2006:18

LICENTIATE THESIS

# Studies of Ester Formation on a Cellulose Matrix

Anna Pantze

Luleå University of Technology
LTU Skellefteå
Division of Wood Science and Technology

2006:18 | ISSN: 1402-1757 | ISRN: LTU-LIC -- 06/18 -- SE

# LICENTIATE THESIS

# Studies of Ester Formation on a Cellulose Matrix

Anna Pantze

Luleå University of Technology
Div. of Wood Science and Technology
LTU Skellefteå
931 87 Skellefteå, Sweden

# ABSTRACT

In this work a model system has been developed to quantitatively study esterification of cellulosic material during drying and heating in which solid-state conditions can be said to predominate. The formation of ester cross-links in cellulosic or lignocellulosic composite materials during drying and heating is of interest for production of paper and wood composite boards, for wood modification and in giving cotton materials improved characteristics.

The results support the hypothesis that direct ester formation, without anhydride intermediate, occurs between carboxylic acids of suitable structure and cellulosic hydroxyls at elevated temperatures even after such short reaction times as 5 minutes. Ester formation has been observed at temperatures ranging from 90°C to 180°C.

Another important conclusion is that a hydroxy or keto group in alpha position of the carboxylic acids seems to favour ester formation. A critical parameter for ester formation is pH, and the results indicate that $pH < 2$ strongly favours esterification reactions, whereas almost no esters are produced at $pH > 5–6$. In the experiments, low moisture content, higher temperatures and longer reaction times also favour ester formation, with some exceptions. Another interesting finding is that three pyrrolidine structures are produced after esterification and aminolysis of 2-ketobutyric acid. One of the structures indicates that 2-ketobutyric acid is reactive in two positions and could therefore be a potential cross-linker.

Esterifications of five structurally different carboxylic acids—2(R)-hydroxybutyric acid, 2-ketobutyric acid, 3-hydroxybutyric acid, hexanoic acid and veratric acid—have been studied. The carboxylic acids and moisture were added to ordinary cellulosic filter paper. Samples were heated at temperatures ranging from 22°C to 180°C between 5 and 45 minutes. Quantitative analysis of ester formation, in this case between the monocarboxylic acids and the cellulose's hydroxyl groups, was performed using aminolysis/gas chromatography.

## ACKNOWLEDGEMENT

This Licentiate thesis was carried out at Luleå University of Technology, Division of Wood Science and Technology, under supervision of Professor Ulla Westermark and Olov Karlsson.

I would like to acknowledge *Fibernätverket* and *EU Mål 1 Norra Norrland* who have founded my work.

I would also like to thank LTU for financial supporting me through Arena Global Resources Research School.

## PREFACE

Att jag skulle börja forska och så småningom skriva en licentiatavhandling var kanske inte helt väntat.

Under mina första utbildningsår var jag nämligen inte så intresserad av att lära mig nya saker. När vi i tredje klass skulle lära oss engelska ansåg jag det helt onödigt. Min fröken förklarade vänligt att det kunde behövas i ett framtida jobb. ”I så fall ska jag bli städerska” var då mitt svar och min ärliga avsikt. Vid tioårsåldern deklarerade jag även ”Det jag inte kan, det kan jag inte lära mig!”

Någonstans på vägen har jag i alla fall börja tycka det är intressant att lära mig nya saker och idag är det riktigt kul att forska.

En viktig drivkraft i mitt nuvarande forskningsarbete är tron på att min forskning ska kunna vara till hjälp i utvecklingen av mer miljövänliga trä produkter. Jag har även turen att ha en handledare som drivs av att försöka hitta miljömässigt bättre alternativ. Ullas drivkraft, energi och idéer tillsammans med Olovs lugna åsikter har varit ovärderliga för mitt arbete.

Under min tid på LTU har jag inte bara lärt mig mer om trä utan också fått möjlighet att delta i forskarskolan jordens resurser tillsammans med andra naturvetare, jurister, ekonomer och samhällsvetare. Den har varit mycket viktig för mig och alla dessa smarta och miljömedvetna människor ger mig framtidstro.

Jag vill också passa på och tacka alla trevliga och roliga människor vid LTU för att ni valt att jobba just här. Polengänget, Carmen, Dennis, Hansson, Bystedt och alla andra – det är roligt att träffa er varje dag. Calle, som tog sej tid att hjälpa till när jag höll på att bli galen på mitt analysinstrument får en guldstjärna– utan din hjälp kunde jag ha smulat sönder instrumentet och min forskningskarriär varit över…

Brian Reedy – Tack, för att du granskat min Svengelska.

Till sist vill jag skänka en tanke till de jag älskar Fredrik, Ida och Alva. Utan er vore allt annat meningslöst.

Skellefteå, Mars 2005

Anna Pantze

## LIST OF PAPERS

| | |
|---|---|
| I | Pantze A., Westermark U., Karlsson O. A model system to study esterification reactions in cellulosic or lignocellulosic material. Submitted to Holzforschung. |
| II | Pantze A., Westermark U., Karlsson O. Studies of ester formation on cellulosic material. Submitted to Holzforschung. |
| III | Pantze A., Westermark U., Karlsson O. (2005) Formation of ester cross linkage in lignocellulosic materials during drying and heating. In proceedings: 13th ISWFPC, Auckland, New Zealand. APPITA. May 16-19. p. 297-300. |

# TABLE OF CONTENTS

ABSTRACT
ACKNOWLEDGMENTS
PREFACE
LIST OF PAPERS

**PAPERS I - III**

# INTRODUCTION

Wood is a renewable and environmentally friendly material, and an increased use of material from renewable sources is highly desired for a sustainable development. In some applications, more homogeneous or formable wood products such as particleboard, MDF, HDF or OBS are needed to replace, for example, plastics or other materials. However, wood composite products such as particle- and fibreboard contain10%–15% glue, mostly based on formaldehyde/urea or isocyanates. Neither of these chemicals can be considered environmentally friendly. Our research group has developed wood particleboard and fibreboard produced without glue (Westermark and Karlsson 2003b). The process is based on oxidation of wood material with hydrogen peroxide and an iron catalyst, followed by pressing at elevated temperatures. This new type of environmentally friendly produced boards has good mechanical properties and low swelling.

The fibre adhesion mechanism of the boards is unclear. More insight would be helpful to further improve the bonding and the quality of these new boards. It is likely that esterification is one of the reactions involved in the autoadhesion mechanism. Very little is known of direct esterification in solid-state conditions, and a more basic knowledge could also be useful in understanding other types of processes in wood, paper and textile modifications.

## Objectives

The main objective of this work was to find support for the hypothesis that direct ester formation, without anhydride intermediate, occurs between carboxylic and hydroxylic groups in solid materials at elevated temperatures. A secondary goal was to study how moisture content, structurally different carboxylic acids, pH, reaction time and temperature influence ester formation.

To accomplish this, a model system has been developed in which carboxylic acids are esterified on cellulosic hydroxyls and the esters produced are quantified.

## Limitations

As all experiments have been performed in a model system, this work can only support, and not prove, ester formation in the environmentally friendly boards or similar processes.

## BACKGROUND

This background will focus on: firstly, the environmentally friendly boards, the oxidation process and suggested adhesion mechanism; secondly, other processes where knowledge of direct ester formation can be useful; thirdly, different analysis techniques in which esters can be determined. Many different analysis techniques were considered before choosing a model system and aminolysis/gas chromatography.

### Environmentally friendly wood particle- or fibreboard

The process for giving wood particles or fibres self-bonding properties and producing boards is not complicated. More detailed descriptions can be found in two conference proceedings (Karlsson and Westermark 2002; Westermark and Karlsson 2003a). Basically, a ferrous solution is sprayed over the wood material followed by the addition of hydrogen peroxide. After oxidative treatment, the wood material is dried at about 60ºC. It is then possible to store this dried activated material for weeks before the actual boards are manufactured. Just before pressing, the moisture content of the activated material is adjusted to around 12% by spraying of water. Fibre or wood particles are thereafter poured into a press form and pressed with ~2.6 MPa at ~170 ºC for ~2 minutes. After release of pressure, the boards are allowed to cool at room temperature to reach final hardness.

The fibre adhesion mechanism of the boards is unclear, but some interesting facts regarding the process parameters and unpublished studies of the boards are presented here. Higher hydrogen peroxide charge during oxidation led to an increase of strength or internal bonding (IB). A lower amount of catalysts, on the other hand, slowed down oxidation, but similar strength properties were ultimately obtained. This indicates that the number of bonding points is higher in boards prepared from wood material activated with larger amounts of oxidants. Another fact is that the number of acidic groups in dried activated material increases with higher charges of hydrogen peroxide. Acid content in the pressed boards is also generally around 30% lower than in the activated material before pressing. This can result from evaporation of volatile acids, degradation or esterification of acids. These initial unpublished studies raised the question whether ester formation can be an important bonding mechanism in the boards. However, other types of mechanisms may also be involved. Understanding the oxidation mechanism is important to understanding what types of bonding mechanisms one can expect.

#### *Oxidation of wood constituents with hydrogen peroxide and ferrous ions*

The main constituents of wood are cellulose (40%–45%), hemicellulose (20%–30%) and lignin (20%–32%). Minor amounts of extractives are also present in wood. Cellulose is a linear polysaccharide composed of glucose units, while hemicellulose is a branched polysaccharide built up of different monomeric sugars such as xylose, mannose and glucose. Lignin is a complex, branched polyphenylpropanoid formed by radical coupling between phenylpropane units. These three main constituents of wood have the possibility to react with active species during oxidation.

The oxidation solution used in producing the environmentally friendly boards with hydrogen peroxide and dissolved iron is called Fenton's reagent. The ferrous ions (Fe (II)/Fe (III)) decompose hydrogen peroxide ($H_2O_2$), and it has been suggested that reactive species such as different oxygen radicals ($HO^\bullet$, $HO_2^\bullet$, etc.) are formed (Walling 1975). The stoichiometry of Fenton's reagent is complex, and all reactive species formed have the ability react with the wood material.

Reaction studies in which Fenton's reagent or hydroxyl radicals oxidize lignin-like aromatic substances indicate that these oxidizing agents are very nonselective (Hamilton *et al.* 1966; Gierer *et al.* 1992). Formation of radicals and further oxidation to different structures such as carboxyls, carbonyls, hydroxyls and ketones have been reported (Nguyen 1982; Gierer *et al.* 1992; Widsten *et al.* 2003). In Figure 1, four introduced functionalities in oxidized lignin-like structures are shown.

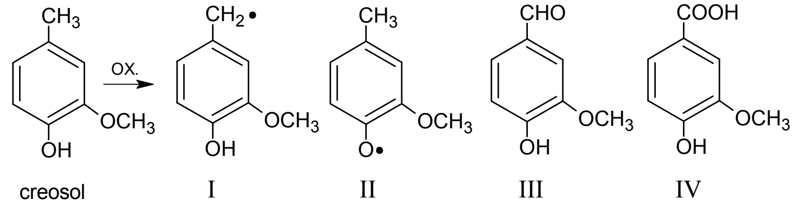


**Figure 1.** *Examples of the sorts of lignin-like structures that can form after oxidation with hydroxyl radicals (Gierer et al. 1992). The introduced functions are benzyl radical (I), phenoxy radical (II), aldehyde group (III) and carboxylic group (IV).*

Studies of how Fenton's reagent reacts with and oxidizes carbohydrates (building blocks in cellulose and hemicellulose) also indicate it to be nonselective and able to produce many different substances. Formation of radicals and further oxidation to functional groups such as carboxylic acids, aldehydes and ketones has been reported for different sugars (Moody 1964; Fry 1998). Among the substances reported to have been found are dialdehydoglucose, glucosuloses, gluconic acid, oxalic acid, formaldehyde, 2-ketogluconic acid and many more. The oxidation seems to both introduce functional groups and degrade the carbohydrates.

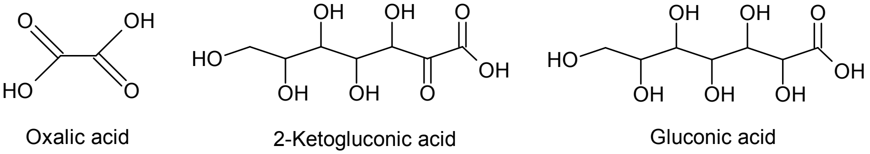


**Figure 2.** *Three examples of carboxylic acids found after oxidation of glucose with Fenton's reagent (Moody 1964).*

## Adhesion mechanisms

After oxidation, different functionalities such as radicals, carboxyls, carbonyls and ketones probably exist together with a natural abundance of hydroxyls in cellulose and lignin. A covalent bonding is expected in the adhesion mechanism, as the boards have some resistance to swelling. Some possible adhesion mechanisms are proposed below.

In 2003, Widsten *et al.* suggested that radicals coupling between lignin units (Figure 3 a) take part in the adhesion mechanism for environmentally friendly fibreboards oxidized with hydrogen peroxide. However, increased radical levels did not automatically increase strength proportionately. This indicates that at least one additional adhesion mechanism is important. Another problem with the radical theory is the fact that radicals are not known to be very stable. In experiments with irradiated beech, only 10% of the radicals survived room temperature (Fischer 1987), and the oxidized wood material can be stored for weeks before pressing the environmentally friendly boards.

Formation of hemiacetal or acetal linkage (Figure 3 b and c) is another possibility, as both carbonyl and hydroxyl groups are likely to be present within the activated material. Acetals are more stable, and water is released when the second hydroxyl reacts with a hemiacetal. If two hydroxyl groups are close enough to carbonyl, the removal of water at higher temperature should force the reaction in Figure 3 towards more acetals. Also, the presence of ketones could possibly form ketals and hemiketals in the same way, and the removal of water should also force this reaction towards more ketals.

Ester linkage (Figure 3 d) seems like a very interesting alternative, as discussed earlier, and this works is therefore focused on esterification. The removal of water at higher temperatures should, as for acetals, also force the reaction in Figure 3 towards more esters.

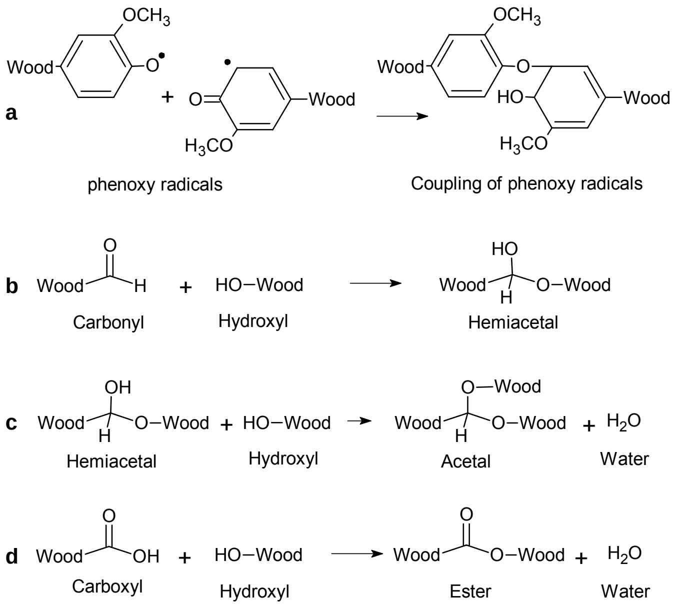


**Figure 3.** *Some proposed adhesion mechanisms in the environmentally friendly boards.*

## Other processes where direct ester formation could be important

There are also other interesting areas where knowledge of ester formation during drying and heating under solid-state conditions may well be useful.

### *Ester cross-linkage one reason behind hornification in paper processes?*

The formation of natural ester cross-links is an interesting issue for the paper industry. The term hornification is used to describe the irreversible structural changes that occur in fibres during drying (Weise 1998). In pulping processes, cellulose hydroxyls are present together with several carboxylic acids, such as metasaccharinic acid, which is formed after alkaline degradation of polysaccharides in kraft pulping, and gluconic acid, which is formed in bleaching processes (Sjöström 1992). When wood pulp fibres are dried, the fibre walls are irreversibly linked together, and the original water-swollen state can never be regained. Ester cross-linking is often cited when discussing hornification (Ruffini 1966), but the experimental evidence for such reactions is not very strong. The only experimental support found is analyses of lactones (Slavik and Kucerova 1969).

### *Improvement of wet strength in paper and durable press finish of cotton by esterification*

In the 1960s, research within the textile industry started to focus on cross-linking of cellulose with different carboxylic acids (Gagliardi and Shippee 1963; Rowland *et al.* 1967). The polycarboxylic acids react with hydroxyl groups of cellulose after high-temperature drying and curing. From the beginning, many different acids were tested. Today, mostly polycarboxylic acids such as butanetetracarboxylic acid or citric acid are used to improve both the durable press finish of cotton and the wet performance of paper (Welch 1988; Welch and Andrews 1989; Caulfield 1994; Zhou *et al.* 1995; Morris *et al.* 1996; Lee and Kim 2001).

The esterification process used in both cases is more or less the same—the cotton or paper is immersed in a solution containing polycarboxylic acids and catalysts and then dried and further cured at approximately 180°C for 1–3 minutes. The esterification reactions take place in solid-state systems and at the same temperatures and reaction times as for environmentally friendly boards.

