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REACTIVITY OF DISSOLVING PULPS:

A MEASURE BASED ON ACETYLATION KINETICS

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Resumen

La celulosa es el polímero más abundante en el planeta, y como tal, es ampliamente usado. Entre sus usos más comunes se encuentran la producción de cartón y papel hechos a partir de pulpa de celulosa. Sin embargo, existe una producción menor pero importante de derivados de celulosa obtenidos a partir de la producción de pulpas de disolución (*dissolving pulps*), es decir, pulpas con alto contenido de celulosa. En el caso de las pulpas para papel y cartón, el proceso más común el proceso Kraft, junto con otros procesos minoritarios. Por el contrario, el proceso de sulfito ácido es el principal método usado en la producción de pulpas de disolución. Debido a la derivatización aplicada a las pulpas, el proceso Kraft normal no es apropiado para la producción de pulpa de disolución, y por lo tanto el proceso es modificado, añadiéndose una hidrólisis previa, resultando el proceso Kraft con Prehidrólisis (PHK, su sigla en inglés). La reactividad de la celulosa es usualmente uno de los parámetros más importantes para determinar la calidad de pulpas de disolución. Es uno de los principales datos considerados en la producción de derivados de la celulosa, como viscosa o acetato de celulosa, y también un parámetro fundamental en la producción de bioetanol. La reactividad es un concepto relacionado con la accesibilidad de los grupos hidroxilo en proceso de conversión determinado. Por ejemplo, la reactividad de la pulpa de celulosa respecto al proceso de formación de viscosa se determina por el método de Fock o el método del valor de filtro de viscosa. Sin embargo,

estos métodos llevan mucho tiempo y no están claramente relacionados. Entre los productos de derivatización de la celulosa, el acetato de celulosa es uno de los más importantes. Por lo tanto, diversas aplicaciones del acetato de celulosa son de importancia industrial y nuevas aplicaciones son desarrolladas continuamente. De esta forma, la producción industrial y el mecanismo de acetilación son considerados.

En este estudio, la reactividad de muestras de pulpa de celulosa se determinó mediante la cinética de acetilación, mientras que la accesibilidad se estudió mediante ^{31}P-NMR, aunque en este último estudio los resultados no fueron satisfactorios. Para el desarrollo del método de acetilación, se usaron pulpas de diferentes orígenes: dos pulpas de disolución de *Eucalyptus*, una producida por proceso del sulfito ácido y la otra mediante el Kraft con Prehidrólisis; una pulpa de disolución de madera blanda hecha con el proceso de sulfito ácido; dos pulpas para papel, una de madera dura hecha con el proceso Kraft y la otra de madera blanda hecha con el proceso de sulfito ácido; y por último, una pulpa de disolución de madera blanda, cuyo proceso era desconocido. El estudio de la cinética de acetilación implicó la reacción de celulosa con anhídrido acético catalizada con ácido sulfúrico a una temperatura determinada. El grado de sustitución (DS) se determinó mediante HPLC y luego mediante la técnica FT-IR. La Distribución de la Masa Molar y composición de carbohidratos también se analizaron y se correlacionaron con la velocidad de reacción. En conclusión, el método de acetilación

demostró ser adecuado para determinar la reactividad de muestras de pulpas de forma reproducible. Los resultados revelaron una clara diferencia entre la reactividad de las pulpas.

Se realizó una presentación oral de los resultados obtenidos para las pulpas de *Eucalyptus* en el Sexto Coloquio Internacional en Pulpa de *Eucalyptus* (Bonfiglio & Sixta, 2013).

Abstract

Cellulose is the most abundant polymer in the planet, and as such, it is widely used. Among its most common uses is as board and paper made from cellulose pulp. However, there is a smaller but significant production of specialized cellulose derivatives obtained from the production of dissolving pulps, i.e. pulps with high cellulose content. In the case of pulps intended for board and paper, the most common process is the Kraft process, with some other minor processes. On the contrary, the acid sulfite process is the principal method used in the production of dissolving pulps. Due to the derivatization applied to the pulps, the normal Kraft pulp process is not suitable for dissolving pulp, and therefore a modification of the process is made, the Prehydrolysis Kraft process (PHK). The reactivity of cellulose is usually one of the most important parameters used in the determination of the quality of dissolving pulps. It is a main input in the production of cellulose derivatives, such as viscose or cellulose acetate, and also a key parameter in the production of bioethanol. Reactivity is a concept related to the accessibility of hydroxyl groups in a defined conversion process. Pulp reactivity towards the viscose process is, for example, determined through Fock's method or the viscose filter value. However, these methods are time-consuming and they are not clearly inter-related. Amid the products of derivatization of cellulose, the cellulose acetate is ranked among the most important. Therefore, several applications of cellulose acetate are of industrial

importance and new applications are developed continuously. The industrial production and the mechanism of acetylation are reviewed.

In this study, the reactivity of cellulose samples was determined by the kinetics of acetylation, and the accessibility was studied by ^{31}P-NMR, although in this latter study the results were unsatisfactory. For the development of the acetylation method, pulps from different origins were used: two *Eucalyptus* dissolving pulps, one produced by the Acid Sulfite (AS) process and the other by the pre-hydrolysis Kraft (PHK) process; a softwood acid sulfite dissolving pulp; two paper pulps, one hardwood Kraft pulp and the other softwood acid sulfite pulp; and finally, a softwood dissolving pulp, from an unidentified process. The study of the acetylation kinetics involved the reaction of cellulose with acetic anhydride catalyzed by sulfuric acid at a defined temperature. The degree of substitution (DS) was determined by HPLC and separately by the FT-IR technique. Molar Mass Distribution and Carbohydrate composition of the pulps were also analyzed and correlated to the speed of reaction. In conclusion, the acetylation method proved to be adequate to determine the reactivity of pulp samples in a reproducible manner. The results revealed a clear difference in the reactivity of the pulps.

The *Eucalyptus* pulps results and discussion were orally presented in the 6th International Colloqium on *Eucalyptus* Pulp (Bonfiglio & Sixta, 2013).

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Abbreviations

Ac_2O	Acetic Anhydride
AcOH	Acetic acid
AHG	Anhydroglucose Units
AIC	Akaike's Criterion Test
CA	Cellulose Acetate
CCE	Cold Caustic Extraction
$CDCl_3$	Deuterated Chloroform
Cell-OH	Cellulose
DMAc	N, N-dimethylacetamide
DMAP	Dimethylamino pyridine
DP	Degree of Polymerization
DS	Degree of substitution
FT-IR	Fourier Transform Infrared Spectroscopy
FTIR-PAS	Fourier Transform Photoacustic Spectroscopy
H_2SO_4	Sulfuric Acid
HCl	Hydrochloric Acid
HPAEC-PAD	High-Performance Anion-Exchanged Chromatography with Pulsed Amperometric Detection
HPLC	High Performance Liquid Chromatography
HW	Hardwood

LCD	Liquid Crystal Display
LiCl	Lithium Chloride
MALLS	Multi Angle Laser Light Scattering
MCC	Microcrystalline Cellulose
MFC	Microfibrillated Cellulose
MM	Molar Mass
MMD	Molar Mass Distribution
Mn	Number-average molecular weight
Mw	Weight-average molecular weight
Mz	Z-average molecular weight
NaOH	Sodium Hydroxide
NFC	Nanofibrillated Cellulose
NMMO	N-methylmorpholine-N-oxide
NMR	Nuclear Magnetic Resonance
OH	Hydroxyl
PHK	PreHydrolysis Kraft
RI-detection	Refractive Index detection
SEC	Size Exclusion Chromatography
SW	Softwood
VisCBC	Viscose Continuous Batch Cooking

1. INTRODUCTION

The objective in this work is to optimize a method to determine the reactivity of cellulose towards acetylation and to compare the reactivity of several pulps. The method implies the study of the kinetics of acetylation of cellulose and to study the relationship of the speed of acetylation of cellulose with other characteristics of the dissolving pulp. Therefore, Molar Mass Distributions and carbohydrate composition of the pulps are investigated. To evaluate the degree of acetylation this work compares two different methods: by HPLC and by FT-IR. While the former is more exact, the latter has the advantage of being faster and easier, although a calibration is required. Also, it is possible to explain the kinetics of acetylation by two methods, one considering the hydroxyls in the cellulose with the same reactivity, and the other with two groups of hydroxyls.

The high versatility of the cellulose has made of it an essential raw material. It is used for countless purposes and in the production of various materials, from paper to biofuel, in building insulation or in the pharmaceutical industry. Although one of the main uses of cellulose is the production of paper and board, the production of dissolving pulps (pulp cellulose with high cellulose content, made especially for cellulose derivatives) is a growing market, from 3.1 million tons in the year 2000 to more than 4.5 million tons in the year 2010. Among the cellulose derivatives (i.e., the functionalization of cellulose) are the viscose –which

involves the treatment of cellulose with sodium hydroxide and sodium disulfide– and cellulose acetate, used in several applications, like apparel, filters, films, absorbency products, etc.

However, as written above, to use the cellulose as raw material for this production of derivatives, cellulose pulp with high content of cellulose must be used, i.e. a dissolving pulp. High cellulose content of the pulp ensures the quality of the final product, also avoiding problems in the production. So, while the process for the production of paper and board is mainly the Kraft process, for the production of dissolving pulp the main process is the Acid Sulfite process. Nevertheless, a modified Kraft process is used in the production of dissolving pulp. This modification involves the addition of a previous step of hydrolysis, hence the name of this modified process, Prehydrolysis Kraft process.

Cellulose acetate is produced from this dissolving pulp and acetic anhydride, using a catalyzer (usually sulfuric acid). Knowing the reactivity of the dissolving pulp is a fundamental aspect of this industrial production. This knowledge is useful to answer specific questions, like production time, amount of chemicals to be used and the possibility of mixing pulps from different origins, among others. Also, the behavior of the dissolving pulp in acid medium does not have to match necessarily with the reactivity in basic medium –usually referred to the viscose production. Furthermore, the reactivity is related with the concept of accessibility of hydroxyls.

In this thesis, Chapter 2 deals with the structure of cellulose and reactivity related issues and then introduces the industrial processes of dissolving pulp. Later, specific aspects of cellulose acetate –like production and mechanism of acetylation of cellulose- are presented. The experimental details of this work are shown in Chapter 3, including a brief summary of the method development and the derivation of the kinetics of acetylation equations. Although the pulps samples are mostly dissolving pulps, two paper pulps are also studied. Next, the results obtained along with the respective discussion are presented in Chapter 4. In this chapter, the two methods to describe the kinetics of acetylation are examined for all the pulps. Also, two methods to determine the degree of substitution of cellulose are compared, proving that the HPLC method is more exact but the FT-IR faster and easier. Besides, Chapter 4 shows that the filterability and cellulose content are not directly related with the speed of reaction, at some levels at least. On the other hand, it is discussed the possible influence of the polydispersity in the speed of reaction. Finally, Chapters 5 and 6 set out the conclusions and some possible improvements on the method of determination of the kinetics of acetylation, respectively. Last, it may be worth mentioning that the accessibility was studied by ^{31}P-NMR and it is presented in the Appendix 1, although the results were not satisfactory.

2. LITERATURE REVIEW

2.1 Cellulose

2.1.1 Structure

Cellulose, the most common organic polymer on earth, produced by green plants, algae and certain types of bacteria, has been in consequence a companion of humanity since the beginning of our time, used for a range of purposes, from housing and clothing to instruments of communication. It was not, however, until two centuries ago that man started to use it as a chemical raw material for other purposes. (Strunk, 2012; Klemm *et al.*, 1998).

Cellulose is a homopolymer of D-anhydroglucopyranose units (AHG) linked by β-1,4-glycosidic bonds, and it can be considered an isotactic polymer of cellobiose (being cellobiose the repeating unit). The AHG has hydroxyl groups at C-2, C-3 and C-6 that can be regarded as primary and secondary hydroxils, with their typical reactivity. The terminal glucose with a free hydroxyl group at C-4 is the non-reducing end, also capable of undergoing typical aliphatic hydroxyl reactions. On the contrary, the terminal glucose with the C-1 free is present in the form of a semiacetal and it is the reducing end of the cellulose. In the conformation of the AHG, a $^{4}C_{1}$ chair, the free hydroxyl groups are positioned in the equatorial plane and the hydrogen atoms are in the axial plane, as seen in Figure 1.

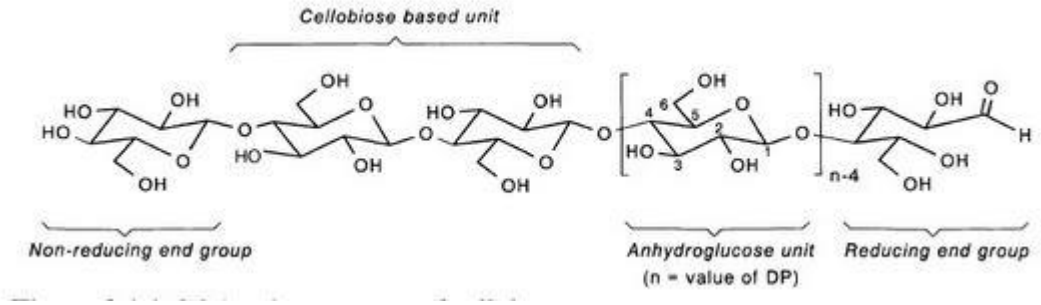

Figure 1 – Molecular structure of cellulose (from Klemm *et al.*, 1998).

Despite the apparent simplicity of the cellulose molecule, the complexity of the system becomes evident when considering the other levels of structure: the supramolecular structure and the morphological structure. At a supramolecular level, the network of inter and intra molecular bonds is responsible for a high proportion of the cellulose properties (Figure 2). In native cellulose (cellulose I) the bonds between the hydroxyl at C-3 and the hydroxyl at C-6 of another cellulose chain are considered the most important from a chemical point of view, although several other bonds are formed. In cellulose I two phases are present, cellulose I_α and cellulose I_β, the latter being the predominant phase in cotton and wood. Also, part of the I_β is converted to I_α after Kraft cooking. On the other hand, cellulose II is obtained by mercerization or by regeneration from solution and the system is even more complicated, with a higher intermolecular crosslinking density (Klemm *et al.*, 1998, Sixta, 2006).

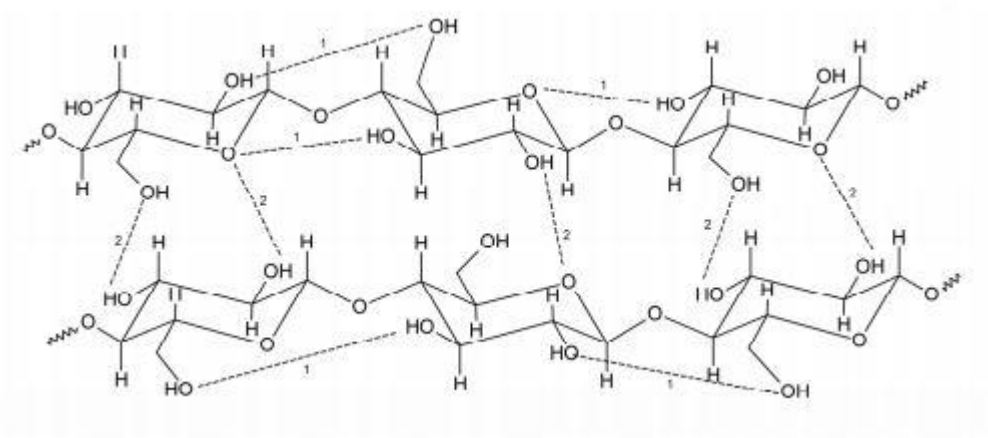

Figure 2. Inter- and intramolecular bonds in cellulose (Baptista *et al.*, 2013)

2.1.2 Reactivity

Pulp reactivity is the key parameter for the dissolving pulp production because it determines the efficiency of the conversion processes and the quality of the resulting products, such as cellulose derivatives or regenerated cellulose fibers. This parameter is related to the accessibility of chemicals to cellulose. However, the first problem that arises when discussing the reactivity of cellulose is that there is no universal method for the characterization of pulp reactivity. Usually, pulp reactivity is specifically determined based on its respective chemical conversion reaction (Klemm *et al.*, 1998, Sixta, 2006).

A complete functionalization of all the hydroxyl groups of cellulose is a hard task, and the majority of the cellulose derivatives produced in the

industry consists of partially modified cellulose with a significant number of free hydroxyl groups. The extent of the reaction is described by the degree of substitution (DS), which indicates the average number of hydroxyl groups modified per AHG. Therefore, a 0 DS means non-substituted cellulose, and the maximum DS is 3, where the possible places of substitution are the hydroxyls placed at C-2, C-3 and C-6 of the AHG.

As with the normal polymer reactions, the reactions of cellulose may be classified as homogeneous reactions - where cellulose is dissolved - or heterogeneous reactions - where cellulose is in a solid and more or less swollen state. With a suitable preparation of the cellulose sample, and adjusting the reaction medium and external conditions, the heterogeneous reactions can behave as quasi-homogeneous bulk reactions. (Klemm *et al.*, 1998).

Regarding the homogeneous reaction of cellulose, its dissolution is a prerequisite; it can be made by means of a nonderivatizing solvent (as *N,N*- dimethylacetamide/LiCl), a derivatizing medium, or by the dissolution of a cellulose derivative in an adequate solvent. Although the reactivity of the hydroxyl groups depends on the conditions of the reaction, it can be assumed that the OH at C-3 has the poorest reactivity, with the C6-OH being the most reactive and C2-OH being variable. (Klemm *et al.*, 1998) (Ramos *et al.*, 2011) (Marson & El Seoud, 1999)

In the heterogeneous reaction, the reactivity of the hydroxyl group in C-3 is supposed to be the lowest of the three hydroxyl groups, with a preference for the C-2 compared to the C-6, which depends on the type of reaction, reagent used and reactivity medium. (Klemm *et al.*, 1998)

Although a higher reactivity can be expected in the amorphous regions, there are previous steps that can minimize this preference. In concordance with this awareness, some studies didn't find that crystallinity affected the reactivity. Nevertheless, it is known that the acetylation starts in the amorphous regions, and is followed by the acetylation of the crystallites. The swelling and mechanical forces applied to the cellulose as previous steps in the production of derivatives can split the hydrogen bonds enhancing the reactivity (Klemm *et al.*, 1998) (Sassi & Chanzy, 1995) (Wollboldt *et al.*, 2010)

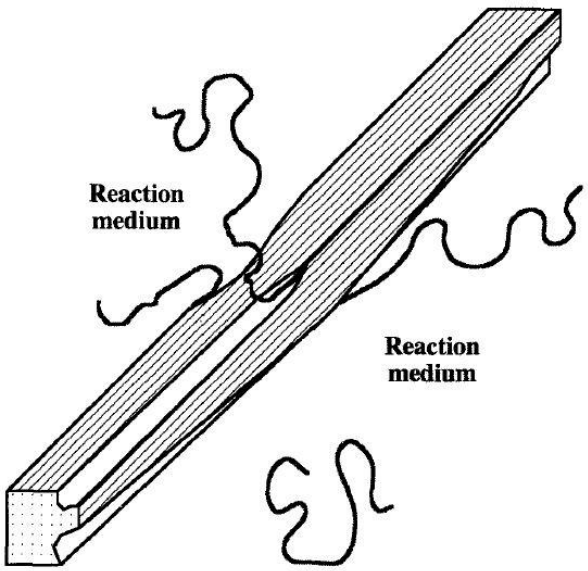

Figure 3. Acetylation of a cellulose crystal. A chain is solubilized due to the acetylation and leaves the crystal (Sassi & Chanzy, 1995)

Different phenomena in the industrial production affect the reactivity of cellulose. Among these, hornification seems to be one of the most important. The hornification that appears when the pulp is dried reduces the reactivity. New bonds between the cellulose molecules are created, thus making reactions more difficult. This process is almost irreversible, although drastic conditions of temperature and pH may reverse the inaccessibility. (Fernandes Dinis *et al.*, 2004) (Pönni *et al.*, 2013)

2.1.3 Methods to measure reactivity

As pointed out, the reactivity is related to the accessibility of hydroxyl groups. This has been addressed by several studies, and some common techniques are applied. For instance, the Water Retention Value can be used as an important input for the accessibility, as well other water sorption methods. Likewise, the exchange of cellulose with deuterium has also been investigated and can be used to characterize cellulose (Frilettte *et al.*, 1948) (Hofstetter *et al*., 2006). Also, the accessibility of cellulose has been studied by means of Phosphurus NMR (Filpponen & Argyropoulos, 2008).

However, the reaction conditions affect the reactivity of cellulose. One of the traditional methods to measure cellulose reactivity is Fock's method (Fock, 1959). In this method, the amount of undissolved cellulose is measured after mixing an excess of sodium hydroxide and carbon disulfide with a pulp sample. Although normal laboratory glassware and equipment are suitable to perform this test, its application is restricted to

alkaline conditions, and no conclusions on the performance of a pulp under acidic conditions can be drawn. The method is also time-demanding and it must usually be used in combination with other methods. Another technique that gives an indication of the processability of pulps in the viscose process is the viscose filter value, applying the method described by Treiber *et al.* (1962). In this method, the filterability of the pre-spinning viscose solution is analyzed by determining the viscose filter value. However, Treiber's method is not necessarily suitable for the characterization of pulp reactivity in different derivatization conditions, such as the cellulose acetylation (Christoffersson *et al.*, 2002) (Javed & Germgård, 2011) (Östberg *et al.*, 2012) (Sixta *et al*., 2004).

For instance, some studies have shown that there is no correlation between the pulp reactivity measured according to the Fock's test and the cellulose or hemicellulose content of the pulp samples (Javed & Germgård, 2011) (Östberg *et al.*, 2012). On the other hand, Christoffersson *et al.* (2002) have shown that the reactivity is higher in pulps with low hemicellulose content and shorter and more soluble in alkali cellulose chains.

There have been different attempts to measure the reactivity by following the kinetics of acetylation. *E.g.* Luo *et al.* (2013), examined the acetylation of cotton linters under heterogeneous conditions, using sulfuric acid as catalyst. In their work, samples were taken from a reaction vessel and added to a solution of magnesium acetate and acetic acid to finish the

reaction. Similarly, acetylation rates were estimated by following the increase in the temperature of the reaction, as in the work of Yang *et al.* (2008). Also, Wollboldt (2011), studied the acetylation kinetics of different pulps after optimizing the experimental conditions, in particular how to finish the reaction. Unfortunately, lack of reproducibility in the results was found.

An important input in the determination of the kinetics is the determination of the Degree of Substitution in the resulting cellulose acetate. Elemental or functional group analyses are usually employed to determine the DS (Klemm *et al.*, 1998) (Vaca-Garcia *et al.*, 2001). The typical volumetric method, called the Eberstadt method, involves the addition of NaOH to produce the alkaline hydrolysis and then a back-titration of the excess with HCl (Subcommittee on Acyl Analysis, Division of Cellulose Chemistry Committee on Standards and Methods of Testing, 1952) (Murray *et al.*, 1931). The most extended spectroscopic technique to determine the DS is the H-NMR in $CDCl_3$ (Buchanan *et al.*, 1987) (Luo *et al.*, 2013) (Satgé *et al.*, 2002). A comparative technique used, where calibration takes place first, is the FT-IR (Sassi & Chanzy, 1995) (Hurtubise, 1962). Samples of known DS are related to the disappearance of the OH signal, creating a calibration curve. The HPLC is used not only as a technique to determine the acetyl functional group, but also as a way to determine the intermolecular acetyl distribution of cellulose triacetate (Asai *et al.*, 2006). In addition, alkaline hydrolysis followed by gas

chromatography-mass spectrometry was also studied, and it was found to be a fast and reliable method (Freire *et al.*, 2005).

