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Laura Kupiainen

DILUTE ACID CATALYSED HYDROLYSIS OF CELLULOSE – EXTENSION TO FORMIC ACID

UNIVERSITY OF OULU GRADUATE SCHOOL;
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FACULTY OF TECHNOLOGY,
DEPARTMENT OF PROCESS AND ENVIRONMENTAL ENGINEERING,
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Abstract

New methods are being sought for the production of chemicals, fuels and energy from renewable biomass. Lignocellulosic biomass consists mainly of cellulose, hemicellulose and lignin. Cellulose and hemicellulose can be converted to their building blocks, i.e. sugars, via hydrolysis. This thesis is focused on glucose production from cellulose by dilute acid hydrolysis. Acid hydrolysis has the drawback of limited glucose yields, but it has the potential to become a short-term solution for biochemical production.

During acid hydrolysis, the cellulose chain is split into glucose, which undergoes further decomposition reactions to hydroxymethylfurfural, levulinic acid, formic acid and by-products like insoluble humins. The present thesis aims to increase our knowledge on complicated acid-catalysed hydrolysis of cellulose. Glucose decomposition and cellulose hydrolysis were studied independently in laboratory experiments. Kinetic modelling was used as a tool to evaluate the results. The effect of the hydrogen ion on the reactions was evaluated using formic or sulphuric acid as a catalyst.

This thesis provides new knowledge of cellulose hydrolysis and glucose decomposition in formic acid, a novel catalyst for high-temperature dilute acid hydrolysis. Glucose yields from cellulose hydrolysed in formic or in sulphuric acid were comparable, indicating that a weak organic acid could function as a cellulose hydrolysis catalyst.

Biomass fibres in the form of wheat straw pulp were hydrolysed more selectively to glucose than a model component, microcrystalline cellulose, using formic acid. Glucose decomposition took place similarly in formic and sulphuric acid when the temperature dependence of the hydrogen ion concentration was taken into account, but a significant difference was found between the reaction rates of cellulose hydrolysis in formic acid and in sulphuric acid. The observations can be explained by changes in the cellulose hydrolysis mechanism. Thus, it is proposed in this thesis that side-reactions from cellulose to non-glucose compounds have a more significant role in the system than has earlier been understood.

Keywords: cellulose hydrolysis, dilute sulphuric acid, formic acid, glucose decomposition, specific acid catalysis, wheat straw pulp

Kupiainen, Laura, Selluloosan happokatalyyttinen hydrolyysi – muurahaishappoon pohjautuva tarkastelu.
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Tiivistelmä

Uusia menetelmiä etsitään kemikaalien, polttoaineiden ja energian valmistamiseen uusiutuvasta biomassasta. Eräs biomassa, ns. lignoselluloosa, koostuu pääasiassa selluloosasta, hemiselluloosasta ja ligniinistä. Selluloosa ja hemiselluloosa voidaan muuttaa hydrolyysin avulla niiden rakennuspalikoikseen eli sokereiksi. Tämä väitöskirja keskittyy glukoosin tuottamiseen selluloosasta laimean happohydrolyysin menetelmällä. Happohydrolyysi kärsii rajoittuneesta glukoosin saannosta, mutta sillä on potentiaalia tulla lyhyen aikavälin ratkaisuksi biokemikaalien tuotannossa.

Happohydrolyysin aikana selluloosaketju pilkkoutuu glukoosiksi, joka reagoi edelleen hajoamisreaktioiden kautta hydroksimetyylifurfuraaliksi, levuliini- ja muurahaishapoiksi ja kiinteäksi sivutuotteeksi. Tämän tutkimuksen tavoitteena on kasvattaa ymmärrystämme monimutkaisesta happokatalysoidusta selluloosan hydrolyysistä. Glukoosin hajoamista ja selluloosan hydrolyysiä tutkittiin erikseen laboratoriokokein. Kineettistä mallinnusta käytettiin työkaluna arvioimaan tuloksia. Vety-ionien vaikutus reaktioihin arvioitiin käyttämällä muurahais- ja rikkihappoja katalyytteinä.

Tämä väitöskirja antaa uutta tietoa selluloosan hydrolyysistä ja glukoosin hajoamisreaktioista muurahaishapossa, joka on uusi katalyytti korkean lämpötilan laimean hapon hydrolyysissä. Glukoosisaannot muurahaishappo-hydrolysoidusta selluloosasta olivat vertailukelpoisia vastaaviin rikkihappo-hydrolyysi saantoihin. Tämä viittaa siihen, että heikko orgaaninen happo voisi toimia selluloosahydrolyysin katalyyttinä.

Kun katalyyttinä käytettiin muurahaishappoa, vehnän oljesta tehdyt kuidut hydrolysoituivat selektiivisemmin glukoosiksi kuin mallikomponenttina toimineen mikrokiteisen selluloosan. Kun vetyionikonsentraation lämpötilariippuvuus otettiin huomioon, glukoosi hajosi samalla tavalla sekä muurahais- että rikkihappokatalyytissä, mutta merkittävä ero havaittiin selluloosahydrolyysin reaktionopeudessa. Havainnot voidaan selittää selluloosahydrolyysin mekanismissa tapahtuvilla muutoksilla. Väitöskirjassa esitetään, että sivureaktioilla selluloosasta ei-glukoosituotteiksi on merkittävä vaikutus systeemiin.