However, polycarboxylic acids have the capability to form an anhydride intermediate (Yang *et al.* 1996), which is considered more effective in esterification than free carboxylic acids. In 1996, using findings based on FT-IR analysis, Yang and Wang claimed that only those carboxylic acids that form cyclic anhydride intermediates esterify cotton cellulose. Others argue that carboxyl groups can esterify cellulose without an anhydride intermediate (Gagliardi and Shippee 1963; Rowland *et al.* 1967; Welch and Peters 1997). That durable press finishes are improved when cured with dicarboxylic acids supports the latter theory, since a dicarboxylic acid only has the ability to form one cyclic anhydride. The second acid in a dicarboxylic acid has no chance to form an anhydride intermediate after the first acid has esterified, as illustrated in Figure 4.

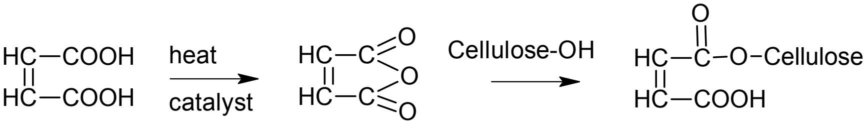


**Figure 4.** *Esterification of one carboxylic group of maleic acid through anhydride intermediate (Welch and Peters 1997).*

*Chemical modification of wood by treatment with anhydrides*

Esterification is a chemical modification of wood that has the potential to improve wood's properties. Most of the research on esterified wood today is concerned with improvement of dimensional stability and resistance to fungal attack and decay (Iwamoto and Itoh 2005; Larsson-Brelid 1998; Rowell 1983) and with improving compatibility in polyethylene/wood-flour composite systems (Oksman *et al.* 1998). Another quality of esterified wood is improved light stability (Chang and Chang 2001).

Anhydrides together with catalysts are known to be very reactive. The reaction of acetic anhydride and succinic anhydride on wood is presented in Figure 5. During treatment the wood is soaked in anhydride solution and heat is applied for some hours before left-over chemicals are washed away and the wood is dried and heated to around 120°C for hours. In treatments with acetic anhydride, the hydrophilic hydroxyl groups are replaced by an ester link and a more hydrophobic methyl group (-COOCH3). The wood becomes more water resistant, which improves its dimensional stability and decay resistance. For every ester, a corresponding acid is produced, and if the produced acids were also to form ester links to hydroxyl groups of wood, the process would be more effective.

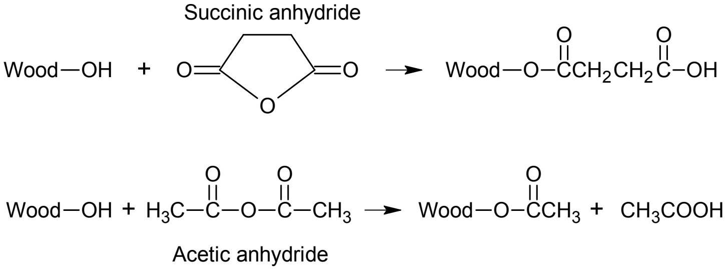


**Figure 5.** *Modification reactions between wood and succinic or acetic anhydride.*

In treatments with cyclic anhydrides such as succinic anhydride, the situation is slightly different. The carboxylic acid formed with esterification is now attached to the wood, and the acid function is not especially hydrophobic. If the free acid also were to esterify, not only the hydrophobic properties would be improved, but also an extra cross-link would stabilize the material even better.

So, knowledge of direct esterification can be useful in understanding many aspects of wood modification.

## Techniques to analyse esters in solid materials

Chemical analysis of materials is not an easy task, and no magic black box exists in which a material can be scanned and all functional groups, chemical structures and bonds are determined. It is necessary to know what type of substances or functional groups, etc., are expected and whether qualitative or quantitative analyses are needed. Problems with interfering effects from similar functional groups in the matrix (in this case wood components) also need to be solved.

Ideally, ester linkages in a pressed board of wood or fibres should be directly quantitatively determined. However, the material is solid, and the expected ester linkages are part of the complex network of lignin, hemicellulose and cellulose. This makes reliable direct quantification difficult.

Commonly used methods for ester analysis in cellulose and lignocellulosic material are discussed below, as well as the theory of aminolysis.

### *Fourier transform infrared spectroscopy (FT-IR)*

This technique is commonly used for ester analysis in cellulosic or lignocellulosic material (Yang 1993b; Yang *et al.* 1996; Chang and Chang 2001; Tjeerdsma and Militz 2005). An advantage of FT-IR analysis is the possibility to analyse solid samples and qualitatively determine esters. However, caution is needed when interpreting the spectra, as bands can overlap. Quantitative measurements of ester linkage in wood or cellulose are too unreliable with this technique.

The principle operation of FT-IR is based on chemical bonds' absorption of infrared energy at specific frequencies (or wavelengths) allowing the basic structure of compounds to be determined. Different functional groups, aromatic structures or other functions absorb specific wavelengths and can be identified with the help of libraries of reference spectra.

A problem in ester analyses with FT-IR is the overlap in wavelengths at around 1730 $cm^{-1}$ where both ester carbonyls (C = O) and carboxyl carbonyls (C = O) absorb. Signals from free carboxylic acids can therefore be mistaken as signals from esters. One common solution to this problem is to wash the sample with deionized water and a base 0,1 M NaOH (Yang and Wang 1996). In this procedure the carboxyl group is converted into a carboxylate anion that absorbs at 1585 $cm^{-1}$ and thus does not overlap with the esters anymore. In this procedure it is necessary to make sure that all free acids are converted to anions and that no esters have been hydrolyzed in the alkaline solution. There are also studies in which the authors argue that absorption bands don't overlap, that ester carbonyl stretching is between1729 and 1748 $cm^{-1}$ and that peaks at 1710–1725 $cm^{-1}$ arise from the carboxyl carbonyl stretching groups (Matuana *et al.* 2001).

Study of a handbook of spectrometric identification (Silverstein *et al.* 1981) reveals that the absorption bands of esters and carboxylic acids overlap. Different esters (acetates, aromatic esters, etc.) also give small differences in the absorption band and a broadening of the absorption area. Aldehydes and ketones also absorb around a wavelength of 1730 $cm^{-1}$.

### *Nuclear magnetic resonance (NMR)*

Nuclear Magnetic Resonance spectroscopy is another powerful and complex analytical tool. NMR can be used both for solution and in solid state (CP/MAS $^{13}C$-NMR). Basically, the nucleus of carbons ($^{13}C$) is exposed to a magnetic field. The nucleus shields the magnetic field, and the different shifts are functions of the nucleus and its environment.

The application of both liquid and solid $^{13}C$-NMR in lignocellulosic characterization has grown in the past decades. One reason is that carbon atoms of functional groups that contain oxygen, such as carbonyl and aldehyde, and aromatic ring substitutes can be observed. Another reason is the development of solid-state $^{13}C$ cross-polarization magic angle spinning (CP/MAS $^{13}C$-NMR). However, drawbacks to solid-phase NMR are lower sensitivity and the lack of proportionality between intensity of signals and concentration.

Ester formation has been confirmed in wood treated with acetic or other anhydrides with the help of CP/MAS $^{13}C$-NMR and FT-IR (Chang and Chang 2001). The appearance of bands at around 173 ppm is claimed to arise from the introduced carbonyl group (C=O) of the ester. This study also shows another nice feature of $^{13}C$-NMR. The different carbons in cellulose have different spins, and the relative intensity of the band showed that esterification preferably occurs in the C-6 position of cellulose.

In a characterization study of heat-treated wood, the CP/MAS $^{13}$C-NMR signal at 175 ppm (the carbonyl signal) was assigned to the carboxyl group in acetic acid obtained from deacetylation of hemicellulose (Tjeerdsma *et al.* 1998). These two examples show that $^{13}$C-NMR suffers from the same problems as FT-IR when it comes to ester analysis. It is difficult to know if the carbonyl (C=O) signal arises from carboxylic groups or from ester groups. The signals from esters and carboxylic acids lies around 170–180 ppm, and the shift positions are influenced by closeness to other functionalities such as aromatics, etc. (Silverstein *et al.* 1981).

Hence this technique is a very powerful tool in the search for functional groups or linkages or other structural features within lignocellulosic material. Comparing the spectra with reference spectra from model studies provides the opportunity to search for chemical changes in all types of wood modification processes. However, caution is needed when interpreting the spectra, as bands overlap and quantitative analyses of esters in solid, complex lignocellulosic material are not possible.

### *Titration and ion exchange methods*

In titrations, functional groups such as carboxylic acids are determined. The quantification of ester groups requires therefore several steps. First, samples are treated with alkali to hydrolyze all esters to carboxylic acids, which are determined by titration. The result is then compared with carboxylic acid content from a second sample that not has been alkali treated.

In wood material, carboxylic acids begin to dissociate at pH above 2–3, and the different types of alcoholic groups found are such weak acids that they ionize only under alkaline conditions (pH > 9). In principle this means that the total ion exchange capacity of the wood material is equivalent to the total amount of carboxylic acids. The most common titration method is based on hydrogen exchange, wherein the sample is treated with an abundance of acid to convert all carboxylic acids to hydrogen ion form. The milled wood material is then carefully washed with deionized water to remove excess free acid. Thereafter, an abundance of salt (NaCl) is added, and hydrogen ions, liberated in the exchange of H+ for Na+, are titrated potentiometrically. One source of errors with this method is the tendency of certain carboxylic groups to form lactones during acid treatment.

An alternative method in which lactonization is avoided and detection sensitivity is high is an ion exchange method in which a divalent salt ($Mg^{2+}$) is used (Sjöström *et al.* 1965). The photometrical titration curves this method results in are sharp, and the accuracy is good.

The problems with titration methods are firstly to know that all esters are hydrolyzed to carboxylate ions in the reference sample secondly to know that all acids are carboxylated before exchange ions are added and that all ions are exchanged. Another problem is that in fibres or wood particle suspensions, the acids are often found in the porous structure of the fibre walls. When these acids dissociate, the hydrogen tends to stay in the fibre phase and does not reach the external solution where titration is performed. This is called Donnan potential (Stenius and Vuorinen 1999). The Donnan potential can interfere with both conductometric and potentiometric titrations.

In a study of esterification of uronic acid, some of the titration problems mentioned above were solved (Filippov and Chernei 2002). Special attention was paid to ensure the complete hydrolysis of ester groups and the substitution of $Cu^{2+}$ ions for the hydrogen ions of carboxyl groups. The parameters in question were monitored by IR spectroscopy. The $Cu^{2+}$ ions were then measured photometrically after formation of a copper-ammonium complex, and the amount of esters was calculated from carboxylic groups in hydrolyzed and nonhydrolyzed samples. This method was an attractive alternative, as quantitative analysis of esters should be possible within wood material. However, every sample has to be carefully granulated, and the whole procedure with hydrolyzation, ion exchange, etc., would entail a lot of work.

### *Aminolysis*

Aminolysis, an analytical method used to analyse or remove acetyl groups in pyridine/pyrrolidine solution, has been presented by Månsson and Westfelt (1980). They demonstrated that aminolysis of cellulose esters produces amides of pyrrolidine (see Figure 6). Samaranayake and Glasser (1993) demonstrated that aminolysis of larger and bulkier esters also produces corresponding pyrrolidine structures.

The pyrrolidine structures are analysed with gas a chromatograph equipped with a flame ionization detector/mass spectrometer (GC-FID/MS). In principle, the compounds to be analysed are separated according to their boiling point and polarity in the gas chromatographic part and thereafter detected with FID or MS. In FID, the organic compounds are ionized within the hot flame, and the ion current produced is measured. More carbons basically generate higher currents. In MS the compounds are both fragmentized and ionized by an electric beam. Charged ions are then separated by differences in their mass-to-charge ratio. Ions are detected with an electron multiplier. MS provides information about both quantity and structure. Every component raises a mass spectrum that can be regarded as a sort of fingerprint. GC-FID and GC-MS are very reliable techniques, and the use of internal standards and calibration curves produces accurate quantitative analyses.

The only problem with this Aminolysis/GC-FID/MS method is that ester linkage between two wood components will not produce a free amide of pyrrolidine. Only esters such as cellulose acetals form a free amide pyrrolidine in the reaction solvent that can be determined with GC-FID.

# METHODS

No reliable analysis technique for quantification of ester linkages within environmentally friendly boards was found. Instead, a model system that allows reliable quantitative analysis of ester formation was developed. The model system imitates the conditions of the different processes mentioned earlier (board pressing, cross-linking of cotton and paper, hornification and wood modification) in which direct ester formation may occur. The conditions include a solid matrix, low moisture levels and elevated temperatures that also induce drying in the presence of hydroxyl and carboxyl groups.

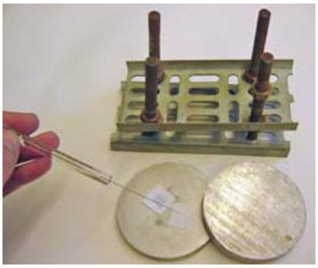


**Figure 6.** *A carboxylic acid is added to the filter paper on the aluminium plate. The frame that clamps the two plates together during esterification is in the background.*

In Paper I the model system is described in detail. In brief, a carboxylic acid is added to filter paper together with moisture. The filter paper is thereafter clamped between two aluminium plates in a frame (Figure 6). The sample is heated, and esters are formed. Aminolysis is applied to the esterified paper. Theoretically, one mol of ester produces one mol of corresponding pyrrolidine structure. The reaction solvent including pyrrolidine derivatives is then analyzed and quantified with GC-FID/MS. The esterification and aminolysis is illustrated in Figure 7.

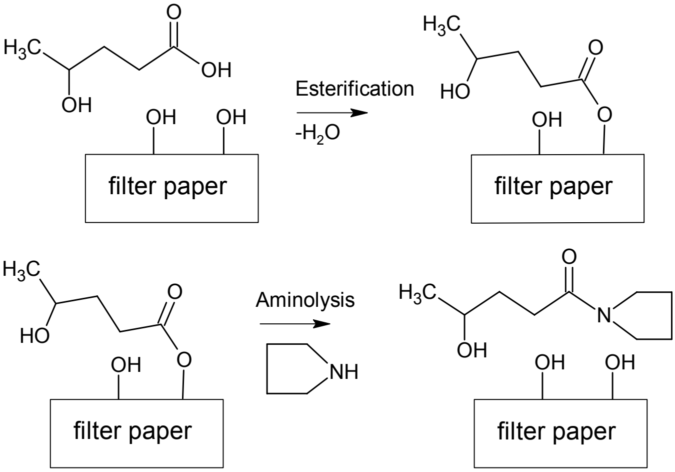


**Figure 7.** *Illustration of both the esterification of 3-hydroxybutyric acid on filter paper and the aminolysis, in which the ester is transformed to a corresponding pyrrolidine structure.*

The esterifications of five different monocarboxylic acids have been studied in this thesis, namely 3-hydroxybutyric acid, (R)-2-hydroxybutyric acid, 2-ketobutyric acid, hexanoic acid and veratric acid (see Figure 8). The experiments are described in detail in Papers I and II. Factors such as moisture content, structurally different carboxylic acids, pH, reaction time, temperature and gradual/constant heating have been examined.

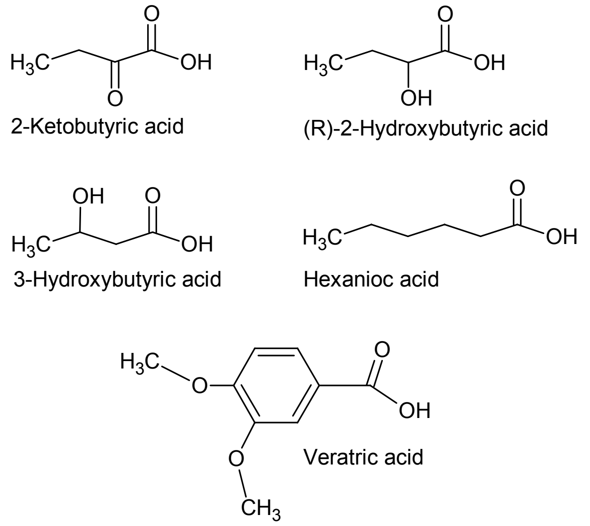


**Figure 8.** *Monocarboxylic acids used for studies of esterification.*

## RESULTS AND DISCUSSION

The results from studies with the model system strongly support the occurrence of ester formation in solid-state material during drying and heating at acidic pH (Paper I and Paper II).

An important quality of the model system is the fact that moisture can evaporate during esterification. Tests with samples heated in closed vials showed no esterification reactions at all. Aminolysis of the esters and analysis with GC-FID/MS produces repeatable and reliable quantifications, and all duplicates are in good agreement.

### Influence of moisture on ester formation

Moisture is important for the formation of esters (see Figure 9), and the influence of moisture on esterification of two structurally different acids has been examined.

As discussed earlier, ester formation should always, theoretically, be favoured by lower moisture content. This is true for 3-hydroxybutyric acid, which esterifies better with decreasing moisture content down to 13% initial moisture content. Unfortunately, experiments with moisture content lower than 13% are impossible, as the acid is dissolved in water.