2.2 Dissolving pulp

2.2.1 Introduction

A pulp with high cellulose content is called a dissolving grade pulp. Until World War II it was produced from purified cotton linters or using the acid sulfite process with higher temperature and acidity along with prolonged cooking. The aim of this process was to remove the majority of the hemicelluloses, which cannot be done by the regular Kraft pulping process, where the presence of pentosans in the final product may interfere with the chemical conversion of cellulose into viscose, cellulose ethers or acetates. However, the abundance and variety of species of hardwoods made their use economically attractive. Therefore, the prehydrolysis Kraft (PHK) process was developed during World War II in Germany; in this process, the prehydrolysis step introduced liberates organic acids from the wood, which in turn hydrolyze the hemicellulose to produce water-soluble carbohydrates. (Sixta, 2006) (Charles, 1963)

When the pulp is used for chemical conversion to produce regenerated fibers or cellulose derivatives, it is called a dissolving grade pulp. It represents around the 2 to 3 % of the total wood pulp production, and there has been a remarkable shift in the demand during the last few years, as can be observed in the figure 4 (Sixta H. , 2006) (Patrick, 2011).

The production is mainly done by acid sulfite cooking and prehydrolysis Kraft process, the former being the dominant system. Although the minor production of dissolving grade pulp compared to the paper grade pulp, there is a high demand for cellulose purity and reactivity which explains the "*advanced state of technology within the pulp industry*" (Sixta, 2006). As a result of this, new dissolving pulp processes are developed continuously (Sixta *et al.*, 2013).

Around 85-88% of the total dissolving pulp market is produced from wood-derived celluloses, with the remaining amount based on cotton linters. Table 1 shows a summary of the principal processes and products derived from dissolving pulps (Strunk, 2012)

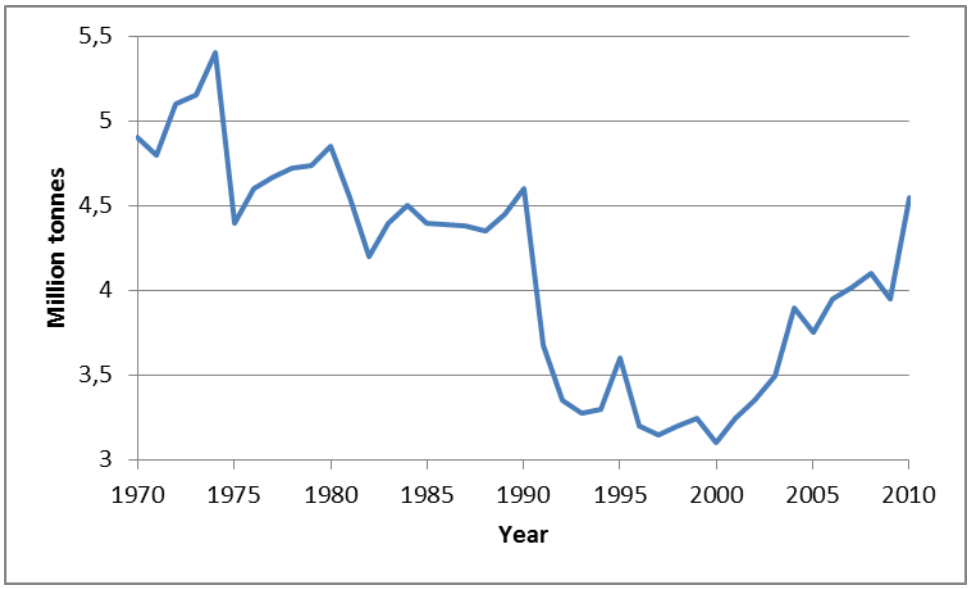

Figure 4. World dissolving pulp demand, 1970-2010, RISI, *Outlook For Global Dissolving Pulp Market*, 2011 (From Patrick, 2011)

Table 1 Some products and the corresponding process made with the dissolving pulp (Strunk, 2012)

Process	Product Segment	Products			
Etherification	Ethers	Food additives	Binders	Glues	
		Pharmacy	Oil drilling		
Nitration	Nitrates	Explosives	Lacquers	Celluloid	
Acetylation	Acetates	Filament	Tow	Mouldings	Films
Xanthation	Viscose	Filament	Rayon Staple	Cord and Industrial yarn	
		Cellophane films	Sponge products	Sausage casings	
Other Chemicals	$CuO + NH_4OH$	Cupra			
	$ZnCl_2$	Vulcan Fiber			
	NMMO	Lyocell / Tencell			
	H_2SO_4	Parchment			
	Resins	Paper laminates			
Other treatments	Mechanical + Grinding	MFC, NFC	Papers		
	Grinding	MCC			

In order to obtain a high quality dissolving grade pulp from softwoods and hardwoods, drastic conditions in pulping and bleaching operations must be applied, as even small amounts of impurities may affect several aspects of the outcome; e.g. residual impurities can affect the filterability of viscose. Even so, the complete removal of noncellulosic impurities would

be a very expensive and environmentally harmful task, and therefore the demands of the cellulose products are satisfied by adjusting the refining processes. (Sixta, 2006)

The main problem of dissolving pulps is to determine their suitability, which can be done only by simulating the conversion process to the final products. There are several methods for evaluating the pulp quality, and analytical methods are continuously developed to provide a rapid and reliable assessment of the quality of the dissolving pulp. (Sixta, 2006).

Usually, the characteristics demanded in dissolving pulp are that it should have high brightness, low amount of impurities such as resins, waxes and salts, and high alpha cellulose (which in turn helps to avoid the spinneret plugging and improves the spinning properties) (Steinmeier, 2004). Also, hemicelluloses in the dissolving pulp are detrimental to the properties of the cellulose acetate. E.g. glucomannans favor the formation of cellulose acetate haze, affect the measurement of viscose and contribute to poor behavior during filtration. Xylans affect mainly the color, and it must be taken into account that all dissolving pulps have higher xylan content in the surface layer than in the inner fiber wall. Physical properties of the pulp sheet are controlled, too: homogeneity of the fibres, density variations and moisture content may affect the activation of the cellulose (Steinmeier, 2004, Sixta, 2006).

Taking into account the two main processes of production of dissolving pulp, a brief review of the raw material and principal aspects that may be related to the reactivity of the pulps is made in the sections below.

2.2.2 Sulfite dissolving pulp

Comparatively, the main reason of today's existence of the sulfite process is the production of dissolving pulps. A higher pulp yield, better bleachability and higher reactivity are among the competitive advantages of this process versus prehydrolysis kraft pulp. (Sixta, 2006)

2.2.2.1. Raw material

Not all species are suitable for acid sulfite pulping, as it is the most sensitive process to the raw material. Many softwood species and some hardwood species may have problems in the production, such as high screenings and high residual lignin content, limited impregnation, etc. Among the hardwoods, low resin content and high density are desirable and therefore suitable for dissolving pulp production with the acid sulfite process. Different *Eucalyptus* species are suitable and used to produce dissolving pulps. In the case of pines or larches, modifications of the acid sulfite process with the introduction of previous stages with low acidity have been developed. (Sixta, 2006)

2.2.2.2. Process

The delignifying medium in the Sulfite Chemical Pulping is bisulfite, with common cations being calcium, magnesium, sodium and ammonium. The precipitation of calcium sulfite hinders the use of calcium (it can be used in the pH 1-2 ranges); this, among other reasons, has restricted the use of the acid calcium bisulfite process to a few pulp mills with complete by-product recovery. Nowadays, magnesium is the most common base used in sulfite pulping. (Sixta, 2006)

In the acid sulfite cooking, the cooking conditions and the chemical composition of the cooking chemicals almost determine the composition of the sulfite liquor spent, which in turn has influence on the reactions involved. The $[H^+]\cdot[HSO_3^-]$ affects the degree of delignification and the $[H^+]$ affects the rate of cellulose hydrolysis. (Sixta, 2006)

The reactions occurring in the cooking media can be classified in four types (Sixta, 2006):

- sulfonation, which is the basis of the delignification. The lignin is transformed into hydrophilic compounds in order to dissolve it in the cooking liquor.
- In the case of carbohydrates, and in particular hemicelluloses, hydrolysis is the main reaction, which also occurs in the bonds between lignin and carbohydrate. The hydrolysis of galactan under acidic conditions is faster than that of xylan, which in turn is faster

than the hydrolysis of mannan, with the hydrolysis of cellulose being the slowest. In the case of hardwoods the presence of glucuronic acid side chains diminishes the rate of hydrolysis of the xylans. (Figure 5)

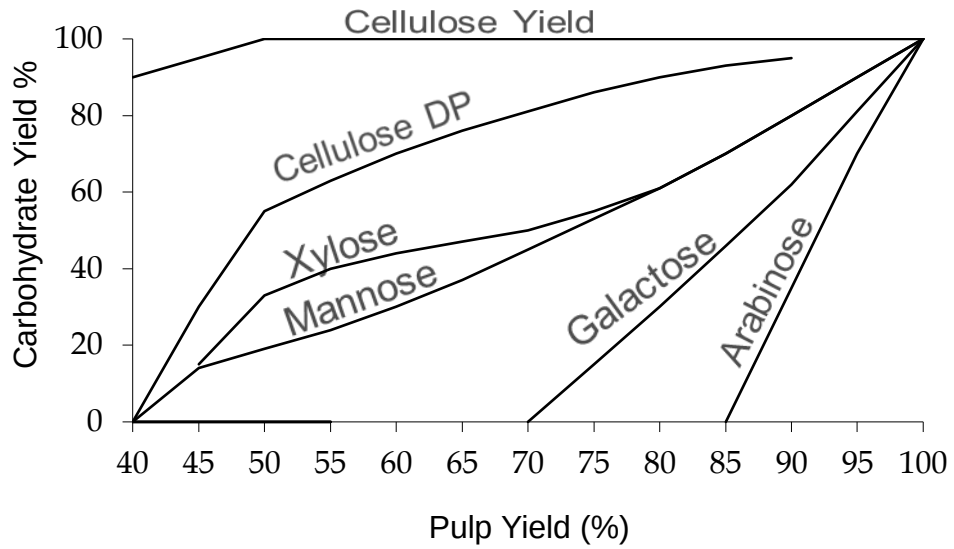

Figure 5. Carbohydrate degradation phenomena during sulfite cooking of spruce (from School of Environmental and Forest Sciences, College of the Environment, University of Washington)

On the other hand, the influence of the temperature can be observed in the comparison of carbohydrate degradation and delignification rate, the former being the most affected one.

- The third type of reaction is the condensation reactions, as can be seen in the Figure 6.

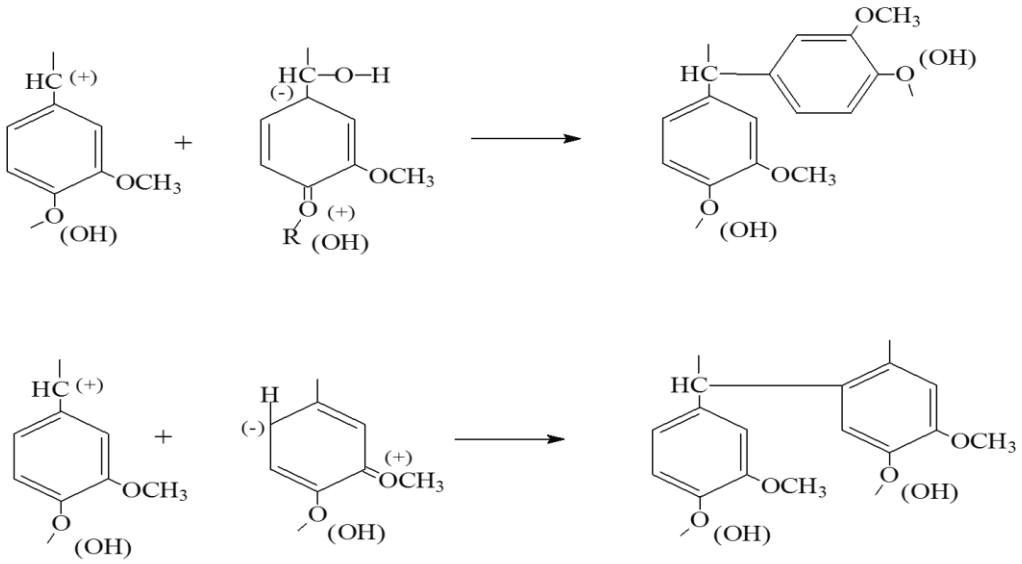

Figure 6. Condensation reactions of lignin. The top formula is a β-1 and the bottom lignin is a β-6 (from School of Environmental and Forest Sciences, College of the Environment, University of Washington)

- Also, redox processes occur in the cooking liquor.

2.2.3 PreHydrolysis Kraft (PHK)

2.2.3.1 Raw material

The more common wood species used in PHK pulps are *Eucalyptus*, beech, pine and mixed American hardwood, with more than 70 % of the pulps made from hardwood species. Aspen, birch, bamboo (Yang *et al.*, 2008), bagasse, salai and reed have also been used as dissolving pulps. Straw and other annual plants containing silica are not suitable because the silica cannot be removed sufficiently. (Sixta, 2006)

With regard to the chemical composition of some wood species, it was demonstrated that a high concentration of glucan has a positive

impact on yield and purity. Also, the residual hemicellulose content, as xylan and mannan, has a direct influence on pulp yield. As a consequence, if the intention of the process for dissolving pulp is focused on lowering the hemicellulose content, high yield losses are expected, as happens with spruce. (Sixta, 2006)

2.2.3.2 Process

When producing dissolving pulp using the Kraft process, a prehydrolysis step is introduced. This previous step usually involves the application of cold white liquor from the causticizing plant, heating-up and cooking. However, this traditional approach may affect the production of dissolving pulp negatively. The water used in prehydrolysis may form highly reactive intermediates, which in turn form compounds that deposit on any accessible surface. Also, the heating-up phases require large amounts of steam which leads to a prolongation of cooking and affects the economy of the process. (Sixta, 2006)

A single modification, *i.e* changing the prehydrolysis water with steam resulted in "*very poor delignification, bleachability and reactivity of the dissolving pulps*". A process to overcome this problem has been developed (Visbatch process) combining the advantages of displacement technology and steam prehydrolysis. In this process the prehydrolysis is finished by adding hot white liquor and hot black liquor to the digester, neutralizing organic acids and fragmentizing oligo and monosaccharides. Delignification starts with this extraction of the acidic constituents.

Following, the neutralization liquor is displaced from the bottom to the top, expelling acid-volatile substances. (Sixta, 2006)

In a modification of the Visbatch process (VisCBC), the parameters of the process are adjusted in order to minimize the variations in temperature, pressure and OH ion concentrations. This process avoids excessive cellulose degradation and levels the pulp quality, while guaranteeing a high delignification rate along with the prevention of the xylan reprecipitation. (Sixta, 2006)

In the prehydrolysis step and in the posterior neutralization, the majority of the hemicelluloses are degraded. The ensuing alkaline process steps contribute to the solubilization. To ensure the degradation of polysaccharides and to prevent a recondensation and precipitation of carbohydrates and lignin compounds, a sufficient supply of Effective Alkali is required. After the neutralization step, depending on the process, the hot displacement or cooking stage may be applied. Cellulose yield loss is highest during the neutralization and hot displacement, an effect that may be corrected by lowering the temperature level. (Sixta, 2006).

The conditions during prehydrolysis determine the purity of the dissolving pulp. The removal of xylan is dependent of the intensity of the prehydrolysis, (soft conditions are enough); also, this dependence reveals the presence of at least two types of xylans. However, lowering the xylan content below 2 % implies high yield losses and significant reductions in

viscosity. When the prehydrolysis conditions involve P-factors higher than 600, massive cellulose degradation is verified. The degradation of cellulose is also confirmed measuring the R-values (R-18 and R-10). (Sixta, 2006).

In the final phase of alkaline pulping dissolved hemicelluloses –as xylan- are taken back by the fibers from the solution. This, as said, may be affecting the manufacture of cellulose acetate, such as colour. (Sixta, 2006).

Another aspect of the PHK dissolving pulp production is the benefit of the integration with a bioethanol process. Bioethanol can be produced from cellulose and hemicelluloses by acid-catalyzed hydrolysis to mono-sugars, and fermenting them to ethanol. Ensuring that enough prehydrolyzate can be separated from the wood chips prior to Kraft pulping, the production of bioethanol can be done with several positive aspects. (Kautto *et al.*, 2010)

2.3 Cellulose acetate

2.3.1 History and uses

According to Rustemeyer (Rustemeyer, 2004), the first mention of cellulose acetate was in 1865, when Schützemberger synthesized it by heating cellulose and acetic anhydride. In 1879, it was discovered that, CA could be produced at room temperature with sulfuric acid as catalyst. Next, the first patents for cellulose triacetate were applied in 1894, and in the

following years the industry supported the investigation with generous resources but with poor results, due to several aspects affecting the economy of the cellulose acetate production. Finally, the commercial success arrived in 1904 and 1905, with the use of a mixture of di- and triacetate in the field of coating for airplanes. In the years previous to World War I, and even during the war, the cellulose diacetate was a highly demanded product and the industry was prosperous (Rustemeyer, 2004).

After World War I, the demand for aviation applications was reduced, so new uses of the cellulose acetate were investigated. It was in the textile market that the cellulose acetate industry found a rapid growth, where the Dreyfus brothers made the first merchandizing of the spinning of cellulose acetate fibers; this growth continued until the 50's and 60's, when it slowed down, with a peak in 1971 (Steinmann, 1998). On the other hand, in1952 cellulose acetate was introduced in cigarette filters, where it found a significant success. Nowadays, plastic applications of cellulose acetate are highly demanded, in items such as tool handles, toothbrush handles, toys, etc. Photographic film and professional motion picture films are also made of cellulose acetate, as well other usages, e.g. LCD flat screens. (Rustemeyer, 2004; Steinmann, 1998). Unconventional applications of the cellulose acetate are continuously found, as nanocomposites of cellulose acetate –which have been studied with positive results (Suetsugu *et al.*, 2009)- or as an adsorbent for selective recovery of metals (Yang *et al.*, 2014).

The cellulose acetates (CAs) are among the most important and widely used cellulose derivatives (Figure 7). The fact that CAs are biocompatible and biodegradable, and that they are derived from a renewable source, represents a competitive advantage versus synthetic fibers, in particular those derived from petroleum; eventually, the anticipated lack of petroleum makes cellulosic fibers more attractive. (Steinmann, 1998).

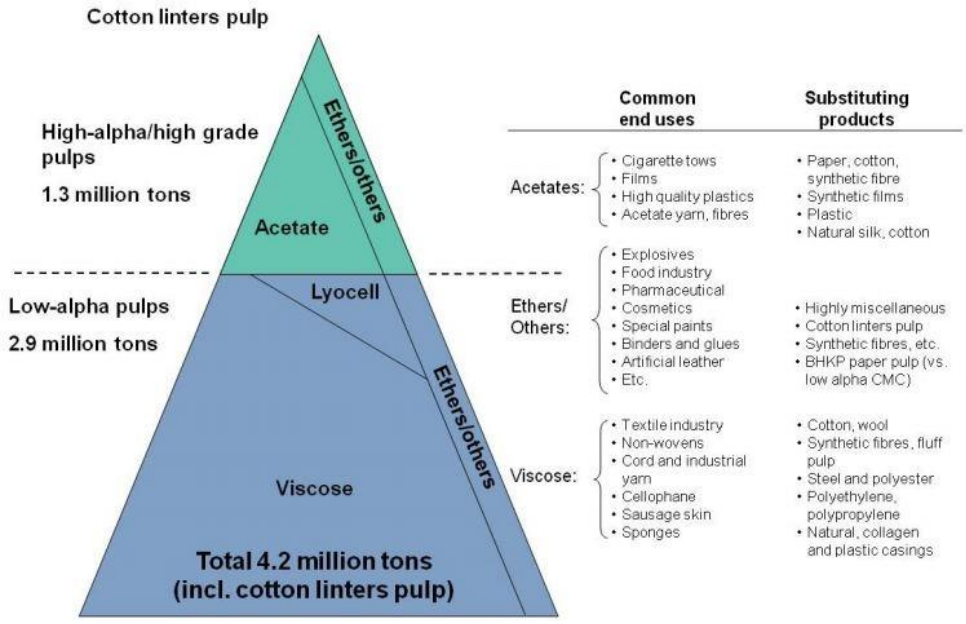

Figure 7. Dissolving pulp end use segments, source *Pöyry* from Flickinger *et al*. (2011)

There are several characteristics that make the cellulose acetate fibers better than others: according to Steinmann (1998), fabrics made of cellulose acetate have an "*excellent hand, dye to brilliant, attractive shades, and are soft and comfortable*", the "*sparkling clarity*" of cellulose

acetate plastics and films unmatched by any other polymer; they also have an excellent performance in cigarette smoke filters. (Steinmann, 1998)

2.3.2 Cellulose acetylation

The industrial acetylation of cellulose is a heterogeneous reaction, and therefore it is influenced by the accessibility of the cellulose molecules and also by the propensity of the individual cellulose crystallites to acetylate. Macro and micro morphology of the cellulose fibers affect the course and mechanism of the reaction with a mutual interaction between these aspects. The penetration of the reagent and the cleavage of hydrogen bonds are the decisive parameters. To facilitate accessibility, the fiber bundles are separated into individual fibers by gentle mechanical treatment, followed by a thorough impregnation in pure acetic acid. (Sassi & Chanzy, 1995) (Klemm *et al.*, 1998)

The reaction of cellulose to cellulose triacetate may be schematically seen in the Figure 8.

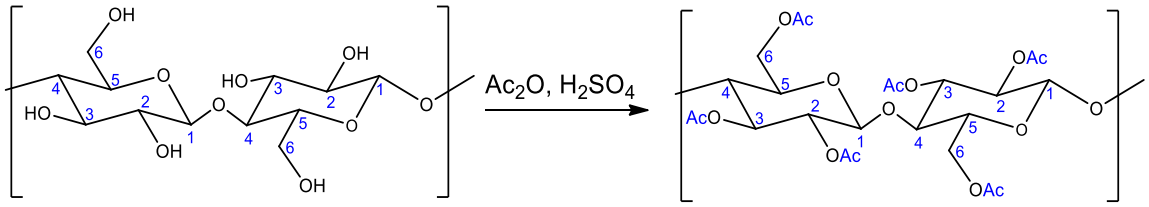

Figure 8. Schematic transformation of cellulose to triacetate cellulose with acetic anhydride, using sulfuric acid as catalyst

The formation of cellulose sulfate is the first step in the mechanism of acetylation with sulfuric acid. In the next step, cellulose is trans-

esterified from sulfate to acetate in the presence of acetic anhydride. Several studies have shown that in the absence of an activating acid, there is little or no acetylation (Akim, 1967) (Malm *et al.*, 1946). Nevertheless, different studies of the acetylation under atypical conditions have been carried out, such as a solvent-free acetylation with acetic anhydride using iodine as a catalyst (Li *et al.*, 2009) (Cheng *et al.*, 2010)

Two mechanisms for acetylation are more or less accepted for the acetylation of cellulose with sulfuric acid as catalyst (Steinmeier, 2004) (Steinmann, 1998). A first step common to both involves the formation of cellulose sulfate

$$\text{Cell-OH} + H_2SO_4 + Ac_2O \longrightarrow \text{Cell-O-}SO_2OH + 2\ \text{AcOH}$$

In the first mechanism the sulfate of cellulose sulfate cedes a proton to the acetic anhydride, to finally form the cellulose acetate (Figure 9).