Asiasanat: glukoosi, happohydrolyysi, laimea rikkihappo, muurahaishappo, selluloosa, spesifinen happokatalyysi, vehnän olki sellu

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Finally, my warmest thanks go to my family for supporting and encouraging me during my studies and research.

Oulu, October 2012 Laura Kupiainen

List of symbols and abbreviations

Latin symbols

A	pre-exponential factor ($M^{-m}min^{-1}$)
C_a	acid term (mol/l)
C_c	cellulose concentration (mol/l)
C_{H+}	concentration of hydrogen ions (mol/l)
CrI	crystallinity index
E_a	activation energy (kJ/mol)
k_i	rate constant of reaction i (min^{-1})
m	reaction order for acid term
$K_{a,FA}$	dissociation constant of formic acid
$K_{a,SA}$	dissociation constant of sulphuric acid
$K_{a,HSO}$	dissociation constant of bisulphate ion
m_c	mass of cellulose (g)
MW_g	molar mass of glucose (g/mol)
V	volume of solution (l)
k_{H2O}	solvent factor (min^{-1})
k_{H+}	acid factor ($M^{-1}min^{-1}$)
T	reaction temperature (K)
R	gas constant (J/mol·K)

Abbreviations

FA	formic acid
HMF	hydroxymethylfurfural
HPLC	high performance liquid chromatography
LA	levulinic acid
MC	microcrystalline cellulose
XRD	X-ray diffraction

List of original papers

The thesis is based on the following publications:

I Kupiainen L, Ahola J & Tanskanen J (2010) Comparison of formic and sulfuric acids as a glucose decomposition catalyst. Industrial & Engineering Chemistry Research 49(18): 8444–8449.

II Kupiainen L, Ahola J & Tanskanen J (2012) Distinct effect of formic and sulfuric acids on cellulose hydrolysis at high temperature. Industrial & Engineering Chemistry Research 51(8): 3295–3300.

III Kupiainen L, Ahola J & Tanskanen J (2011) Kinetics of glucose decomposition in formic acid. Chemical Engineering Research and Design 89(12): 2706–2713.

IV Kupiainen L, Ahola J & Tanskanen J (2012) Kinetics of formic acid catalyzed cellulose hydrolysis. Manuscript.

V Kupiainen L, Ahola J & Tanskanen J (2012) Hydrolysis of organosolv wheat pulp in formic acid at high temperature for glucose production. Bioresource Technology 116: 29–35.

All the listed publications were written by the author of this thesis, whose main responsibilities were the experimentation, data analysis and reporting of the results.

Table of contents

1 Introduction

1.1 Background

Today's society is based on the use of fossil resources. For example, crude oil is processed in an oil refinery into more useful fractions, which form the basis for the petrochemical industry or the production of transportation fuels. However, crude oil in particular is regarded with negativity due to the problems caused by its limited availability as well as the environmental impacts related to its use. Thus, new resources for the production of chemicals, fuels and energy are clearly required, and the use of these resources should be more sustainable and environment-friendly than the current situation.

One such potential resource is biomass. According to directive 2009/28/EC, biomass is defined as a "biodegradable fraction of products, waste and residues from biological origin from agriculture (including vegetal and animal substances), forestry and related industry". Therefore, biomass is a renewable, domestic and even cheap raw material abundantly available on Earth. Currently, 10% of global primary energy consumption is supplied from biomass, which is mainly used by burning (Bauen *et al.* 2009). In 2050, about 20–80% of the potential world primary energy demand could be covered by sustainable biomass potential (Bauen *et al.* 2009).

Not only an energy source, biomass is also a promising raw material for the production of chemicals. Together with sustainable technologies, the use of biomass would promote a shift of society towards the bioeconomy. However, the features of biomass pose challenges to conversion technologies. Technology should enable the processing of material that has a very complex and resistant structure and allow the efficient exploitation of every part of biomass, in which the relative portions of the different parts vary greatly depending on the source.

Terrestrial biomass is composed of carbohydrates (75% of annually produced biomass by photosynthesis), lignin (20%) and other natural compounds (5%) such as fats and proteins (Lichtenthaler 2010). This enables a wide variety of products. Lignin, a complex polyphenol, has a high heat of combustion value and is most straightforwardly burned to release energy. There is also a future opportunity to produce higher value lignin products in the form of macromolecules, aromatics and phenol monomers (Bozell *et al.* 2007). Carbohydrates, i.e. hemicellulose and cellulose in this context, are natural polymers of different sugars, cellulose being

the most abundant individual component in biomass. The National Renewable Energy Laboratory and Pacific Northwest National Laboratory in the USA have assessed the most promising carbohydrate-based chemicals, which possess the potential to be converted into new families of useful molecules (Werpy & Petersen 2004). Eight of these twelve molecules can be produced from glucose, which is a basic unit of the cellulose polymer.

