schott pH electrode. The electrode was kept approximately 2 minutes in the cooking liquor to wait for the steady results.

The amount of dissolved lignin was measured from the filtrates by (Shimadzu UV-2550) UV-spectrophotometer. The pH of the samples was neutral, so the chosen wavelength for measurements was 280 nm (Uprichard & Benfell 2004). Additionally, the absorptivity for dissolved neutral sulphite lignin was set to 16.5 L/(g*cm) (Sjöström et al. 1962). The DLC was quantified by using equation 1.

$$Lignin\left[\frac{g}{L}\right] = \frac{A*DF}{a*l} \tag{1}$$

Where	A	is the absorbance at 280 nm
	DF	is the dilution factor
	a [L/(g*cm)]	is the absorptivity
	l [cm]	is the length of the cuvette

The MWD of dissolved lignin was performed by size-exclusion chromatography (SEC). SEC analyses were carried out using a HPLC system (Waters Corp., Milford, MA) equipped with 8 × 3000 mm MCX 1000 and 100 000 å columns (Polymer Standard Services, Mainz, Germany) and a Waters 2998 UV detector (Waters Corp., Milford, MA) set at 280 nm using 0.1 M NaOH eluent (0.5 mL/min flow rate). For the SEC analysis, the filtrate samples were diluted with 0.1 M NaOH, followed by filtration through a 0.45 µm polytetrafluoroethylene (PTFE) syringe filter. Results were calculated relative to polystyrenesulfonate sodium salt standard using Waters Empower 3 software. The MWD analyses were provided by VTT.

7 RESULTS AND DISCUSSION

The objective of the experimental part was to carry out the trials and determine whether antioxidant mechanism of AHQ is present in the lignin coupling reactions. The experiments were successfully completed, so in that sense the goal was achieved. On the other hand, it is difficult to say for sure whether antioxidant effect of AHQ is present or not. The results are expressed in order of the internal logic of the topic.

7.1 Stage 1: Reduction of additives

Stage 1 was important in order to indicate that the cooking liquor is capable of reducing the chosen additives. Immediately after the addition of AQ into the reaction solution, there was no observable color transition in the mixture. AQ-2-sulfonic acid, AQ-1-sulfonic acid, AQ-2-carboxylic acid, and AQ-1,5-disulfonic acid showed behavior which was similar to AQ's. Thus each of the solutions of these additives were blank right after the addition of chemicals. However, with 2-hydroxy-1,4-naphthoquinone and 2,5-dihydroxy-1,4-benzoquinone the color transition was extremely rapid, and the color changed in a few seconds. Figure 26 shows how the reduction (color change) took place for AQ.

Figure 26. Reduction of AQ – 0 min (left) and after 30 min (right).

As it can be seen, there are no big differences between these two pictures of AQ. Perhaps sodium sulphite was unable to provide conditions reducing enough for AQ, or maybe reduction requires more heat. However, with other additives the difference in colors is much more visible (Appendix 2).

The additives were chosen for this study according to their varying redox potentials, but also because of their structural similarity to AQ. Thus the variation in reduction sensitivity of the used additives seems to be very interesting. In addition, it must take into account that AQ, as well as AQ-2-carboxylic acid are both insoluble to aqueous solutions, albeit water

solubility of AQ-2-carboxylic acid is diagnosed to increase with higher temperature (Tsai 1993). Table 7 combines the information received from the experiments and from the literature.

Table 7. General information and the observable results of the quinones.

Sample name	E° (V)	Transition time (min)	Starting color	Final color	Water solubility
AQ	0.155	30	blank	slightly green	no
AQ-2-sulfonic acid	0.187	20	blank	bright yellow	yes
AQ-1-sulfonic acid	0.195	30	blank	light red	yes
AQ-2-carboxylic acid	0.213	20	blank	slightly red	no*
AQ-1,5-disulfonic acid	0.239	30	blank	light yellow	yes
2-hydroxy-1,4-NQ	0.360	30	orange	deep red	yes
2,5-dihydroxy-1,4-BQ	0.441	30	red	deep red	yes

(*temp. dependent)

According to this table, all the additives were reduced quite differently in the presence of sodium sulphite. As expected, AQ and AQ-2-carboxylic acid showed especially small color changes due to their poor solubility to reaction solution. Solutions with AQ-2-sulfonic acid and AQ-1,5-disulfonic acid turned to yellow which was a bit strange. The explanation for this color change was probably a successful dissolution of the chemicals, but it might signify something else.

Transition time of each chemical reflects the total time for stable color transitions. In the other words, 30 min transition time signifies that there were no observable differences in solution color after 30 minutes. However the maximum time used in these trials was 60 minutes so it is possible that there could have been some kind of color transition after 60 min exposure. Altogether, according to the results, 2-hydroxy-1,4-naphthoquinone and 2,5-dihydroxy-1,4-benzoquinone are the only quinones that sodium sulphite could fully reduce in the used conditions (100°C, pH 8). In other words, these chemicals turned deep red which indicates full reduction in pH 8. Other quinones do not react that easily with sodium sulphite which could mean that the “normal” (fully oxidized) form of these additives requires something else in order to get reduced. From the perspective of the antioxidant mechanism, effective reduction of additives is essential and therefore the quinones with higher redox potential seem to have more antioxidant potential.

7.2 Total yield & pulp yield

The significance of total yield to the antioxidant mechanism is rather indirect. High total yield could refer to a poor pulping additive or an excellent pulping additive depending on the pulp content and the lignin content of the cooked chips. Hence, total yield as such does not reveal much, but as the reject/accept content and lignin content are known, there is more information to make a rationalized decision about the significance towards antioxidant mechanism. Thus, to some extent, total yield reflects on the amount of lignin solubilized, and thereby makes it meaningful for the antioxidant mechanism.