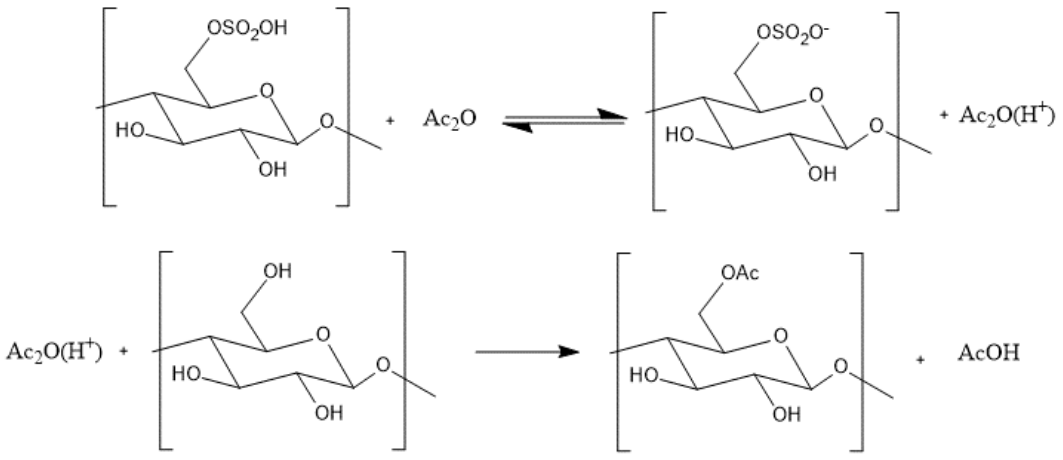

Figure 9. First mechanism proposed of the acetylation

In the second mechanism, a cellulose acetosulfate may be formed previously (Figure 10).

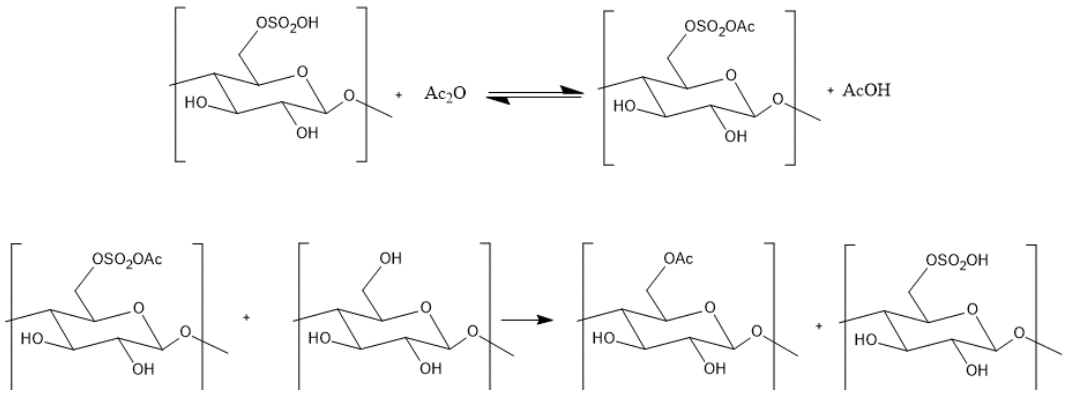

Figure 10. Second mechanism proposed of the acetylation

Esterification is an equilibrium reaction, meaning that it also involves hydrolysis. The presence of water in the system promotes that hydrolysis, which in turn is prevented by an excess of acetic anhydride (Steinmeier, 2004).

2.3.3 Industrial production

The Acetic Acid Process is the modern industrial process for cellulose acetylation manufacturing. A schematic diagram of the cellulose acetate process is shown in Figure 11. In this process, the acetylation of cellulose is carried out by using acetic anhydride and an acid catalyst. The acid catalyst (usually sulfuric acid) is one of the variables of the acetylation process, where it can be added in low amounts, as in the Drum or

Rhodiaceta process (less than 2% catalyst by weight), in medium amounts, 4-8% catalyst, or as in the Dreyfus process, 11-15% catalyst. (Steinmeier, 2004; Steinmann, 1998). In the medium and high catalyst processes the sulfuric acid acts also as a solvating agent, which enhances the solubility in the final (triacetate) stage; nevertheless, these levels affect the viscosity of cellulose and cellulose acetate, promoting a faster degradation. (Steinmeier, 2004)

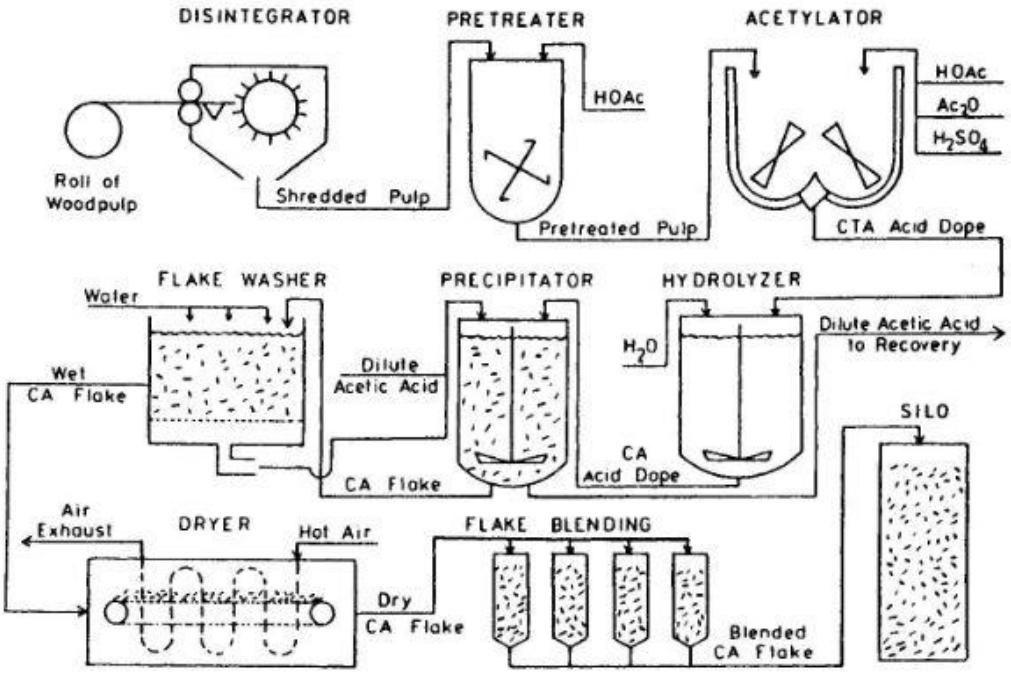

Figure 11. Cellulose Acetate process, from Steinmann (1998)

In the acetylation of cellulose, the activation of the cellulose is a very important step. The target of the activation is that all cellulose hydroxyl groups have a homogeneous accessibility, considering for example that cellulose has a non-crystalline and crystalline phases

organized in microfibrils, where the accessibility in the amorphous phases is allegedly better than in the crystalline phases (Steinmeier, 2004). As said, the greater the accessibility, the easier the reactants reach the interior of the cellulose. Therefore, the first step in the activation of the wood pulp is to disintegrate it mechanically and to open the cellulose fibres by swelling (Steinmeier, 2004).

In addition to this, a homogeneous distribution of the catalyst has to be achieved. Therefore, another step involved in the activation of cellulose is to mix thoroughly the sulfuric acid with the cellulose and acetic acid system, where cellulose sulfate ester is partially formed. Although to achieve the best activation it is preferable for the cellulose to be completely dissolved, i.e. to acetylate in a homogeneous reaction, in the industry none of the solvents that are capable of this are used, mostly because of the economic reasons (Steinmeier, 2004).

The final step in the industrial acetylation includes the acetic hydrolysis of cellulose triacetate with water. When the desired DS is reached –which can be followed by kinetic data or by measuring the acetyl value of the acetic dope– the reaction is stopped by the addition of salts (Steinmeier, 2004)

3. EXPERIMENTAL PART

The experimental part of this Master's Thesis work consists of a comparison of acetylation kinetics between different pulp samples (after optimization of the acetylation procedure). Structural aspects of the pulps, as the Molar Mass Distribution (MMD) and the Carbohydrate composition were studied.

Also the accessibility was studied by phosphorus NMR, which is revised in the Appendix 1, due to unsatisfactory results.

3.1 Samples

Commercial pulp samples from different origins.

Table 2. Samples analyzed.

Pulp Sample Identification	Raw material	Industrial Process	Filter value	Particle (ppm)
Bahia	Hardwood - Eucalyptus	PHK	582	2.3
Saiccor	Hardwood – Eucalyptus	Sulfite	430	4.7
Domsjö	Softwood – Spruce	Sulfite	291	20.3
Paskov paper	Softwood - Spruce	Sulfite	316	7.9
Botnia paper[a]	Hardwood – Birch	Kraft	-	-
Softwood FE2035	Softwood	-	64	82

[a] Although Botnia is now Metsa Fiber, it will be referred in this work as Botnia paper, since it was the original identification of the pulp.

3.2 Methods

3.2.1 Method development

Since the introduction of commercial-scale manufacture of cellulose acetate in 1905 (Rustemeyer, 2004), several studies on the acetylation mechanism and kinetics have been conducted over the years. Quite recently, Wollboldt (2011) optimized the precipitation conditions of the resulting cellulose acetate based in a procedure developed by Obermaier (Obermaier, 2001), which has been adopted. Also, the procedure used to obtain full cellulose/catalyst contact has been assured, as described by Griskey (1965). Besides, this study confirmed the influence of the concentration of the activating acid (Malm *et al.*, 1946) on the acetylation rate. Therefore, the percentage of sulfuric acid in the activating acid was adjusted so it would be the same in all the samples. Nevertheless, some assessments were available in the higher level (0.6% sulfuric acid in the activating acid), that are reported in this work to verify the influence of the catalyst. The study also showed that the volume of the aliquot taken from the reaction vessel affected the reaction rate, as the ratios of reactants could be changed. In this case the amounts of the reactants were augmented and the aliquot was reduced to diminish this possible effect.

Finally, it should be mentioned that in both assessments of DS by HPLC and FT-IR, the existence of a degradation of the different Cellulose Acetates could have been detrimental to this study, as some measurements made some time later yield uneven results; they were not

considered in this work. A review made by Puls *et al.* (2011) enumerates various causes for the degradation of cellulose acetates.

3.2.2 Acetylation

After cutting 7.5 g of the pulp (o.d. weight) into small pieces, a 350 mL volume of glacial acetic acid was added. Then, the pulp was disintegrated by vigorous mechanical stirring. The suspension was filtrated; the wet pulp cake was put in a screw-capped Duran bottle and glacial acetic acid was added until the weight was 82.5 g (pulp and acetic acid). 37.5 mL of the activation acid (0.3 % sulfuric acid in acetic acid) was added and shaken for 2 hours. After the activated pulp was taken to a target temperature (25 °C or 30 °C) in a temperature-controlled glass reaction vessel equipped with a magnetic stirrer, 75 mL of acetic anhydride was added to trigger the reaction. Small aliquots were taken at specified times and poured into a 100-mL sodium acetate solution (40 g/L) to stop the reaction. This mixture was stirred for 30 minutes, filtered and washed. Finally, it was dried at 50 °C in a vacuum oven.

3.2.3 Determination of the Degree of Substitution by HPLC

A 40 - 50 mg sample of the previously dried cellulose acetate was filled into a screw-capped 10 mL vial. 0.5 mL of 72.2 % sulfuric acid was

added under vigorous stirring and the closed vial was heated 3 – 3.5 h in a water bath at 25 °C (with vigorous stirring at 15 minutes and after 1 hour). The vial with a magnetic stirrer was heated at 110 °C in a heating block, finishing the reaction after 90 minutes by cooling the vial in a water bath. The content of the vial was diluted in a volumetric flask (200 - 250 mL). The resulting acetic acid was determined using a Dionex Ultimate 3000 HPLC, flow rate 0.6 mL/min, Acclaim® OA column, diode array detector, and processing the signal with software Chromeleon. The quantified combined acetic acid was calculated as the Degree of Substitution according to Equations 1 and 2:

$$\frac{Combined\ acetic\ acid\ (\%)}{1.395} = Acetyl\ content\ (\%) \qquad \text{Equation 1}$$

$$DS = \frac{3.86 \times Acetyl\ content\ (\%)}{102.4 - Acetyl\ content\ (\%)} \qquad \text{Equation 2}$$

Table 3 shows the corresponding values and Figure 12 is the graphical representation. A reference cellulose acetate from Sigma-Aldrich with 39.7 wt % acetyl was used to verify the method.

Table 3. Correspondence between the different terms used (from Comprehensive Cellulose Chemistry, Klemm et al, 1998)

Degree of Substitution	Acetyl content (%)	Combined acetic acid (%)
0	0	0
0.50	11.7	16.3
0.75	16.7	23.2
1.00	21.1	29.4
1.50	28.7	40.0
2.00	35.0	48.8
2.50	40.0	56.2
3.00	44.8	62.5

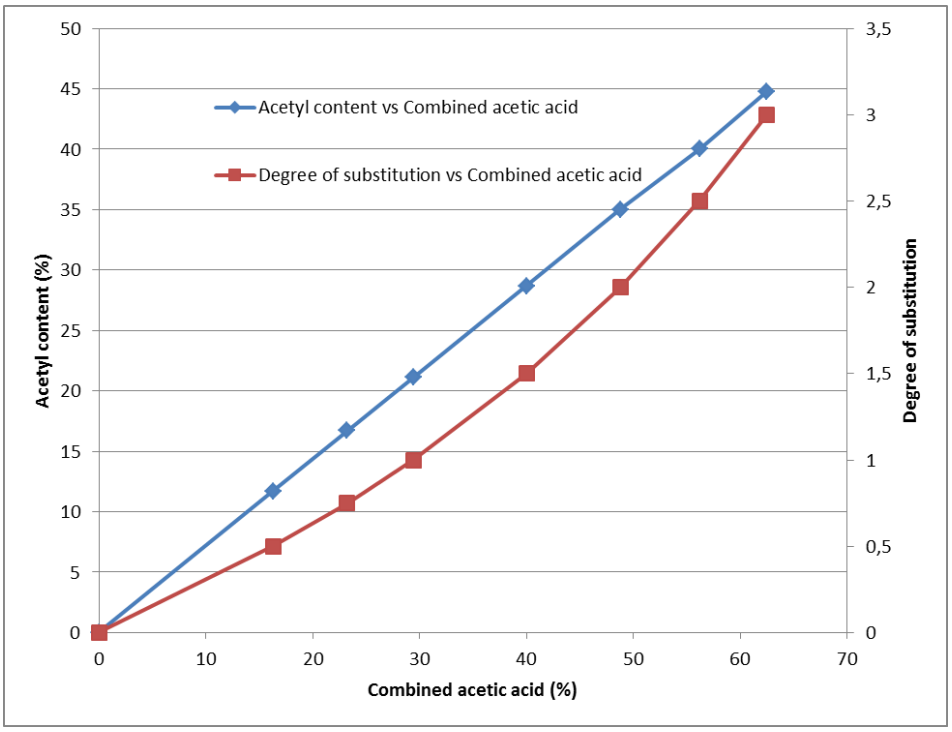

Figure 12. Relationship between the different terms applied to the degree of substitution of cellulose.

3.2.4 Determination of the Degree of Substitution by FT-IR

A calibration was done by plotting the absorbance ratio at the height of the C=O stretching band (1750 cm^{-1}) to the absorbance at the O-H stretching band height (3400 cm^{-1}) versus the degree of substitution determined by HPLC of acetylated cellulose samples, performing a Fourier Transform infrared spectroscopy with photoacoustic detection (FTIR-PAS). The equipment was a Bio-Rad FTS 6000 spectrometer with a MTEC 300 photoacoustic detector (PAS) at a constant mirror velocity of 5 KHz, 1.2 kHz filter and 8 cm^{-1} resolution. The acetylated sample was put into a detection cell placed in the PAS detector after having collected the background spectrum. A minimum of 200 scans were collected for each sample and the resulting spectra were normalized to 1060 cm^{-1}.

3.2.5 Molar Mass Distribution

The molar mass distribution of pulps was determined by gel permeation chromatography (GPC). About 500 mg of the pulp sample was accurately weighed in a sample bottle. Prior to their analyses, the samples were activated by a water – acetone – N, N-dimethylacetamide (DMAc) sequence. Approximately 50 ml of MilliQ-water were added to the pulp sample. The samples were kept in water under gentle stirring for more than 6 hours. The water-activated sample was filtered and rinsed with acetone before it was transferred to a dry bottle where acetone was added

and stirred for more than 2 hours. After removing the acetone by filtration, the residue was immersed in 20 – 40 ml DMAc and kept there for at least 16 hours. The activated samples (50 mg each) were dissolved in 90 g/L lithium chloride (LiCl) containing DMAc at room temperature and under gentle stirring. The samples were then diluted to 9 g/L LiCl with DMAc, filtered through 0.2 µm syringe filters, and analyzed in a Dionex Ultimate 3000 system equipped with a guard column, four analytical columns (PLgel Mixed-A, 7.5 x 300 mm) and RI-detection (Shodex RI-101). Flow rate and temperature were 0.75 ml/min and 25 °C, respectively. Narrow pullulan standards (343 Da - 2500 kDa, PSS GmbH) were used to calibrate the system. The molar masses (MM) of the pullulan standards were modified to match those of cellulose ($MM_{cellulose} = q \cdot MM^{p}_{pullulan}$), following recommendations from literature (Berggren, Berthold, Sjöholm, & Lindström, 2003). The coefficients $q = 12.19$ and $p = 0.78$ were found by a least-squares method, using the data published in their report.

3.2.6 Carbohydrate analysis

The chemical composition of the pulps was determined after a total hydrolysis, applying the analytical method NREL/TP-510-42618. The obtained monosaccharides were determined by HPAEC-PAD in a Dionex ICS-3000 System.

3.3 Acetylation Kinetics

2.3.1 Model 1

Under the given conditions of acetylation, a first order (or pseudo first order) reaction can be assumed, since acetic anhydride was added in excess. Therefore, :

$$-\frac{d(OH)}{dt} = -k \cdot [OH] \qquad \text{Equation 3}$$

Considering the three hydroxyl groups available per Anhydroglucose Unit (AHG) (C-2, C-3 and C-6), the integrated form at t_0=0 and $[OH]_0$=3:

$$\ln \frac{(OH)}{3} = -k \cdot t \qquad \text{Equation 4}$$

Therefore, the decrease of hydroxyl groups can be described with

$$[OH] = 3 \cdot e^{-k \cdot t} \qquad \text{Equation 5}$$

3.3.2 Model 2

A second kinetic model for the acetylation reaction was tested, assuming different reactivities of the OH groups. In this case, the OH groups are divided in two fractions, one slowly reacting (OH_s with a rate constant k_s) and one fast reacting (OH_f with k_f). Both fractions react in a first order homogeneus reaction, where the rate of the acetylation is expressed as the addition of the two reactions.

So, for the slow fraction

$$-\frac{d(OH)_s}{dt} = -k \cdot [OH]_s \qquad \text{Equation 6}$$

$$[OH]_s = [OH]_{s\,o} \cdot e^{-k \cdot t} \qquad \text{Equation 7}$$

For the fast fraction

$$-\frac{d(OH)_f}{dt} = -k \cdot [OH]_f \qquad \text{Equation 8}$$

$$[OH]_f = [OH]_{f\,o} \cdot e^{-k \cdot t} \qquad \text{Equation 9}$$

With the implication that

$$[OH]_{total} = [OH]_s + [OH]_f = 3 \text{ for initial conditions} \qquad \text{Equation 10}$$

And considering a new parameter A, representing the fraction of 'slow' OH-groups to the total OH-groups:

$$A = \frac{[OH]_s}{[OH]_{total}} \qquad \text{Equation 11}$$

and therefore

$$1 - A = \frac{[OH]_f}{[OH]_{total}} \qquad \text{Equation 12}$$

The decrease of hydroxyl groups can be expressed as:

$$[OH] = 3 \cdot \left[A \cdot Exp(-k_s \cdot t) + (1 - A) \cdot Exp\left(-k_f \cdot t\right)\right] \qquad \text{Equation 13}$$

4. RESULTS AND DISCUSSION

4.1 Molar Mass Distribution

Figure 13 shows the Molar Mass distributions of the different pulps. In favor of greater clarity, the individual results are presented in Figure 14 to 19, also showing the two different ways of evaluating the Size Exclusion Chromatography (SEC) results. In the traditional way, the molar masses are expressed as Pullulan equivalents, while in the second way the molar masses are expressed as cellulose equivalents. As shown in the Experimental Part, an empirical equation was used to transfer the Pullulan molar mass equivalents to the cellulose molar mass equivalents. The latter were determined by Multi Angle Laser Light Scattering (MALLS) detection. Table 4 shows the numerical calculations of the different parameters derived from this test, and Table 5 shows the polydispersity.