Among the numerous conversion technologies developed for biomass exploitation, hydrolysis is a method that converts carbohydrates into their building blocks, i.e. sugars. Cellulose hydrolysis in particular has been studied extensively using concentrated or dilute sulphuric acid (Sherrard & Kressman 1945; Taherzadeh & Karimi 2007) as a catalyst. However, despite the long history of acid-catalysed cellulose hydrolysis, its commercial breakthrough in peacetime has not yet taken place. There are several barriers that noticeably impede the broader use of acid hydrolysis. In concentrated acid hydrolysis, the separation of sugars from sulphuric acid and the acid recovery are challenging tasks. In the dilute acid hydrolysis that takes place at higher temperature, glucose decomposition limits the product yield. In addition, both methods require a neutralization step for sulphuric acid, which creates an environmental problem due to the formation of gypsum. Although encouraging results with regard to glucose yield have recently been achieved with extreme low sulphuric acid concentrations (Gurgel *et al.* 2012) that are favourable due to minimum gypsum formation, replacement of sulphuric acid with a sulphur-free catalyst would be advantageous. Furthermore, one reason for the difficulties may be the complicated nature of cellulose hydrolysis and the fact that efforts are more on building a production process rather than understanding in depth what happens during hydrolysis. However, understanding the phenomena is the key to developing an efficient process.

1.2 Scope and objectives

This thesis is focused on the conversion of the cellulosic part of biomass to glucose using acid hydrolysis at high temperature. Fig. 1 presents how glucose is formed from cellulose in a series of acid-catalysed reactions. First, cellulose is broken down to glucose, which decomposes further into hydroxymethylfurfural (HMF). HMF reacts then to produce levulinic and formic acids. The aim of the thesis is to increase our knowledge of the phenomena that take place in acid-catalysed cellulose hydrolysis. For this purpose, formic acid was selected as an

acid catalyst for hydrolysis. Previously, formic acid has been studied for example as a pulping chemical (Sundquist & Poppius-Levlin 1998) and as a pretreatment chemical for bioethanol production (Sindhu *et al.* 2010), but rarely as a hydrolysis chemical at high temperatures. Therefore, dilute sulphuric acid is also included in this study alongside formic acid.

The overall aim of the thesis is achieved by considering the following sub-objectives:

1. Assessment of the difference between formic and sulphuric acids in cellulose hydrolysis and glucose decomposition
2. Development of a kinetic model for cellulose hydrolysis and glucose formation in formic acid
3. Study of the hydrolysis of biomass fibres in formic acid.

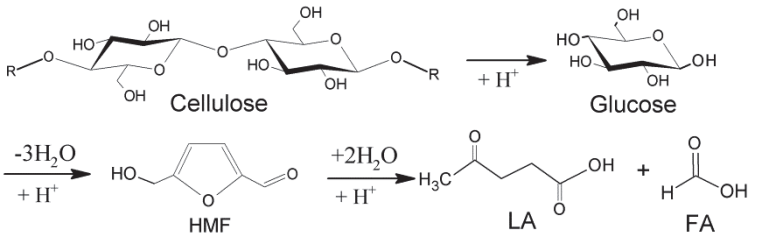

Fig. 1. Acid-catalysed cellulose hydrolysis to glucose. HMF = hydroxymethylfurfural, LA = levulinic acid, FA = formic acid.

Due to the complicated nature of the research subject, cellulose hydrolysis phenomena are divided into two parts: 1) glucose decomposition and 2) cellulose hydrolysis. These parts are studied independently by executing laboratory experiments in batch reactors and using kinetic modelling as a tool for data analysis. The outline of the thesis is illustrated in Fig. 2. Glucose decomposition reactions are studied in Papers I and III, whereas the hydrolysis of microcrystalline cellulose is studied in Paper II. The cellulose hydrolysis and glucose decomposition models are compiled in Paper IV. Microcrystalline cellulose was selected as a model component to study the hydrolysis reaction. Therefore, the hydrolysis of biomass fibres in formic acid is also dealt with in Paper V.

Formic acid, i.e. a weak organic acid, differs greatly from diprotic sulphuric acid. As shown in Figure 1, both cellulose hydrolysis and glucose decomposition

are catalysed by hydrogen ions. Since the emphasis of the thesis is on acid catalysis, special attention is given to the calculation of the prevailing hydrogen ion concentration at the reaction temperature.