As it can be seen in Figure 27, the total yield is smallest with AQ in each time category. This phenomenon is explained through the capability of AQ to degrade wood chips faster than the other additives of this experiment. The supporting evidence for this argument is that the pulp yield for AQ is notably higher at the same time (Fig. 28). However, at this point, it cannot be said if the yield loss for total yield is because of lignin solubilization or carbohydrate solubilization.

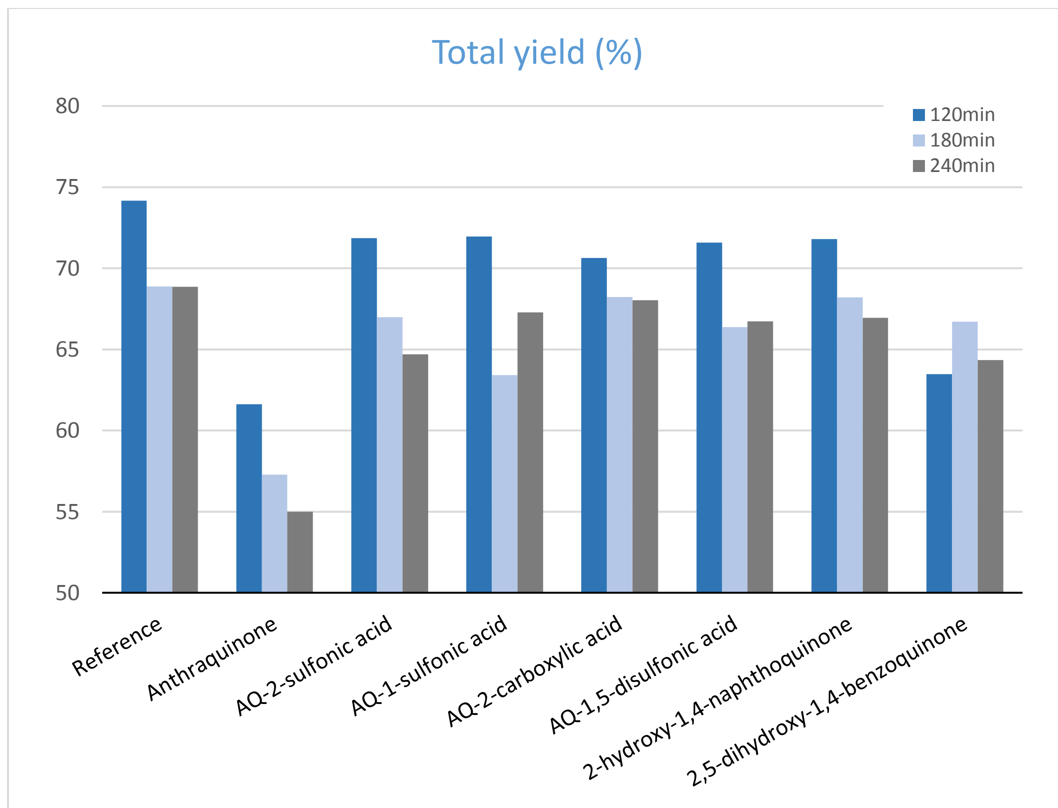

Figure 27. Total yields of cooked wood chips.

Figure 28 expresses the precise reject/accept results for 120 min, 180 min and 240 min cooks. In the case of AQ, there is a clear indication of more complete defibration of wood chips and with remaining quinones, the wood

chips of AQ-2-carboxylic acid showed slightly higher accept content than the rest of the samples. Otherwise there are no notable differences in comparison to reference samples where additives were not present.