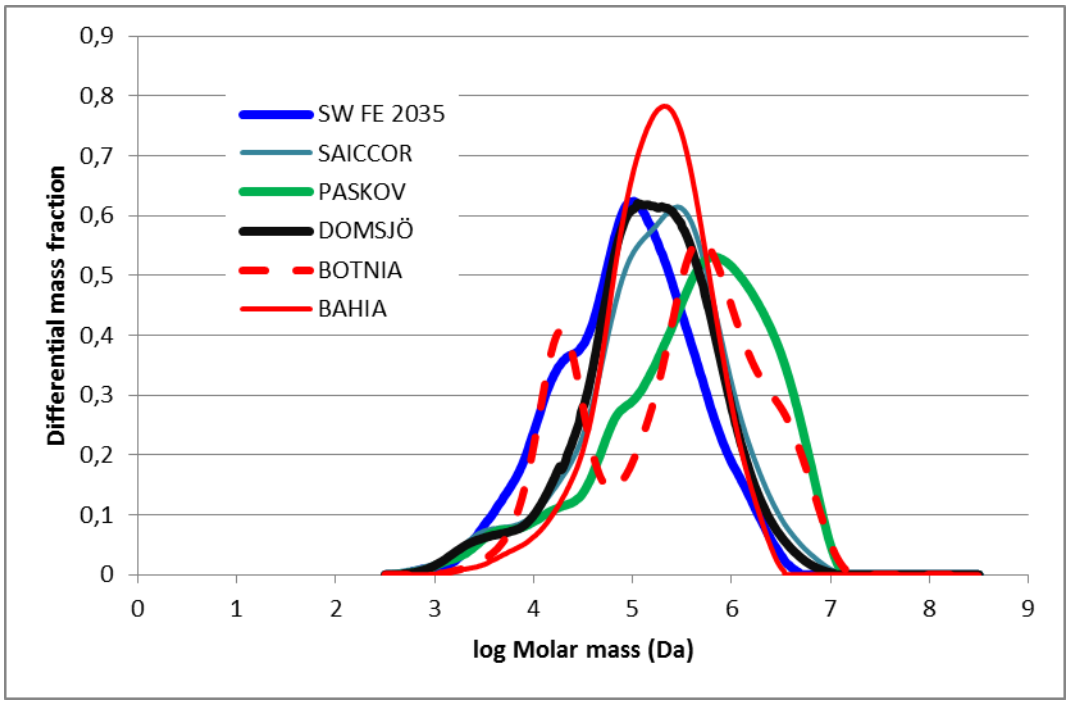

Figure 13. Molar mass distributions of the different pulps studied. SEC-MALLS has been used to obtain the results

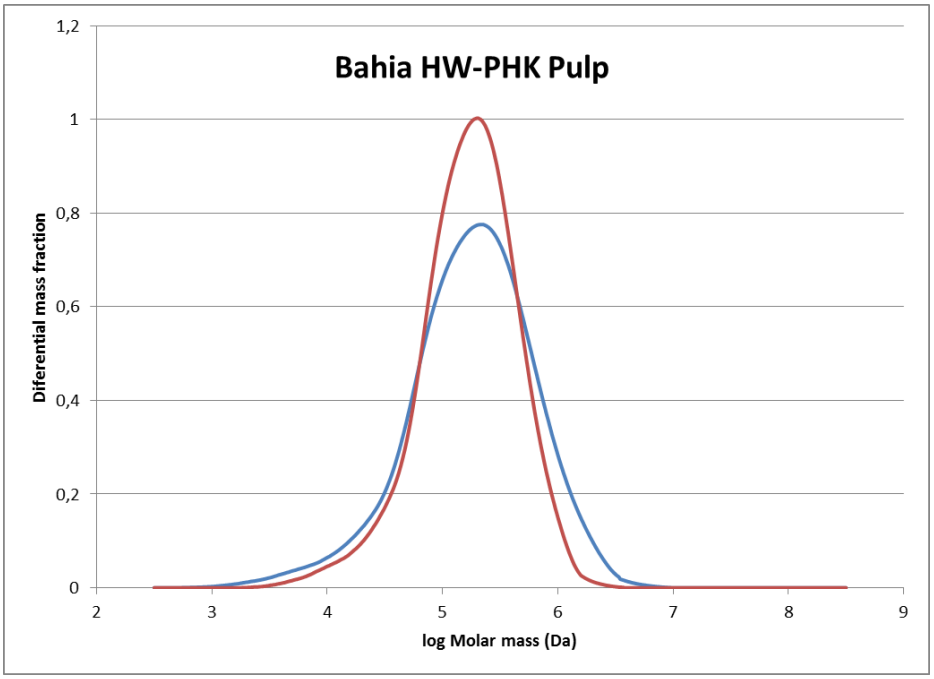

Figure 14. Molar Mass Distribution of the Bahia HW-PHK pulp. The red curve represents the data obtained with SEC-MALLS, while the blue curve is the result relative to Pullulan standards

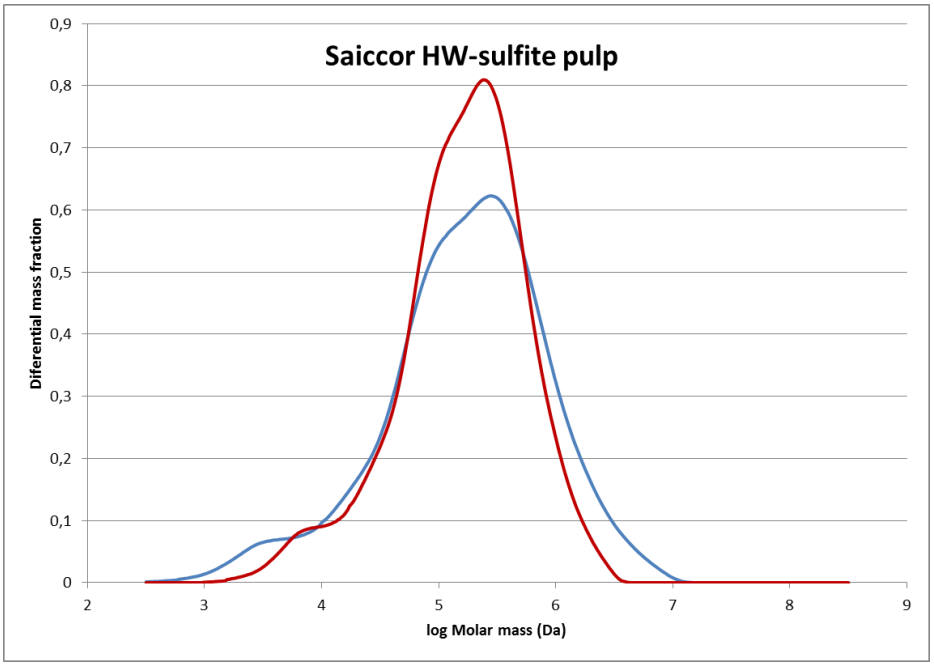

Figure 15. Molar Mass Distribution of the Saiccor HW-sulfite pulp. The red curve represents the data obtained with SEC-MALLS; the blue curve is the result relative to Pullulan standards

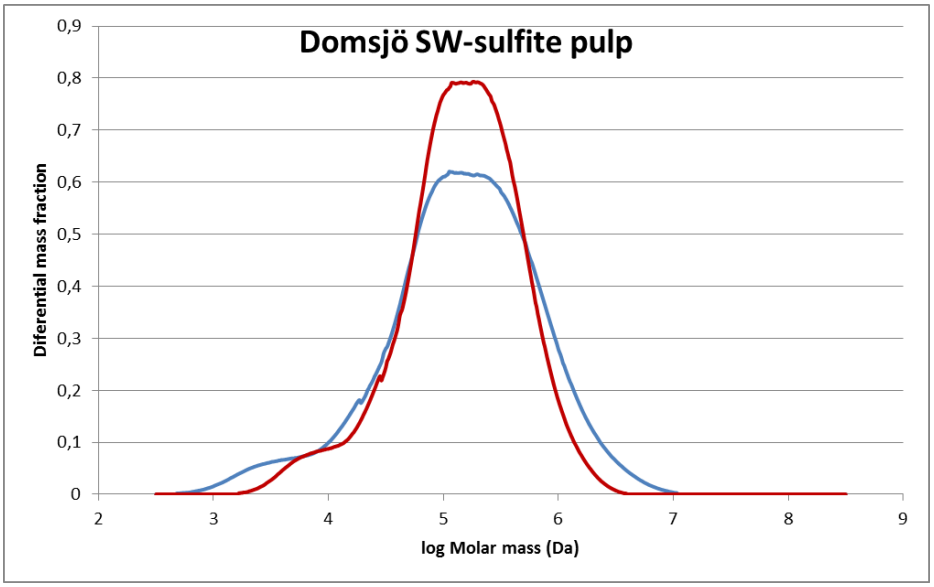

Figure 16. Molar Mass Distribution of the Domsjö SW-sulfite pulp. The red curve represents the data obtained with SEC-MALLS, the blue curve is the result relative to Pullulan standards.

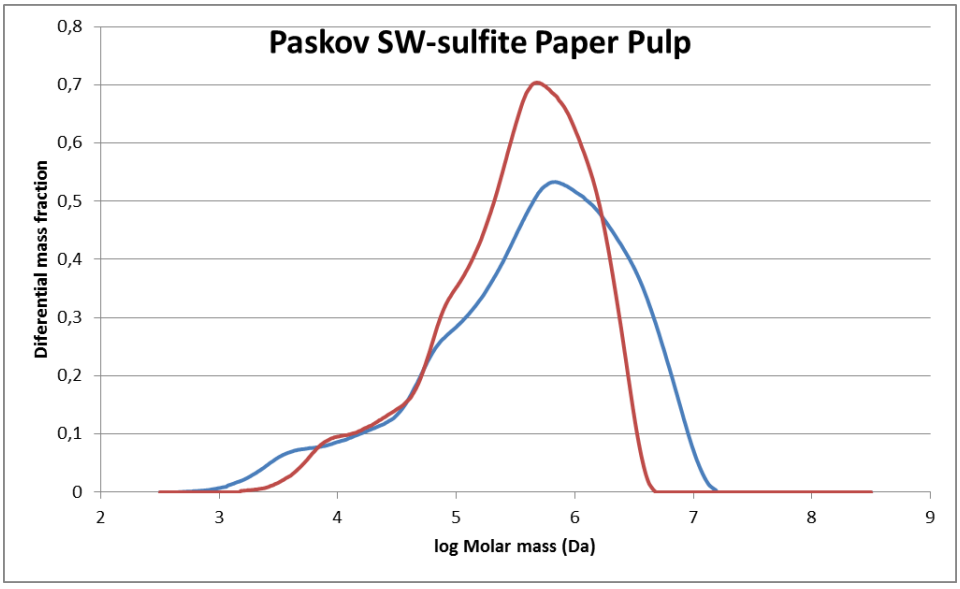

Figure 17. Molar Mass Distribution of the Paskov SW-sulfite paper pulp. The red curve represents the data obtained with SEC-MALLS, the blue curve is the result relative to Pullulan standards.

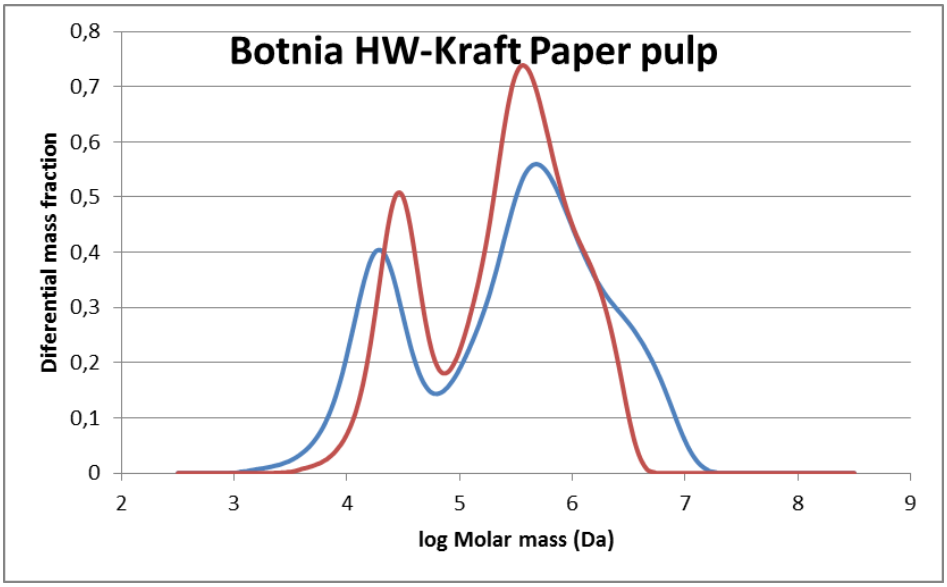

Figure 18. Molar Mass Distribution of the Botnia HW-Kraft paper pulp. The red curve represents the data obtained with SEC-MALLS, the blue curve is the result relative to Pullulan standards.

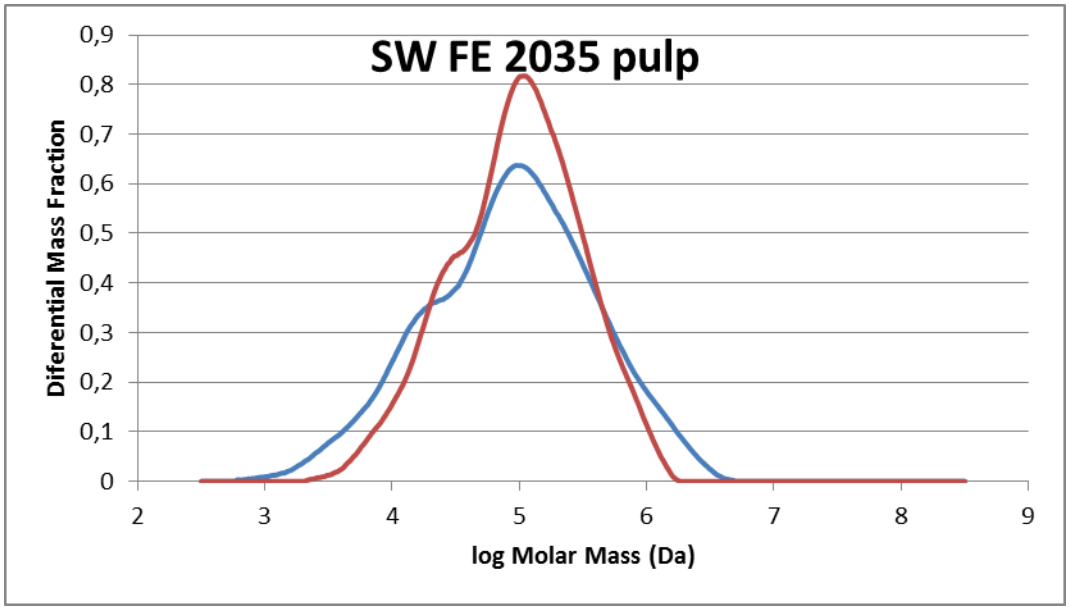

Figure 19. Molar Mass Distribution of the Softwood FE 2035 (without data about its process). The red curve represents the data obtained with SEC-MALLS, the blue curve is the result relative to Pullulan standards.

Table 4. Molar Mass Distributions of the pulps (relative MALLS)

Pulp	Mn (10^3)	Mw (10^3)	Mz (10^3)	Mz+1 (10^3)	DP50	DP100	DP2000
Bahia HW-PHK	91	250	495	830	0,007	0,023	0,246
Saiccor HW-sulfite	57	299	763	1365	0,029	0,058	0,292
Domsjö SW-sulfite	57	257	650	1206	0,028	0,056	0,246
Paskov SW-sulfite paper	79	639	1399	1981	0,023	0,052	0,552
Botnia HW-Kraft paper	72	518	1340	2019	0,007	0,041	0,464
Softwood FE2035	45	173	427	698	0,024	0,081	0,149

Table 5. Polydispersity calculated as Mw/Mn

	Polydispersity index
Bahia HW PHK	2.7
Saiccor HW sulfite	5.2
Domsjö SW sulfite	4.5
Paskov SW sulfite paper	8.1
Botnia HW Kraft paper	7.2
Softwood FE2035	3.8

As expected, the molecular distribution of the pulp produced by the PHK process (Bahia Pulp) is more uniform than that produced by the acid sulfite cooking process, which typically shows a multimodal distribution. In the case of the Softwood FE2035, where there was no information about the process or raw material available, it can be inferred from the MMD that it was produced by the acid sulfite process. However, this pulp may have undergone a modified process in order to improve the reactivity, as will be discussed in the further sections. Considering only the molar mass distribution, it can be suspected that this pulp experienced the removal of short chain-material. A process that may match with these characteristics could be the cold caustic extraction (CCE) (Sixta, 2006). In support of this presumption, the low filter value and the high particle content in the spinning dope –as shown in Table 2- is characteristic of pulps produced by CCE (Schild & Sixta, 2011).

Comparing two acid sulfite pulps with different raw material –i.e. one with hardwood (Saiccor pulp) and the other with softwood (Domsjö pulp)- the differences are minor. However, based on the numerical values corresponding to the degree of polymerization shown in Table 4 it is clear that the hardwood pulp has a higher proportion of long chains (expressed as the weight fraction of DP> 2000).

The MMD of the Botnia Pulp (now Metsä Fiber), which is a Kraft paper pulp, shows the typical bimodal character with its minimum between the cellulose and hemicellulose content. This will be also represented in the carbohydrate composition and in the reactivity as studied.

4.2 Carbohydrate composition of the different pulps studied

Table 6. Carbohydrate composition

Pulp	Type	Glucose	Xylose	Mannose
Bahia HW PHK	Hardwood	95.8	2.1	-
Saiccor HW sulfite	Hardwood	92.0	1.4	-
Domsjö SW sulfite	Softwood	97.7	0.4	0.9
Paskov SW sulfite paper	Softwood	85.2	3.2	5.4
Botnia HW Kraft paper	Hardwood	74.4	23.5	-
Softwood FE2035	Softwood	88.6	5.1	3.5

The results of the carbohydrate composition of the different pulps studied reflect the raw material used and the process involved, as shown in Table 6. All the softwood pulps appear to have mannose as sugar monomer of their hemicelluloses, an element that is not present in the hardwood pulps. It also shows the purification process used to produce a dissolving pulp applied to the Bahia, Saiccor and Domsjö pulps, with a higher amount of cellulose.

The Botnia paper pulp has the highest amount of hemicelluloses, which explains the previously discussed MMD. Of course, this (the low cellulose content) is explained by the fact that this is a paper pulp that does not require high cellulose contents. The Paskov pulp was also a paper pulp, and therefore its behavior was similar.

The higher percentage of cellulose in the PHK pulp was expected, and it could be suggested that purity may influence reactivity, at least at baseline conditions (see the kinetic model discussed next). However, although the values for the PHK pulp are reasonable, in the case of the Saiccor HW-sulfite pulp the xylan content is questionable. Typical values for the sulfite pulps lie around 3-4 % (Christov et al., 2000; Sixta, 2006), thus, this result should be revised in future work.

4.3 Acetylation kinetics measured by HPLC

4.3.1 PHK and Acid Sulfite Pulps (Bahia and Saiccor)

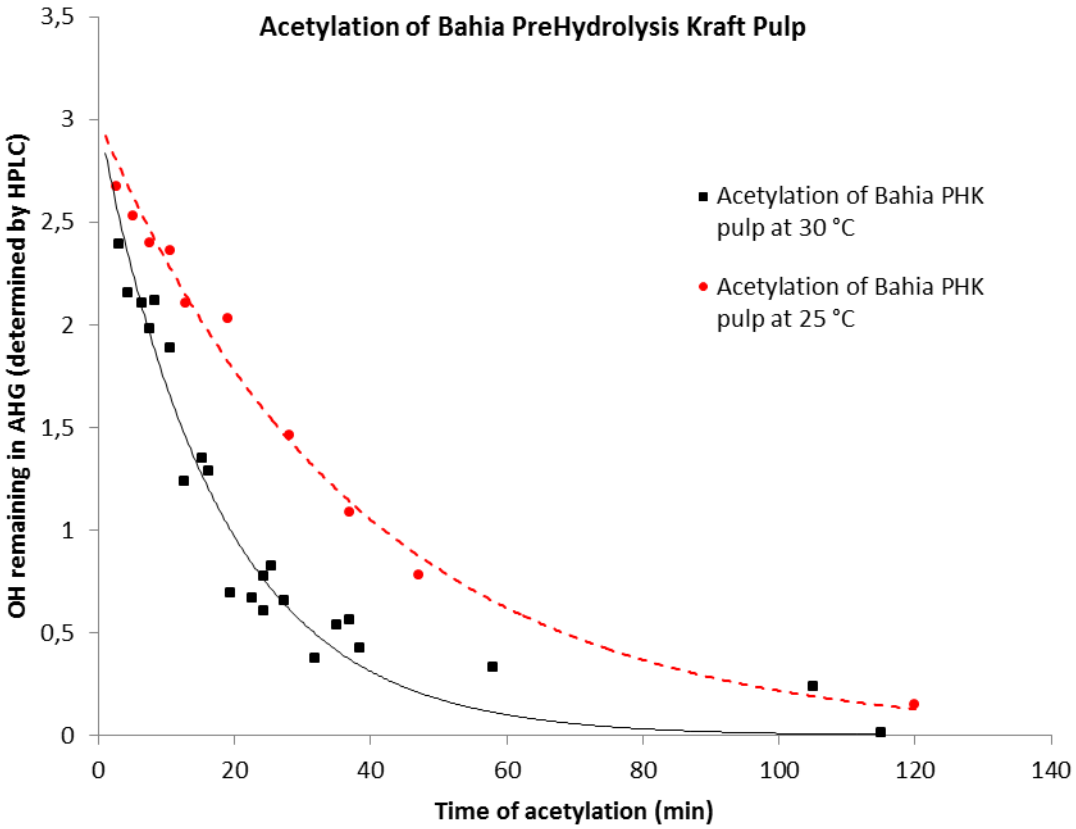

Figure 20. OH remaining in the AHG unit vs time of acetylation for the Pre-Hydrolysis Kraft Pulp at two different temperatures (25 °C and 30 °C)

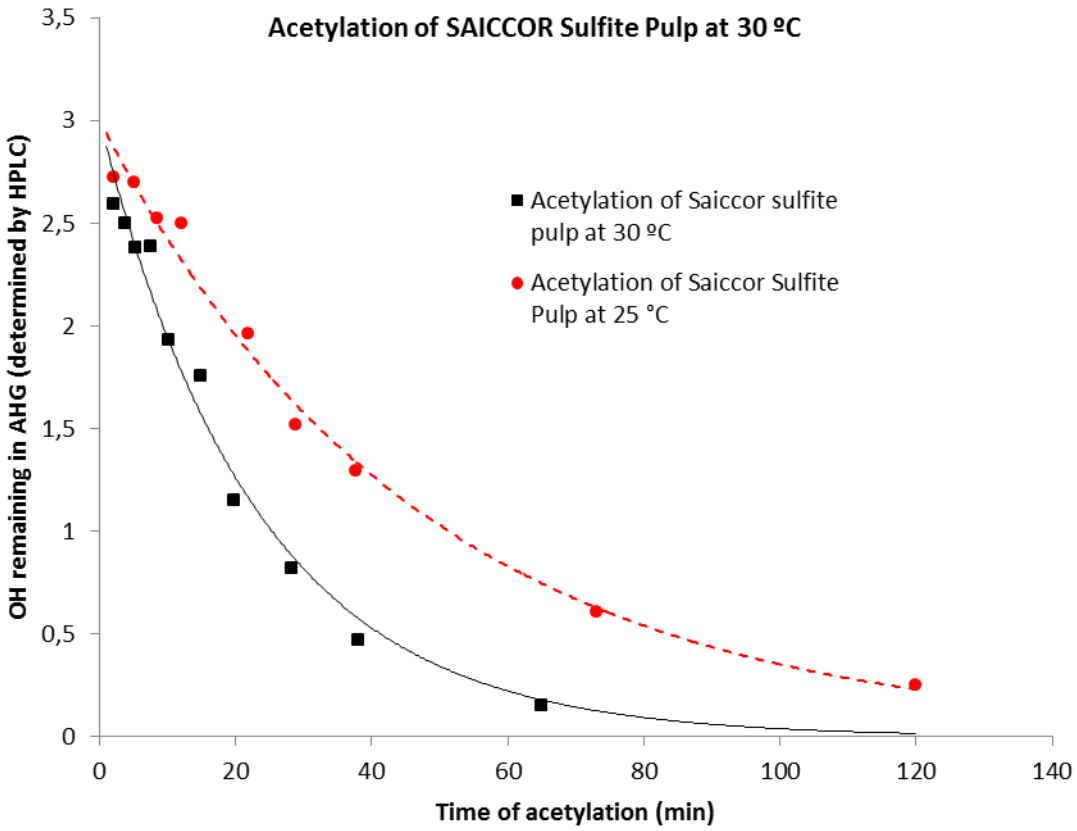

Figure 21. OH remaining in the AHG unit vs time of acetylation for the Saiccor Sulfite Pulp at two different temperatures (25 °C and 30 °C)

Figure 20 and Figure 21 show the reaction profiles for two Eucalyptus pulps, the Bahia PHK pulp and the Saiccor sulfite pulp towards acetylation for the temperatures tested, i.e., 25 °C and 30 °C. In both figures, the lines represent the non-linear curve fit, using Equation 5. Table 7 presents the kinetic constants calculated for each reaction. As expected, the speed of reaction (i.e. the reactivity) for the pulps increases as temperature increases. It becomes apparent that the increase in the two pulps is of similar order, meaning that the constant at 30 °C is almost twice

the constant at 25 °C. A duplication of the rate constants within a 5-degree range is consistent with the presence of the catalyst, and hence it is a minor indicator of the accuracy of the method. Also logical are the error values for the kinetic constants, where the standard errors for the lower temperature are lower than the errors at higher temperatures (0.0011 and 0.0010 min^{-1} at 25 °C *versus* 0.0023 for both pulps at 30 °C). This effect should be attributed to a more controlled reaction, where similar values can be interpreted as indicators of the precision of the method. The values of the activation energy shown in Table 7 are only rough estimates, because they were calculated on the basis of just two temperature levels; the higher values observed in this work compared to those in previous studies would be explained by this error (Griskey, 1965) (Luo *et al.*, 2013). The effect of the diffusion of the reagents was eliminated by the excess of acetic acid and acetic anhydride, and by the sufficient stirring. The high rate/temperature dependence may be interpreted as a confirmation of the chemically controlled reaction (Levenspiel, 1986)

Table 7. Kinetic constants of acetylation using Equation 5, Model 1. DS determined by HPLC.