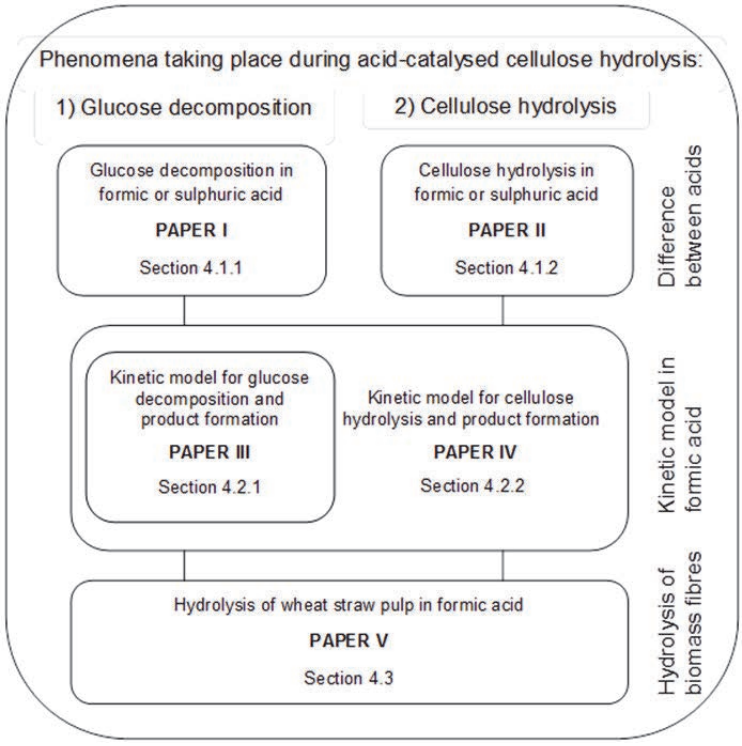

Fig. 2. Outline of the thesis.

1.3 Dissertation structure

The subsequent Chapters 2–5 present the current understanding of acid-catalysed cellulose hydrolysis and glucose decomposition and show the new findings obtained during this research. In Chapter 2, the research subject is described based on the information obtained from the literature. A brief survey is given separately for both glucose decomposition and cellulose hydrolysis. Moreover, the concept of specific acid catalysis, which was used as the basis for the kinetic model, is described briefly. The methods that have been used to achieve the aim of the thesis are summarised in Chapter 3. In Chapter 4, the main results are

shown and their reliability and significance is evaluated through discussion. Finally, conclusions are given in Chapter 5. The proposals for future research arising from this thesis are also dealt with in the last chapter.

2 Literature survey

2.1 Glucose decomposition phenomena

D-glucose, $C_6H_{12}O_6$, is the most abundant sugar on earth. It occurs free in plant juices, honey and blood; as a component in oligosaccharides, e.g. in sucrose; and in polysaccharides, e.g. in starch and cellulose (McIlroy 1967). It is a colourless, crystalline solid that readily dissolves in water. In aqueous solutions (at room temperature), over 99% of glucose exists in two cyclic forms, α-D-glucopyranose and β-D-glucopyranose, which change from one form to the other through acyclic aldehyde (McIlroy 1967, Schenck 2007). This reaction is called mutarotation.

2.1.1 Glucose decomposition reactions

Glucose chemistry is extremely complicated. Acid-catalysed glucose decomposition at high temperature can include reversion reactions (Thompson *et al.* 1954, Pilath *et al.* 2010), condensation reactions (Sumerskii *et al.* 2010, Patil *et al.* 2011), isomerisation reactions (Usuki *et al.* 2007) and dehydration reactions. The main reaction pathway is dehydration. Dehydration of glucose results in 5-hydroxymethyl-2-furfural (HMF), which undergoes a rehydration step to levulinic acid (LA) and formic acid (FA), as illustrated in Fig. 3. The role of side-reactions with reversion products increases at low temperatures and high initial glucose concentrations (Pilath *et al.* 2010), which are the opposite of the conditions used in the experimental part of this thesis. In highly acidic conditions, it has been possible to identify reversion products 1,6-anhydro-β-D-glucofuranose, isomaltose, levoglucosan and gentiobiose at the initial stage of the glucose decomposition reaction, but quantitative analysis was not successful due to low concentrations (Girisuta *et al.* 2006b). Condensation reactions result in water-insoluble products, known as humins. They can originate from HMF, glucose intermediates and/or glucose itself (Girisuta *et al.* 2006a, Sumerskii *et al.* 2010, McKibbins *et al.* 1962, Baugh & McCarty 1988).

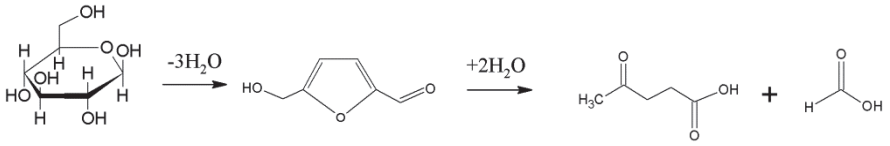

Fig. 3. Glucose decomposition in acidic media. (Paper III © Elsevier)

Based on the literature, it seems that the isomerisation of glucose to fructose plays an important role in glucose decomposition to HMF from the mechanistic viewpoint. However, the detailed mechanism of glucose decomposition (dehydration) is unknown. There are two mechanistic pathways proposed in the literature for hexose dehydration: a pathway via an acyclic intermediate and a pathway via a cyclic intermediate (Corma *et al.* 2007). The former proceeds via an enediol intermediate between glucose to fructose in the isomerisation reaction (Harris & Feather 1975, Mednick 1962); the latter proceeds via a fructofuranose ring originating from fructose (Antal *et al.* 1990).