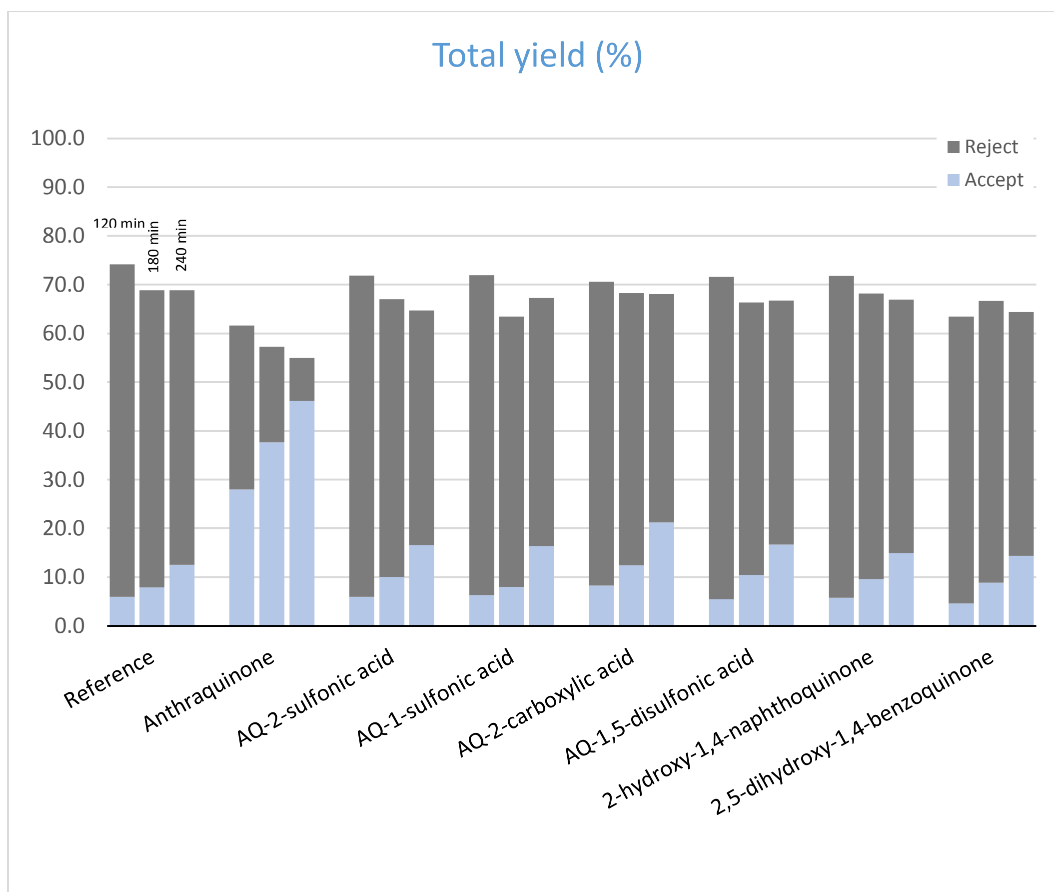

Figure 28. Total yields + accept and reject contents of cooked wood chips.

The influence of cooking time with respect to pulp yields can also be viewed from the figure above. As expected the pulp content increased along with the increased cooking time. Unexpectedly, in the case of AQ-1-sulfonic acid and 2,5-dihydroxy-1,4-benzoquinone the total yield increased along with time. This could be explained by lignin condensation reactions or otherwise there have been some covert losses/supplements during experiments. All in all, the results indicate that AQ, as well as AQ-2-carboxylic acid are the most effective quinones of defibrating the wood chips. This could be a signal of more effective solubilization of lignin.

7.3 Kappa number

Kappa numbers were determined from each accept sample in order to give an idea how much there are lignin left in the pulp. There are few things which have to be assimilated before comparing kappa numbers to each other. First of all, kappa number determinations have been done for the accept samples, not for the total samples. As can be seen in Figure 28, the pulp

yields are different and there is a difference when performing kappa number for reference sample (pulp yield ~12%) in contrast to AQ sample (pulp yield ~46%). Secondly, kappa number is not unequivocally the definition for lignin content. There are other factors such as extractives and hexenuronic acids that have an influence on kappa number.

Anyhow, kappa numbers show relatively small changes when compared to reference samples (Fig. 29). Although the reference, as well as AQ-2-sulfonic acid and AQ-2-carboxylic acid samples expressed slightly strange results (by getting higher kappa numbers at 180 min cook), the changes are yet quite subtle.

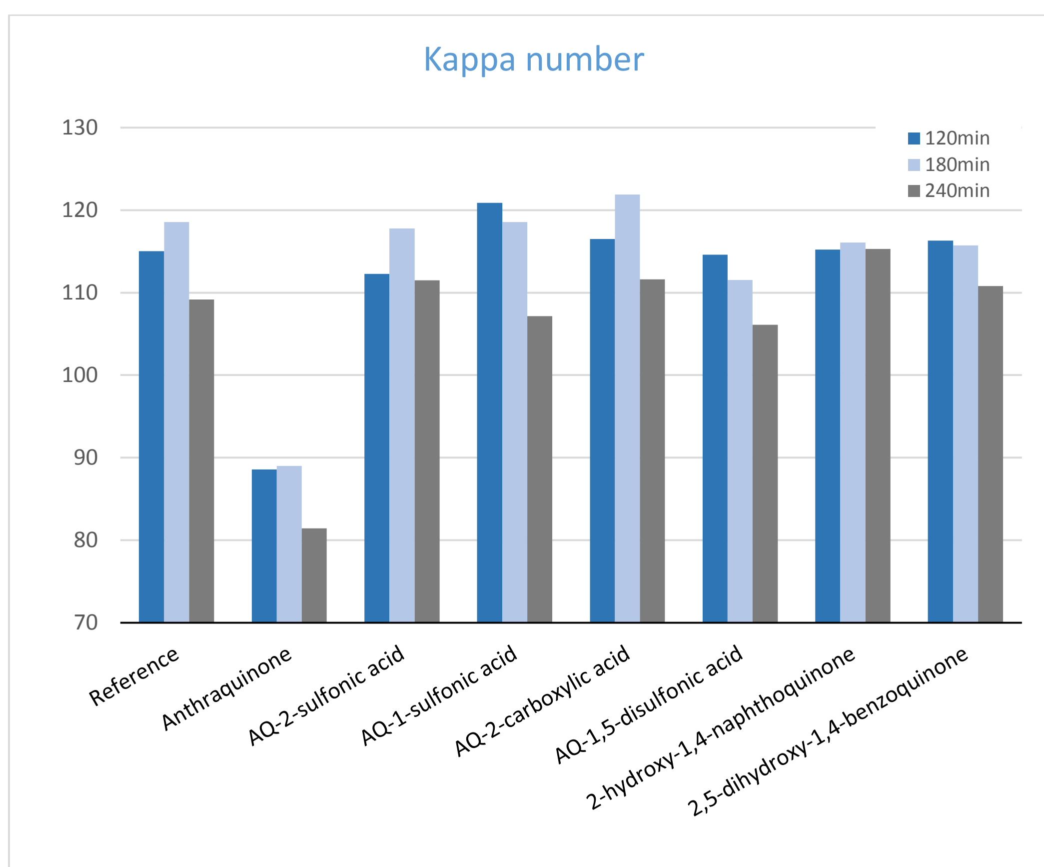

Figure 29. Influence of cooking time to kappa numbers.

It is possible that small rises in kappa numbers are due to increased condensation of lignin, but errors could be derived from the measurements as well. Either from insufficient homogenization of the pulp samples or possibly due to the utilized standard (SCAN-C 1:00) which is intended for samples whose kappa numbers are between 5 and 100. Additionally, a few bark particles existed among the used wood chips which may have caused some variation in the results. However, the smaller kappa number of AQ is most probably a consequence from the more effective delignification, but it might be partly derived from the antioxidant mechanism as well.