Hexanoic acid, on the other hand, yields maximum ester formation at about 20% initial moisture content, with ester formation slowly decreasing at higher moisture contents. It is possible that hexanoic acids, which mismatch with the polarity of cellulose more than the hydroxyl acids, needs a better mobility of the cellulose hydroxyls for esterification. Higher moisture content increases the mobility of cellulose hydroxyls, but increased moisture content also shifts the theoretical equilibrium towards the production of fewer esters (see Figure 7). A moisture content around 20% may balance these two phenomena for hexanoic acid.

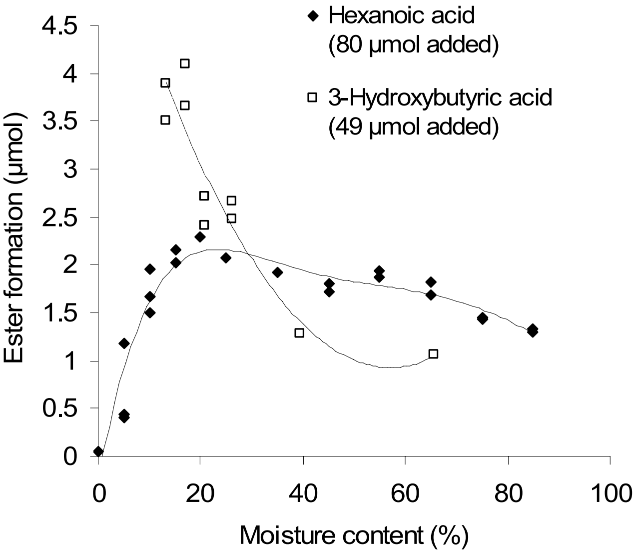
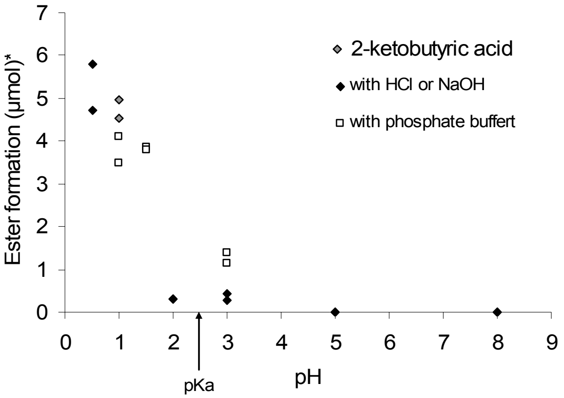


**Figure 9.** *Ester formation as a function of moisture content. Samples with 3-hydroxybutyric acid were gradually heated to 180°C over a period of 30 minutes, whilst the samples with hexanoic acid were gradually heated to 180°C over a period of 45 minutes.*

## Influence of pH and phosphate buffer on ester formation

The influence of pH on ester formation has been studied for 3-hydroxybutyric acid, 2-ketobutyric acid and hexanoic acid. All acids showed the highest esterification rate at pH below 2 (see Figures 10 and 11 and Paper II for hexanoic acid). The reactivity of 2-ketobutyric acid is very pH dependent. It is efficient in ester formation at pH < 2, but in less acidic conditions this acid is as slow in ester formation as the less effective hexanoic acid. Hexanoic acid and 3-hydroxybutyric acid follow the same pattern and are also favoured at pH < 2. Above pH 2, ester formation stabilizes at half optimum around their pKa (see Paper II) until esterification drops at pH 5–6. This drop in esterification efficiency at pH 5–6 can also be seen in esterification reactions through cyclic anhydride intermediate (Yang 1993a).

Phosphorous and phosphoric acid have earlier been suggested to increase ester formation by the classical proton-catalyzed mechanism of esterification (Welch and Peters 1997). In the samples with 3-hydroxybutyric acid and phosphate buffer, more esters were obtained than for samples without buffer at the same pH (2–3). For the other acids the effect of phosphate is not that obvious. One explanation of the effect of phosphoric and phosphorous acid on esterification can be transesterification. This means that the phosphorous-containing acids first esterify a hydroxyl group in the cellulose, and then this ester is replaced by the carboxylic acid through transesterification. Transesterification is likely, and in experiments with caprolactone, a cyclic ester, the same amounts of esters were found on the filter paper as in experiments with hexanoic acid. However, further experiments are needed for a more thorough understanding of the effect of phosphate.



*The amount of esters is the sum of 1b and 1c in Figure 14.

**Figure 10.** *Ester formation of 49 µmol of 2-ketobutyric acid when starting pH is set by addition of water, HCl, NaOH or phosphate buffer. Samples were heated gradually from 22°C to 180°C for 30 minutes, and moisture content was 26%.*

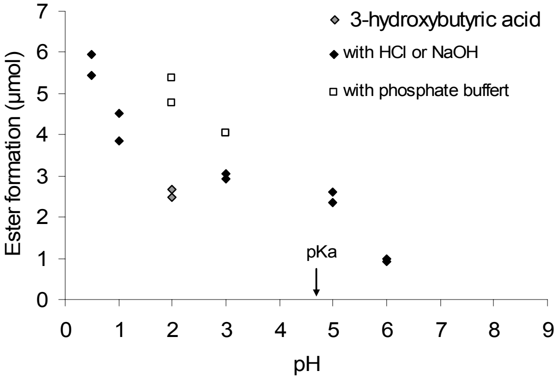


**Figure 11.** *Ester formation of 49 µmol of 3-hydroxybutyric acid when the starting pH is set by addition of water, HCl, NaOH or phosphate buffer. Samples were heated gradually from 22°C to 180°C for 30 minutes, and moisture content was 26%.*

## Influence of time/temperature and structurally different acids on ester formation

Basically, two different heating methods were used in the experiments—constant heating at 180ºC for 5 minutes or gradual heating from 22°–180ºC. In the initial experiments in this work, only hexanoic acid and a longer gradual heating scheme were used. The gradual heating scheme is illustrated in Figure12. Hexanoic acid was chosen, as aminolysis and analysis had been performed on this alkanoate before (Samaranayake and Glasser 1993). However, the esterification efficiency seemed low, exceedingly long heating sequences were needed in order to produce esters. Therefore, more polar acids that could be expected after oxidative treatment and shorter reaction times were tested. Veratric acid, which should represent oxidized lignin, showed no esterification at all, but the three structurally different butyric acids formed considerably more esters than hexanoic acid (see Table 1).

Another question arose when acids with higher esterification rates were tested. How effective at ester formation are these acids? To answer this question, butanoic anhydride was used together with a catalyst to establish a "maximum" in formed ester groups within the model system (Paper I). The "maximum" amount of esters formed from the anhydride was approximately 9.5 µmol. This indicates the maximum amount of hydroxyls that can be esterified with a 49-µmol charge of acid (see Table 1)

**Table 1.** *Ester formation with gradual and constant heating*

| Carboxylic acid | µmol added | µmol of esters formed after 30 min gradual heating to 180°C | µmol of esters formed after 5 min constant heating at180°C |
|---|---|---|---|
| 2(R)-hydroxybutyric acid | 49 | 6.8; 7.7 | 2.2; 2.0 |
| 3-hydroxybutyric acid | 49 | 3.6; 4.1 | 0.9; 1.0 |
| 2-ketobutyric acid | 49 | 4.4*; 4.4* | 1.4*; 1.2* |
| hexanoic acid | 49 | 0.7; 0.6 | no sample |
| veratric acid | 49 | 0 | 0 |
| maximum butyric anhydride | 49 | 8.8**; 9.7** | 8.8**; 9.7** |

*The amount of esters is the sum of the two identified final substances in Figure 14.
**Maximum amount of esters formed after 30 minutes gradual heating to 180ºC (Paper I).

The results presented in Table 1 show that the more effective acids produce high quantities of esters even after as short reaction times as 5 minutes at 180 ºC. The amount of esters formed from 2(R)-hydroxybutyric acid after this short reaction time reaches 20% of the "maximum" amount. Also, 2-ketobutyric acid and 3-hydroxybutyric acid show high values of ester formation after this short reaction time.

A hydroxyl or keto group in alpha position of the carboxylic acids seems to favour ester formation, as 2(R)-hydroxybutyric acid and 2-ketobutyric acid produce somewhat more esters than 3-hydroxybutyric acid.

Another object of this work was to examine the dependence of structurally different acids on ester formation. This is illustrated in Figure 12, which shows esterification when samples are gradually heated over 5 to 45 minutes. The temperature curve of the gradual heating is also shown in Figure 12. A very interesting phenomenon is the effect of temperature on the esterification reaction for the different acids. At temperatures ranging from 155°C to 180ºC, (R)-2-hydroxybutyric acid is most effective in ester formation. The 2-ketobutyric acid is most effective at temperatures ranging from 90ºC to 155ºC. The fact that this acid esterifies at lower temperatures is interesting when considering hornification problems.

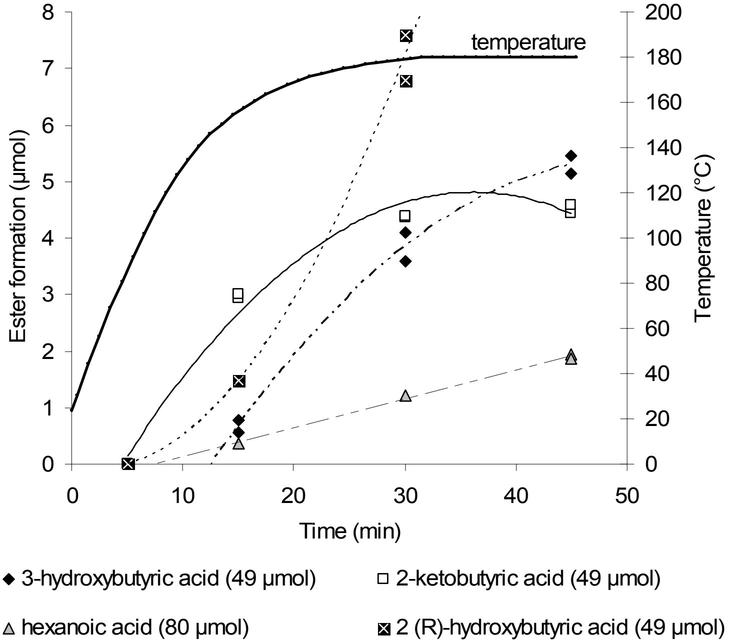


**Figure 12.** *Ester formation after gradual heating from 22°C to 180°C. To all samples, 49 µmol acid and 13% moisture were added, except for hexanoic acid, which had a moisture content of 55% and 80 µmol of acid added. For 2-ketobutyric acid, the ester formation (µmol) is the calculated sum of the two identified final substances in Figure 14.*

### *Esterification and aminolysis of 2-ketobutyric acid*

Esterification and aminolysis of 2-ketobutyric acid does not follow the expected pattern. After aminolysis, three products, absent in the blanks, instead of one, are found. The expected reaction and product, illustrated in Figure 13, is not found.

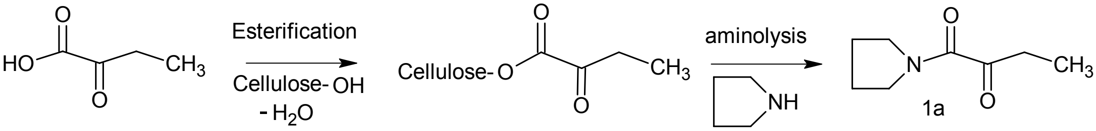


**Figure 13.** *The expected product is not found after esterification and aminolysis of 2-ketobutyric acid.*

Two substances have been identified, and the third is still unknown. The substances are illustrated in Figure 14. The unexpected outcome of ester formation with 2-ketobutyric acid affects quantification, and in all tables and figures, ester formation of 2-ketobutyric acid is reported as the sum of 1b and 1c. However, this should have only a minor influence on the results, as the peak area of 1d in the chromatogram is considerably smaller than the area of compounds 1b and 1c. In Paper II the identification and quantification of the two 2-keto esters are described in detail.

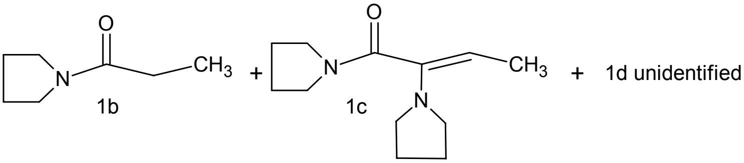


**Figure 14.** *Products, two tentatively identified, after esterification and aminolysis of 2-ketobutyric acid.*

The mechanistic reaction pathways in esterification and aminolysis of 2-ketobutyric acid are unclear. Propanoyl pyrrolidine, 1b, indicates that a hydroxyl group of cellulose has formed an ester by reacting with the keto function under release of formic acid. Another explanation could be degradation of 2-ketobutyric acid into propionic acid followed by esterification with paper hydroxyls.

Product 1c, with two pyrrolidine units attached, is very interesting. The 2-ketobutyric acid seems to be very reactive in two positions and can perhaps act as a cross-linker between two separate hydroxyl groups of cellulose. The fact that a pyrrolidine unit has reacted not only with the ester but also with the keto function raises the question whether a cellulosic hydroxyl can react in the same way. If the keto acid were to react with two hydroxyls, it could probably not be released during aminolysis and would therefore not be found during analysis. However, the mechanistic pathways for products 1b, 1c and 1d need further study.

## CONCLUSIONS

- This work presents a versatile model system capable of quantifying esterification reactions on a solid matrix such as cellulose or lignocellulose.
- The results confirm that extensive ester formation occurs in materials with low moisture levels at 180 ºC even for reaction times as short as 5 minutes when both hydroxyl and carboxyl groups are present.
- Low moisture levels and lower pH increase ester formation.
- Structural differences of the carboxylic acids are important, and a hydroxyl or keto group in alpha position of the carboxylic acids amplifies ester formation in a solid-state system.
- The mechanistic pathway for esterification and aminolysis of 2-ketobutyric acid is still unclear, but one of the structures produced indicates that this ester is reactive in two positions and could therefore be a potential cross-linker.
- The results indicate that ester formation can be one of the adhesion mechanisms in the production of environmentally friendly fibre- or particleboard produced without glue. The results also indicate that direct esterification is a mechanism that could exists side by side with esterification through an anhydride intermediate in cross-linking for improved durable press finish of cotton and wet performance of paper.

### Future work

Other possible adhesion mechanism, such as the reaction of aldehydes in materials with low moisture levels and elevated temperatures, would also be interesting to study. Removal of water at higher temperature should force the equilibrium towards more acetals in the same way as for esters.

Another interesting issue that needs more study is the reactions and esterifications of 2-ketobutyric acid.

## LITERATURE REFERENCES

Caulfield, D. F. 1994. Ester crosslinking to improve wet performance of paper using multifunctional carboxylic acids, butanetetracarboxylic and citric acid. *Tappi Journal* 77:205–211.

Chang, S.-T. and Chang, H.-T. 2001. Comparisons of the photostability of esterified wood. *Polym. Degrad. Stab.* 71(2):261–266.

Filippov, M. P. and Chernei, G. V. 2002. Determination of the Content and Degree of Esterification of Uronic Acids in Plant Tissues and Products of Their Processing. *Appl. Biochem. Microbiol.* 38:68–71.

Fisher, K. 1987. Changes in lignin and cellulose by irradiation. *Makromol. Chem. Macromol. Symp.* 12:303–322.

Fry, S. C. 1998. Oxidative scission of plant cell wall polysaccharides by ascorbate-induced hydroxyl radicals. *Biochem. J.* 332:507–515.

Gagliardi, D. D. and Shippee, F. B. 1963. Crosslinking of Cellulose with Polycarboxylic Acids. *Am. Dyest. Rep.* 52:300–303.

Gierer, J., Yang, E. and Reitberger, T. 1992. The reactions of hydroxyl radicals with aromatic rings in lignins, Studied with Creosol and 4-methylveratrol. *Holzforschung* 46:495–504.

Hamilton G. A., Hanifin J. W. Jr. and Friedman J. P. 1966. The Hydroxylation of Aromatic Compounds by Hydrogen Peroxide in the Presence of Catalytic Amounts of Ferric Ion and Catechol. Product Studies, Mechanism, and Relation to Some Enzymic Reactions. *J. Am. Chem. Soc.* 88(22):5269–5272.

Iwamoto, Y. and Itoh, T. 2005. Vapor phase reactions of wood with maleic anhydride (I): dimensional stability and durability of treated wood. *J. of Wood Sci.* 51:595–600.

Kapusniak, J. 2005. Thermal Solid State Reactions of Potato Starch with α-Hydroxy Acids. *J. Polym. Environ.* 13(4):307–318.

Karlsson, O. and Westermark, U. (2002) Resin-free particleboard by oxidation of wood. *Proc. The 6th Pacific Rim Bio-Based Composites Symposium* 1:149_153

Larsson-Brelid, P. 1998. *Acetylation of solid wood Wood properties and process development*. Doctoral thesis. Chalmers University of Technology.

Lee, E. S. and Kim, H. J. 2001. Durable press finish of cotton/polyester fabrics with 1,2,3,4-butanetetracarboxylic acid and sodium propionate. *J. Appl. Polym. Sci.* 81(3):654–661.