2.1.2 Kinetics of glucose decomposition

The overall kinetics of glucose decomposition and product formation in acidic conditions has been widely studied using different reaction schemes. The most simplified reaction scheme includes only the disappearance of glucose (Saeman 1945, Thompson & Grethlein 1979, Bienkowski *et al.* 1987, Malester *et al.* 1992). These schemes are often a part of cellulose hydrolysis studies making it possible to predict the maximum glucose yield from cellulose. However, including decomposition products in the reaction schemes would give valuable information about the system. There are various schemes including product formation from glucose. For example, Baugh & McCarty (1988) and Girisuta *et al.* (2006b) included the side-reactions with humins in the reaction scheme, whereas Conner *et al.* (1985) took irreversible decomposition reaction and reversion reactions into account and Pilath *et al.* (2010) modelled the kinetics of 11 reversion reactions and the HMF formation reaction in their extensive study.

Generally, the overall reaction of glucose decomposition in sulphuric acid follows pseudo-first-order kinetics with respect to glucose concentration (Bienkowski *et al.* 1987, McKibbins *et al.* 1962, Baugh & McCarty 1988, Xiang *et al.* 2004). According to the studies by Kuster & Baan (1977), McGibbins *et al.* (1962) and Girisuta *et al.* (2006a), the apparent reaction order of HMF rehydration is also very close to 1. Conventionally, the reaction order, *m*, is used for the acid in an Arrhenius-type, empirical relation called Saeman's equation.

The equation includes an acid term, C_a, besides a pre-exponential factor, A, as follows (Saeman 1945):

$$k_i = AC_a^m e^{-\frac{E_a}{RT}}. \quad (1)$$

The acid term is described by the amount of catalyst (Saeman 1945, McKibbins *et al.* 1962, Chan *et al.* 2006) or by the hydrogen ion concentration (Mosier *et al.* 2002, Girisuta *et al.* 2006b).

2.2 Cellulose hydrolysis phenomena

Cellulose hydrolysis has been a subject of extensive research since H. Braconnot discovered in 1819 that sugars could be formed by treating wood with concentrated sulphuric acid. In 1855, G.F. Melsens noticed that this conversion could be carried out with dilute sulphuric acid. The reactivity of cellulose in chemical reactions as well as its typical chemical properties are basically determined by its structure. The structure of cellulose has been considered at different levels in the literature. Different approaches are also used to study the kinetics of cellulose hydrolysis.

2.2.1 Crystalline cellulose and its hydrolysis

At the molecular level, cellulose is an unbranched polymer consisting of anhydrous β-D-glucopyranose units that are linked by β-1,4-glycosidic bonds. The actual repeating unit of cellulose is cellobiose. Native as well as treated cellulose polymers are of various chain lengths; the degree of polymerization, i.e. the number of monomeric units in a polymer, can vary for example from 500 to 10 000 depending on the cellulose source and the isolation method (Fan *et al.* 1987).

Cellulose chains form intra- and intermolecular hydrogen bonds between hydroxyl groups, and between hydroxyl groups and cyclic oxygen. At the supermolecular level, this ability to form hydrogen bonds results in the basic structural unit of cellulose fibres, an elementary fibril, in which cellulose chains are organized in parallel through a hydrogen bond network. Elementary fibrils aggregate into fibre bundles called microfibrils. Within the microfibrils, higher ordered (crystalline) regions caused by hydrogen bonds alternate with less ordered (amorphous) regions, in which cellulose chains show much less

orientation with respect to each other. There are no clearly defined boundaries between crystalline and amorphous regions. (Fan *et al.* 1987, Krässig *et al.* 2007, Browning 1963) At a macro level, cellulose forms the cell walls of a plant in close association with hemicellulose and lignin (Nimz *et al.* 2000).

Similarly to the cellulose structure, phenomena related to cellulose hydrolysis can be considered at several levels. At the molecular level, the proposed mechanism of acid-catalyzed cellulose hydrolysis starts with the protonation of oxygen in a β-1,4-glycosidic bond or the protonation of cyclic oxygen in a glucopyranose ring (Krässig *et al.* 2007, Fan *et al.* 1987). The former continues with the splitting of the glycosidic bond and a reaction with water, as illustrated in Fig. 4. The latter takes place through a ring-opening phase. During hydrolysis, long cellulose chains degrade to shorter polymers step by step, finally producing glucose monomers.

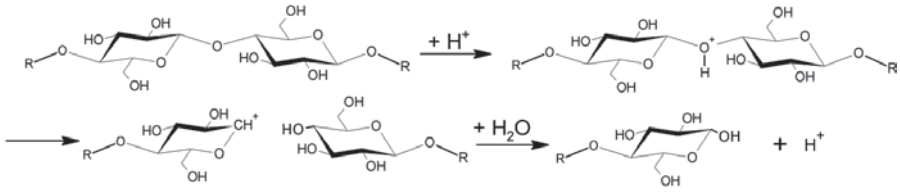

Fig. 4. Proposed mechanism of cellulose hydrolysis. (Paper II © ACS)

The reactivity and therefore the kinetics of cellulose hydrolysis are affected by its structural properties. Although the basic hydrolysis reaction takes place at the molecular level via glycosidic bonds, the supermolecular structure of cellulose affects the overall reaction. Cellulose hydrolysis is hindered by its crystalline structure: the access of hydrogen ions and water molecules to the glycosidic bonds is limited due to the crystalline regions of cellulose. Water cannot dissolve cellulose, but water molecules can penetrate the cellulose structure and cause swelling of the fibres. Swelling by the action of water has an *inter*fibrillar character: it opens the interstices between fibrils and swells the less-ordered regions, but not the crystalline areas. (Krässig *et al.* 2007, Browning 1963) The water-cellulose interaction has been studied extensively. For instance, a correlation has been found between water vapour adsorption and cellulose crystallinity (Mihranyan *et al.* 2004, Kocherbitov *et al.* 2008). Furthermore, cellulose is insoluble in dilute acids. Therefore, for example, dilute sulphuric acid catalysed cellulose hydrolysis has a heterogeneous nature.