7.4 Final pH of filtrate

Although initial pH of the sodium sulphite (Na_2SO_3) solution was set to 8, there is a clear evidence that pH drops after the cooking has started. Figure 30 illustrates that during 120 minutes pulping, pH is distinctly dropped. However, when the cooking time is extended, pH rises up simultaneously.

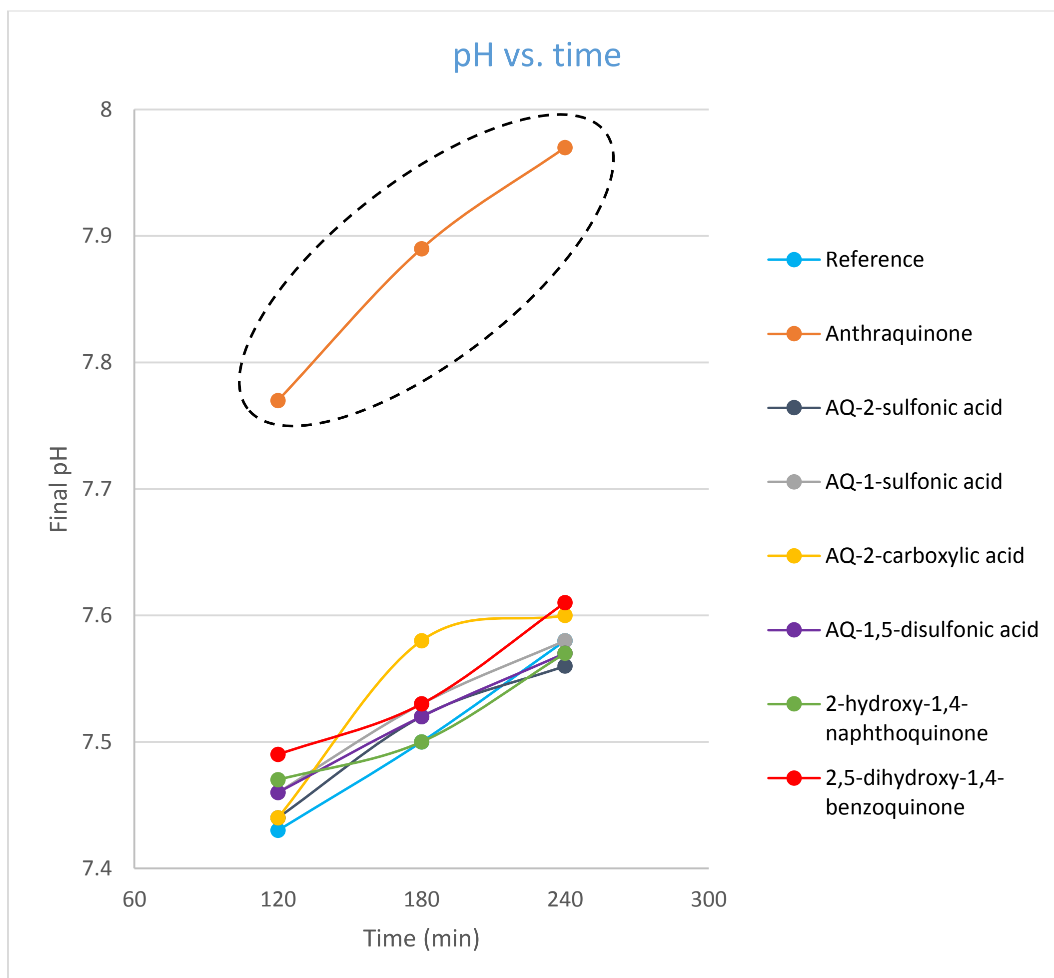

Figure 30. Influence of cooking time to pH.

The drop in pH is expected and is supposedly related to the loss of the buffer capacity of the solution. However, the differences in pH increase were interesting. It was surprising that the pH-slope for AQ is notably steeper than for the other quinones used in the experiments. The higher basicity of AQ samples might be derived from the accelerated sulfonation of the organic material (carbohydrate & lignin). This is extremely intriguing phenomenon and it could be part of the explanation why AQ is so effective pulping additive. From the perspective of the antioxidant mechanism it is difficult to draw any conclusions from the pH differences of the filtrates.

7.5 Dissolved lignin content

Along with the molecular weight distribution (MWD) of dissolved lignin, the results of the dissolved lignin content (DLC) are probably the most essential for determination of the antioxidant mechanism. The reason for this is obviously very simple. When the lignin is dissolved, it is not condensed. However, it is difficult to see from the graph what is really happening. When the cooking is extended, more lignin might be dissolved, but simultaneously more lignin coupling might occur as well. Figure 31 expresses the influence of redox potential to dissolved lignin content.