Pulp Sample	Temperature of acetylation (°C)	k (min^{-1})	Standard error (min^{-1})	R^2	Activation Energy ($kJ \cdot mol^{-1}$)
Bahia PHK pulp	25	0.0262	0.0011	0.974	112.9
	30	0.0565	0.0023	0.950	
Saiccor Sulfite pulp	25	0.0214	0.0010	0.982	103.5
	30	0.0433	0.0023	0.972	
Domsjö Sulfite pulp	30	0.0499	0.0020	0.961	-
Paskov Paper Sulfite Pulp	30	0.0435	0.0021	0.968	-
Botnia Kraft paper pulp	30	0.0398	0.0029	0.893	-

The study of the reactivities of these two pulps by the second kinetic model (two different hydroxyl groups) revealed some interesting aspects, as shown in Table 8. In the case of the PHK pulp, the fraction of 'slow' OH groups decreases with increasing temperature, which is to be expected. This may be indicating that there are some superficial or hidden OH groups that become significantly more reactive when the temperature is increased, as shown by the calculated k_s. Although rather high, the calculated k_f may be indicating a pre-disposition of some OH groups to acetylation in the activation step. In the case of the sulfite pulp, the fraction

of ‘slow’ OH groups is 1, and therefore they react uniformly, despite the differences in the polydispersity compared to the PHK. According to the k_f calculated, the minor number of fast OH groups in the sulfite pulp at 25 °C have almost the same rate of reaction as the slow OH groups (and therefore, meaning that all the OH have almost the same reactivity at this temperature, too). However, the increase in the k_f at 30 °C is consistent with a residual presence of fast OH groups that clearly enhance their reactivity when a higher temperature is set. As expected, these results show higher k_f value of the PHK pulp versus the sulfite pulp. Nevertheless, statistical tests applied proved that the preferred method is the one that involves only one kind of OH groups (Table 8 and Appendix 3).

Table 8. Kinetic parameters using Equation 13, Model 2. DS determined by HPLC.

Pulp Sample	Temperature of acetylation (°C)	k_s (min^{-1})	k_f (min^{-1})	A	R^2	Model preference
Bahia HW-PHK pulp	25	0.0251	136	0.98	0.974	1
	30	0.0545	6127	0.97	0.946	1
Saiccor HW-Sulfite pulp	25	0.0214	0.0215	1	0.975	1
	30	0.0434	296	1	0.963	1
Domsjö SW-Sulfite pulp	30	0.0427	13.3	0.93	0.987	*AIC: 1 F-test: 2
Paskov SW-sulfite Paper pulp	30	0.0368	20.1	0.92	0.993	2
Botnia HW-Kraft Paper pulp	30	0.0294	0.511	0.85	0.991	*AIC: 1 F-test: 2

**AIC: Akaike’s Criterion Test*

4.3.2 Acid Sulfite Pulp (Domsjö)

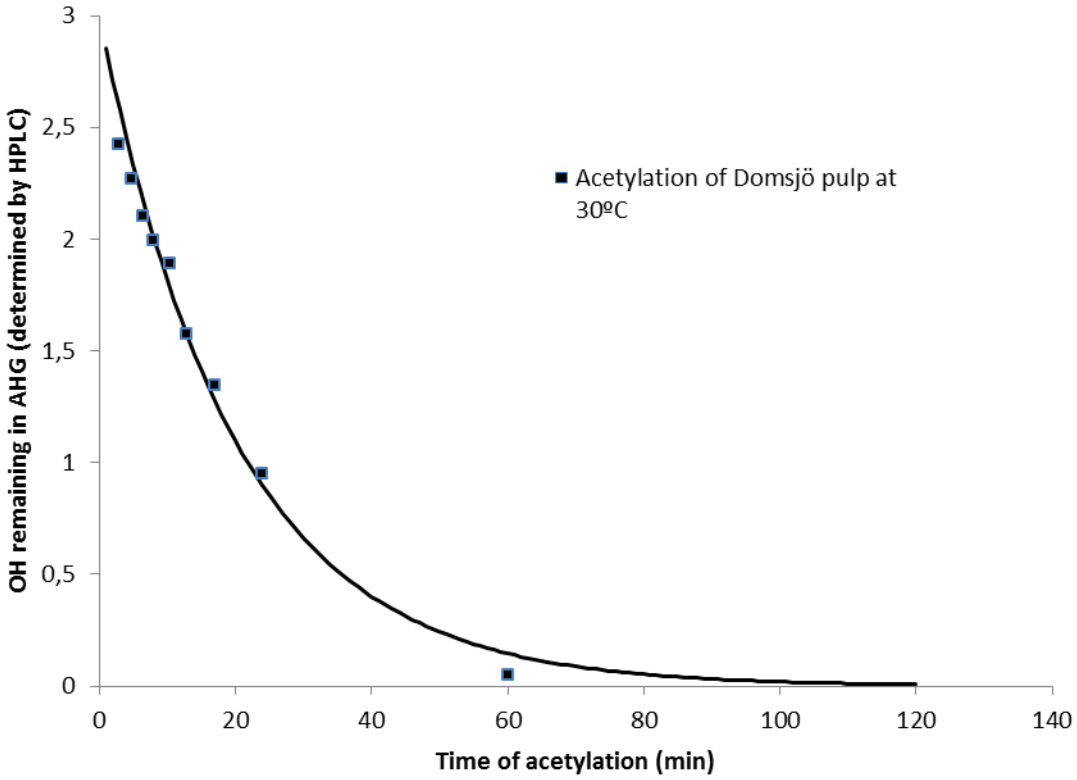

Figure 22. OH remaining in the AHG unit vs time of acetylation for the Domsjö Sulfite Pulp Pulp at 30 °C

Figure 22 shows the reactivity profile at 30 ºC for the Domsjö Sulfite Pulp, a dissolving pulp that uses spruce as raw material. The value of the kinetic constant for this pulp is 0.0499 min^{-1}, in between of the two previous pulps studied. An attempt to explain the higher reactivity of this pulp compared to the Saiccor sulfite pulp is consistent with one of the assumptions: the lower presence of long chains of cellulose of the Domsjö pulp makes it more suitable to reaction -not impeded by the shorter chains, as in the Saiccor pulp. In the same order are the values of the standard error, as expected. In the case of this pulp, the kinetic study by

the second model revealed an improvement of the R-square (Table 8, 0.961 to 0.987). Also according to this model, the Domsjö Sulfite pulp had a comparatively higher amount of fast OH (7 %), although their k_f is the lowest of the three pulps discussed so far. The F-test, which assumes the models are nested, gave preference to this second model of acetylation, probably directly related to the higher amount of fast OH (the statistical comparison is made in the Appendix 3).

4.3.3 The paper pulps: acid sulfite softwood pulp (Paskov) and Kraft hardwood pulp (Botnia)

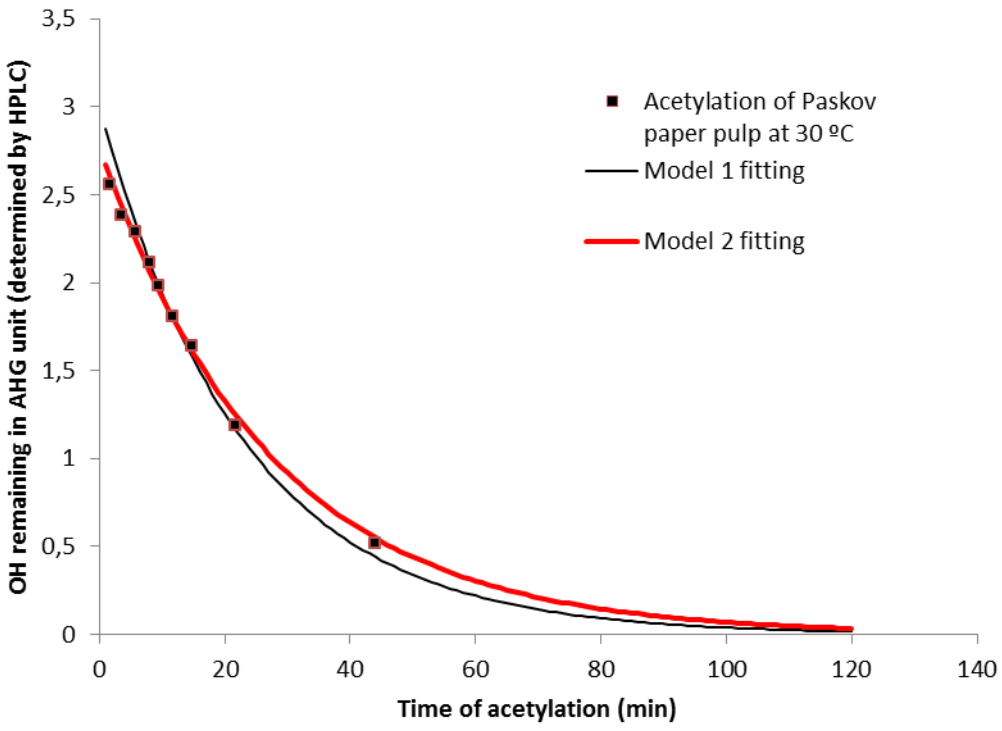

Figure 23. OH remaining in the AHG unit vs time of acetylation for the Paskov Paper Sulfite Pulp at 30 °C

The reaction graph for the Paskov Paper Pulp is shown in Figure 23. According to the first model shown in Table 7 the speed of the reaction at 30 ºC (as the k value) is the lowest of all the sulfite pulps studied. Starting with the obvious, this pulp is not intended for dissolving pulp specialties and, in the same vein, the higher percentage of hemicelluloses and the lower content of cellulose found (Table 6) may be indicating a relationship between these two aspects. Consideration of the second kinetic model results in a higher R-square that can be seen graphically in Figure 23, suggesting that this model provides a better interpretation of the reaction path.

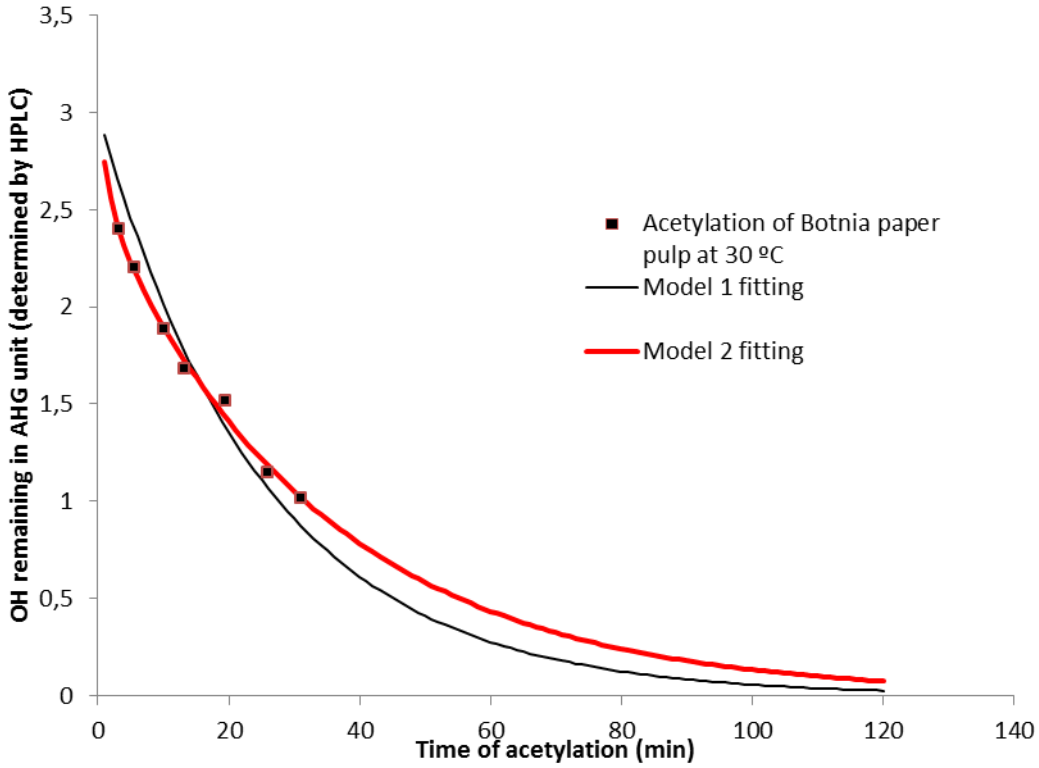

Figure 24. OH remaining in the AHG unit vs time of acetylation for the Botnia Paper Kraft Pulp at 30 °C- comparing model 1 fitting and model 2 fitting

In the case of the Botnia Paper Pulp, the profile of the reaction is plotted in Figure 24. As it can be seen, there is a clear difference in the fitting curves when applying model 1 or model 2. The statistical tests applied showed a preference for the second model (Table 8 and Appendix 3)

The preference of these two paper pulps for the second kinetic model might be explained by the higher amount of hemicelluloses, although other characteristics of the paper pulps should be studied.

4.3.4 The unidentified Softwood pulp (The influence of the activation acid in the speed of reaction)

Table 9 shows the kinetic parameters according to the first model for the acetylation of a softwood pulp (identified as FE2035, with no other known characteristics), doubling the percentage of sulfuric acid in the activation acid. Figure 25 shows the graphic representation of these acetylations. There is a significant change in the speed of the reaction as the percentage increases, although the kinetic constant is not the double.

Table 9. Reactivity of the Softwood FE2035 pulp at 30 °C, model 1

Pulp Sample	Percentage of Sulfuric in the activation acid (%)	k (min^{-1})	Standard error (min^{-1})	R^2
Softwood FE2035	0.30	0.0610	0.0022	0.972
	0.60	0.0893	0.0029	0.974

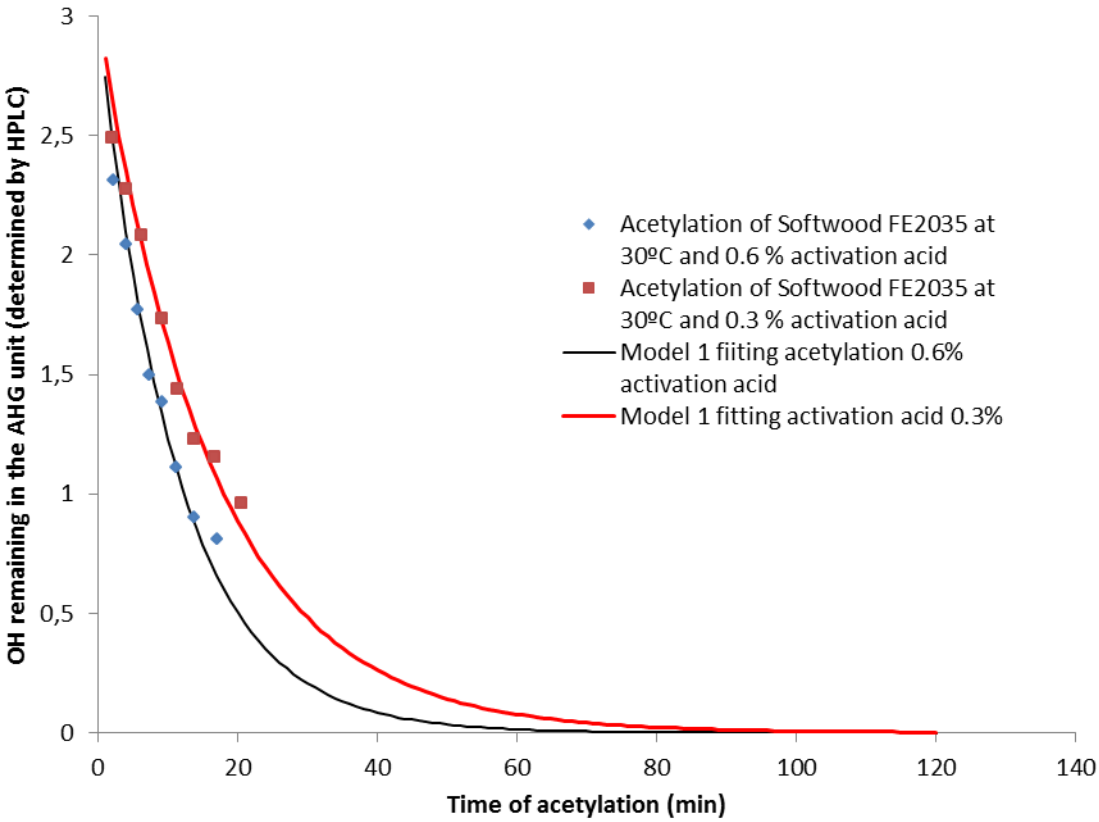

Figure 25. Acetylation of Softwood FE2035 at 30 ºC with two different activation acid concentration.

As Table 10 shows, the kinetic parameters calculated considering two different OH groups reflect some characteristics worth noticing. First of all, it shows a better adjustment (R-square) compared to model 1, although the statistics tests applied still gave a preference to the first model. Nevertheless, there is evidence of a higher amount of fast OH calculated as the percentage of sulfuric acid increases, an aspect consistent with what is expected in the reaction and supportive of the model. However, the fast OH groups at 0.60 % sulfuric acid in the

activation had a lower kinetic constant than the fast OH group at 0.30 % (sulfuric acid in activation acid), unlike the case of the increase in the temperature where the kinetic constant of the fast OH groups is also increased.

Table 10. Reactivity of the Softwood FE2035 pulp at 30 ºC, model 2.

Pulp Sample	Percentage of Sulfuric in the activation acid (%)	k_s (min^{-1})	k_f (min^{-1})	A	R^2	Model preference
Softwood FE2035	0.30	0.0546	2455	0.94	0.984	1
	0.60	0.0786	696	0.92	0.991	*AIC: 1 F-test: 2

**AIC: Akaike's Criterion Test*

4.4 Comparing different properties versus the kinetic constant

A comparison between the kinetic data found and other parameters highlight some interesting aspects.

4.4.1 Filterability

First, the filterability *versus* the kinetic constant (considering only the first model) at 30 ºC is shown in Figure 26. According to this figure, there is not a direct relationship between these two parameters for all the pulps studied (there was no data about the filterability of the Botnia pulp).

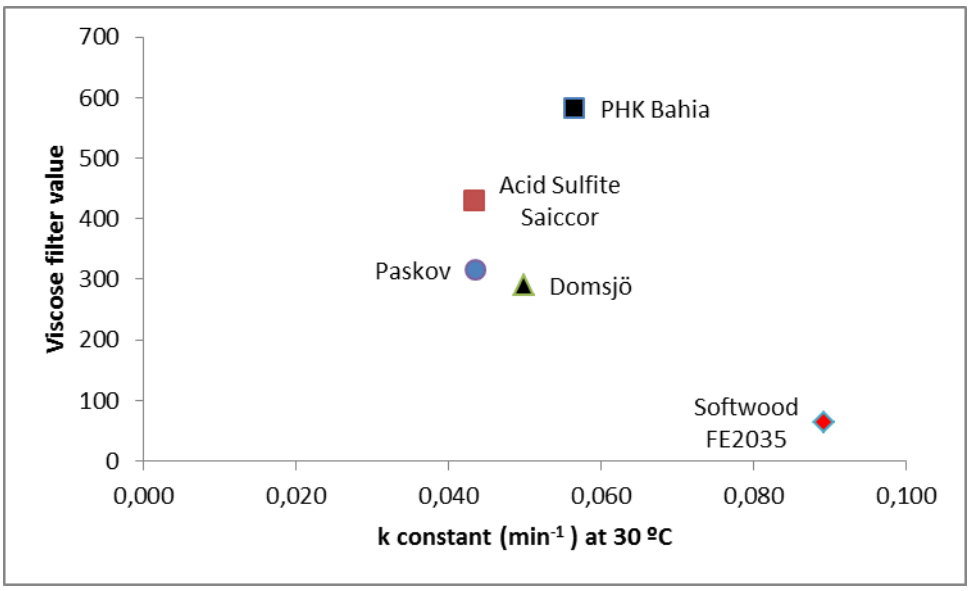

Figure 26. Viscose filter value vs the calculated kinetic constant (model 1) at 30ºC

However, where the combination of filterability and particle lay in the *very good to excellent* quality of viscose (Sixta *et al.*, 2004) –i.e. for the two Eucalyptus pulps, Bahia and Saiccor-, the kinetic results gave proportional results, as can be seen in Figure 27. There, considering the Acid Sulfite Saiccor as 100 % for the Treiber Value, kinetic constant at 30 ºC and 25 ºC (model 1), the higher reactivity of the PHK Bahia pulp is in the same order for the three tests considered: 35 %, 30% and 22 % respectively. Also interesting, yet expected, is the smaller difference at 25 ºC than at 30 ºC -30 % more reactive at 30 ºC and 22 % more reactive at 25 ºC.