2.2.2 Kinetics of dilute acid cellulose hydrolysis

The kinetics of dilute acid hydrolysis have been studied in a wide range of reaction conditions from different perspectives. Qi *et al.* (2009) developed a model for the random rupture of glycosidic bonds and Petterson *et al.* (2003) included a transport term in the hydrolysis model. In this thesis, cellulose is treated as one lump. Thus the hydrolysis phenomenon is simplified by assuming that cellulose hydrolysis is pseudo-homogeneous. Saeman (1945) found that the pseudo-homogeneous dilute acid hydrolysis of Douglas fir follows first-order kinetics at 170–190 °C in 0.4–1.6% H_2SO_4. Hydrolysis was described with two reactions in series: one for cellulose hydrolysis and another for glucose decomposition. Later Fagan *et al.* (1971) proved that Saeman's equation is also valid for other biomass materials (Kraft paper) at temperatures up to 240°C. Since Saeman's extensive kinetic study, dilute-acid cellulose hydrolysis has been studied for different raw materials in a wide range of reaction conditions (180–240 °C, 0.05–4.4% H_2SO_4) on laboratory scale in batch reactors (Fagan *et al.* 1971, Ranganathan *et al.* 1985, Malester *et al.* 1992), plug flow reactors (Thompson & Grethlein 1979, McParland *et al.* 1982, Franzidis *et al.* 1983) and semi-batch flow reactors (Mok *et al.* 1992, Torget *et al.* 2000).

Researchers have detected hydrolysable products, i.e. oligomers, before glucose (Abatzoglou *et al.* 1986) and non-hydrolysable soluble products that do not produce glucose (Mok *et al.* 1992). In addition, Bouchard *et al.* (1989) found modifications that take place in cellulose during acid hydrolysis. However, they did not discuss the possible effects of formation of humins on cellulosic residues. Girisuta *et al.* (2007) modelled cellulose hydrolysis including a side-reaction with non-glucose products, and Conner *et al.* (1985) assumed different reaction rates for easily hydrolysable and resistant cellulose parts. However, most kinetic studies assume that cellulose reacts directly into glucose.

Similarly to the kinetics of glucose decomposition, the rate constant of cellulose hydrolysis can be expressed with an Arrhenius-type, empirical relation that includes an acid term besides a pre-exponential factor (Eq. 1). Usually the acid term, C_a, is described by the catalyst amount in weight percent (Saeman 1945, Fagan *et al.* 1971, Thompson & Grethelein 1979, McParland *et al.* 1982, Franzidis *et al.* 1983, Ranganathan *et al.* 1985, Abatzoglou *et al.* 1986, Abatzoglou *et al.* 1990) or by the hydrogen ion concentration (Conner *et al.* 1985, Malester *et al.* 1992, Mosier *et al.* 2002, Girisuta *et al.* 2007). Although Malester *et al.* (1988) have stated the disadvantages of using the acid amount rather than

the hydrogen ion concentration; the latter approach is not commonly used for the kinetic modelling of dilute acid cellulose hydrolysis. The disadvantages are the difficulty of comparing different acid catalysts, the difference between acid concentration and hydrogen ion concentration of diprotic acids, and the neutralizing capacity of some biomass materials. Moreover, only Girisuta *et al.* (2006b) have used the hydrogen ion concentration of sulphuric acid at the reaction temperature.

2.3 Concept of specific acid catalysis

Let us consider a homogeneous reaction catalysed in an acidic, aqueous environment. The following definitions can be made. *Specific acid catalysis* is related to a reaction in which a proton donated only from H_3O^+ is involved. *General acid catalysis* is related to a reaction in which a proton donated from other species, i.e. undissociated acid or water, is involved. (Gates 1992) In some cases, a base can also be involved in the reaction. An example of this *acid-base catalysis* is glucose mutarotation, which requires both an acid (a proton donor) and a base (a proton acceptor) to occur; it takes place in water for example due to the acidic and basic nature of water (Panchenkov & Lebedev 1976).

The observed rate constant depends on the rate of the uncatalysed reaction taking place in the solvent and the concentrations of catalytic ions and molecules involved in the reaction. If the reaction is catalysed by hydrogen ions and hydroxyl ions (acid-base catalysis), the rate constant is

$$k = k_{H2O} + k_{H+}C_{H+} + k_{OH-}C_{OH-} . \quad (2)$$

In very acidic conditions, the base term in Eq. 2 becomes negligible compared to the acid term, due to the low concentration of hydroxyl ions. If we assume that the temperature dependence of the solvent factor and the acid factor follows the Arrhenius equation, and that the factors have the same activation energy, E_a, then the rate constant can be formulated as

$$k = \left(k_{H2O} + k_{H+}C_{H+}\right)e^{-\frac{E_a}{RT}}, \quad (3)$$

where k_{H2O} is the solvent factor, k_{H+} the acid factor, T is the reaction temperature and R is the gas constant.