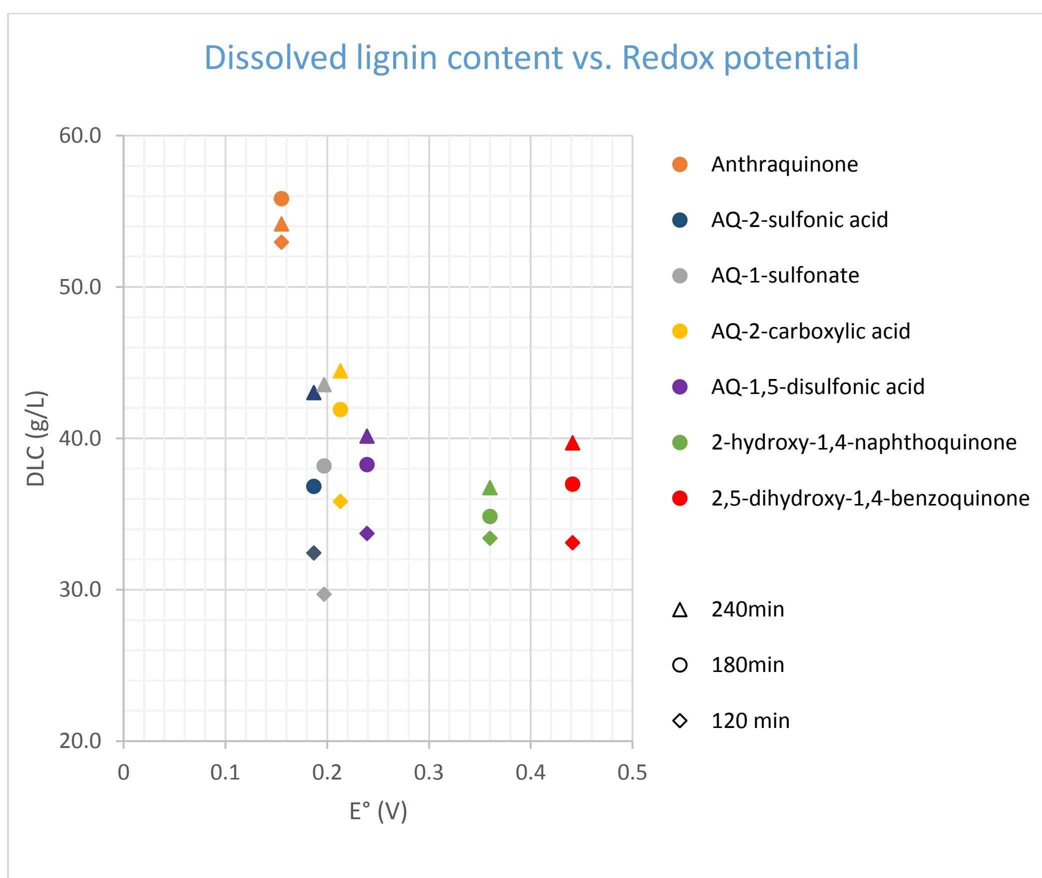

Figure 31. Influence of redox potential to dissolved lignin content.

As shown in Figure 31, it seems that lower redox potential and longer cooking time gives higher DLC. Quickly viewed it is a good generalization, but further exploration reveals that the relationship between redox potential and DLC is not that straightforward. For some reason, dissolved lignin content drops for AQ after cooking is extended from 180 min to 240 min. This kind of behavior indicate that dissolved lignin radicals could have coupled with lignin particles thus lowering the DLC of the sample.

One option might be that due to high DLC of 180 min AQ cook, all the AQ is depleted and there are no free AQ/AHQ remaining in the cook for further

delignification. This finding could support the idea that AQ/AHQ could create permanent adducts in the cook.

Anyhow, there are two additives which have caused clearly observable discrepancies from the general DLC trend. These two quinones are AQ, with the highest DLC and 2-hydroxy-1,4-naphthoquinone, with the lowest DLC. The comparison of 2-hydroxy-1,4-naphthoquinone to the reference sample shows that the lignin condensation could be even boosted in the case of 2-hydroxy-1,4-naphthoquinone, or on the other hand the quinone might alternatively protect lignin against delignification. The results of the DLCs are shown in Table 8.

Table 8. Dissolved lignin contents of different additives.

Sample name	Dissolved lignin content (g/L)		
	Cook 1 (120 min)	Cook 2 (180 min)	Cook 3 (240 min)
Reference	30.8	37.6	43.8
AQ	53	55.8	54.2
AQ-2-sulfonic acid	32.4	36.8	43
AQ-1-sulfonic acid	29.7	38.2	43.6
AQ-2-carboxylic acid	35.8	41.9	44.5
AQ-1,5-disulfonic acid	33.7	38.3	40.2
2-hydroxy-1,4-NQ	33.4	34.8	36.7
2,5-dihydroxy-1,4-BQ	33.1	37	39.7

7.6 Molecular weight distribution of dissolved lignin

Low molecular weight for AQ was expected in order to support the antioxidant mechanism. The reason for this expectation was that lignin which have a low molecular weight is generally in dissolved form. However, when the dissolved lignin content is higher, there are also more radicals to be neutralized. Nonetheless Figure 32 illustrates the average molecular weight of four carefully selected filtrate samples: Reference, AQ, AQ-2-

carboxylic acid, and 2-hydroxy-1,4-naphthoquinone. Each of these samples were 240 min cooking samples and they were selected because they presented interesting results in previous measurements of this study. The results were acquired from VTT.