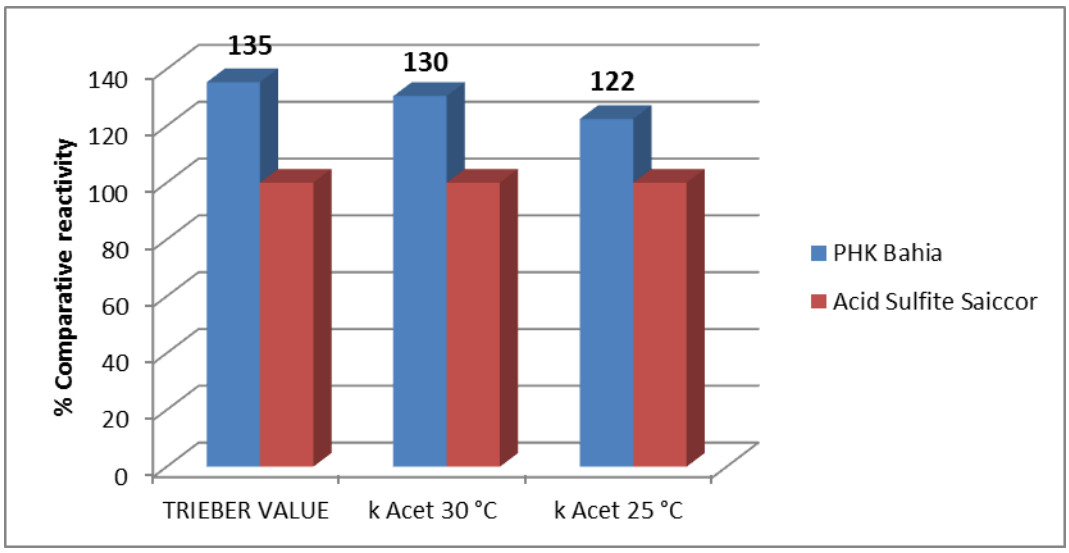

Figure 27. Relative reactivity of the Eucalyptus pulps, according to the Treiber value and the calculated kinetic constants

4.4.2 Polydispersity, Degree of Polymerization and Cellulose content

Figure 28 compares the polydispersity of the pulp to the kinetic constants. Although it can't be affirmed categorically, there seems to be a general trend involving these two properties, where a lower polydispersity correlates with a higher kinetic constant (speed of reaction). The clear exceptions of the Softwood FE2035 –with a higher polydispersity and a higher reactivity than the Bahia pulp- and the Paskov pulp –with the highest polydispersity, but more reactive than the Botnia pulp and similar to the Saiccor pulp- make this assumption worth of reconfirmation with more pulps.

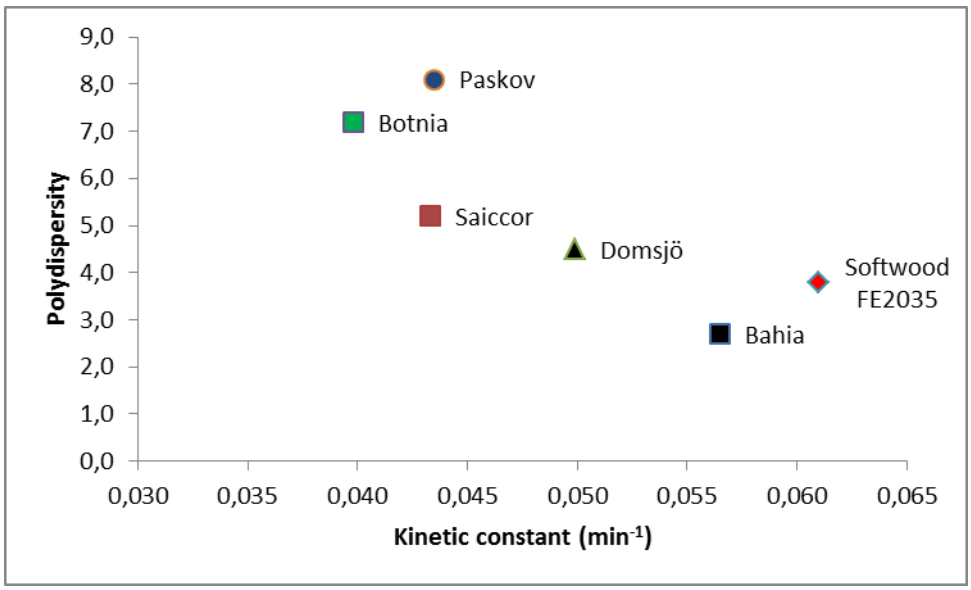

Figure 28. Polydispersity vs kinetic constant.

A similar trend can be seen when the percentage of the degree of polymerization analyzed is higher than 2000, as in Figure 29. It could be suggested that the short chain material reacts faster, making it more difficult for the long molecules to react with the acetic anhydride. Nevertheless, explaining the various reactivities solely by the aspects studied in this work will not be entirely satisfactory. Several aspects can be affecting the reactivity of the pulps, including hornification and the ultrastructure of cellulose.

A similar comparison can be made with the percentage of cellulose, with the important caveat that these results were not entirely trustable. Figure 30 shows a comparable behavior, making it difficult to draw conclusions. In four of the six pulps, the higher the content of cellulose, the faster the reaction. In the rest of the pulps, it is just the opposite.

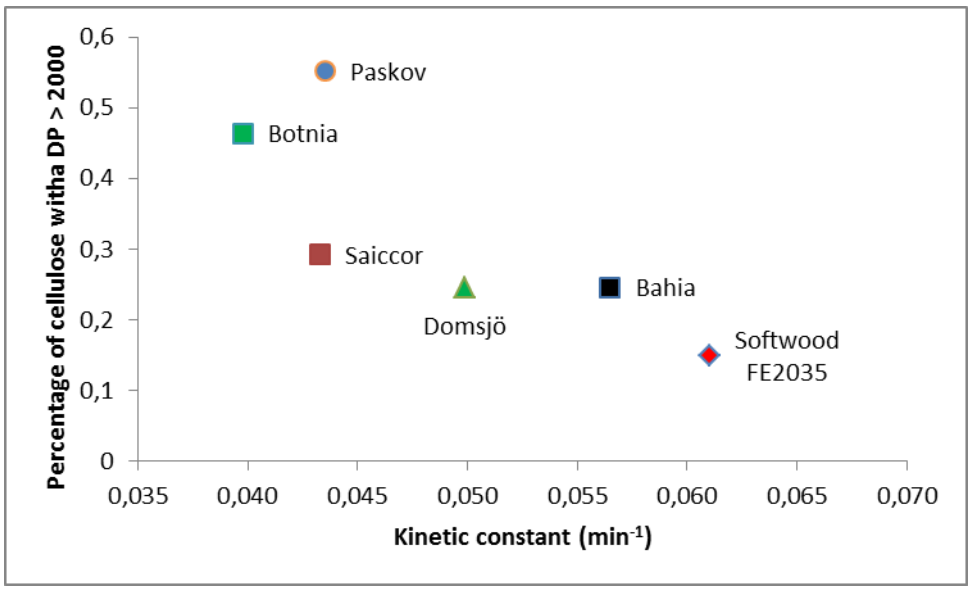

Figure 29. Fraction of cellulose with a Degree of Polymerization higher than 2000 vs the kinetic constant

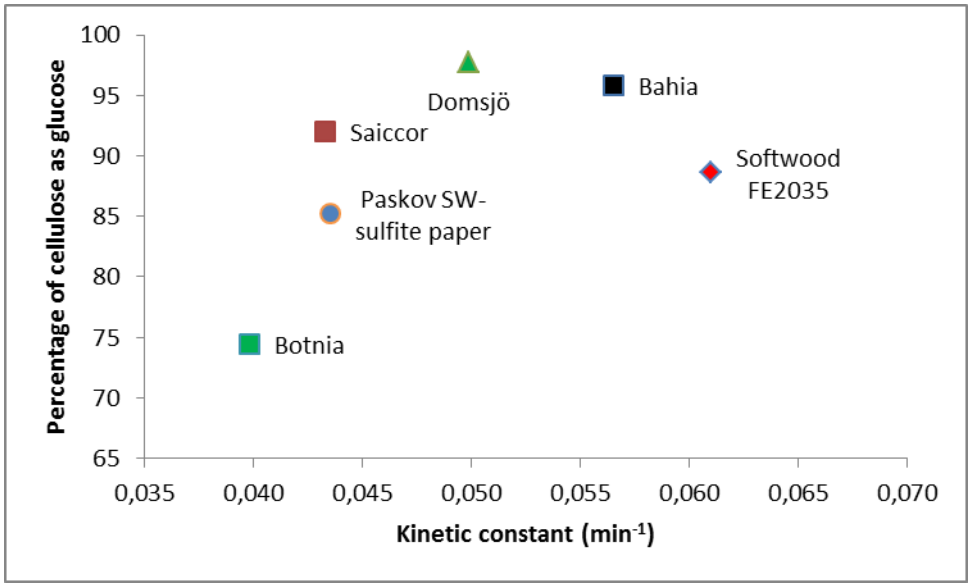

Figure 30. Impact of the cellulose content on the kinetic constant

4.5 Determination of the kinetic values by FT – IR

4.5.1 FT-IR Calibration

The determination of the Degree of Substitution of cellulose by HPLC is a highly precise method, although rather slow. To speed up this determination, a calibration with FT-IR and PAS detector was carried out.

Although the FT-IR can be used to monitor the acetylation of the different phases of cellulose (Sassi *et al.*, 2000), the usefulness in this study lies in the relationship of the FT-IR signals to the DS. Sassy and Chanzy (1995), Hurtubise (1962), and Wollboldt (2011), among others, have investigated the behavior of the C=O/O-H Ratio to the Degree of Substitution, but they reached different results (i.e. the ratio of the signals corresponding to different DS was different for all the studies, including this one). The calibration curve of this study is shown in Figure 31 reflecting a quite large dispersion of the points, and probably not suitable for a high- precision kinetic study.

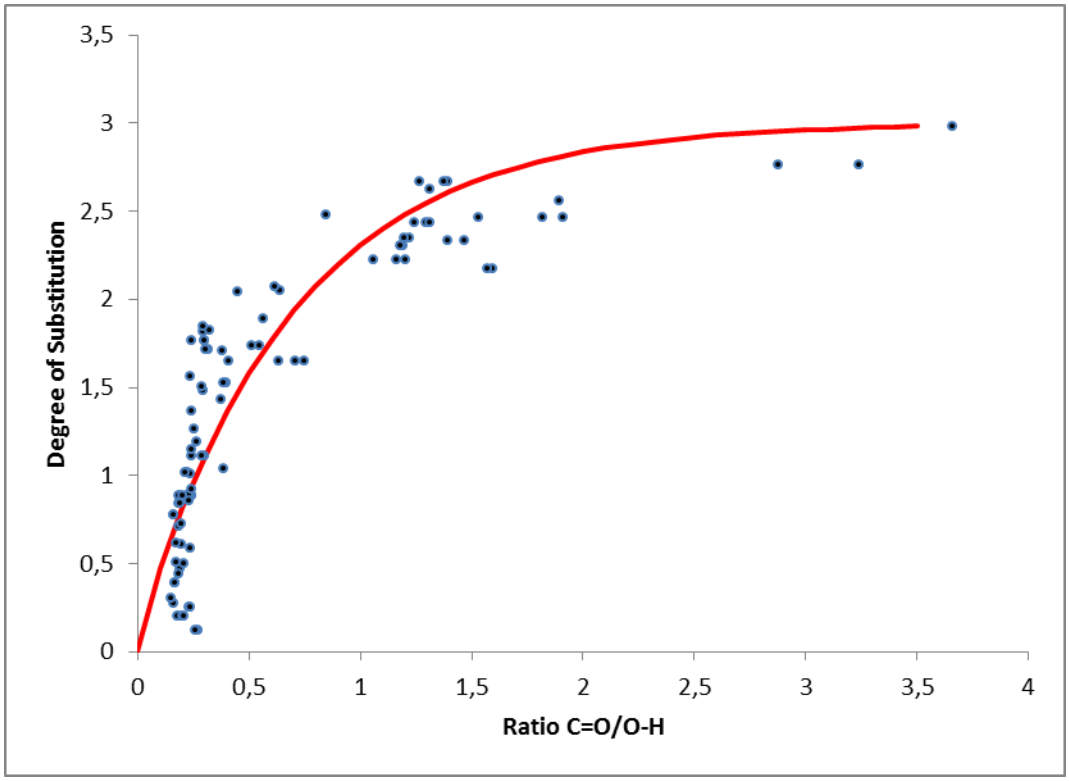

Figure 31. IR calibration: C=O at 1750 cm^{-1} / O-H at 3400 cm^{-1} ratio versus the Degree of Substitution determined by HPLC. The fitting curve is expressed in Equation 15**.**

Considering that the final degree of substitution is 3, the points in Figure 31 are fitted to an asymptotic curve of the type

$$y = a - b * c^{x}$$ Equation 14

After fitting and replacing the *a*, *b* and *c* parameters for the actual values, the equation takes the form below

$$Degree\ of\ substitution = 3 - 2.913 * 0.238^{Ratio\ C=O/O-H}$$ Equation 15

Figure 32 shows the FT-IR spectra of the cellulose acetates from acetylation-free cellulose to fully-acetylated cellulose. It shows a peak at 3400 cm^{-1} that represents the O-H stretching as it gradually disappears,

and the peak at 1750 cm^{-1} that represents the C=O stretching. As a result of the acetylation, this latter peak should be increasing, and so should the ratio of the peaks. However and unfortunately, it is not a smooth transition, which in turn affects the calibration, as discussed above. Another aspect that affects calibration can be deduced from Figure 31, where the smaller DSs have a small C=O/O-H ratio range, and the higher DSs have a greater range: big changes in the DS may not be clearly differentiated in the ratio, and the opposite also applies: big ratio changes are not consistent with changes in the DS.

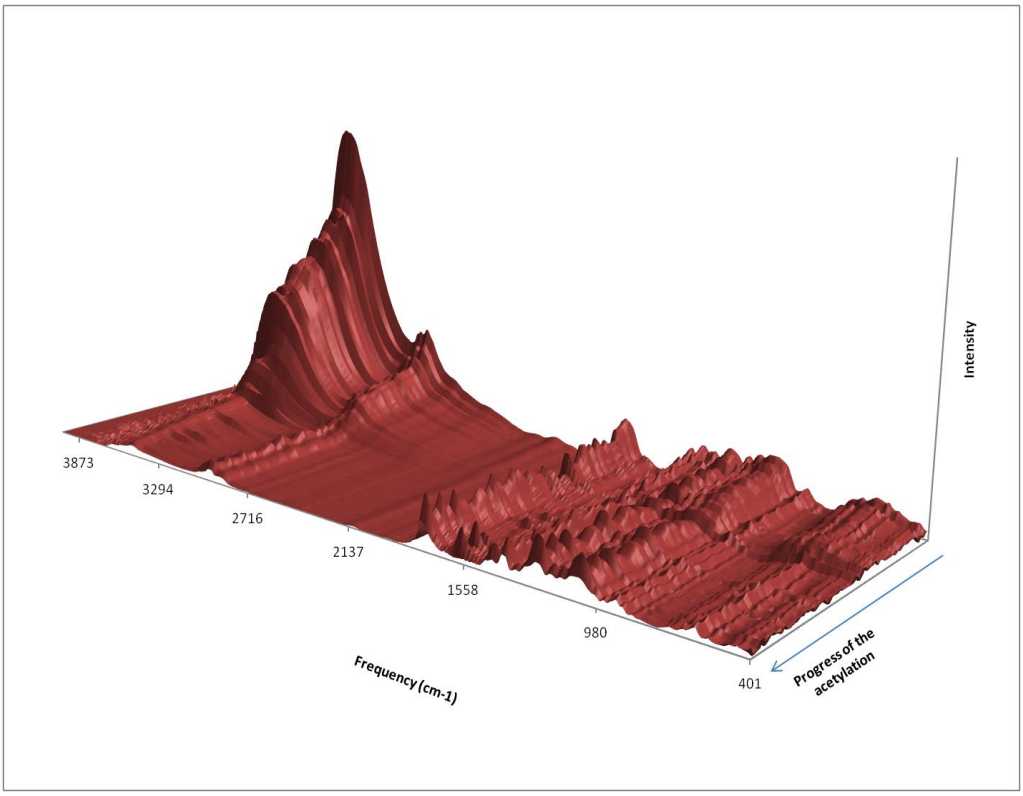

Figure 32- FT-IR of the different cellulose acetates obtained.

4.5.2 Kinetics of acetylation using the FT-IR calibration

Table 11 shows a calculation of the kinetic parameters of acetylation of the pulps using the FT-IR calibration. Although the precision of the parameters is not as good as using the DS determined by HPLC, it must be pointed out that the FT-IR allowed more points to be studied in each curve. Moreover, some curves that were not available by the HPLC technique became available with the FT-IR technique. These new curves are the acetylation of the pulps Botnia and Domsjö at 25 ºC and the acetylation of the Paskov pulp at 30 ºC using 0.60 % of sulfuric acid in the activating acid. In the case of Botnia and Domsjö, the new kinetic values are logical and consistent with the previous data obtained for other pulps, since there is a decrease of the speed of reaction. Moreover, the reductions for both pulps are in the same order to the previously discussed pulps. Also logical is the kinetic value of the Paskov with 0.60 % of sulfuric acid, with a high kinetic constant similar to the case of the Softwood FE2035, mentioned above.

Table 11. Kinetic parameters of the pulps using the FT-IR calibration

Pulp Sample	Temperature of acetylation (°C)	k (min^{-1})	Standard error (min^{-1})	R^2
Bahia HW-PHK pulp	25	0.0286	0.0024	0.849
	30	0.0591	0.0025	0.861
Saiccor HW-sulfite pulp	25	0.0201	0.0020	0.823
	30	0.0415	0.0021	0.881
Domsjô SW-sulfite pulp	25	0.0363 [a]	0.0038 [a]	0.783 [a]
	30	0.0441	0.0031	0.919
Botnia HW-Kraft paper pulp	25	0.0241 [a]	0.0025 [a]	0.780 [a]
	30	0.0375	0.0059	0.857
Paskov SW-sulfite paper pulp	30 [b]	0.0901 [b]	0.0082 [b]	0.890 [b]
	30	0.0394	0.0036	0.884
Softwood FE2035	30 [b]	0.0798 [b]	0.0062 [b]	0.837 [b]
	30	0.0348	0.0030	0.788

a. These kinetic values were not determined by HPLC.

b. The percentage of sulfuric acid in the activation acid was 0.6%. All the other determinations had 0.3% sulfuric acid.

4.5.3 Comparison of the FT-IR and HPLC kinetic constants

Figure 33 shows the comparison of the kinetic constants as assessed by the two different methods. It can be seen that most of the constants determined by HPLC have a good correspondence with the constants determined by FT-IR.

Moreover, it can be seen that the error made with the FT-IR method is generally higher than the error made with the HPLC determination of the DS. Nevertheless, in some determinations the lower precision of the FT-IR method is compensated by the higher amount of points available to build a curve.

However, there is a clear outlier identified as the Softwood FE2035 using 0.3% of sulfuric acid in the activation acid. In this point, the kinetic constant determined by the FT-IR method is significantly lower than the one determined by HPLC.

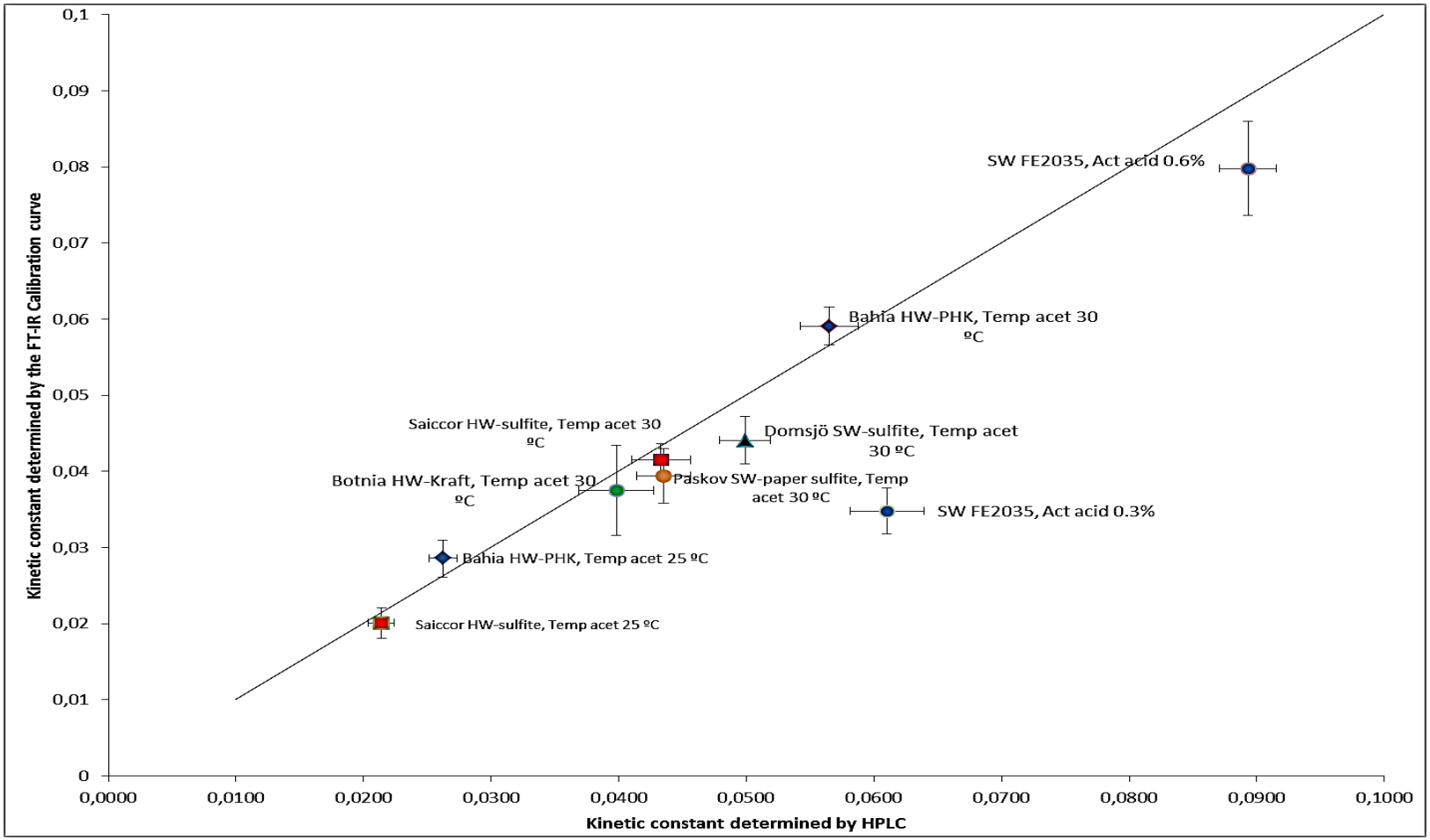

Figure 33. Comparison of the kinetic constants determined by HPLC and by FT-IR. The line represents 'the perfect calibration', *i.e.* same kinetic constant by both methods.

However, the reason behind this unexpected behavior is not certain. A detailed analysis of the FT-IR spectra of the Softwood FE2035 doesn't show any important difference to the other pulps spectra during acetylation. On the other hand, considering that eight out of nine determinations were fine according to the FT-IR calibration and one was outside the tolerance, it could be suggested that the FT-IR measurement for the Softwood FE2035 acetylated pulps was not right. An unnoticed deterioration of the acetylated samples may be the cause for this totally unpredicted behavior.

Either way, this determination is easier, faster and probably cheaper than the determination by HPLC; likewise, in the particular case of this work, more points became available for the kinetic study. Despite the problems mentioned, it shows the same tendency as earlier results, which may encourage a better study of the FT-IR technique and spectra. Principal Components or using different frequencies and ranges (Saad *et al.*, 1980) may be investigated. Also, as supported by Casarano *et al.* (2011), it may be necessary to work with a homogeneous mixture in a supporting KBr matrix, but this could reduce the practicality of this method.