Acid-base catalysis has not been applied for cellulose hydrolysis, probably because of its heterogeneous nature, whereas acid-base catalysis has been

considered in some studies of glucose decomposition at high temperature. McKibbins *et al.* (1962) mentioned the three parts of rate constants, i.e. acid, base and uncatalysed constants, in the context of glucose decomposition. Baugh & McCarty (1988) actually used them and estimated the values over a pH range of 1–4 and temperatures of 170–230 °C. They concluded that glucose decomposition is solvent catalysed at a pH range of 2–2.5, hydrogen ion catalysed at pH values below 2 and hydroxyl ion catalysed above 3 (at room temperature). Xiang *et al.* (2004) ignored the base catalysed term and estimated the kinetic values of glucose decomposition according to the specific acid catalysis model at a pH range of 1.5–2.2 (at room temperature) and temperatures of 180–230 °C.

2.4 Overview of formic acid in biomass exploitation

Formic acid, CH_2O_2, is the strongest monocarboxylic acid with a pK_a value of 3.8. It is a volatile organic acid that can be separated by thermal operations. Previously, formic acid had been utilized in several ways to convert biomass into useful products. A formic acid based pulping process, known as the MILOX process, has been developed for woody and non-wood biomass (Sundquist & Poppius-Levlin 1998). In pulping, formic acid is used in high concentrations of up to 90% (v/v) and at moderate temperatures of 100–130 °C (Dapia *et al.* 2002, Tu *et al.* 2008, Li *et al.* 2012). Formic acid can selectively delignify biomass with minor effects on cellulose (Lam *et al.* 2001, Dapia *et al.* 2002).

Formic acid has been lately studied as a pretreatment agent prior to enzymatic hydrolysis with a sulphuric acid catalyst or acetic acid (Sindhu *et al.* 2010, Vanderghem *et al.* 2012). In these studies, the optimum conditions were a moderate temperature (107–121 °C) and formic acid concentration (40–60%), resulting in good delignification and hemicellulose removal combined with low removal of cellulose. In contrast, at high temperatures (150–200 °C) and lower formic acid concentrations (e.g. 8% (w/w)), raw material was successfully pretreated without any additional chemicals (Jian *et al.* 2009, Marzialetti *et al.* 2011). Under these conditions, lignin and cellulose were almost unaffected (Jian *et al.* 2009).

Only very few researchers have tested formic acid with a view to hydrolysing cellulose directly (Sun *et al.* 2007, Asaoka & Funazukuri 2011). Sun *et al.* (2007) hydrolysed cotton cellulose at a high formic acid concentration (78% (w/w)) with an addition of hydrochloric acid. The reaction time was long (2–9 h) due to the low temperature (55–65 °C). It was stated that formic acid can affect the

crystalline parts of cellulose (Sun & Lin 2010). Asaoka & Funazukuri (2011) hydrolysed cotton cellulose at 250–270 °C using 0.1–1% (w/w) formic acid solutions.

2.5 Summary

Acid-catalysed cellulose hydrolysis and glucose decomposition form an interesting but complex research subject. The possible reactions of cellulose hydrolysis and glucose decomposition in acidic conditions are summarised in Fig. 5. In the batch experiments used in this thesis, it is unlikely that oligomers could survive in high concentrations due to the long reaction times. For example, Abatzoglou *et al.* (1986), who found oligomers, used reaction times of 30–90 s. However, the existence of other by-products from cellulose cannot be excluded.

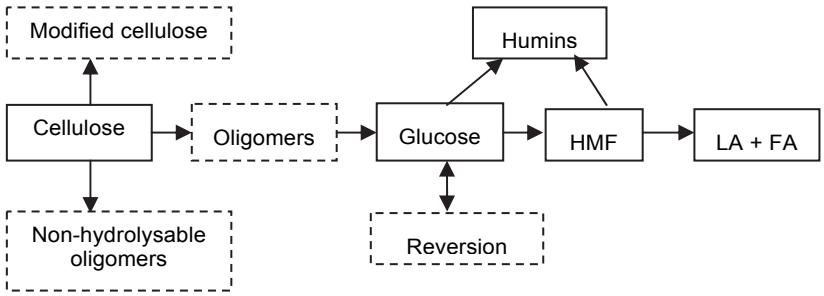

Fig. 5. Possible reactions in acid-catalysed cellulose hydrolysis.

Numerous studies have been carried out concerning the kinetics of cellulose hydrolysis or glucose decomposition. It is common to all these studies that their rate constants lean on the empirical Saeman's equation that dates from 1945. Due to the complexity of acidic cellulose and glucose systems, simplified, empirical models are sensible. Despite the importance of the hydrogen ion concentration on an acid-catalysed reaction, only a few studies have paid attention to the temperature dependence of the pH. Girisuta *et al.* (2007) modelled sulphuric acid catalyzed levulinic acid production with hydrogen ion concentrations calculated at the reaction temperature, Li *et al.* (2009) estimated pH changes in a high-temperature liquid water application for fructose decomposition, and Kootstra *et al.* (2009) explained the increasing difference of rate constants between fumaric and maleic acids by the increasing pH difference.