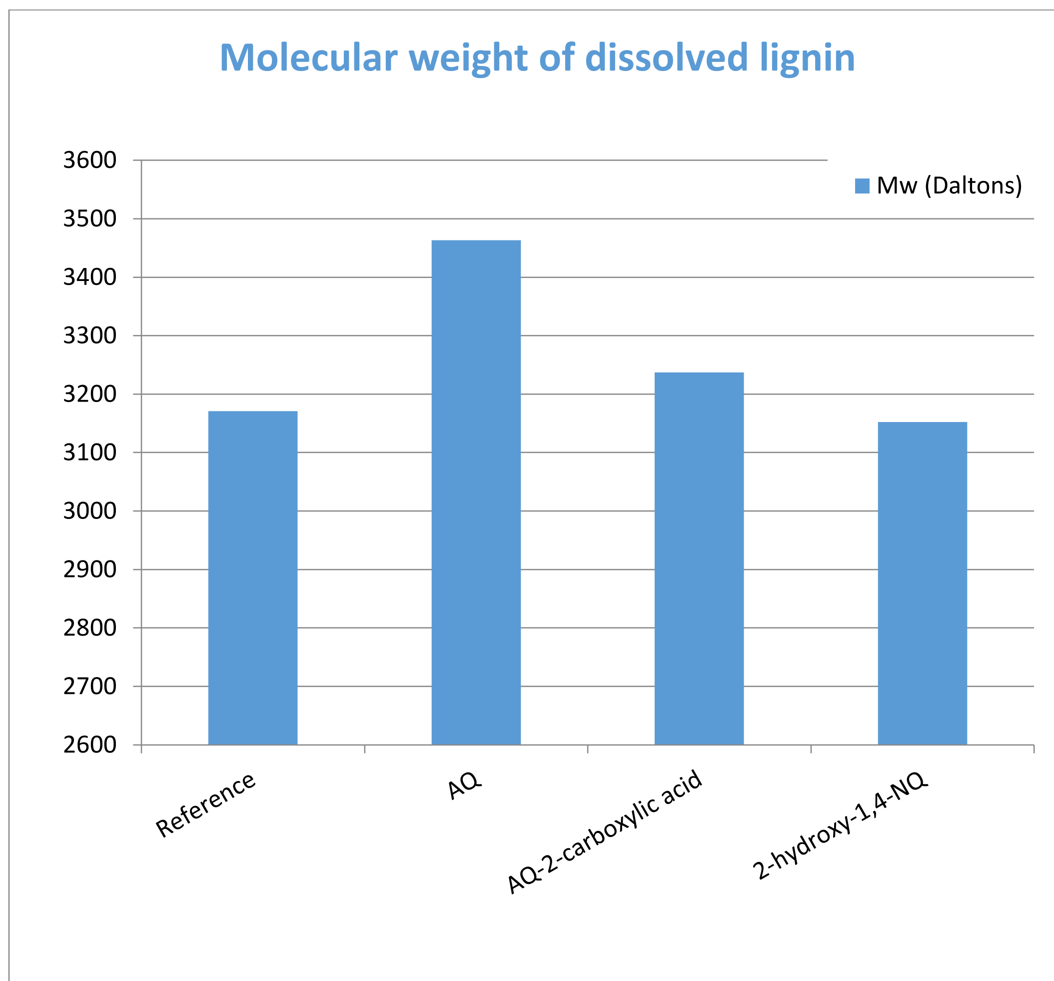

Figure 32. Average molecular weights of dissolved lignin.

As it can be seen, the average molecular weights of dissolved lignin differ with different quinones. Surprisingly, dissolved lignin of AQ did not have the smallest average molecular weight lignin but largest which might refer to AHQ's ability to solubilize greater lignin particles. According to these results, it appears that AQ does not have antioxidant mechanism towards dissolved lignin. However, it is possible that there is a certain kind of antioxidant mechanism present that inhibits the coupling of the bigger lignin molecules, but with these methods it is impossible to say whether it exists. If antioxidant mechanism exists for AQ, its power is most likely based on the protection of high molecular weight lignin polymers. Otherwise the evidence supporting antioxidant mechanism for AQ seems to be unlikely. Table 9 lists the results of the SEC analysis. The logarithmic scale of MWD is demonstrated in Appendix 3.

Table 9. The results of the molecular weight distribution of dissolved lignin.

Sample name	Mn (Daltons)	Mw (Daltons)	Mz (Daltons)	MP (Daltons)	Poly-dispersity
Reference (1)	1368	3163	11260	1247	2.31182
Reference (2)	1373	3179	11617	1248	2.31589
AQ (1)	1396	3541	19186	1219	2.53717
AQ (2)	1400	3386	14037	1226	2.41787
AQ-2-carboxylic acid (1)	1375	3239	12229	1246	2.35530
AQ-2-carboxylic acid (2)	1377	3235	12144	1244	2.35018
2-hydroxy-1,4-NQ (1)	1353	3198	12964	1251	2.36326
2-hydroxy-1,4-NQ (2)	1372	3107	10611	1250	2.26532

8 CONCLUSIONS

Along with the comprehensive literature review, the aim of this thesis was to investigate if the antioxidant mechanism of AQ is present during neutral sulphite pulping of wood chips.

According to literature, it is unclear what causes the carcinogenicity of AQ. No reliable human data exists, so the carcinogenic potential to humans is still unexplained. Thus the hazardous exposure levels to humans are difficult to define. The synergism of PS and AQ has been proven, but the reasons for the effect is blurred. Nonetheless it seems that the altered reaction conditions might provide the hidden answer for AQ/PS synergism. Multiple suggestions have been made in order to understand AQ working mechanism, but the mechanism is still unsolved. However the reason(s) behind AQ's effectiveness seems to be related to lignin degradation and not to retardation of lignin condensation.

This study investigated experimentally the lignin degradation mechanism, and according to research hypothesis, the delignification efficiency of AQ could be partly explained through antioxidant mechanism. The results showed the potential of AQ as a powerful pulping additive, but the evidence supporting the antioxidant hypothesis was scarce.

Although the antioxidant mechanism seems to have no influence on AQ working mechanism, it cannot be fully discarded. This work strengthened the idea that there is something exceptional in anthraquinone. AQ demonstrated the best performance of the used quinones while having the smallest redox potential. AQ also showed notably higher molecular weight for dissolved lignin, which could refer to AQ's ability to solubilize lignin which molecular size is bigger. Furthermore the differences in final pH of the filtrate samples was an interesting finding. Increased pH of the AQ filtrates might originate from the more effective lignin sulfonation, which could further cause the accelerated delignification effect of AQ.

Thus, further research is needed in order to understand why the results were as demonstrated. The future's AQ studies should be focused on issues mentioned in this work. Does AQ's effect result from the sulfonation of organic matter? Why AQ accelerates the sulfonation? Are there a link between redox potential and delignification? How does the redox potential of additives vary in different conditions? Does polarity have any function in lignin degradation? What about stability and selectivity of the quinones used in this study?