5. CONCLUSIONS

The kinetic method to determine the reactivity of cellulose towards acetylation gave reliable results mainly depending on the technique used to determine the degree of substitution (DS) for the acetyl groups on cellulose. The FT-IR technique can be used for the determination of the DS.

However, as implemented, the FT-IR technique was not suitable for the determination of kinetic parameters. Yet, it can be used for the fast and rough estimation of the reactivity.

It was also found that the OH groups within the anhydroglucose (AHG) unit react almost uniformly. However, in some cases, there was an indication that a given fraction of the OH groups react far faster than the others. While the proportion of these groups is low, the amount and the velocity of reaction increased significantly with elevated temperature.

Within the pulps studied, no clear correlation between the viscose value and the velocity of reaction towards acetylation was identified. Similar trend was observed for the cellulose content. Nevertheless, lower polydispersity and lower content of chains with a high degree of polymerization seemed to yield faster acetylation rates.

6. FUTURE WORK

After having proved that the acetylation method is reliable, it could be improved if some aspects of the experimental part were upgraded. In particular, if the method for taking the aliquots from the reaction vessel could be mechanized, the determinations of cellulose might become more accurate. The temperature could be better controlled and the time points could be more accurately determined.

The carbohydrate composition should be re-studied and improved. An intensive study of the hemicelluloses content of the different pulps is another aspect that can contribute to the better understanding of the different relationships.

Besides the obvious fact that more pulps can be used to confirm or dismiss some of the comparisons studied, tests such as viscose, yellowness and other tests used to characterize dissolving pulps should be useful as well.

APPENDIX 1 – Determination of cellulose hydroxyl accessibility by using phosphitylation and quantitative ^{31}P-NMR Spectroscopy

Introduction

In addition to studying reactivity through the kinetics of acetylation, the study included the accessibility of hydroxyl groups. The technique used involved the phosphitylation of cellulose and the measurement of the remaining phosphitylating reagent, as proposed by Filpponen and Argyropoulos (Filpponen & Argyropoulos, 2008).

In this method, the free hydroxyls react with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane [P(II)] (Figure 34)

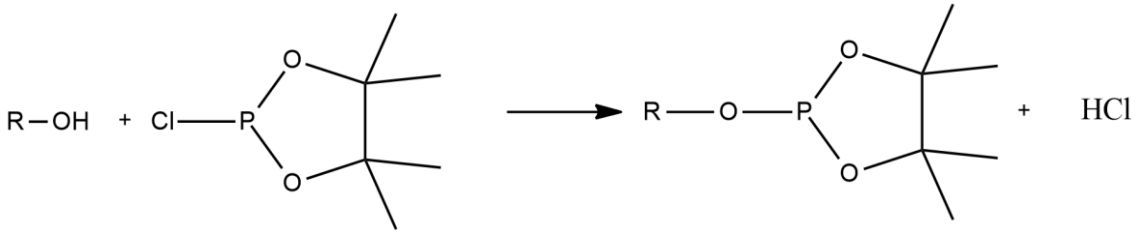

Figure 34. Reaction between 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphos-pholane [P(II)] and a hydroxyl group.

Instead of determining the hydroxyl groups by solubilization due to the phosphitylation, the method proposed in this work determines the amount of unreacted phosphitylating agent. Therefore, the free phosphitylating agent relates inversely with the amount of reacted

cellulose. The amount of free phosphitylating agent is monitored by ^{31}P-NMR.

^{31}P-NMR is a widely known technique, used for several purposes. The advantages of this technique lie in different aspects. The spin quantum of 1/2 of the phosphorus nucleus will give a single spectral line. Also, ^{31}P is the only natural isotope of the element. (Quin & Williams, 2004). Of particular interest in the field of this study, the determination of the DS by this method (King *et al.*, 2010) is to be highlighted.

Materials and methods

The samples of cellulose studied were the same as in the acetylation part (Table 2).

The method was applied following the indications recommended by Filpponen & Argyropoulos (2008)

Phosphitylation of Cellulose

Reactions were carried out in 50 mL pre-dried Schlenk flasks equipped with a magnetic stirrer, an Argon inlet and a septum for reagent addition via a stainless steel syringe. A previously grinded and oven dried cellulose sample (100 mg) was suspended in 15 mL of freshly distilled THF, 5 mL of dry pyridine containing 0.03 mmoles of 4-(dimethylamino) pyridine (DMAP) and 5 mL of dry chloroform containing 100 µL of guaiacol (0.9 mmol, internal standard). Then 600 µL of 2-chloro-4,4,5,5-tetramethyl-

1,3,2-dioxaphospho-lane [P(II)] were added slowly via the septum under slight agitation. The reaction kinetics was monitored by taking aliquots (600 µL) from the reaction mixture at specific times and then determining the amount of remaining phosphitylation reagent using quantitative 31P NMR spectroscopy. Clean and transparent samples for the NMR analysis were taken by allowing the cellulose to settle in the bottom of the reaction flask prior to sampling (by turning off the magnetic stirrer). In all experiments one flask containing all the chemicals but no cellulose was kept apart as a blank. The use of this reference sample allowed taking into account the slow decomposition kinetics of the phosphitylation reagent.

Quantitative 31P NMR of Remaining P(II)

Aliquots of 600 µL of the reaction mixture, prepared as described above, were transferred into an NMR tube containing 0.57 mg of chromium(III) acetylacetonate (relaxation agent) dissolved in 50 µL of deuterated chloroform. The quantitative 31P NMR spectra were acquired as soon as the samples were collected using a Varian Unity Innova 600 spectrometer (600 MHz proton frequency) equipped with a 5 mm direct detection broadband probe-head. A total of 512 scans were acquired for each sample with a 10.0 second relaxation delay time (d1).

Reactivity Calculations

The amount of reactive hydroxyls was calculated based on the theoretical value of 18.5 mmol of hydroxyl groups present per gram of AHG.

Results and discussion

All the spectra obtained by ^{31}P-NMR are like those seen in Figure 35, which is the spectrum obtained from one of the samples.

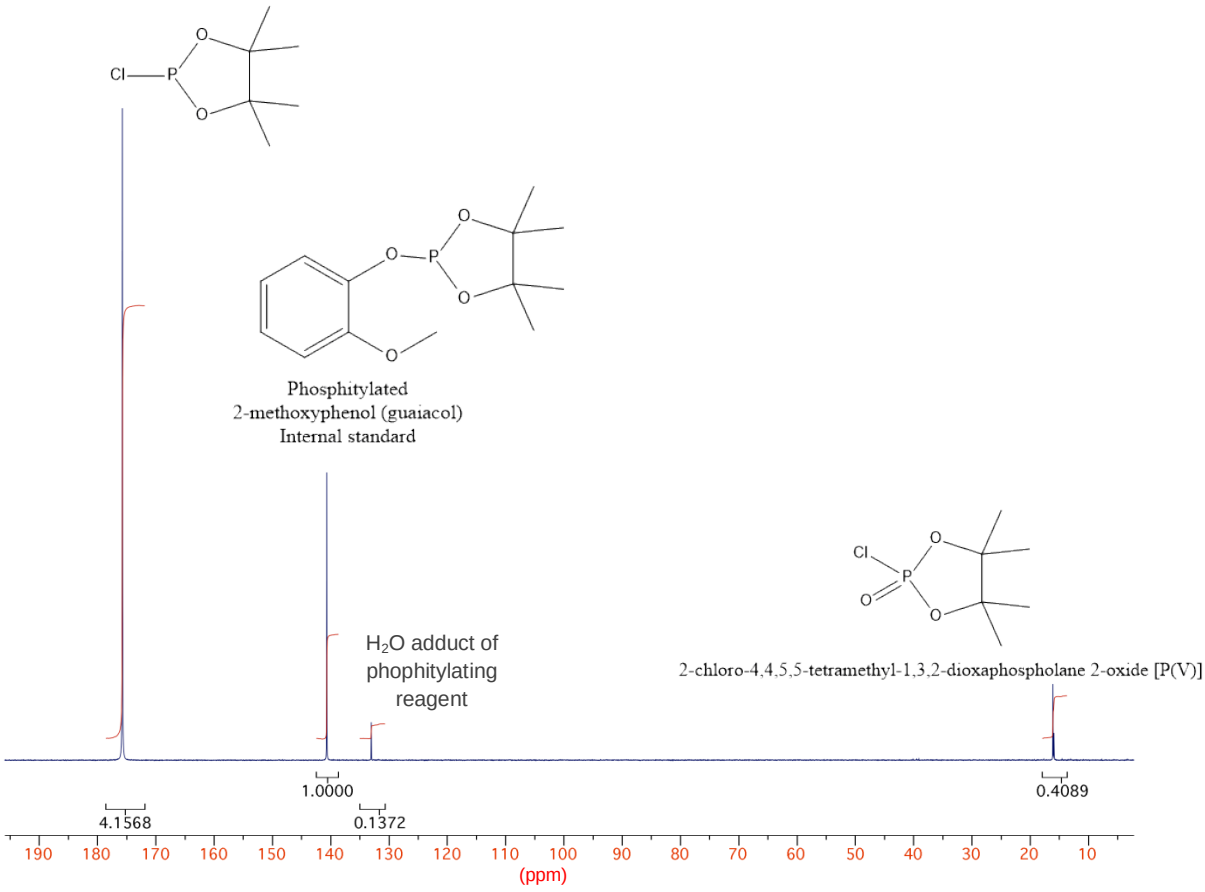

Figure 35. Typical quantitative ^{31}P-NMR spectrum of remaining phosphitylation reagent

The amount of reacted hydroxyls can be calculated, and therefore the reaction can be monitored.

Unfortunately, as shown in Figure 36, the results were unacceptable because of a number of issues: for several pulps the amount of reactive hydroxyls was negative, which is obviously illogical. In addition, as time elapses, the amount of reactive hydroxyls should be increasing until they reach a maximum. As has already been seen, that is not the case for every pulp; even so, there are some pulps that show a minimum in the middle of the time studied (at 5 minutes). Similarly, the repetitions of the Bahia pulp didn't provide the same results, showing an uneven behavior.

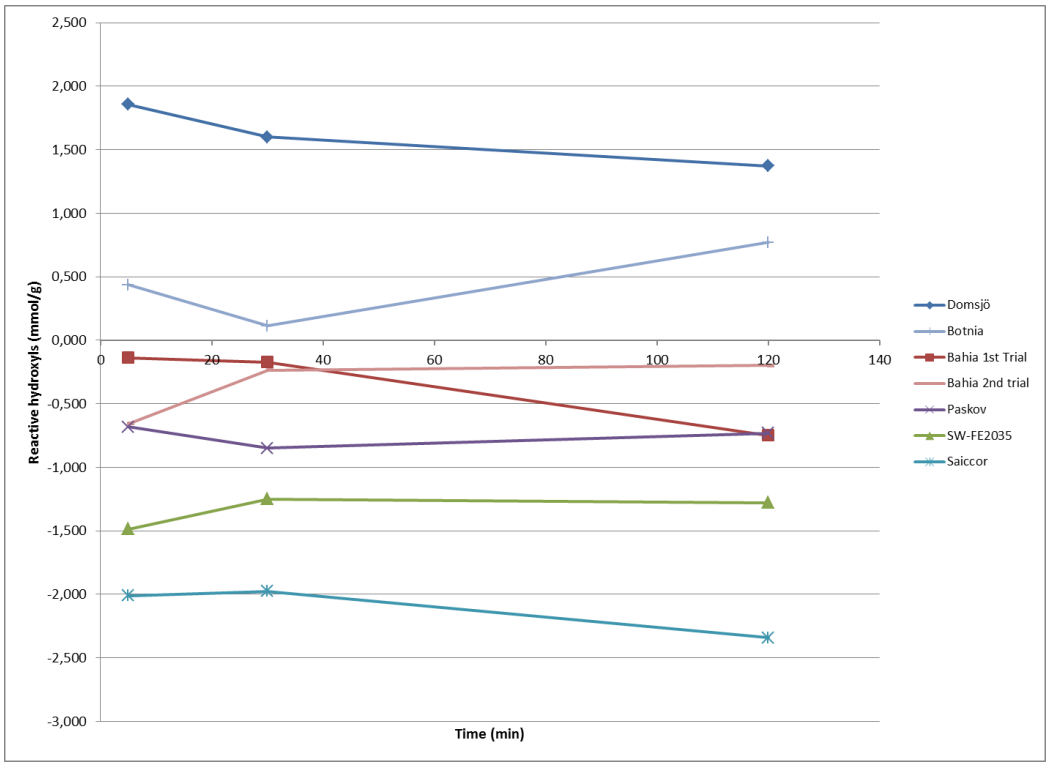

Figure 36. Reactive hydroxyls vs time for the different pulps

Even assuming that the response at 30 minutes is correct (since it is the point where both trials of Bahia pulp obtain similar results), and considering a wrong correction due to unidentified issues (but making the same wrong correction in all cases, i.e. with a systematic error), there is no correlation between these results and those previously obtained by acetylation, as seen in Figure 37.

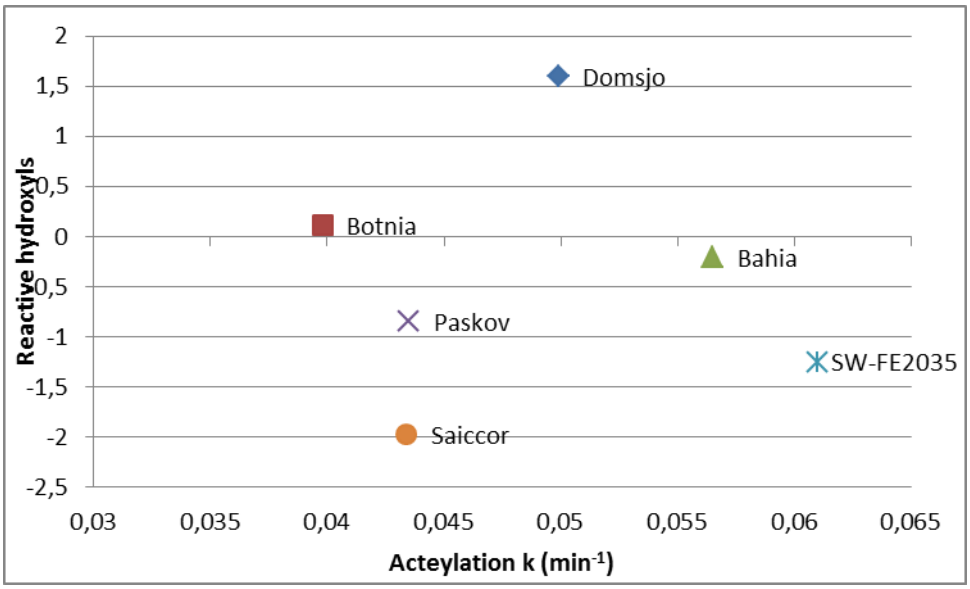

Figure 37. Correlation between the acetylation constant and the reactive hydroxyls as determined

The reasons behind this unexpected behavior are unclear. Discarding gross mistakes, and assuming the theoretical correctness, the problems might be searched at the moment of following the reaction, i.e. practical aspects of the method. *E.g.*, something about the preparation of cellulose, as the grinding or the time involved in the measurements can be held responsible. Otherwise, the adducts formed in the reaction vessel

might be solubilized and mask the real amount of cellulose reactive. Anyhow, this method should be revised and some corrections would probably be made. On the speculation side, maybe changing the actual object of study, *i.e.* studying the phosphitylated cellulose itself could be a solution.

APPENDIX 2- Determination of structural carbohydrates and lignin in biomass

Procedure Title: Determination of Structural Carbohydrates and Lignin in Biomass

Laboratory Analytical Procedure

1. Introduction

1.1 Carbohydrates and lignin make up a major portion of biomass samples. These constituents must be measured as part of a comprehensive biomass analysis, Carbohydrates can be structural or non-structural. Structural carbohydrates are bound in the matrix of the biomass, while non-structural carbohydrates can be removed using extraction or washing steps. Lignin is a complex phenolic polymer.

1.2 Portions of this procedure are substantially similar to ASTM E1758-01 "Standard method for the Determination of Carbohydrates by HPLC.

1.3 This procedure is suitable for samples that do not contain extractives. This procedure uses a two-step acid hydrolysis to fractionate the biomass into forms that are more easily quantified. The lignin fractionates into acid insoluble material and acid soluble material. The acid insoluble material may also include ash and protein, which must be accounted for during gravimetric analysis. The acid soluble lignin is measured by UV-Vis spectroscopy. During hydrolysis the polymeric carbohydrates are hydrolyzed into the monomeric forms, which are soluble in the hydrolysis liquid. They are then measured by HPLC. Protein may also partition into the liquid fraction. A measure of acetyl content is necessary for biomass containing hemicellulose with a xylan backbone, but not biomass containing a mannan backbone. Acetate is measured by HPLC.

2. Scope

2.1 This procedure is appropriate for extractives free biomass, which includes biomass that has been extracted using LAP "Determination of Extractives in Biomass", as well as process solids containing no extractives. Results are reported on an oven dry weight basis. Results may be reported on an as received biomass basis or an extractives free basis, depending on type of biomass used. LAP "Preparation of Samples for Biomass Compositional Analysis" should be used prior to this procedure.

2.2 This procedure is appropriate for biomass containing the components listed throughout the procedure. Any biomass containing other interfering components not listed must be further investigated.

2.3 A measure of acetyl content is necessary for biomass containing hemicellulose with a xylan backbone, but not biomass containing a mannan backbone.

2.4 All analyses should be performed in accordance with an appropriate laboratory specific Quality Assurance Plan (QAP).

3. Terminology

3.1 *Oven dry weight (ODW)*- the weight of biomass mathematically corrected for the amount of moisture present in the sample at the time of weighing
3.2 *Prepared biomass*- biomass prepared according to LAP "Preparation of Samples for Biomass Compositional Analysis".
3.3 *Extractives free biomass* - Biomass after exhaustive water and ethanol extraction (refer to LAP "Determination of Extractives in Biomass").
3.4 *Acid insoluble lignin*- the residue remaining on a medium porosity filtering crucible after a two step hydrolysis, with correction for acid insoluble ash and acid insoluble protein, if necessary.
3.5 *Structural carbohydrates*-Polymeric carbohydrates, namely cellulose and hemicellulose.
3.6 *Non-structural components*- Non-chemically bound components of biomass that include but are not limited to sucrose, nitrate/nitrites, protein, ash, chlorophyll, and waxes.

4. Significance and Use

4.1 This procedure is used, possibly in conjunction with other procedures, to determine the amount of structural carbohydrates and lignin in a solid biomass sample.

5. Interferences

5.1 This procedure has been optimized for the particle size range specified in LAP "Preparation of Samples for Biomass Composotional Analysis". Deviation to a smaller particle size may result in a low bias in carbohydrate content (and consequent high lignin bias) due to excessive carbohydrate degradation. Deviation to a larger particle size may also result in a low bias in carbohydrate content (and consequent high lignin bias) due to incomplete hydrolysis of polymeric sugars to monomeric sugars.
5.2 Samples containing extractives are not suitable for this procedure. Extractives will partition irreproducibly, resulting in a high lignin bias.
5.3 Samples with an ash content above 10 wt % may not be suitable for this procedure, as the sample may contain soil or other minerals that will interfere with appropriate acid concentrations and may catalyze side reactions.
5.4 Samples with a moisture content above 10 wt % may not be suitable for this procedure, as the excess moisture will interfere with appropriate acid concentrations. Samples should be dried (air-dried or oven dried at less than 40°C) prior to this procedure.
5.5 Samples containing protein will bias the acid insoluble lignin high unless the protein is accounted for in the gravimetric determination of acid insoluble material. An independent nitrogen analysis is required to estimate the protein content of the residue. The protein estimate is then subtracted from the acid insoluble residue measurement. Physical separation of the acid insoluble protein from the acid insoluble lignin is beyond the scope of this procedure.
5.6 This procedure is not suitable for samples containing added acid, base, or catalyst.
5.7 Certain guard columns for carbohydrate quantification may cause artifact peaks. Individual carbohydrates should be run on new columns and guard columns to verify to absence of artifact peaks.

6. Apparatus

6.1 Analytical balance, accurate to 0.1 mg
6.2 Convection drying oven, with temperature control of 105 ± 3°C
6.3 Muffle furnace, equipped with a thermostat, set to 575 ± 25 °C or equipped with optional ramping program
6.4 Water bath, set at 30 ± 3 °C
6.5 Autoclave, suitable for autoclaving liquids, set to 121 ± 3 °C

6.6 Filtration setup, equipped with a vacuum source and vacuum adaptors for crucibles
6.7 Desiccator containing desiccant
6.8 HPLC system equipped with refractive index detector and the following columns:
6.8.1 Shodex sugar SP0810 or Biorad Aminex HPX-87P column (or equivalent) with ionic form H^+/CO_3^- deashing guard column
6.8.2 Biorad Aminex HPX-87H column (or equivalent) equipped with an appropriate guard column
6.9 UV-Visible spectrophotometer, diode array or single wavelength, with high purity quartz cuvettes of pathlength 1 cm
6.10 Automatic burette, capable of dispensing 84.00 mL water, optional

7. Reagents and materials

7.1 Reagents
7.1.1 Sulfuric acid, 72% w/w (specific gravity 1.6338 at 20°C)- (also commercially available as a reagent for the determination of fluorine, from Fluka #00647)
7.1.2 Calcium carbonate, ACS reagent grade
7.1.3 Water, purified, 0.2 µm filtered
7.1.4 High purity standards : D-cellobiose, D(+)glucose, D(+)xylose, D(+)galactose, L(+)arabinose, and D(+)mannose
7.1.5 Second set of high purity standards, as listed above, from a different source (manufacturer or lot), to be used to prepare calibration verification standards (CVS)
7.2 Materials

7.2.1 QA standard, well characterized, such as a National Institute of Standards and Technology (NIST) biomass standard or another well characterized sample of similar composition to the samples being analyzed
7.2.2 Pressure tubes, minimum 90 mL capacity, glass, with screw on Teflon caps and o-ring seals (Ace glass # 8648-30 tube with #5845-47 plug, or equivalent)
7.2.3 Teflon stir rods sized to fit in pressure tubes and approximately 5 cm longer than pressure tubes
7.2.4 Filtering crucibles, 25 mL, porcelain, medium porosity, Coors #60531 or equivalent
7.2.5 Bottles, wide mouth, 50 mL
7.2.6 Filtration flasks, 250 mL
7.2.7 Erlenmeyer flasks, 50 mL
7.2.8 Adjustable pipettors, covering ranges of 0.02 to 5.00 mL and 84.00 mL
7.2.9 pH paper, range 4-9
7.2.10 Disposable syringes, 3 mL, fitted with 0.2 µm syringe filters
7.2.11 Autosampler vials with crimp top seals to fit

8. ES&H Considerations and Hazards

8.1 Sulfuric acid is corrosive and should be handled with care.
8.2 Use caution when handling hot pressure tubes after removal from the autoclave, as the pressurized tubes can cause an explosion hazard.
8.3 When placing crucibles in a furnace or removing them, use appropriate personal protective equipment, including heat resistant gloves.
8.4 Operate all equipment in accordance with the manual and NREL Safe Operating Procedures
8.5 Follow all applicable NREL chemical handling procedures

9. Sampling, Test Specimens and Test Units

9.1 Care must be taken to ensure a representative sample is taken for analysis.
9.2 LAP "Preparation of Samples of Biomass Compositional Analysis" should be performed prior to this analysis. Samples must have a minimum total solids content of 85%.
9.3 LAP "Determination of Extractives in Biomass" should be performed prior to this analysis if extractives are present in the sample.
9.4 LAP "Determination of Solids in Biomass" should be performed at the same time that samples for this analysis are weighed out.
9.5 This procedure is suitable for samples that have been air dried or lyophilized. Samples dried at a temperature of 45°C or higher are not suitable for this procedure.
9.6 Steps 9.2 to 9.4 should be applied to the QA standard

10. Procedure

10.1 Prepare the sample for analysis and hydrolyze

10.1.1 Place an appropriate number of filtering crucibles in the muffle furnace at 575 ±25 °C for a minimum of four hours. Remove the crucibles from the furnace directly into a desiccator and cool for a specific period of time, one hour is recommended. Weigh the crucibles to the nearest 0.1 mg and record this weight. It is important to keep the crucibles in a specified order, if they are not marked with identifiers. Permanent marking decals are available from Wale Apparatus. Do not mark the bottom of the filtering crucible with a porcelain marker, as this will impede filtration.