Matuana, L. M., Balatinecz, J. J., Sodhi, R. N. S. and Park, C.B. 2001. Surface characterization of esterified cellulosic fibers by XPS and FTIR Spectroscopy. *Wood Sci. Technol.* 35:191–201.

Moody, G. J. 1964. The actions of hydrogen peroxide on carbohydrates and related compounds. *Advances in Carbohydr. Chem.* 19:149-179

Morris, C. E., Morris, N. M. and Trask-Morell, B. J. 1996. Interaction of *meso*-1,2,3,4-Butanetetracarboxylic Acid with Phosphorus-Containing Catalysts for Esterification Cross-Linking of Cellulose. *Ind. Eng. Chem. Res.* 35(3):950–953.

Månsson, P. and Westfelt, L. J. 1980. Selective Aminolysis of Mixed Esters of Cellulose, *J. Appl. Polym. Sci.* 25:1533–1540.

Nguyen, T. 1982. The role of lignin in surface-activated bonding of lignocellulose characterized by differential scanning calorimetry. *J. Adhes.* 14(3–4):371–388.

Oksman, K., Lindberg, H. and Holmgren, A. 1998. Nature and location of SEBS-MA compatibilizer in polyethylene-wood flour composites**.** *J. Appl. Polym. Sci.* 69:201–209.

Rowell, R. M. 1983. Chemical modification of wood: a review. *Forest Products Abstracts* 6(12):363–382.

Rowland, S. P., Welch, C. M., Brannan, M. A. F. and Gallagher D. M. 1967. Introduction of Ester Cross Links into Cotton Cellulose by a Rapid Curing Process. *Text. Res. J.* 37: 933–941

Ruffini, G. (1966) Improvement in bonding of wood pulps by the presence of acidic groups. *Svensk Papperstidn.* 69:72–76.

Samaranayake, G. and Glasser, W. G. .1993. Cellulose derivatives with low DS. II. Analysis of Alkanoates. *Carbohydr. Polym.* 22:79–86.

Silverstein, R. M., Bassler, G. C. and Morrill, T. C. 1981. *Spectrometric identification of organic compounds*. Fourth edition. New York: John Wiley & Sons, Inc.

Sjöström, E., Janson, J. and Haglund, P. and Enström, B.1965. The acidic groups in wood and pulp as measured by ion exchange. *J. Pol. Sci.* 11:221–241.

Sjöström, E. 1992. *Wood Chemistry- Fundamentals and applications*. San Diego: Academic Press, Inc.

Slavik, I.. and Kucerova, M. 1969. Time profile of lactone and ester formation in cellulose upon acidification and drying. *Faserforschung und Textiltechnik* 20:346–347.

Stenius, P. and Vuorinen, T. 1999. Direct characterization of chemical properties of fibres. *Analytical Methods in Wood Chemistry, Pulping and Papermaking*. Sjöström, E. and Alén, R., eds. Heidelberg: Springer –Verlag.

Tjeerdsma, B. F., Boonstra, M., Pizzi, A., Tekely, P. and Militz H. 1998. Characterisation of thermally modified wood: molecular reasons for wood performance improvement. *Holz als Roh- und Werkstoff* 56:149–153.

Tjeerdsma, B. F. and Militz, H. 2005. Chemical changes in hydrothermal treated wood: FTIR analysis of combined hydrothermal and dry heat-treated wood. *Holz als Roh- und Werkstoff* 63(2):102–111

Walling, C. 1975. Fenton's reagent revisited. *Acc. Chem. Res.* 8:125–131.

Weise, U. 1998. Hornification – mechanism and terminology. *Paperi ja Puu/Paper and Timber* 80:110–115.

Welch, C. M. 1988. Tetracarboxylic Acids as Formaldehyde-Free Durable Press Finishing Agents part I: Catalyst, Additive and Durability Studies. *Text. Res. J.* 58:480–488.

Welch, C. M. and Andrews B. A. K. 1989. Ester crosslinks: A route to high performance nonformaldehyde finishing of cotton. Text. Chem. Color. 21:13–18.

Welch, C. M. and Peters, J. G. 1997. Mixed Polycarboxylic Acids and Mixed Catalyst in Formaldehyde-Free Durable Press Finishing. *Text. Chem. and Color.* 29:23–27.

Westermark, U. and Karlsson, O. 2003a. Auto-Adhesive Bonding by Oxidative Treatment of Wood. *Proc. 12th International Symposium on Wood and Pulping Chemistry* 1:365–368.

Westermark, U. and Karlsson, O. 2003b. "Lignocellulose product". *European Patent Application*, EP1308556.

Widsten, P., Qvintus-Leino, P., Tuominen, S. and Laine, J.E. 2003. Manufacture of fiberboard from wood fibers activated with Fenton's reagent ($H_2O_2/FeSO_4$). *Holzforschung* 57:447–452.

Yang, C. Q. 1993a. Effect of pH on Nonformaldehyde Durable Press Finishing of Cotton Fabric: FT-IR Spectroscopy Study. *Textile Res. J.* 63(7):420–430.

Yang, C. Q. 1993b. Infrared spectroscopy studies of the effects of the catalyst on ester cross-linking of cellulose by poly(carboxylic acids). *J. Appl. Polym. Sci.* 50(12):2047–2053.

Yang, C., Q., Wang, X. 1996. Formation of Cyclic Anhydride Intermediates and Esterification of Cotton Cellulose by Multifunctional Carboxylic Acids: An Infrared Spectroscopy Study. *Textile Res. J.* 66:595–603.

Yang, C. Q., Xu, Y. and Wang, D. 1996. FT-IR Spectroscopy Study of the Polycarboxylic Acids Used for Paper Wet Strength Improvement. *Ind. Eng. Chem. Res.* 35:4037–4042.

Zhou, Y.J., Luner, P. and Caluwe, P. 1995. Mechanism of Crosslinking of Papers with Polyfunctional Carboxylic Acids. *J. Appl. Polym. Sci.* 58:1523–1534.

# Paper I

# A MODEL SYSTEM TO STUDY ESTERIFICATION REACTIONS IN CELLULOSIC OR LIGNOCELLULOSIC MATERIAL

Anna Pantze, Ulla Westermark and Olov Karlsson

Luleå University ofTechnology, Div. of Wood Science
and Technology, LTU Skellefteå,931 87 Skellefteå, SWEDEN
e-mail: anna.pantze@ltu.se

Keywords: Carboxylic acid, cellulose, drying, esterification, GC-FID, GC-MS, lignocellulose, heating, reactivity, solid state reaction

## ABSTRACT

The formation of natural ester cross-linkages in cellulosic or lignocellulosic composite materials during drying and heating is of interest for production of paper and of wood composite boards and in giving cotton materials improved characteristics. A model system has been developed to quantitatively study esterification of cellulosic material during drying and heating when solid-state conditions can be said to predominate.

In the experiments, hexanoic acid and 3-hydroxybutyric acid were added to ordinary filter paper. Moisture content was adjusted, and samples were heated to temperatures ranging from 85°C to 180°C for between 15 and 45 minutes. Quantitative analysis of ester formation, in this case between the monocarboxylic acids and the cellulose's hydroxyl groups, was performed using aminolysis/gas chromatography. The influence of the acids' structure, moisture content, temperature and reaction time on ester formation was studied. The 3-hydroxybutyric acid was surprisingly effective in ester formation. This acid matches the polarity of cellulose and is one third as effective in ester formation as butyric anhydride with catalysts. The results indicate that direct esterification of monocarboxylic acid can be an important reaction in lignocellulosic material at elevated temperatures.

## INTRODUCTION

Ester linkage is a covalent bond that can cross-link and stabilize different materials. Cellulosic and lignocellulosic materials contain considerable numbers of hydroxyl groups. They are also rich in carboxylic groups, especially after oxidative treatments. Under suitable conditions, such as heating and drying, esterification reactions can probably occur between hydroxyl and carboxyl groups within the material. In the production of wood and paper composites, moisture is normally present, but solid-state conditions can be said to rule. Historically, the nature of esterification reactions has been thoroughly studied in liquid systems. However, knowledge of esterification reactions in solid-state processes is poor.

Techniques for production of environmentally friendly fibre- and particleboards produced without glue have recently been developed (Karlsson and Westermark 2002; Westermark and Karlsson 2003b; Widsten *et al.* 2003). In this new process, fibres or wood particles are oxidized with hydrogen peroxide in the presence of a catalyst. The oxidized material is formed into sheets and pressed in a hot press at approximately 170°C for 1–3 minutes, resulting in very good bonding between the fibres. The fibre adhesion mechanisms of the boards are not fully understood, but ester cross-linking, coupling of radicals, condensation reactions and hydrogen bonding have all been suggested (Widsten *et al.* 2003).

Better understanding of the adhesion mechanism is needed in order to further improve the bonding and the quality of these new environmentally friendly boards. Earlier studies in our laboratory indicate that ester linkage may be one of the adhesion mechanisms. The theory is supported by unpublished quantitative titrations of the oxidized material. The oxidized wood particles and their water-soluble parts show a 30% reduction in carboxylic acid content after pressing, which points to ester formation.

The formation of natural ester cross-links is also an interesting issue for the paper industry. The term hornification is used to describe the irreversible structural changes that occur in fibres during drying (Weise 1998). When wood-pulp fibres are dried, the fibre walls are irreversibly linked together, and the original water-swollen state can never be regained. It is important to overcome the effects of hornification in order to preserve and regain the properties of paper fibres, especially when recycling. Ester cross-linking is often cited when discussing hornification (Ruffini 1966), but the experimental evidence for such reactions is not very strong. The only experimental support found is analyses of lactones (Slavik and Kucerova 1969)

In the textile and paper industry, polycarboxylic acids that react with hydroxyl groups of cellulose are used as cross-linking agents. Acids such as butanetetracarboxylic acid or citric acid are used to improve the wet performance of paper (Caulfield 1994) and to give cotton a durable press finish (Welch 1988; Welch and Andrew 1989; Welch and Peters 1997; Choi and Welch 1994). The esterification process used in both cases is more or less the same—the cotton or paper is immersed in a solution containing polycarboxylic acids and catalysts and then dried and further cured at approximately 180°C for 1–3 minutes. The esterification reactions take place in solid-state systems and at the same temperatures and reaction time as for boards as described above. However, polycarboxylic acids have the ability to form an anhydride intermediate (Yang *et al.* 1996), which is more effective in esterification than free carboxylic acids. In 1996, using findings based on FT-IR analysis, Yang and Wang claimed that only those carboxylic acids that form cyclic anhydride intermediates esterify cotton cellulose. Others argue that carboxyl groups can esterify cellulose by a simple hydrogen ion catalyst mechanism (Rowland *et al.* 1967; Welch and Peters 1997).

The ester linkage produced within the solid material in the different types of processes mentioned above is very difficult to measure quantitatively. The processes are, however, similar and include low moisture levels, elevated temperatures and the presence of both hydroxyl and carboxyl groups. A model system that imitates these conditions and at the same time allows reliable quantitative analysis of ester formation can shed some light on the basic reactivity. If suitable carboxylic acids that not are capable of forming cyclic anhydride intermediates are used in the model system, the question of whether or not direct esterification occurs can be addressed.

Knowledge of how moisture, reaction time, heat, pH and different catalysts affect the esterification process can help to achieve better self-adhesion properties in environmentally friendly fibre- and particleboards. Better knowledge of esterification reactions will also help to improve understanding of hornification, wet performance of paper and durable press finish of cotton fabrics.

The aim of this work has been to evolve a simple model system where esterification reactions during drying and heating could be quantitatively studied. A further aim was to investigate how the basic parameters of moisture content, reaction time and heating influence direct esterification in cellulosic material.

## MATERIALS

The chemicals used in the experiments were hexanoic acid, 3-hydroxybutyric acid, butyryl chloride and hexanoyl chloride, all from Aldrich; 1-methylnaphtalene, pyridine, pyrrolidine and ethyl butyrate from Merck; and butyric anhydride from Fluka. Chromatography on silica gel was performed using PLC plates (20- x 20-cm silica gel 60 $F_{254}$, 2 mm) from Merck. The filter paper used was from Munktell (15 cm, OOH). The two round aluminium plates used in esterification were 9 mm thick and 70 mm in diameter. To measure the temperature, a PC-logger (2100 INTAB Sweden) with thin sensors was used. The pH was measured using a commercial pH meter (744 Metrohm). Analysis involved the use of a gas chromatograph equipped with mass spectrometer (Shimadzu GCMS-QP5050) and a gas chromatograph with flame ionization detector (Shimadzu GC-2014 FID). Both the instruments were equipped with 30-meter columns from Supelco (Equity 1701). The temperature program used was 40ºC 1 min, 40°–250ºC at 10ºC/min, 250ºC 5 min.

## METHODS

Each sample consisted of two pieces of paper 15 x 15 mm cut out of filter paper. To achieve initial moisture content close to 0%, all the samples were dried at 103ºC overnight and stored in a dessicator. The dry weight of each sample was 38 ± 2 mg.

The two monocarboxylic acids used to study direct ester formation with the hydroxyl groups of the filter paper were hexanoic acid and 3-hydroxybutyric acid. Hexanoic acid was used because it has a relatively high boiling point (> 200°C) and therefore wouldn’t evaporate when the samples were heated. Another reason for choosing this acid was that the aminolysis technique had been performed with this alkanoate before (Samaranayake and Glasser 1993). The 3-hydroxybutyric acid used is more hydrophilic and has a boiling point of 130°C at reduced pressure (12 mm Hg). Butyric anhydride was used to evaluate the efficiency of direct esterification.

An outline of the model system developed is shown in Figure 1.

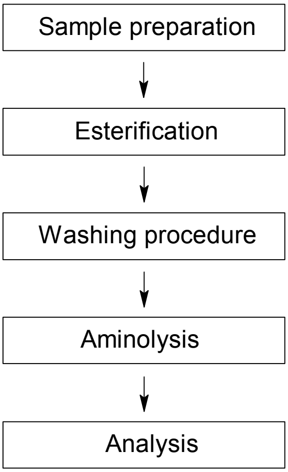


**Figure 1.** Outline of the method

*Sample preparation*

The moisture content for each sample was adjusted in the range 0% to 80%, and the carboxylic acid or anhydride (2.5 to 45 µl) was added using a syringe. The hexanoic acid and butyric anhydride were added in a concentrated form, and the 3-hydroxybutyric acid was dissolved in deionised water to 48%.

To obtain the required moisture content, different techniques were used. For samples with hexanoic acid, the filter paper was wetted in deionised water and then allowed to dry on a balance until a precalculated weight was achieved. The filter papers were then put on a thin Teflon film placed on an aluminium plate. The hexanoic acid was then quickly added before a second Teflon film and aluminium plate were placed on top of the sample.

For samples with 3-hydroxybutyric acid, the dry filter paper was taken directly from the dessicator and put on the thin Teflon film, which, as before, was placed on the aluminium plate. Then moisture content was adjusted by adding deionised water with a syringe. The required amount of water was determined from equation 1. The 3-hydroxy acid was quickly added, and the second Teflon film and aluminium plate were placed on top of the prepared sample.

Equation 1 Moisture content % = (weight of water / weight of dry sample) • 100

For the samples prepared with butyric anhydride, no moisture was added, but 12.5 µl of catalyst (3 droplets concentrated sulphuric acid in 7.5 ml acetic acid) were added. The sample was clamped between the Teflon films and aluminium plates as previously described. The catalyst system used was a modification of previously described methods for production of cellulose acetate (Hart *et al.* 1999). Blanks were prepared in the same way as the samples.

*Esterification*

During esterification, the acids or anhydride form ester linkages to the hydroxyl groups of the filter paper. This is illustrated in Figures 2 and 3.

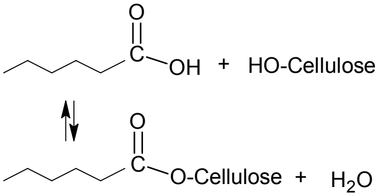


**Figure 2.** The esterification reaction between hexanoic acid and a cellulose hydroxyl group.

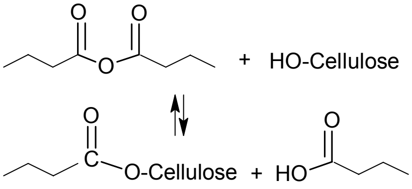


**Figure 3.** The esterification reaction between butyric anhydride and a cellulose hydroxyl group.

The samples prepared as described earlier where clamped between the two aluminium plates forced together with a small frame. The esterification was performed in an oven for periods of 10 to 45 minutes. The temperature of the oven was 180°C except in temperature experiments with hexanoic acid where oven temperatures of 85°C, 100°C, 120°C and 150°C were used. The temperature of the samples increased gradually from room temperature to oven temperature. Measurements of temperature between the aluminium plates covered with Teflon films are presented in Figure 4. It is important to note that moisture can evaporate from all samples since a 1-mm gap remains between the aluminium plates.

The prepared blanks were placed between the two aluminium plates and kept there for at least 45 minutes at room temperature.