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LIST OF APPENDICES

Appendix 1: Standards and methods used in the experiments

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Appendix 1

Standards and methods used in the experiments.

Determination	Method
Chip dry matter content	SCAN-CM 39:94
Pulp dry matter content	SCAN-C 3:78
Total yield	Gravimetric
Reject	Gravimetric
Accept (pulp)	Gravimetric
Kappa number	SCAN-C 1:00
Reduction of additives	Look at pages 34 & 39 and Appendix 2
Dissolved lignin content	UV-VIS Spectrophotometer
Molecular weight distribution of lignin	Size-Exclusion Chromatography (SEC)

Appendix 2

Demonstration of the reduction of additives.

AQ – 0 min (left side) and 30 min (right side)

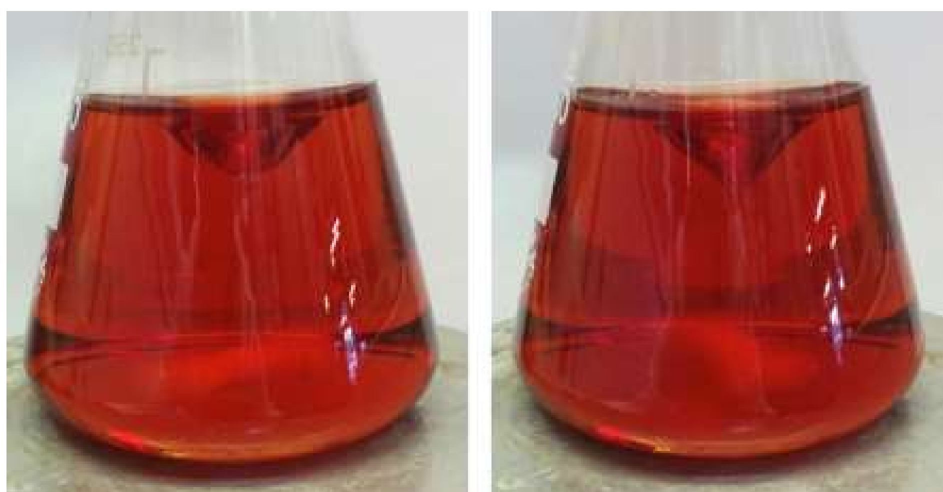
AQ-2-sulfonic acid – 0 min (left side) and 20 min (right side)

AQ-1-sulfonic acid – 0 min (left side) and 30 min (right side)

AQ-2-carboxylic acid – 0 min (left side) and 20 min (right side)

AQ-1,5-disulfonic acid – 0 min (left side) and 30 min (right side)

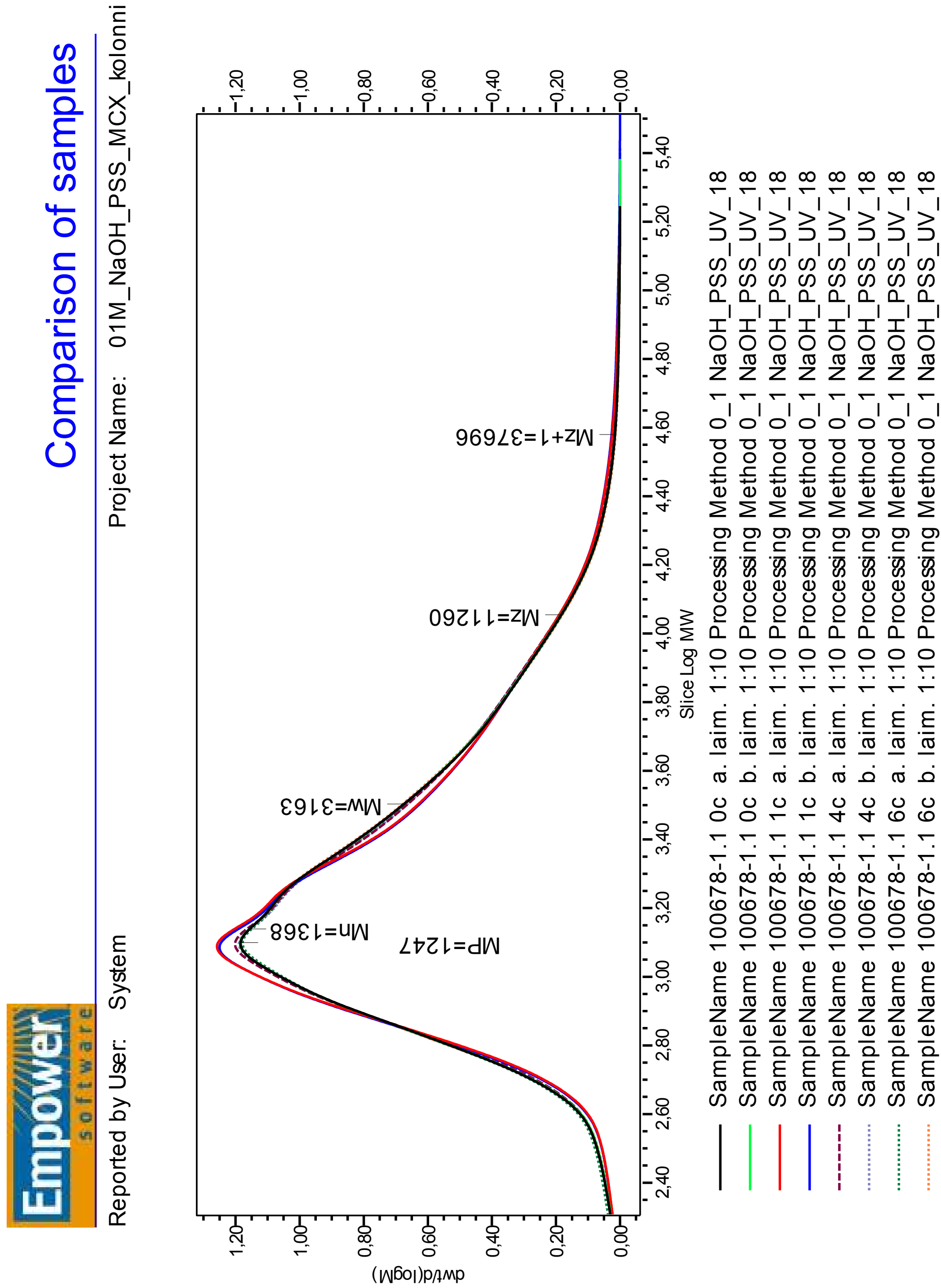
2-hydroxy-1,4-NQ – 0 min (left side) and 30 min (right side)