10.1.2 Place the crucible back into the muffle furnace at 575 ± 25 ^{o}C and ash to constant weight. Constant weight is defined as less than ± 0.3 mg change in the weight upon one hour of re-heating the crucible.

10.1.3 Weigh 300.0 ± 10.0 mg of the sample or QA standard into a tared pressure tube. Record the weight to the nearest 0.1 mg. Label the pressure tube with a permanent marker. LAP "Determination of Total Solids in Biomass" should be performed at the same time, to accurately measure the percent solids for correction. Each sample should be analyzed in duplicate, at minimum. The recommended batch size is three to six samples and a QA standard, all run in duplicate.

10.1.4 Add 3.00 ± 0.01 mL (or 4.92 ± 0.01 g) of 72% sulfuric acid to each pressure tube. Use a Teflon stir rod to mix for one minute, or until the sample is thoroughly mixed.

10.1.5 Place the pressure tube in a water bath set at 30 ± 3 °C and incubate the sample for 60 ± 5 minutes. Using the stir rod, stir the sample every five to ten minutes without removing the sample from the bath. Stirring is essential to ensure even acid to particle contact and uniform hydrolysis.

10.1.6 Upon completion of the 60-minute hydrolysis, remove the tubes from the water bath. Dilute the acid to a 4% concentration by adding 84.00 ± 0.04 mL deionized water using an automatic burette. Dilution can also be done by adding 84.00 ± 0.04 g of purified water using a balance accurate to 0.01 g. Screw the Teflon caps on securely. Mix the sample by inverting the tube several times to eliminate phase separation between high and low concentration acid layers.

Note: The volume of the 4% solution will be 86.73 ml, as demonstrated in the following calculations.

Density 72% H_2SO_4= $d_{72\%\ H2S04}$= 1.6338 g/ml
Density H_20= d_{H20}= 1.00 g/ml
Density 4% H_2SO_4 = $d_{4\%\ H2S04}$ = 1.025 g/ml

1. The weight of 3.00 ml 72% H_2SO_4 is:

3.00 ml 72% H_2SO_4 x $d_{72\%\ H2S04}$= 4.90 g 72% H_2SO_4

2. The composition of 3 ml of 72% H_2SO_4 is:
   4.90 g 72% H_2SO_4 x 72% (acid wt) = 3.53 g acid
   4.90 g 72% H_2SO_4 x 28% (water wt) = 1.37 g water
3. The concentration of H_2SO_4 after dilution is:
   3.53 g acid / (84.00 g H_20 + 4.90 g 72% H_2SO_4) = 3.97 % H_2SO_4 (w/w)
4. The total volume of solution present after dilution is:
   (4.90 g H_2SO_4 + 84.00 g H_20) x $(d_{4\%\ H2S04})^{-1}$ = 86.73 ml

10.1.7 Prepare a set of sugar recovery standards (SRS) that will be taken through the remaining hydrolysis and used to correct for losses due to destruction of sugars during dilute acid hydrolysis. SRS should include D-(+)glucose, D-(+)xylose, D-(+)galactose, -L(+)arabinose, and D-(+)mannose. SRS sugar concentrations should be chosen to most closely resemble the concentrations of sugars in the test sample. Weigh out the required amounts of each sugar, to the nearest 0.1 mg, and add 10.0 mL deionized water. Add 348 µL of 72% sulfuric acid. Transfer the SRS to a pressure tube and cap tightly.

10.1.7.1 A fresh SRS is not required for every analysis. A large batch of sugar recovery standards may be produced, filtered through 0.2 µm filters, dispensed in 10.0 mL aliquots into sealed containers, and labeled. They may be stored in a freezer and removed when needed. Thaw and vortex the frozen SRS prior to use. If frozen SRS are used, the appropriate amount of acid must be added to the thawed sample and vortexed prior to transferring to a pressure tube.

10.1.8 Place the tubes in an autoclave safe rack, and place the rack in the autoclave. Autoclave the sealed samples and sugar recovery standards for one hour at 121°C, usually the liquids setting. After completion of the autoclave cycle, allow the hydrolyzates to slowly cool to near room temperature before removing the caps. (If step 10.2 is not performed, draw a 10 mL aliquot of the liquor for use in step 10.5.)

10.2 Analyze the sample for acid insoluble lignin as follows

10.2.1 Vacuum filter the autoclaved hydrolysis solution through one of the previously weighed filtering crucibles. Capture the filtrate in a filtering flask.

10.2.2 Transfer an aliquot, approximately 50 mL, into a sample storage bottle. This sample will be used to determine acid soluble lignin as well as carbohydrates, and acetyl if necessary. Acid soluble lignin determination must be done within six hours of hydrolysis. If the hydrolysis liquor must be stored, it should be stored in a refrigerator for a maximum of two weeks. It is important to collect the liquor aliquot before proceeding to step 10.2.3.

10.2.3 Use deionized water to quantatively transfer all remaining solids out of the pressure tube into the filtering crucible. Rinse the solids with a minimum of 50 mL fresh deionized water. Hot deionized water may be used in place of room temperature water to decrease the filtration time.

10.2.4 Dry the crucible and acid insoluble residue at 105 $\pm$ 3 °C until a constant weight is achieved, usually a minimum of four hours.

10.2.5 Remove the samples from the oven and cool in a desiccator. Record the weight of the crucible and dry residue to the nearest 0.1 mg.

10.2.6 Place the crucibles and residue in the muffle furnace at 575 $\pm$ 25 °C for 24 $\pm$ 6 hours.

10.2.6.1 A furnace with temperature ramping may also be used

Furnace Temperature Ramp Program:

Ramp from room temperature to 105 °C
Hold at 105°C for 12 minutes
Ramp to 250 °C at 10°C / minute
Hold at 250 °C for 30 minutes
Ramp to 575 °C at 20 °C / minute
Hold at 575 °C for 180 minutes
Allow temperature to drop to 105 °C
Hold at 105 °C until samples are removed

10.2.7 Carefully remove the crucible from the furnace directly into a desiccator and cool for a specific amount of time, equal to the initial cool time of the crucibles. Weigh the crucibles and ash to the nearest 0.1 mg and record the weight. Place the crucibles back in the furnace and ash to a constant weight. (The amount of acid insoluble ash is not equal to the total amount of ash in the biomass sample. Refer to LAP "Determination of Ash in Biomass" if total ash is to be determined.)

10.3 Analyze the sample for acid soluble lignin as follows

10.3.1 On a UV-Visible spectrophotometer, run a background of deionized water or 4% sulfuric acid.

10.3.2 Using the hydrolysis liquor aliquot obtained in step 10.2.2, measure the absorbance of the sample at an appropriate wavelength on a UV-Visible spectrophotometer. Refer to section11.3 for suggested wavelength values. Dilute the sample as necessary to bring the absorbance into the range of 0.7 – 1.0, recording the dilution. Deionized water or 4% sulfuric acid may be used to dilute the sample, but the same solvent should be used as a blank. Record the absorbance to three decimal places. Reproducibility should be $\pm$ 0.05 absorbance units. Analyze each sample in duplicate, at minimum. (This step must be done within six hours of hydrolysis.)

10.3.3 Calculate the amount of acid soluble lignin present using calculation 11.3 .

10.4 Analyze the sample for structural carbohydrates

10.4.1 Prepare a series of calibration standards containing the compounds that are to be quantified, referring to Table 1 for suggested concentration range. Use a four point calibration. If standards are prepared outside of the suggested ranges, the new range for these calibration curves must be validated.

10.4.1.1 Table 1- Suggested concentration ranges for 10.4.1 calibration standards

Component	Suggested concentration range (mg/ml)
D-cellobiose	0.1-4.0
D(+)glucose	0.1-4.0
D(+)xylose	0.1-4.0
D(+)galcatose	0.1-4.0
L(+)arabinose	0.1-4.0
D(+)mannose	0.1-4.0
CVS	Middle of linear range, concentration not equal to a calibration point (2.5 suggested)

10.4.1.2 A fresh set of standards is not required for every analysis. A large batch of standards may be produced, filtered through 0.2 μm filters into autosampler vials, sealed and labeled. The standards and CVS samples may be stored in a freezer and removed when needed. Thaw and vortex frozen standards prior to use. During every use, standards and CVS samples should be observed for unusual concentration behavior. Unusual concentrations may mean that the samples are compromised or volatile components have been lost. Assuming sufficient volume, standards and CVS samples should not have more than 12 injections drawn from a single vial. In a chilled autosampler chamber, the lifetime of standards and CVS samples is approximately three to four days.

10.4.2 Prepare an independent calibration verification standard (CVS) for each set of calibration standards. Use reagents from a source or lot other than that used in preparing the calibration standards. Prepare the CVS at a concentration that falls in the middle of the validated range of the calibration curve. The CVS should be analyzed on the HPLC after each calibration set and at regular intervals throughout the sequence, bracketing groups of samples. The CVS is used to verify the quality and stability of the calibration curve(s) throughout the run.

10.4.3 Using the hydrolysis liquor obtained in step 10.2.2, transfer an approximately 20 mL aliquot of each liquor to a 50 mL Erlenmeyer flask.

10.4.4 Use calcium carbonate to neutralize each sample to pH 5 – 6. Avoid neutralizing to a pH greater that 6 by monitoring with pH paper. Add the calcium carbonate slowly after reaching a pH of 4. Swirl the sample frequently. After reaching pH 5 – 6, stop calcium carbonate addition, allow the sample to settle, and decant off the supernatant. The pH of the liquid after settling will be approximately 7. (Samples should never be allowed to exceed a pH of 9, as this will result in a loss of sugars.)

10.4.5 Prepare the sample for HPLC analysis by passing the decanted liquid through a 0.2 μm filter into an autosampler vial. Seal and label the vial. Prepare each sample in duplicate, reserving one of the duplicates for analysis later if necessary. If necessary, neutralized samples may be stored in the refrigerator for three or four days. After this time, the samples should be considered compromised due to potential microbial growth. After cold storage, check the samples for the presence of a precipitate. Samples containing a precipitate should be refiltered, while still cold, through a 0.2 μm filters.

10.4.6 Analyze the calibration standards, CVS, and samples by HPLC using a Shodex sugar SP0810 or Biorad Aminex HPX-87P column equipped with the appropriate guard column.

HPLC conditions:
Injection volume: 10 – 50 μL, dependent on concentration and detector limits
Mobile phase: HPLC grade water, 0.2 μm filtered and degassed
Flow rate: 0.6 mL / minute
Column temperature: 80 - 85°C
Detector temperature: as close to column temperature as possible
Detector: refractive index
Run time: 35 minutes
Note: The deashing guard column should be placed outside of the heating unit and kept at ambient temperature. This will prevent artifact peaks in the chromatogram.

10.4.7 Check test sample chromatograms for presence of cellobiose and oligomeric sugars. Levels of cellobiose greater than 3 mg/mL indicate incomplete hydrolysis. Fresh samples should be hydrolyzed and analyzed.

10.4.8 Check test sample chromatograms for the presence of peaks eluting before cellobiose (retention time of 4-5 minutes using recommended conditions). These peaks may indicate high levels of sugar degradations products in the previous sample, which is indicative of over hydrolysis. All samples from batches showing evidence of over-hydrolysis should have fresh samples hydrolyzed and analyzed.

10.5 Analyze the sample for acetyl content if necessary

10.5.1 Prepare 0.005 M (0.01 N) sulfuric acid for use as a HPLC mobile phase. In a 2L volumetric flask, add 2.00 mL of standardized 10 N sulfuric acid and bring to volume with HPLC grade water. Filter through a 0.2 μm filter and degas before use. If 10N sulfuric acid is not available, concentrated sulfuric acid may also be used. 278 μl concentrated sulfuric acid brought to volume in a 1L volumetric flask with HPLC grade water will also produce 0.005 M sulfuric acid.

10.5.2 Prepare a series of calibration standards containing the compounds that are to be quantified. Acetic acid is recommended, formic acid and levulinic acid are optional. A range of 0.02 to 0.5 mg/mL is suggested. An evenly spaced four point calibration is suggested. If standards are prepared outside of the suggested ranges, the new range for these calibration curves must be validated.

10.5.3 Prepare an independent calibration verification standard (CVS) for each set of calibration standards, using components obtained from a source other than that used in preparing the calibration standards. The CVS must contain precisely known amounts of each compound contained in the calibration standards, at a concentration that falls in the middle of the validated range of the calibration curve. The CVS should be analyzed on the HPLC after each calibration set and at regular intervals throughout the sequence, bracketing groups of samples. The CVS is used to verify the quality and stability of the calibration curve(s) throughout the run.

10.5.4 Prepare the sample for HPLC analysis by passing a small aliquot of the liquor collected in step 10.2.2 through a 0.2 μm filter into an autosampler vial. Seal and label the vial. If it is suspected that the sample concentrations may exceed the calibration range, dilute the samples as needed, recording the dilution. The concentrations should be corrected for dilution after running.

10.5.5 Analyze the calibration standards, CVS, and samples by HPLC using a Biorad Aminex HPX-87H column equipped with the appropriate guard column.

HPLC conditions:
Sample volume: 50 μL
Mobile phase: 0.005 M sulfuric acid, 0.2 μm filtered and degassed
Flow rate: 0.6 mL / minute
Column temperature: 55 -65°C
Detector temperature: as close to column temperature as possible
Detector: refractive index
Run time: 50 minutes

APPENDIX 3- Modelling comparison (one group of OH vs two groups)

Bahia pulp- 30 ºC

Fit Comparison of Models (18.7.2012 17:10:37)

Description

	Model1	Model2
Input Data	[Book1]"vs OH"!A[1:22],[Book1]"vs OH"!B[1:22],--	[Book1]Sheet2!A[1:22],[Book1]Sheet2!B[1:22],--
Fit Report	[Book1]FitNL1!	[Book1]"FitNL6 vs OH"!
Equation	A * exp(-k * x)	3*(A*exp(-kf*x) + (1-A)*exp(-ks*x))
Function	pruebak (User)	ohdec (User)
Number of Points	22	22
Number of Parameters	1	3

Preferred Model

	Model Name
AIC	Model1
F-Test	Model1

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,56783	22	1	-75,82198	0,93272
Model2	0,556	22	3	-70,56357	0,06728

Model1 has lower AIC value and so is more likely to be correct.
This model is 13.8628 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	0,20203	2	19	0,8188

At the 0.05 significance level, Model1 is more likely to be correct.
Note: The F-test results assume the two models are nested.

Bahia Pulp- 25 ºC

Fit Comparison of Models (18.7.2012 17:49:23)

Description

	Model1	Model2
Input Data	[Book2]Sheet1!A,[Book2]Sheet1!B,--	[Book2]Sheet1!A,[Book2]Sheet1!B,--
Fit Report	[Book2]FitNL2!	[Book2]FitNL1!
Equation	A * exp(-k * x)	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))
Function	pruebak (User)	ohdec (User)
Number of Points	9	9
Number of Parameters	1	3

Preferred Model

	Model Name
AIC	Model1
F-Test	Model1

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,09251	9	1	-35,19893	0,99614
Model2	0,08377	9	3	-24,09181	0,00386

Model1 has lower AIC value and so is more likely to be correct.
This model is 258.156 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	0,31289	2	6	0,74258

At the 0.05 significance level, Model1 is more likely to be correct.
Note: The F-test results assume the two models are nested.

Saiccor pulp – 30 ºC

Fit Comparison of Models (20.7.2012 11:45:34)

Description

	Model1	Model2
Input Data	[Book3]Sheet1!A[1:9],[Book3]Sheet1!B[1:9],--	[Book3]Sheet1!A[1:9],[Book3]Sheet1!B[1:9],--
Fit Report	[Book3]FitNL2!	[Book3]FitNL1!
Equation	A * exp(-k * x)	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))
Function	pruebak (User)	ohdec (User)
Number of Points	9	9
Number of Parameters	1	3

Preferred Model

	Model Name
AIC	Model1
F-Test	No conclusion

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,13733	9	1	-31,64347	0,99753
Model2	0,13735	9	3	-19,64192	0,00247

Model1 has lower AIC value and so is more likely to be correct.
This model is 403.741 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	-5,15039E-4	2	6	--

There is not enough information to draw conclusion

Saiccor pulp- 25 ºC

Fit Comparison of Models (20.7.2012 14:32:07)

Description

	Model1	Model2
Input Data	[Book4]Sheet1!A[1:8],[Book4]Sheet1!B[1:8],--	[Book4]Sheet1!A[1:8],[Book4]Sheet1!B[1:8],--
Fit Report	[Book4]FitNL2!	[Book4]FitNL1!
Equation	A * exp(-k * x)	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))
Function	pruebak (User)	ohdec (User)
Number of Points	8	8
Number of Parameters	1	3

Preferred Model

	Model Name
AIC	Model1
F-Test	No conclusion

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,07457	8	1	-31,00416	0,99943
Model2	0,07468	8	3	-16,05815	5,67896E-4

Model1 has lower AIC value and so is more likely to be correct.
This model is 1759.89 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	-0,00396	2	5	--

There is not enough information to draw conclusion

Domsjö pulp

Fit Comparison of Models (18.7.2012 17:39:38)

Description

	Model1	Model2
Input Data	[Book8]Sheet1!A[1:8],[Book8]Sheet1!B[1:8],--	[Book8]Sheet1!A[1:8],[Book8]Sheet1!B[1:8],--
Fit Report	[Book8]FitNL2!	[Book8]FitNL1!
Equation	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))	A * exp(-k * x)
Function	ohdec (User)	pruebak (User)
Number of Points	8	8
Number of Parameters	3	1

Preferred Model

	Model Name
AIC	Model2
F-Test	Model1

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,0158	8	3	-28,48504	0,14925
Model2	0,06612	8	1	-31,9661	0,85075

Model2 has lower AIC value and so is more likely to be correct.
This model is 5.70036 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	7,96279	2	5	0,02791

At the 0.05 significance level, Model1 is more likely to be correct.
Note: The F-test results assume the two models are nested.

Botnia paper pulp

Fit Comparison of Models (18.7.2012 17:47:21)

Description

	Model1	Model2
Input Data	[Book9]Sheet1!A[1:7],[Book9]Sheet1!B[1:7],--	[Book9]Sheet1!A[1:7],[Book9]Sheet1!B[1:7],--
Fit Report	[Book9]FitNL2!	[Book9]FitNL1!
Equation	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))	A * exp(-k * x)
Function	ohdec (User)	pruebak (User)
Number of Points	7	7
Number of Parameters	3	1

Preferred Model

	Model Name
AIC	Model2
F-Test	Model1

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,00998	7	3	-17,87451	0,3513
Model2	0,16816	7	1	-19,10113	0,6487

Model2 has lower AIC value and so is more likely to be correct.
This model is 1.84653 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	31,71409	2	4	0,00352

At the 0.05 significance level, Model1 is more likely to be correct.
Note: The F-test results assume the two models are nested.

Paskov paper pulp – 0.3 % Sulfuric acid in activation acid

Fit Comparison of Models (18.7.2012 17:15:24)

Description

	Model1	Model2
Input Data	[Book7]Sheet1!A[1:9],[Book7]Sheet1!B[1:9],--	[Book7]Sheet1!A[1:9],[Book7]Sheet1!B[1:9],--
Fit Report	[Book7]FitNL2!	[Book7]FitNL1!
Equation	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))	A * exp(-k * x)
Function	ohdec (User)	pruebak (User)
Number of Points	9	9
Number of Parameters	3	1

Preferred Model

	Model Name
AIC	Model1
F-Test	Model1

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,01824	9	3	-37,81146	0,86637
Model2	0,10484	9	1	-34,07297	0,13363

Model1 has lower AIC value and so is more likely to be correct.
This model is 6.48339 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	14,24174	2	6	0,00527

At the 0.05 significance level, Model1 is more likely to be correct.
Note: The F-test results assume the two models are nested.

Softwood FE 2035 – 0.3 % Sulfuric acid in activation acid

Fit Comparison of Models (18.7.2012 17:06:03)

Description

	Model1	Model2
Input Data	[Book5]Sheet1!A[1:8],[Book5]Sheet1!B[1:8],--	[Book5]Sheet1!A[1:8],[Book5]Sheet1!B[1:8],--
Fit Report	[Book5]FitNL1!	[Book5]FitNL2!
Equation	A * exp(-k * x)	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))
Function	pruebak (User)	ohdec (User)
Number of Points	8	8
Number of Parameters	1	3

Preferred Model

	Model Name
AIC	Model1
F-Test	Model1

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,06227	8	1	-32,4459	0,97778
Model2	0,0248	8	3	-24,87713	0,02222

Model1 has lower AIC value and so is more likely to be correct.
This model is 44.0086 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	3,7768	2	5	0,10012

At the 0.05 significance level, Model1 is more likely to be correct.
Note: The F-test results assume the two models are nested.

Softwood FE 2035 – 0.6 % Sulfuric acid in activation acid

Fit Comparison of Models (20.7.2012 19:35:25)

Description

	Model1	Model2
Input Data	[Book6]Sheet1!A[1:8],[Book6]Sheet1!B[1:8],--	[Book6]Sheet1!A[1:8],[Book6]Sheet1!B[1:8],--
Fit Report	[Book6]FitNL1!	[Book6]FitNL2!
Equation	A * exp(-k * x)	3*(A*exp(-ks*x) + (1-A)*exp(-kf*x))
Function	pruebak (User)	ohdec (User)
Number of Points	8	8
Number of Parameters	1	3

Preferred Model

	Model Name
AIC	Model1
F-Test	Model2

Akaike's Information Criterion Test (AIC)

	RSS	N	Params	AIC	Akaike Weight
Model1	0,05298	8	1	-33,73799	0,84512
Model2	0,01252	8	3	-30,34435	0,15488

Model1 has lower AIC value and so is more likely to be correct.
This model is 5.45655 times more likely to be correct.

F-test

	F	Numer.DF	Denom.DF	Prob > F
	8,07775	2	5	0,02716

At the 0.05 significance level, Model2 is more likely to be correct.
Note: The F-test results assume the two models are nested.

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