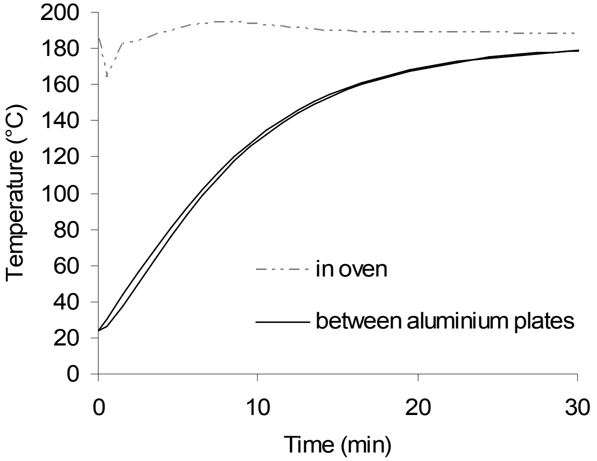


**Figure 4.** The measured temperature in the oven and between the aluminium plates as a function of time. The oven temperature was 180°C.

*Washing procedure*

After esterification, the samples were marked with scissor cuts along their edges. Six samples were then washed together with a blank. Washing was carried out using a Büchner funnel, cold tap water (1 L) followed by acetone (0.05 L). This sequence was repeated three times. After the washing procedure, the samples were allowed to dry.

*Aminolysis*

During aminolysis, pyrrolidine reacts with the esters. Theoretically one mol ester forms one mol hexanoyl pyrrolidine, 3-hydroxy-butyryl pyrrolidine or butyryl pyrrolidine. The aminolysis reaction of hexanoic ester is shown in Figure 5. The aminolysis was a modification of previously described methods (Månsson and Westfelt 1980; Samaranayake and Glasser 1993). Samples or blanks were cut into small pieces and placed in an 8-ml vial. An internal standard was added to each vial together with 1 ml of pyridine/pyrrolidine solution (1:1). The vials were capped and heated to 80°C in a sand bath for 72 hours. The samples used to obtain a calibration curve were prepared and heated in the same way as the ordinary samples. However, instead of the filter paper, known concentrations of synthesized hexanoyl pyrrolidine or butyryl pyrrolidine were added together with pyridine/pyrrolidine (1:1) and the internal standard.

Ethyl butyrate (10 μl) dissolved in ethanol (1:10) was used as an internal standard for hexanoyl pyrrolidine and 2 μl 1-methylnaphtalene dissolved in dioxane (1:10) were used as an internal standard for 3-hydroxy-butyryl pyrrolidine and butyryl pyrrolidine.

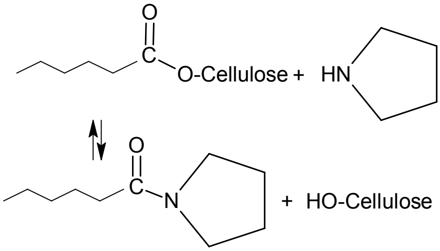


**Figure 5.** Aminolysis of cellulose hexanoate. Pyrrolidine reacts with the ester and forms hexanoyl pyrrolidine.

*Analysis*

After cooling, 1 µl of the reaction mixture was injected into the gas chromatograph. Analysis of hexanoyl pyrrolidine was performed using a gas chromatograph equipped with mass spectrometer (GC-MS). Analyses of the 3-hydroxy-butyryl pyrrolidine and butyryl pyrrolidine were performed using a gas chromatograph with flame ionization detector (GC-FID). The calibration curve for butyryl pyrrolidine was used to quantify both butyryl and 3-hydroxy-butyryl pyrrolidine. As a consequence of the FID mechanism, each carbon atom capable of hydrogenation yields almost the same signal. This means that the overall FID response for butyryl pyrrolidine and 3-hydroxy-butyryl pyrrolidine should be almost the same (Poole and Poole 1995).

*Synthesis of butyryl pyrrolidine and hexanoyl pyrrolidine used in calibration curves*

Butyryl chloride or hexanoyl pyrrolidine (2 ml) was dissolved in dichloromethane (10 ml). This was slowly added to an ice-cold solution of pyrrolidine (4.8 ml or 3.6 ml, 3 equivalent/acid chloride) in dichloromethane (30 ml). The mixture was kept at room temperature and subsequently stirred overnight. The procedures for cleaning and concentrating the two pyrrolidines differ.

The reaction mixture with butyryl pyrrolidine was washed with saturated potassium carbonate solution and filtered. The filtrate was evaporated, and the resulting product was purified by chromatography on silica gel using methanol as eluent. The synthesized butyryl pyrrolidine raised a single peak when analysed with GC-MS.

The reaction mixture with hexanoyl pyrrolidine was washed with 3 • 5 ml 3M HCl to remove excess pyrrolidine. The dichloromethane layer was separated and washed with 5% sodium bicarbonate followed by water until neutral pH was achieved. The mixture was evaporated, and hexanoyl pyrrolidine was isolated by chromatography in the same way as the butyryl pyrrolidine. Hexanoyl pyrrolidine raised a single peak with GC-MS and showed a clean NMR spectrum.

The preparations of butyryl pyrrolidine and hexanoyl pyrrolidine are modifications of methods described previously (Månsson and Westfelt 1980; Samaranayake and Glasser 1993)

### *Measurements of pH*

For three samples, pH was measured before and after esterification. The samples were prepared as ordinary samples with hexanoic acid, butyric acid or butyric anhydride with catalyst. However, instead of heating, the samples were cut into pieces and placed in a test tube. A magnet stirrer and 2 ml deionised water were added, and after 5 minutes, pH was measured. A second set of samples was esterified as described earlier at 180°C for 30 minutes. After the esterification, the samples were cut into pieces and the pH was measured as before.

### *Butylation with butyric anhydride*

An isolated test was performed to make sure that the esterification efficiency of butyric anhydrides with catalyst was as high as for acetic anhydride. Filter papers were placed in a solution containing butyric anhydride (5 ml), acetic acid (7.5 ml) and concentrated sulphuric acid (3 droplets). The solution was then heated at 70ºC for 20 minutes. The white filter paper was transformed into a transparent gel of cellulose butyrate. The method used (Harts *et al.* 1999) is for acetylation of cellulose. The test confirmed that replacing acetic anhydride with butyric anhydride also easily produces a cellulose ester.

## RESULTS AND DISCUSSION

It has previously been claimed that only esters, and not free acids, react with pyrrolidine in the aminolysis (Månsson 1980). An exception to this rule was formic acid. However, initial tests showed high values of hexanoyl pyrrolidine for both samples and blanks when no washing was carried out. The conclusion from this is that free hexanoic acids do react with pyrrolidine, and therefore all samples were carefully washed to remove any remaining free acid before aminolysis.

### *Influence of moisture and acid concentration on ester formation*

Moisture is important for the formation of esters (see Figure 6). In the esterification reaction illustrated in Figure 2, one mole of water is produced for every mole of ester. Removal of water shifts the equilibrium in favour of more esters, and, theoretically, ester formation should always be favoured by lower moisture content.

This is certainly true for 3-hydroxybutyric acid, which esterifies better with decreasing moisture content. The fact that the acid is dissolved in water (48%) makes experiments with moisture content lower than 13% impossible. Hexanoic acid, on the other hand, yields maximum ester formation at about 20% moisture, with ester formation slowly decreasing at higher moisture contents. In samples with hexanoic acid and a moisture content under 5%, ester formation was almost zero. The difference between these two acids is probably due to the different polarity and size of the acids. The ester formation maximum for hexanoic acid may be due to the presence of water leading to better mobility of the cellulose hydroxyls. This increased mobility makes it easier for the acids to find a favourable hydroxyl group to react with. Whilst higher moisture content gives better mobility, it also shifts the equilibrium towards the production of fewer esters (see Figure 2). A moisture content around 20% may balance these two phenomena.

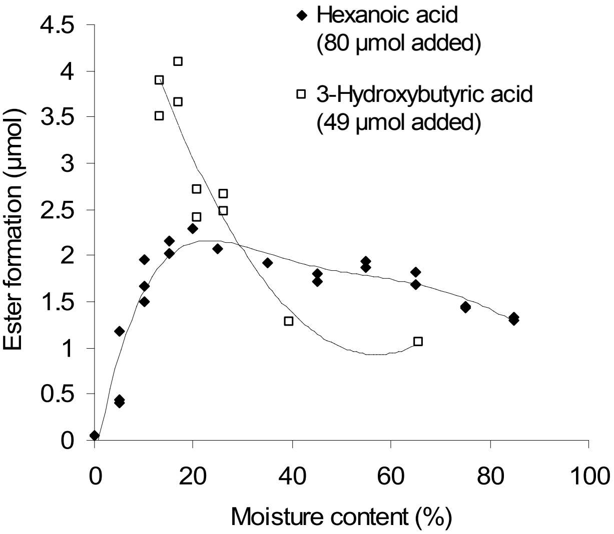


**Figure 6.** Ester formation as a function of moisture content. Samples with 3-hydroxybutyric acid were gradually heated to 180°C over a period of 30 minutes, whilst the samples with hexanoic acid were gradually heated to 180°C over a period of 45 minutes.

The amount of esters formed is also dependent on the amount of acid added and the number of available hydroxyl groups. Figure 7 shows the effect of different amounts of added hexanoic acid. It is apparent that increasing additions of hexanoic acid increase the formation of esters. These results support that the model system is reliable. The ester formation, as a function of added acid, seems to be linear to start with, becoming more asymptotic with additions over 160 µmol (20 µl). As a consequence, 80 µmol (10µl) hexanoic acid was used in the moisture, time and temperature experiments.

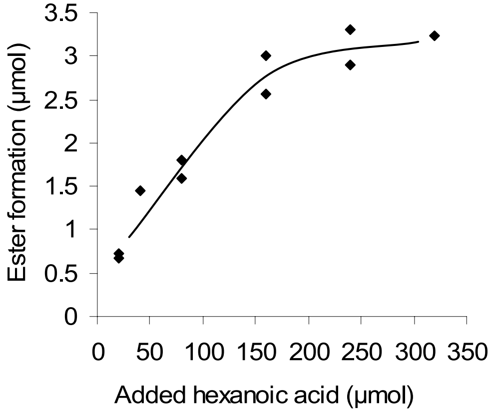


**Figure 7.** Ester formation as a function of added hexanoic acid. All samples had an initial moisture content of 45% and were gradually heated to 180°C over a period of 45 minutes.

*Influence of time and temperature on ester formation*
Esterification reactions are, as are most reactions, favoured by higher temperatures and longer reaction times, which can also be seen in our experiments in the present work (see Figure 8).

The esterification of hexanoic acid was investigated with gradual heating to five different temperatures (85°C, 100°C, 120°C, 150°C and 180ºC). Three different reaction times (15, 30 and 45 minutes) were also studied. The relationship between ester formation and reaction time is linear for all the temperatures used. It is also obvious that a temperature of 150ºC or higher is needed if at least 1% of the added hexanoic acid is to esterify within 45 minutes. The lower temperatures of 100ºC and 120ºC show rather low degrees of esterification. Even in experiments with gradual heating to 85ºC for 30 or 45 minutes, some esters formed, but less than 0.01% of the added hexanoic acid esterified. In these time and temperature experiments, only hexanoic acid was used, and the 3-hydroxybutyric acid would probably show higher levels of esterification at low temperatures. The fact that hexanoic acid is less effective at forming esters than 3-hydroxybutyric acid is discussed later.

In the processes for pressing environmentally friendly boards, improving wet performance of paper or improving the durable press finish for cotton, shorter reaction times of 1–5 minutes are used, in contrast to the 15–45 minutes used in the present work. The gradual heating in our experiments is slow, and after 15 minutes the temperature has only reached 150°C when target temperature of the oven is 180°C. In further studies, constant heating and shorter reaction times will be tested using the model system. However, the results produced thus far indicate that esterification can be an important bonding mechanism for the environmentally friendly boards as well as for cross-linking in paper and cotton.

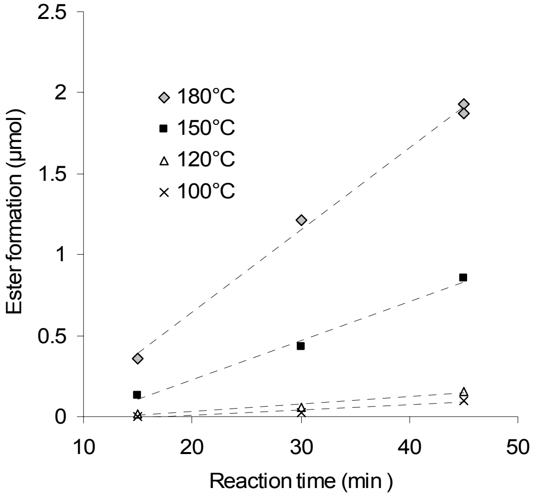


**Figure 8.** The effects of temperature and reaction time on esterification of 10 µl (80 µmol) hexanoic acid. The heating is gradual from 22°C (room temperature) to the target temperature. All samples had a moisture content of 55%.

*Evaluation of esterification efficiency*

The esterification efficiency of hexanoic and 3-hydroxybutyric acid was evaluated by comparing the amount ester linkages formed with esterification of butyric anhydride (see Table 1).

In acylation of cellulose with anhydride, almost all available hydroxyl groups are esterified. Methods for producing cellulose acetate with acetic anhydride are well known; acetic anhydride in acetic acid with concentrated sulphuric acid as a catalyst is one of them (Hart *et al.* 1999). In our experiments, butyric anhydride was used instead of acetic anhydride with acetic acid and concentrated sulphur acid as catalysts. Firstly, experiments were carried out to find a reaction time that was long enough for all available hydroxyl groups to react with the added butyric anhydride. A plateau value for ester formation for the anhydride was found after 30 minutes at 180°C, indicating that all available hydroxyl groups had reacted. Therefore, a period of 30 minutes at 180°C was used when comparing esterification efficiency as shown in Table 1.

Butyric anhydride is three times more effective than 3-hydroxybutyric acid at ester formation and fifteen times more effective than hexanoic acid. The esterification efficiency of 3-hydroxybutyric acid is surprisingly high compared to the very effective anhydride. This indicates that direct esterification of monocarboxylic acid can be an important reaction in lignocellulosic material at elevated temperatures.

The structure of the acid seems to be very important. Hexanoic acid is not as effective as 3-hydroxybutyric acid, probably due to its less polar structure or the lack of a hydroxyl group close to the carboxyl function. Further studies on the influence of other types of carboxylic acid on esterification will be published later.

As pH is likely to play an important role in esterification, it was measured for all samples in Table 1. A difference of about one-half pH unit after heating shouldn’t affect the results significantly. Furthermore, pKa values for the hexanoic acid (4.8) and 3-hydroxybutyric acid (4.7) are almost the same. It is also important to note that the pKa of both acids is above the reaction pH.

**Table 1**. A comparison in esterification efficiency between 3-hydroxybutyric acid, hexanoic acid and butyric anhydride with acid catalyst. Samples were gradually heated to 180°C over a period of 30 minutes.

| Additions | acid/anhydride µmol added | µmol ester formed | pH before heating | pH after heating |
|---|---|---|---|---|
| Butyric anhydride with acid catalyst * | 49 | 8.8; 9.7 | — | 3.9 |
| 3-Hydroxybutyric acid ** | 49 | 3.1; 3.0 | 3 | 3.2 |
| Hexanoic acid *** | 40 | 0.6; 0.7 | 3.2 | 3.5 |

* 8.3 µl butyric anhydride and 12.5 µl from 7.5 ml acetic acid and 3 droplets concentrated sulphur acid.
** 10 µl of 3-hydroxybutyric acid (48%). Moisture content 13%
*** 5 µl of hexanoic acid and 10 µl deionized water. Moisture content 26%

*The model system*

This work presents a simple model system that allows quantification of esterification reactions in cellulosic or lignocellulosic material during drying and heating. In our experiments, ordinary filter paper was chosen as the reaction medium. It is, however, possible to replace the filter paper with lignocellulosic material and even wood particles in future experiments. Additionally, the added carboxylic acids can be chosen from a wide range of acids and properties, such as pKa, or additional functional groups besides the carboxylic function can be altered. Aminolysis of the esters and analysis with gas chromatograph produced repeatable and reliable quantifications, and all duplicates showed a good correspondence. Thus the model system seems versatile and stable.

In the model system, solid-state conditions can be said to predominate. This, together with experimental temperatures of around 180°C, makes the conditions similar to those found in industrial processes (Welch 1988; Welch and Andrew 1989; Welch and Peters 1997; Choi and Welch 1994; Caulfield 1994; Westermark and Karlsson 2003a; Widsten *et al.* 2003). Another important quality of the model system is the fact that moisture can evaporate during esterification, which is also true for all the modern production processes mentioned above. Preliminary tests with samples heated in closed vials showed no esterification reactions at all.

## CONCLUSIONS

This work presents a versatile model system capable of quantifying esterification reactions in predominantly solid-state systems such as cellulosic or lignocellulosic material. Several different carboxylic acids can be tested for their ability to form ester linkage with the hydroxyl groups in cellulose. It would also be possible to examine the effects of different pH or catalysts on ester formation in future studies with the model system.

The results presented strongly support the conclusion that direct esterification can occur during drying and heating. Ester formation is favoured both by higher temperatures and longer reaction times. Moisture content is also an important factor for esterification. Ester formation increases with decreasing moisture content for 3-hydroxybutyric acid. Hexanoic acid demonstrates maximum esterification efficiency at around 20% moisture content.