2,5-dihydroxy-1,4-BQ – 0 min (left side) and 30 min (right side)

Appendix 3

The molecular weight distribution of dissolved lignin.



Where 0c is Reference, 1c is AQ, 4c is AQ-2-carboxylic acid, and 6c is 2-hydroxy-1,4-naphthoquinone.

Explanations for abbreviations used in MWD of dissolved lignin:

Mn
Number average molecular weight for the distribution.

Mp
Peak molecular weight for the distribution.

Mv
Viscosity average molecular weight for the distribution.

Mw
Weight average molecular weight for the distribution.

Mz
Z-average molecular weight for the distribution.

Mz+1
Z+1 average molecular weight for the distribution

Appendix 4

Detailed cooking parameters and results.

Cooking #	Additive	CAS #	E° (V)	Additive charge on o.d. wood (%)	Na2SO3 charge on o.d. wood (%)	Temp. (°C)	Time (min)	Initial pH	Final pH	Dissolved Lignin Content (g/L)	Dilution Factor	Molecural weight (Daltons)	Total yield (%)	Pulp Yield (%)	Reject yield (%)	Kappa #
0a	Reference	-	-	0	50	170	120	8.0	7.43	30.8	1250		74	5.9	68.2	115
0b	Reference	-	-	0	50	170	180	8.0	7.50	37.6	1250		69	7.9	61.0	119
0c	Reference	-	-	0	50	170	240	8.0	7.58	43.8	1250	3163	69	12.5	56.3	109
1a	Anthraquinone	84-65-1	0.155	0.1	50	170	120	8.0	7.77	53.0	1250		62	28.0	33.6	89
1b	Anthraquinone	84-65-1	0.155	0.1	50	170	180	8.0	7.89	55.8	1250		57	37.7	19.6	89
1c	Anthraquinone	84-65-1	0.155	0.1	50	170	240	8.0	7.97	54.2	1250	3541	55	46.2	8.8	81
2a	AQ-2-sulfonic acid	131-08-8	0.187	0.1	50	170	120	8.0	7.44	32.4	1250		72	6.0	65.9	112
2b	AQ-2-sulfonic acid	131-08-8	0.187	0.1	50	170	180	8.0	7.52	36.8	1250		67	10.0	57.0	118
2c	AQ-2-sulfonic acid	131-08-8	0.187	0.1	50	170	240	8.0	7.56	43.0	1250		65	16.5	48.2	112
3a	AQ-1-sulfonate	128-56-3	0.197	0.1	50	170	120	8.0	7.46	29.7	1250		72	6.3	65.6	121
3b	AQ-1-sulfonate	128-56-3	0.197	0.1	50	170	180	8.0	7.53	38.2	1250		63	8.0	55.4	119
3c	AQ-1-sulfonate	128-56-3	0.197	0.1	50	170	240	8.0	7.58	43.6	1250		67	16.4	50.9	107
4a	AQ-2-carboxylic acid	117-78-2	0.213	0.1	50	170	120	8.0	7.44	35.8	1250		71	8.3	62.4	117
4b	AQ-2-carboxylic acid	117-78-2	0.213	0.1	50	170	180	8.0	7.58	41.9	1250		68	12.4	55.8	122
4c	AQ-2-carboxylic acid	117-78-2	0.213	0.1	50	170	240	8.0	7.60	44.5	1250	3239	68	21.2	46.8	112
5a	AQ-1,5-disulfonic acid	853-35-0	0.239	0.1	50	170	120	8.0	7.46	33.7	1250		72	5.4	66.2	115
5b	AQ-1,5-disulfonic acid	853-35-0	0.239	0.1	50	170	180	8.0	7.52	38.3	1250		66	10.4	55.9	112
5c	AQ-1,5-disulfonic acid	853-35-0	0.239	0.1	50	170	240	8.0	7.57	40.2	1250		67	16.7	50.1	106
6a	2-hydroxy-1,4-naphthoquinone	83-72-7	0.360	0.1	50	170	120	8.0	7.47	33.4	1250		72	5.8	66.0	115
6b	2-hydroxy-1,4-naphthoquinone	83-72-7	0.360	0.1	50	170	180	8.0	7.50	34.8	1250		68	9.6	58.6	116
6c	2-hydroxy-1,4-naphthoquinone	83-72-7	0.360	0.1	50	170	240	8.0	7.57	36.7	1250	3198	67	14.9	52.0	115
7a	2,5-dihydroxy-1,4-benzoquinone	615-94-1	0.441	0.1	50	170	120	8.0	7.49	33.1	1250		63	4.6	58.9	116
7b	2,5-dihydroxy-1,4-benzoquinone	615-94-1	0.441	0.1	50	170	180	8.0	7.53	37.0	1250		67	8.9	57.9	116
7c	2,5-dihydroxy-1,4-benzoquinone	615-94-1	0.441	0.1	50	170	240	8.0	7.61	39.7	1250		64	14.3	50.0	111