Another important factor for esterification efficiency is the structure and the polarity of the acid. The 3-hydroxybutyric acid is more effective than hexanoic acid. Esterification efficiency for 3-hydroxybutyric acid is surprisingly high compared to the anhydride, which is widely recognized for its efficiency. In comparison, 3-hydroxybutyric acid esterifies one hydroxyl group when the butyric anhydride esterifies three. This indicates that direct esterification of monocarboxylic acid can be an important reaction in lignocellulosic material during drying and heating.

The results also indicate that direct ester formation can be one of the principal bonding mechanisms in environmentally friendly particle- or fibreboard (Westermark and Karlsson 2003b; Widsten *et al.* 2003). It is also likely that direct ester formation, without an anhydride intermediate, is involved in cross-linking in paper and cotton processes (Welch 1988; Welch and Andrew 1989; Caulfield 1994; Choi and Welch 1994; Welch and Peters 1997). However, more polar acids should be tested before any conclusions regarding esterification efficiency in low temperature ranges are drawn.

## REFERENCES

Caulfield, D.F. (1994) Ester crosslinking to improve wet performance of paper using multifunctional carboxylic acids, butanetetracarboxylic and citric acid. Tappi Journal. 77:205–211

Choi, H., Welch, C.M. (1994) Saturated and Unsaturated Carboxylic Acid Salts as Curing Additives for BTCA Treatment of Cotton. Text. Chem. and Color. 26:23–27

Hart, H.,Craine, L.E., Hart D.J. Laboratory Manual, Organic Chemistry, A short Course, Tenth edition, Houghton Mifflin Company 1999

Karlsson, O., Westermark, U. (2002) Resin-free particleboard by oxidation of wood, Proc. The 6th Pacific Rim Bio-Based Composites Symposium. 1:149–153

Månsson, P., Cellulose grafting by esterification, Stockholm Tekniska Högskola, Doctoral thesis, Stockholm, 1980

Månsson, P., Westfelt, L. (1980) Selective Aminolysis of Mixed Esters of Cellulose, J. Appl. Polym. Sci. 25:1533–1540

Poole, C.F., Poole, S.K. (1995) Chromatography today, Fourth Impresssion, Elsevier Science B.V. pp 260–264

Rowland, S.P., Welch, C.M., Brannan, M.A.F., Gallagher D.M. (1967) Introduction of Ester Cross Links into Cotton Cellulose by a Rapid Curing Process. Text. Res. J. 37:933–941

Ruffini, G. (1966) Improvement in bonding of wood pulps by the presence of acidic groups. Svensk Papperstidn. 69:72–76

Samaranayake, G., Glasser, W.G. (1993) Cellulose derivates with low DS. II. Analysis of alkanoates. Carbohydr. Polym. 22:79–86

Slavik, I., Kucerova, M., (1969) Time profile of lactone and ester formation in cellulose upon acidification and drying. Faserforschung und Textiltechnik. 20:346–347

Weise, U. (1998) Hornification – mechanism and terminology. Paperi ja Puu/Paper and Timber. 80:110–115

Welch, C.M. (1988) Tetracarboxylic Acids as Formaldehyde-Free Durable Press Finishing Agents part I: Catalyst, Additive and Durability Studies. Text. Res. J. 58:480–488

Welch, C.M., Andrews B.A.K. (1989) Ester crosslinks: A route to high performance nonformaldehyde finishing of cotton. Text. Chem. and Color. 21:13–18

Welch, C.M., Peters, J.G. (1997) Mixed Polycarboxylic Acids and Mixed Catalyst in Formaldehyde-Free Durable Press Finishing. Text. Chem. and Color. 29:23–27

Westermark, U., Karlsson O. (2003a). Auto-Adhesive Bonding by Oxidative Treatment of Wood, Proc. 12th International Symposium on Wood and Pulping Chemistry. 1:365–368

Westermark, U., Karlsson, O. (2003b). “Lignocellulose product”. *European Patent Application*, EP1308556

Widsten, P.,Qvintus-Leino, P., Tuominen, S., Laine J.E. (2003) Manufacture of fibreboard from wood fibres activated with Fenton's reagent ($H_2O_2$/$FeSO_4$). Holzforschung 57:447–452

Yang, C.Q., Wang, X. (1996) Formation of Cyclic anhydride intermediates and esterification of cotton cellulose by multifunctional carboxylic acids: an infrared spectroscopy study. Text. Res. J. 66:595–603

Yang, C.Q., Xu, Y., Wang, D. (1996) FT-IR Study of the polycarboxylic acids used for paper wet strength improvement. Ind. Eng. Chem. Res. 35:4037–4042

# Paper II

# STUDIES OF ESTER FORMATION ON CELLULOSIC MATERIAL

Anna Pantze, Ulla Westermark and Olov Karlsson

Luleå University of Technology, Div. of Wood Science
and Technology, LTU Skellefteå,931 87 Skellefteå, SWEDEN
e-mail: anna.pantze@ltu.se

Keywords: Carboxylic acid; cellulose; drying; esterification; heating; reactivity; solid state reaction

## ABSTRACT

This paper describes a study of the formation of ester linkages in cellulosic materials during drying and heating.

The results indicate that direct ester formation, without anhydride intermediate, occurs between carboxylic acids of suitable structure and cellulosic hydroxyls at 180 °C even after reaction times as short as 5 minutes. The 2(R)-hydroxybutyric acid is most effective in ester formation, followed by 2-ketobutyric acid and 3-hydroxybutyric acid. Hexanoic acid is less effective, and veratric acid produces no esters at all. At lower temperatures, 2-ketobutyric acid is the most effective acid in ester formation. One important conclusion is that a hydroxyl or keto group in alpha position of the carboxylic acids favours ester formation. Another interesting finding is that three pyrrolidine structures are produced after esterification and aminolysis of 2-ketobutyric acid. One of the structures indicates that 2-ketobutyric acid is reactive in two positions and could therefore be a potential cross-linker. A critical parameter for ester formation is pH, and the results indicate that pH < 2 strongly favours esterification reactions, whereas almost no esters are produced at pH > 5–6.

All experiments were preformed in a solid-state model system with low moisture content. Esterification of five structurally different carboxylic acids was studied. The carboxylic acids were added to ordinary cellulosic filter paper. Samples were heated constantly at 180°C for 5 minutes or gradually from 22°C to 180°C over periods ranging from 5 to 45 minutes. Quantitative analysis of ester formation, in this case between the mono carboxylic acids and the cellulose's hydroxyl groups, was performed using aminolysis/gas chromatography.

## INTRODUCTION

Ester linkage is a covalent bond that can cross-link and stabilize different materials. Cellulosic and lignocellulosic materials contain considerable numbers of hydroxyl groups and are also rich in carboxylic groups after oxidative treatments.

Ester formation is of interest in production of environmentally friendly fibre- and particleboard produced without glue (Karlsson and Westermark 2002; Westermark and Karlsson 2003; Widsten *et al.* 2003). In these new processes, fibres or wood particles are oxidized with hydrogen peroxide in the presence of a catalyst. The activated material is formed into sheets and pressed at ~170° C for 1–3 minutes, resulting in very good bonding. To further improve the bonding and the quality of these new boards, more insight into the fibre adhesion mechanism would be helpful. Unpublished results of quantitative titrations of carboxylic acids in the material before and after pressing indicate that ester linkage may be one of the adhesion mechanisms.

There are also other interesting areas where knowledge about ester formation during drying and heating may well be useful. In the textile and paper industry, polycarboxylic acids, which have the ability to form a cyclic anhydride intermediate (Yang *et al.* 1996), are used as cross-linking agents to improve the durable press finish of cotton (Welch 1988; Welch and Andrew 1989; Welch and Peters 1997; Choi and Welch 1994) and the wet performance of paper (Caulfield 1994). Ester cross-linking is also often cited when hornification problems in paper production are discussed (Diniz *et al.* 2004; Weise 1998). Measurements of carboxyl content before and after sheeting support this ester theory (Ruffini 1966).

It is difficult to quantitatively measure the produced ester linkage in solid materials, and the knowledge of esterification is therefore poor in the different types of processes mentioned above. The processes are, however, similar and include low moisture levels and elevated temperatures for 1–5 minutes with both hydroxyl and carboxyl groups present.

Recently, a model system that imitates such conditions and also allows reliable quantitative analysis of ester formation has been developed (paper I). The results from studies in this system strongly support the occurrence of ester formation in solid-state material during drying and heating. In the study, esters formed between hydroxyl groups of filter paper and different carboxylic acids have been subjected to aminolysis and quantified. The formation of esters is favoured by higher temperatures (180°C), longer reaction times and low moisture content. Another important finding in this study was that the structure and polarity of the carboxylic acid seems to influence esterification efficiency.

There are, however, still some gaps to fill to further confirm the importance of ester formation for the bonding mechanism in environmentally friendly particle- or fibreboard. In the earlier study (paper I), gradual heating and reaction times no shorter than 15 minutes were been tested. Studies with shorter reaction times that better match drying and hot-pressing processes are needed. Knowledge of how pH or different catalysts affect the esterification process can also help to achieve better self-adhesion properties in environmentally friendly boards.

The aim of this work has been to investigate how esterification efficiency is affected by shorter reaction times and constant heating. A further aim was to investigate how pH and structurally different carboxylic acids influence esterification efficiency in cellulosic material.

## MATERIALS

The chemicals used in the experiments were hexanoic acid, 3-hydroxybutyric acid, (R)-2-hydroxybutyric acid, 2-ketobutyric acid, veratric acid from Aldrich; 1-methylnaphtalene, pyridine, pyrrolidine, ethyl butyrate from Merck; butyric anhydride from Fluka. The filter paper used was from Munktell (15 cm, OOH). The two round aluminium plates used in esterification were 9 mm thick and 70 mm in diameter. The pH was measured using pH indicator strips from Merck (pH 0–14). Analysis was performed on a gas chromatograph equipped with mass spectrometer (Shimadzu GCMS-QP5050) and a gas chromatograph with flame ionization detector (Shimadzu GC-2014 FID). Both the instruments where equipped with 30-meter columns from Supelco, Equity 1701. The same temperature program (40ºC 1min, 40°–250ºC, 10ºC/min, 250ºC 5 min) was used for all analyses except for samples with 2-ketobutyric acid. The program for this analysis was 40ºC 1 min, 40º–100ºC 8ºC/min, 100º–150ºC 5ºC/min, 150º–250ºC 10ºC/min, 250ºC 15 min.

## METHODS

In brief: A carboxylic acid is added on filter paper together with moisture. The sample is heated, and esters are formed. Aminolysis of the esters produces amides of pyrrolidine. The pyrrolidine structures are then analyzed and quantified.

The method for preparation, esterification, washing, aminolysis and quantification of esters is described in detail in previous work (Paper I).

A few differences in the performance need comment, however.

Addition of veratric acid: Veratric acid was dissolved in concentrated ethanol, and this mixture was applied batchwise to the filter paper with a pipette. The ethanol was evaporated and the veratric acid remained as a visible white layer on the surface of the filter paper. This was the only way to apply the acid, as it was impossible to dissolve in a small amount of water. The samples with veratric acid were then dried in a desiccator before adjustment of the moisture content. After esterification with veratric acid, a special washing procedure was adapted including 0.05 L ethanol followed by 1 L water. This was repeated three times.

Adjustment of pH: Different strengths of HCl and NaOH were used for adjustment of pH. Total volumes of 15 µl of solution were mixed with the monocarboxylic acid before application to filter paper with a syringe. Moisture content was kept constant, and pH was measured before esterification. The effects of two phosphate buffers (0.1 M pH 2.1 and 0.2 M pH 5.6) were also tested. Each filter paper was soaked in the buffer (40 µl) and allowed to dry in the desiccator, and then the moisture was adjusted by addition of pH. The pH of the buffer samples was determined in a mixture of 40 µl buffer, the monocarboxylic acid and 10 µl water.

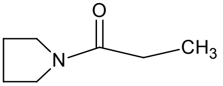
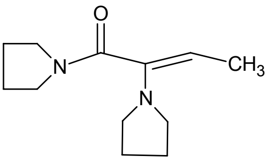
Constant heating: For some of the samples, constant heating at 180°C for 5 minutes was applied instead of gradual heating from room temperature to 180°C (heating time 5 to 30 minutes). For these samples the aluminium plates were preheated in the oven and had a starting temperature of 180°C. Samples where then placed on Teflon films between the preheated aluminium plates and placed in the oven.

Identification and quantification of the pyrrolidine derivative: All pyrrolidine derivates except products 1c and 1d in Figure 5 have been identified by matches with mass spectra of the 1998 National Institute of Standards and Technology (NIST '98) mass spectral library. Product 1c, produced from esters of 2-ketobutyric acid, has been tentatively identified from the mass spectrum shown in Figure 1. In Figure 2 the mass spectrum from the unidentified product 1 d is shown. Pyrrolidine derivatives 1b and 1c (see Figure 5) were quantified, not by calibration curves, but with the predicted effective carbon number (ECN). The formula (Kálla *et al.* 2001) for calculating the amount of pyrrolidine structure from ECN and the reference substance 1-methylnaphtalene is the following:

$$ECN_i = n_s \frac{A_i m_s M_i}{A_s m_i M_s}$$

where $ECN_i$ is predicted from the molecular structure (see Table1), $n_s$ is the carbon number of the reference substance, $M_i$ and $M_s$ are the molecular weights, $m_i$ and $m_s$ are the masses, and $A_i$ and $A_s$ the chromatographic peak areas for the substances of interest and 1-methylnaphtalene, respectively. The ECN number is presented in Table 1. Esters of 2 (R)-hydroxybutyric acid were quantified using the same calibration curve as for 3-hydroxybutyric acid in an the earlier study (paper I)

**Table 1.** The three structures produced after esterification and aminolysis of 2-ketobutyric acid. ECNi numbers determined from the actual number of carbon in the pyrrolidine structures and the change due to functional groups.

| Pyrrolidine structure | Molecular weight | Constant heating* Rel. peak area (%) | Gradual heating** Rel. peak area (%) | No. of Carbon atoms | Functional Groups *** | dECN$_i$*** | ECN$_i$ |
|---|---|---|---|---|---|---|---|
|  1b | 127 | 32 | 19 | 7 | N+K | -1.42 | 5.58 |
|  1c | 208 | 60 | 71 | 12 | N+N+K | -2.04 | 9.96 |
| Unidentified product 1d | 206 | 8 | 10 | - | - | - | - |

* The relative peak areas between the three products after 5 minutes constant heating at 180°C with 13% moisture and 49 µmol 2-ketobutyric acid added.

** The relative peak areas between the three products after 30 minutes gradual heating to 180°C with 13% moisture and 49 µmol 2-ketobutyric acid added.

*** The dECN values are based on the changes -0.62 for nitrogen heterocycles (N) and -0.80 for ketones (K) (Jorgensen *et al.* 1990).

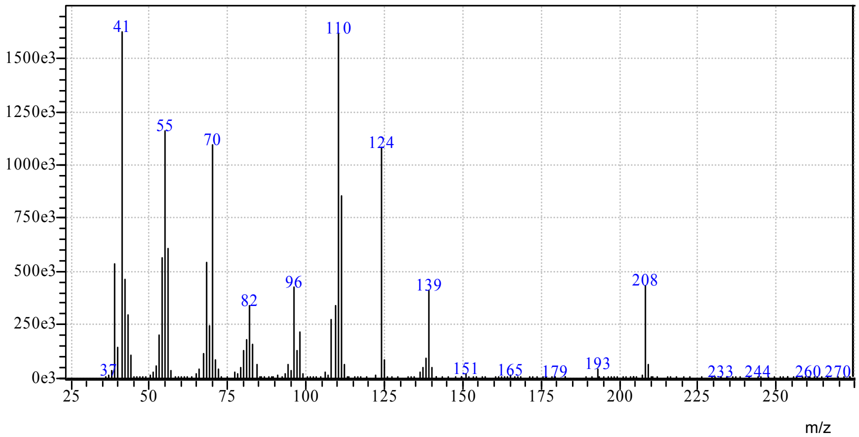


**Figure 1.** Mass spectrum of product 1c illustrated in Table 1.

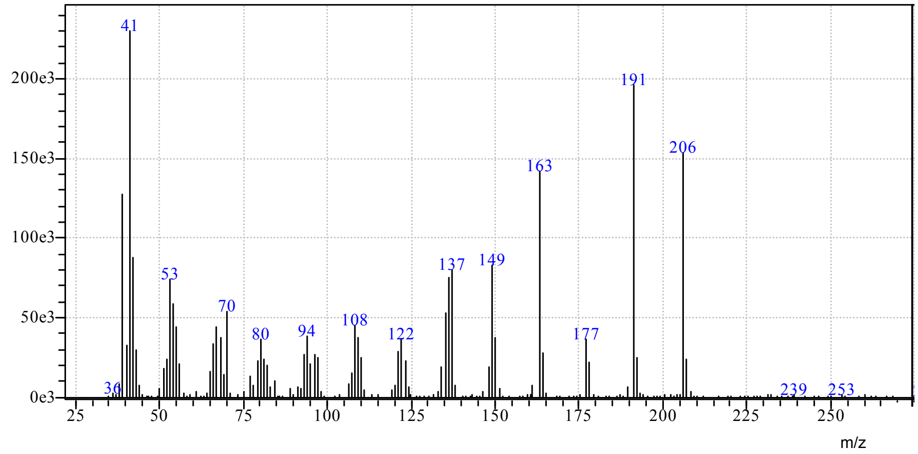


**Figure 2**. Mass spectrum of unidentified product 1d.

## RESULTS AND DISCUSSION

*The influence of time/temperature and structure on esterification efficiency*

One of the main objects of this work was to examine ester formation at short reaction times with several types of carboxylic acids. Basically, two different heating methods have been used in the experiments—constant heating at 180ºC for 5 minutes or gradual heating from 22°–180ºC.

The esterification efficiency after 5 minutes reaction time (constant heating) is presented in Table 2. The most effective of the acids tested for ester formation is 2(R)-hydroxybutyric acid, followed by 2-ketobutyric acid and 3-hydroxybutyric acid. The veratric acid, which should represent oxidized lignin, showed no esterification at all.

In an earlier study, butanoic anhydride together with catalyst was used to establish a "maximum" in ester groups within the model system. A "maximum" between 9 and 10 µmol indicates the maximum amount of hydroxyls that can be esterified at 49-µmol charge of acid (ref 1). The 2(R)-hydroxybutyric acid is very effective in ester formation when samples are constantly heated for 5 minutes (180ºC). The amount of esters formed after this short reaction time reaches 20% of the "maximum". Also, 2-ketobutyric acid and 3-hydroxybutyric acid show high values of ester formation after this short reaction time.

Another object of this work was to examine the time/temperature dependence of different acids on ester formation. This is illustrated in Figure 3, which shows esterification when samples are gradually heated over 5 to 45 minutes. The rising temperature of the gradual heating is also shown in Figure 3.

The 2(R)-hydroxybutyric acid is also the most effective in ester formation after 30 minutes gradual heating and produces twice the amount of esters as 2-ketobutyric acid, followed by 3-hydroxybutyric acid. It is worth noting that ester formation is extensive for all three acids, also compared to the "maximum". The less polar hexanoic acid without any additional functional group is not as efficient as the other acids.

An interesting phenomenon shown in Figure 3 is the effect of temperature on the esterification reaction for the different acids. After 15 minutes gradual heating, 2-ketobutyric acid produces twice the amount of esters as 2(R)-hydroxybutyric acid. However, ester formation of the 2(R)-hydroxybutyric acid accelerates at higher temperatures, and between 155ºC and 180 ºC the ester formation rate is very high (0.4 µmol/minute). The ester formation rate of the keto acid, on the other hand, peaks during the first 15 minutes of gradual heating when the temperature rises from 22ºC to 155ºC. For the keto acid, the rate of ester formation then decreases between 155ºC and 180ºC, and when a sample is heated for 45 minutes, no new esters are produced during the last 15 minutes. One explanation for this could be evaporation at higher temperatures, but a more likely explanation is that the α-ketocarboxylic acid starts to degrade at 150ºC or reacts with cellulosic hydroxyls in two positions and cannot be released by aminolysis (see discussion below). The reactivity of the α-keto acid needs further study.

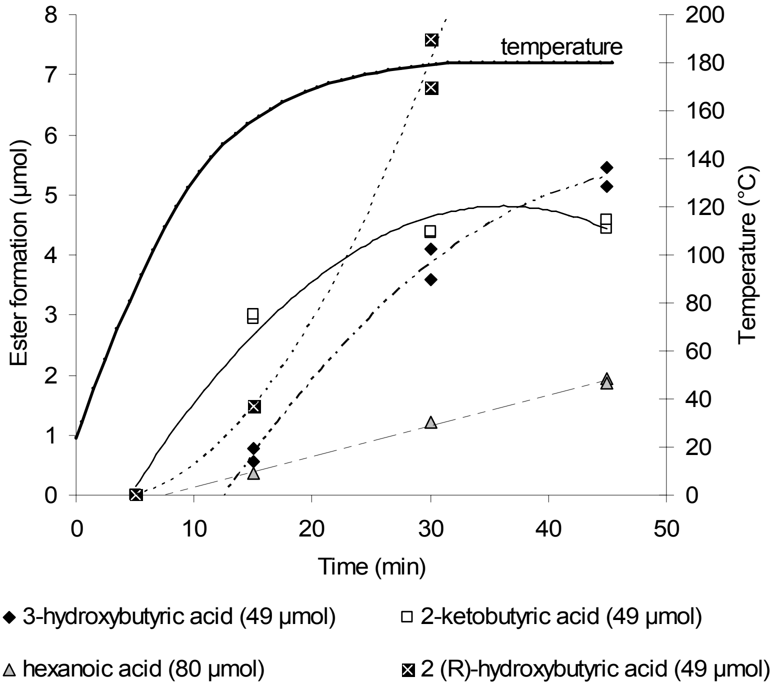


**Figure 3.** Ester formation after gradual heating from 22°C to 180°C. To all samples, 49 µmol acid and 13% moisture were added, hexanoic acid excepted, which had a moisture content of 55% and 80 µmol acid added. For 2-ketobutyric acid the ester formation (µmol) is the calculated sum of the two identified final substances in Figure 3.

The results confirm that ester formation occurs in materials with low moisture levels, at elevated temperature even for reaction times as short as 5 minutes when both hydroxyl and carboxyl groups are present.

It is apparent that both the polarity and the structure of the acids are very important, as veratric acid did not esterify, whereas hexanoic acid shows some ester formation, however low. The more bulky structure of the aromatic esters could be the difference. In addition, the fact that veratric acid is a solid product at room temperature could affect the contact area and therefore ester formation.

The result also shows that hydroxyl or keto groups in alpha position of the carboxylic acids amplify ester formation in a solid-state system. This phenomenon is very interesting with respect to different types of carboxylic acids present in different cellulosic or lignocellulosic matrices.

In wood, natural pectin contains galacturonic acid, which possesses a hydroxyl group in alpha position to the carboxyl function (Westermark *et al.* 1986). In pulping processes, several alpha-hydroxycarboxylic acids, such as metasaccharinic acid and gluconic acids, are formed after alkaline degradation of polysaccharides in kraft pulping or bleaching processes (Sjöström 1992).

Oxidation of sugar with hydrogen peroxide and iron as catalysts can also produce acids with hydroxyl or keto groups in alpha position (Moody 1964). In production of environmentally friendly boards, fibres or wood particles are oxidized with hydrogen peroxide in the presence of iron (II) sulphate (Westermark and Karlsson 2003; Widsten *et al.* 2003), and production of such acids can be expected. It is also likely that carboxylic acids with a hydroxyl group in alpha position can be produced after oxidation of hemicellulose, either in a side group or at the reducing end group.

When glucose units within the cellulose chain are oxidized to carboxylic acids, no hydroxyl or keto group, but one or two oxygen groups, could be linked to the alpha carbon. Such acids have not been examined in this work, but good esterification efficiency could be expected if oxygen's electron-withdrawing properties in alpha position enhance the ester formation of the acid.

All of these acids that can exist in cellulosic or lignocellulosic material have the capability to provide ester cross-linking.

**Table 2.** Ester formation with gradual and constant heating

| Carboxylic acid | umol added | µmol esters formed after 30 min gradual heating to 180 °C | µmol esters formed after 5 min constant heating 180 °C |
|---|---|---|---|
| 2(R)-hydroxybutyric acid | 49 | 6.8 ; 7.7 | 2.2 ; 2.0 |
| 3-hydroxybutyric acid | 49 | 3.6 ; 4.1 | 0.9 ; 1.0 |
| 2-ketobutyric acid | 49 | 4.4*; 4.4* | 1.4* ; 1.2* |
| veratric acid | 49 | no | no |
| maximum butyric anhydride | 49 | 8.8** ; 9.7** | 8.8** ; 9.7** |

*The amount of esters is the sum of the two identified final substances in Figure 5.
**Maximum amount of esters formed after 30 minutes gradual heating to 180°C (Paper I)

### *Esterification and aminolysis of 2-ketobutyric acid*

The esterification and aminolysis of all investigated acids except one were predictable and followed the expected pattern. The exception was 2-ketobutyric acid, which produced three products instead of one. The expected reaction and product from 2-ketobutyric acid, illustrated in Figure 4, was not found when the samples were analyzed.

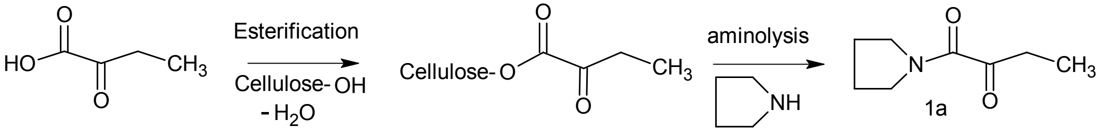


**Figure 4.** Expected products after esterification and aminolysis of 2-ketobutyric acid

Instead, three products, absent in the blanks, were found after aminolysis (see Figure 5). One of the substances could be identified and another of the substances could be tentatively identified after analysis by mass spectroscopy (GC-MS). For identification and mass spectra, see Methods. The third product, 1d, has not been identified. Substance 1d has a molecular weight (see Table 1) pointing to a structure containing two pyrrolidine units as in 1c.

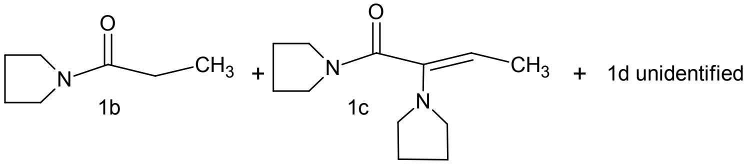


**Figure 5.** Products, two tentatively identified, after esterification and aminolysis of 2-ketobutyric acid

The unexpected outcome of ester formation with 2-ketobutyric acid affects quantification, as no comparable structure could be purchased or easily synthesized. Products 1b and 1c in Figure 5 were quantified using the predicted effective carbon number (ECN). In all tables and figures, ester formation of 2-ketobutyric acid is reported as the sum of 1b and 1c. The unidentified derivative 1d is not included in the sum, but this should have only a minor influence on the results. In Table 1, where the peak areas of the three products for two samples are presented, 1d has a considerably smaller area than 1b and 1c.

The mechanistic pathways in esterification and aminolysis of 2-ketobutyric acid are unclear. Propanoyl pyrrolidine, 1b, indicates that a hydroxyl group of cellulose has formed an ester by reacting with the keto function and under release of formic acid. Another explanation could be degradation of 2-ketobutyric acid into propionic acid followed by esterification with paper hydroxyls.

Product 1c with two pyrrolidine units attached is very interesting. The 2-ketobutyric acid seems to be very reactive in two positions and can perhaps act as a cross-linker between two separate hydroxyl groups of cellulose. The fact that a pyrrolidine unit has reacted not only with the ester but also with the keto function raises the question whether a cellulosic hydroxyl can react in the same way. If the keto acid would react with two hydroxyls, it could not be loosened during aminolysis and could therefore not be analyzed. However, the mechanistic pathways for products 1b, 1c and 1d need further study.

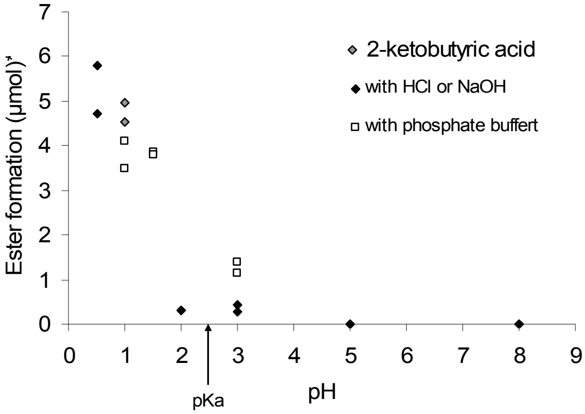
**Table 3.** The $pK_a$ values of the carboxylic acids

| Carboxylic acid | $pK_a$ |
|---|---|
| 2-ketobutyric acid | 2.50 |
| 2(R)-hydroxybutyric acid | 3.65 |
| 3-hydroxybutyric acid | 4.70 |
| hexanoic acid | 4.85 |
| veratric acid | 4.36 |

*Influence of pH on ester formation*

The pH of the samples was altered by additions of various concentration of acid (HCl), base (NaOH) or a buffer (phosphate). The influence of pH on ester formation was studied for three carboxylic acids, and the results are presented in Figures 6, 7 and 8. All acids showed the highest esterification rate at pH below 2. The 2-ketobutyric acid was very efficient in ester formation at pH < 2, but in more basic conditions almost no esters were formed. The 3-hydroxybutyric acid and hexanoic acid form esters in a wider range up to pH 5–6. There also seems to be a plateau in ester formation around pKa of these two acids. No obvious relation between pKa value (see Table 3) of the acids and ester formation efficiency can be discerned. However, it is notable that 2-ketobutyric acid is more acidic itself than 3-hydroxybutyric acid and when no extra acid or base is added is pH 1.

Phosphorous and phosphoric acid have earlier been suggested to increase ester formation by the classical proton-catalyzed mechanism of esterification (Welch and Peters 1997). In a few samples, pH was adjusted by additions of phosphate buffer. In the samples with 3-hydroxybutyric acid and phosphate buffer, more esters were obtained than for samples without buffer at the same pH (2–3). For the other acids the effect of phosphate is not that obvious. The buffer seems to increase ester formation for 2-ketobutyric acid at pH 3, but at pH 1 the ester formation is somewhat lowered. One explanation of the effect of phosphoric and phosphorous acid on esterification can be transesterification. This means that the phosphorous containing acids first esterify a hydroxyl group at the cellulose, and then this ester is replaced by the carboxylic acid through transesterification. However, further experiments are needed for a more thorough understanding of this phosphor effect.



*The amount of esters is the sum of 1b and 1c in Figure 3.

**Figure 6.** Ester formation of 49 µmol 2-ketobutyric acid when pH is altered by addition of water, HCl, NaOH or phosphate buffer. Samples were gradually heated from 22°C to180°C for 30 minutes, and moisture content was 26%.

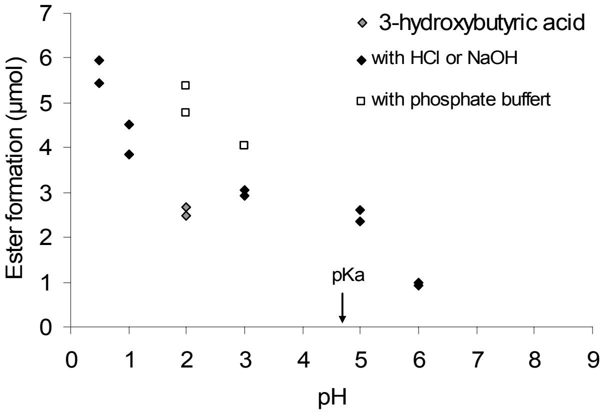


**Figure 7.** Ester formation of 49 µmol 3-hydroxybutyric acid when pH is altered by addition of water, HCl, NaOH or phosphate buffer. Samples were gradually heated from 22°C to 180°C for 30 minutes, and moisture content was 26%.

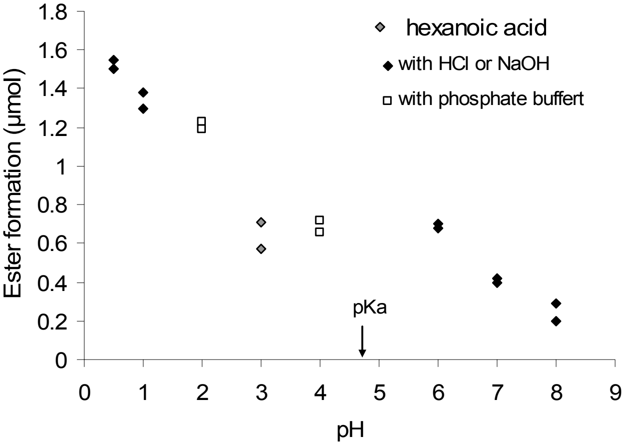


**Figure 8.** Ester formation of 40 µmol hexanoic acid when pH is altered by addition of water, HCl, NaOH or phosphate buffer. Samples were gradually heated from 22°C to 180°C for 30 minutes, and moisture content was 26%.

## CONCLUSIONS

The results confirm extensive ester formation in solid-state materials at low moisture levels and elevated temperature even for reaction times as short as 5 minutes at 180°C when both hydroxyl and carboxyl groups are present. Ester formation can be one of the adhesion mechanisms in the production of environmentally friendly fibre- and particleboard produced without glue. The results also indicate that direct esterification is a mechanism that could exists side by side with esterification through an anhydride intermediate in cross-linking for improved durable press finish of cotton and wet performance of paper. It is also likely that ester formation can occur under conditions similar to when hornification is reported. However, pH is important for ester formation, and the results for the investigated acids indicate that $pH < 2$ strongly favours esterification and that at pH > 5–6 ester formation decreases rapidly. For the special 2-ketobutyric acid, almost no esters are formed at $pH > 2$.

Another important conclusion is that a hydroxyl or keto group in alpha position of the carboxylic acids seems to favour ester formation. In the experiments 2(R)-hydroxybutyric acid is most effective in ester formation at 180°C, but at temperatures below 155°C 2-ketobutyric acid esterifies most rapidly.

Surprisingly, 2-ketobutyric acid produced three products after esterification and aminolysis. The mechanistic pathway for their formation is still unclear, but the results suggest that one of the structures indicates that 2-ketobutyric acid is reactive in two positions and could therefore be a potential cross-linker.

## REFERENCES

Caulfield, D.F. (1994) Ester crosslinking to improve wet performance of paper using multifunctional carboxylic acids, butanetetracarboxylic and citric acid. Tappi Journal. 77:205–211

Choi, H., Welch, C.M. (1994) Saturated and Unsaturated Carboxylic Acid Salts as Curing Addetives for BTCA Treatment of Cotton. Text. Chem. Color. 26:23–27

Diniz, J.M.B.F, Gil, M.H., Castro J.A.A.M. (2004) Hornification- its origin and interpretation in wood pulps, Wood Sci. Technol.. 37:489–494

Hurd, C. D., Raterink, H.R. (1934) The Decomposition of Alpha Keto Acids. J. Am. Chem. Soc. 56:1348–1350

Jorgensen, A.D., Picel, K.C., Stamoudis, V.C. (1990) Prediction of gas chromatography flame ionization response factors from molecular structures. Anal. Chem. 62:683–689

Kállai, M., Veres, Z., Balla, J. (2001) Responses of flame ionization detectors to different homologous series. Chromatographia 54:511–517

Karlsson, O., Westermark, U. (2002) Resin-free particleboard by oxidation of wood, Proc. The 6th Pacific Rim Bio-Based Composites Symposium. 1:149–153

Moody, G.J. (1964) The actions of hydrogen peroxide on carbohydrates and related compound. Advances. in Carbohydr. Chem. 19:149–179

Ruffini, G. (1966) Improvement in bonding of wood pulps by the presence of acidic groups. Svensk Papperstidn. 69:72–76

Sjöström, E. Wood Chemistry- Fundamentals and applications. Academic Press, Inc., San Diego, 1992

Weise, U. (1998) Hornification – mechanism and terminology. Paperi ja Puu/Paper and Timber. 80:110–115

Welch, C.M. (1988) Tetracarboxylic Acids as Formaldehyde-Free Durable Press Finishing Agents part I: Catalyst, Additive and Durability Studies. Textile Res. J. 58:480–488

Welch, C.M., Andrews B.A.K. (1989) Ester crosslinks: A route to high performance nonformaldehyde finishing of cotton. Text. Chem. and Color. 21:13–18

Welch, C.M., Peters, J.G. (1997) Mixed Polycarboxylic Acids and Mixed Catalyst in Formaldehyde-Free Durable Press Finishing. Text. Chem. and Color. 29:23–27

Westermark, U., Hardell, H.-L., Iversen, T. (1986) The content of protein and pectin in the lignified middle lamella / primary wall of spruce fibres. Holzforschung. 40: 65–68 I

Westermark, U., Karlsson O. (2003). Auto-Adhesive Bonding by Oxidative Treatment of Wood, Proc. 12th International Symposium on Wood and Pulping Chemistry. 1:365–368

Westermark, U., Karlsson, O. (2003). “Lignocellulose product”, *European Patent Application*, EP1308556

Widsten, P.,Qvintus-Leino, P., Tuominen, S. and Laine J.E. (2003) Manufacture of fiberboard from wood fibers activated with Fenton's reagent ($H_2O_2$/$FeSO_4$). Holzforschung 57:447–452

Yang, C.Q., Xu, Y., Wang, D. (1996) FT-IR Study of the polycarboxylic acids used for paper wet strenght improvement. Ind. Eng. Chem. Res. 35:4037–4042

# Paper III

# Formation of ester cross linkage in lignocellulosic materials during drying and heating

**ANNA PANTZE, ULLA WESTERMARK AND OLOV KARLSSON**

Department of Wood Technology
Luleå University of Technology
Skellefteå Campus, SE-931 87 Skellefteå, Sweden
E-mail: anna.pantze@ltu.se

## ABSTRACT

The formation of natural ester cross linkages in composite materials during drying and heating is of interest for both paper production and wood chemistry. In this paper a model system has been constructed to quantitatively study esterification of cellulosic material during drying and heating. In the experiments, ordinary filter paper was wetted and allowed to dry to given moisture content and a carboxylic acid, hexanoic acid, was added. The filter paper was then clamped between two aluminium plates and heated at temperatures ranging from 85° C to 180° C for 15 to 45 minutes. Quantitative analysis of ester formation was performed with aminolysis/gas chromatography. The results showed the influence of moisture content, temperature and reaction time on ester formation. In this study an ester formation maximum occurred at 20% moisture content. Under the most favourable conditions, 2,5 % of the added hexanoic acid reacted. Esterification reactions were also favoured by higher temperatures and longer reaction times.

## INTRODUCTION

Lignocellulosic material contains considerable amounts of both hydroxyl- and carboxyl groups. Wood and pulp fibres are especially rich in carboxylic groups after oxidative treatments. Under suitable conditions this can lead to esterification reactions within the material. The nature of esterification reactions in liquids are well known, but esterification reactions in solid state processes have not been studied. During the production of many wood and paper composites some moisture is present but solid state conditions can be said to rule.

In the paper industry the term hornification is used to describe irreversible structural changes that occur in fibres during drying (1). When wood pulps fibres are dried, the fibre walls are irreversibly linked together to some extent and the original water-swollen state can never be regained. This phenomena has often been associated with the formation of hydrogen bonding between cellulose chains when they become more tightly packed during water removal. Another theory suggests that ester cross linkage is the mechanism behind the irreversible pore closure seen in the fibre wall (2). This theory is partly supported by qualitative analyses of lactones carried out in the 1960s. In order to re-cycle paper, it is very important to overcome the hornification problem to regain the properties of the recovered fibres. A quantitative analysis of ester formation at relevant temperatures and drying can shed some light on the basic reactivity of pulp fibres and the problem of hornification.

Understanding esterification reactions is also of interest when studying possible bonding mechanisms in environmentally friendly fibre- and particle-boards produced without glue (3,5). In these new processes, fibres or wood particles are oxidized with hydrogen peroxide and a catalyst. The oxidized material is formed into sheets and pressed in a hot press at ~170° C. The fibre adhesion mechanisms are not fully understood but ester formation can be an important bonding reaction. Basic knowledge of how moisture, heat, pH and different catalysts effects the esterification process can help achieve better self-adhesion properties in such composites.

In this work a model system for the quantitative analysis of esterification during drying and heating is described. The effects of moisture content, temperature and reaction time have also been studied.

## EXPERIMENTAL

### Materials

The chemicals used in the experiments were hexanoic acid (99,5%) and hexanoyl chloride (97%) from Aldrich ; pyridine (99,5%), pyrrolidine (>99%), ethyl butyrate (>98%) from Merck ; ethanol (99,7 vol%) from Primalco and aceton (99,5%) from Prolabo. Each sample consisted of two pieces of 1,5x1,5 cm filter paper (Munktell, OOH). The samples were dried at 105ºC overnight to achieve initial moisture content close to 0%. The dry weight of one sample was around 38 mg.

### Esterification

To obtain the required moisture content for each experiment (0 % to 80 %), the filter paper was wetted and then allowed to dry on a balance. Hexanoic acid (10µl) was then added on the filter paper. The paper was placed between two aluminium plates (9mm thick) and pressed together with a small frame. The sample was then heated in an oven at temperatures ranging from 85° C to 180° C for 15 to 45 minutes. It is important to note that moisture can evaporate from the sample since there remains a slight gap between the aluminium plates. Figure 1 illustrates the esterification reaction.

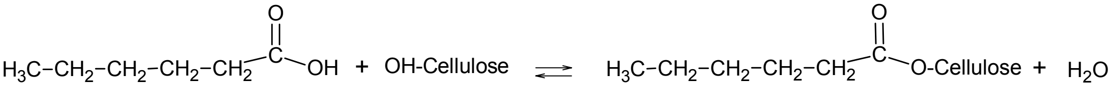


Fig 1. The esterification reaction between hexanoic acid and a cellulose hydroxyl group.

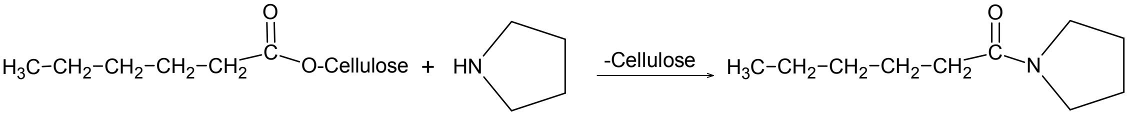


Fig 2. Aminolysis of cellulosehexanoat. Pyrrolidine reacts with the ester and forms hexanoyl pyrrolidine

### Washing procedure

After esterification it was necessary to remove any remaining free hexanoic acid since this reacts with pyrrolidine during aminolysis. The samples were marked with scissor cuts along their edges and then washed together with a blank. Blanks were prepared in the same way as the samples with 10µl hexanoic acid and adequate moisture content, but placed between two cold aluminium plates for at least 45 minutes. Washing was carried out using the following sequence on a büchner funnel; water (1L); acetone (0,05 L); water (1L); ethanol (0,05L); water (1L); acetone (0,05L). After the washing procedure the samples were allowed to dry.

### Analysis

Quantitative analyses of ester formation were performed with aminolysis/gas chromatography (4). Each sample was cut into small pieces and placed in a 1,5 ml vial. Ethylbutyrate dissolved in ethanol (1:10) was used as an internal standard and 10µl of this standard was added to each vial together with 1 ml of pyridine/pyrrolidine solution (1:1).

The vials were capped and then heated to 80° C in a sand bath for 72 h. During aminolysis, pyrrolidine reacts with the esters and forms hexanoyl pyrrolidine and butyryl pyrrolidine (see Figure 2). After cooling, 1µl of the reaction mixture was injected into the gas chromatograph. The samples used for the calibration curve were prepared in the same way as the ordinary samples. Instead of the filter paper, known concentrations of hexanoyl pyrrolidine were added together with pyridine/pyrrolidine and internal standard before the vials were heated. Hexanoyl pyrrolidine was synthesized from hexanoyl chloride (4). The synthesized hexanoyl pyrrolidine raised a single peak in the GC and showed a clean NMR spectrum.
All quantifications were performed on a Shimadzu GCMS-QP5050 with the column Equity1701 from (Supelco AB).

## RESULTS AND DISCUSSION

The primary results presented in this work show the influence of moisture content, temperature and reaction time on ester formation.

The presence of moisture was found to be important for the formation of esters (see Fig. 3). In samples with moisture content under 5%, the ester formation was almost zero. A peak in ester formation occurred at about 20% moisture, with ester formation slowly decreasing at higher moisture contents. In the esterification reaction, one mole of water is produced for every mole of ester and removal of water is necessary to shift the equilibrium in favour of more esters (see Fig. 1). The ester formation maximum seen at 20% moisture content, where approximately 2,5% (2µmol) of the added hexanoic acid has reacted, can be due to water causing better mobility of cellulose hydroxyls. The increased flexibility of the cellulose material makes it easier for the hexanoic acid to find a favourable hydroxyl group to react with. Whilst higher moisture content gives better flexibility it also shift the equilibrium towards the production of fewer esters, i.e. a shift to the left of Fig. 1. The moisture content of 20 % balances the two phenomena and is most favourable for ester formation.

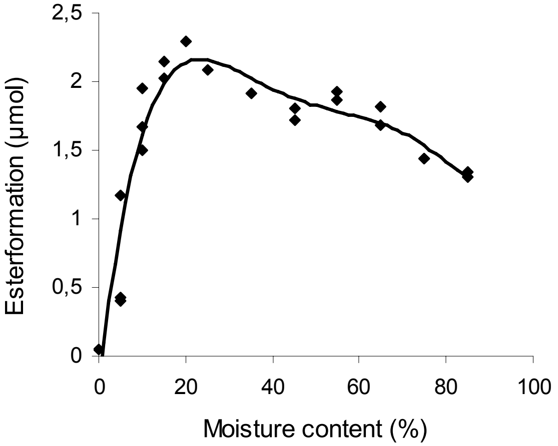


Fig 3. Ester formation as a function of moisture content. All samples in the figure were esterified at 180ºC for 45 minutes.

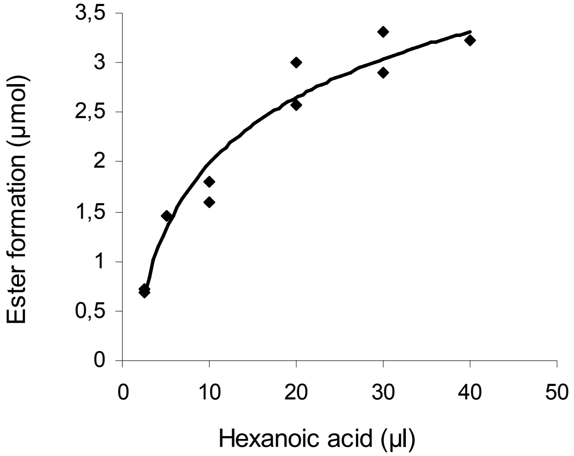


Fig. 4. Ester formation as a function of added hexanoic acid. All samples had an initial moisture content of 45% and were esterified at 180ºC for 45 minutes.

The amount of ester formed is of course dependent on the amount of acid added and the number of available hydroxyl groups. Later experiments showed that amount of esters formed increased linearly with additions of up to 5µl hexanoic acid (Fig. 4). An important conclusion from this is that the addition of 10µl hexanoic acid, used in all the other experiments (Figure 3 and 5), is not optimal and gives an altogether too low percentage of calculated "reacted hexanoic acid". An addition of 5µl hexanoic acid would have given higher values.

Esterification reactions are favoured by higher temperatures and longer reaction times which can be seen in Figure 5. It can be clearly seen that temperatures of 150ºC or above are needed to esterify at least 1 % (0,8µmol) of the hexanoic acid. Another series of experiments was carried out at 85ºC and with process times of 30 and 45 minutes respectively. The moisture content was 15% instead of 55% as for the other samples in Figure 5. Even at this low temperature some esters had been formed, but less than 0,01 % of the hexanoic acid had reacted.

In this first model system hexanoic acid was used as it has a relatively high boiling point (>200° C) and therefore wouldn't evaporate when samples were heated. Another reason for this choice was that the aminolysis technique had been performed with this alkanoat before (4). However, esterification is probably not favoured by the long hydrophobic alkane chain of hexanoic acid which does not match with the polarity of the hydroxyl rich cellulose. Other more hydrophilic acids are to be investigated.

## CONCLUSIONS

The model system used in this work showed that the formation of ester cross linkage in composite materials and paper can occur during drying and heating and that the degree of esterification can be quantified. Under the most favourable conditions about 2,5 % of the added hexanoic acid was esterified in these experiments. It is intended to repeat this work using a more hydrophilic acid to see whether matching the polarity of the hydroxyl groups in cellulose can increase esterification. Further studies will also investigate the influence of pH and the role of catalysts on esterification in lignocellulosic systems.

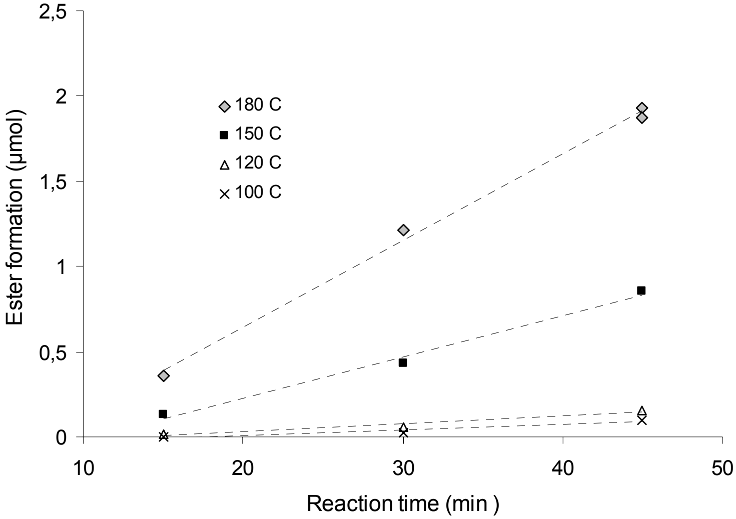


Fig. 5 The effects of temperatures and reaction time on ester formation. All samples had an initial moisture content of 55%

## REFERENCES

1 Weise, U. *Paperi ja Puu/Paper and Timber* **80**(2):110 (1998)

2 Fernandes Diniz J.M.B., Gil M.H. and Castro J.A.A.M. *Wood Science and Technology* **37**(6):489 (2004)

3 Westermark U. and Karlsson O. *A European Patent Application* EP1308556, “Lignocellulose product” (2003)

4 Samaranayake G. and Glasser W.G. *Carbohydrate Polymers* **22**(2):79 (1993)

5 Widsten, P.,Qvintus-Leino, P., Tuominen, S. and Laine *Holzforschung* **57**(4): 447 (2003)