3 Materials and Methods

Acid-catalysed cellulose hydrolysis and glucose decomposition were studied experimentally on laboratory scale. Kinetic modelling was used as a tool to evaluate the data. In this chapter the experimental apparatus, procedures and analysis methods that were used are described briefly. Details can be found in Papers I–V.

3.1 Materials

Aqueous catalyst solutions were prepared in Milli-Q water. Concentrations of formic acid solutions were 5, 10 and 20% (w/w) and concentrations of sulphuric acid solutions were 0.09, 0.21, 0.36 and 0.50% (w/w). Reactant solutions for glucose decomposition experiments (Papers I and III) were prepared beforehand by dissolving a suitable amount of glucose in the catalyst solution. Reactant solutions for the cellulose hydrolysis experiments (Papers II and IV-V) were prepared directly in the reactors. Table 1 summarises the experimental conditions used in this thesis.

Table 1. Experimental conditions.

Publication	Raw material	Catalyst concentration	Catalyst	Temperature
Paper I	10 g/l glucose	5–20% (w/w)	HCOOH	180–220 °C
		0.09–0.50%	H_2SO_4	
		pure	water	
Paper II	100 g/l MC	5–20%	HCOOH	180–220 °C
		0.09–0.50%	H_2SO_4	
		pure	water	
Paper III	10–20 g/l glucose	5–20%	HCOOH	180–220 °C
		pure	water	
Paper IV	10–100 g/l MC[1]	5–20%	HCOOH	180–220 °C
Paper V	20–101 g/l MC	5–20%	HCOOH	180–220 °C
	19–68 g/l pulp			

[1] MC = microcrystalline cellulose

Microcrystalline cellulose (Acros Organics) was used as a model component to study cellulose hydrolysis. Moreover, hydrolysis experiments were also carried out with wheat straw pulp delignified using the formicodeli™ method (Chempolis Ltd, Oulu, Finland).

3.2 Experimental apparatus

All experiments were conducted in batch reactors made of zirconium tubing and designed at the University of Oulu. The internal diameter of each reactor is 2.4 cm, the length is 10 cm and the inner volume of the reactor is about 40 ml.

Two ovens were used for rapid heating and steady temperature control. A preheating oven was set at 410–450 °C (Papers I and III) or 440–470 °C (Papers II and IV–V) depending on the target reaction temperature. A fluidized sand bath (SBL-2D, Techne) was set at the target temperature.

The temperature inside the reactor was monitored using a Pt-100 sensor (Papers I and III) or a PTFE-coated thermo element (Papers II and IV–V). The Pt-100 sensor was sheltered from the reaction media by a zirconium pocket, while the thermo element was inserted directly into the reaction media through a zirconium cap. The temperature was recorded at intervals of 15 s.

3.3 Experimental procedure

The reactant solution containing glucose (Papers I and III) was pipetted into the reactor, or the cellulosic raw material (Papers II and IV–V) was weighed and the acid catalyst solution was pipetted into the reactor. The volume of the solutions was 30 ml.

The reactor was inserted into the preheating oven, which was set at the initial reaction time t_0=0 min. After reaching a temperature of about 10 °C below the target temperature (Papers I and III) or the desired reaction temperature (Papers II and IV–V), the reactor was moved into the fluidized sand bath. A typical heating-up phase is shown in Fig. 6.

The reactor was removed from the sand bath and quenched in a cold water bath to stop the reaction. The temperature measured inside the reactor dropped to below 100 °C in less than 2 min (Papers I and III) or in 0.5 min (Papers II and IV-V). For modelling purposes (Papers III-IV), the final reaction time t was set to the moment when the temperature inside the reactor was below 100 °C. Otherwise, the final reaction time was set to the moment when the reactor was moved to the cold water bath.

The reactor was opened and a liquid sample was taken for pH measurements and HPLC analysis (Papers I and III) or the contents of the reactor were filtered using a Büchner funnel (Papers II and IV–V). In the case of filtering, the liquid

sample was taken from the filtrate, and the cake was washed with deionised water before drying for weighing overnight at 105 °C.

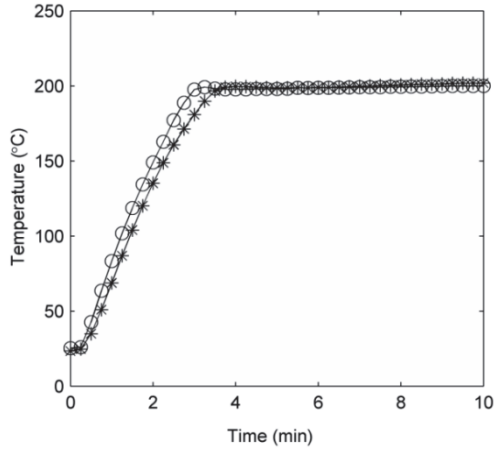

Fig. 6. Temperature profiles for both procedures. Symbols: * Pt-100 sensor, o thermo element.

3.4 Analysis methods

3.4.1 pH measurements

The pH was measured using a SenTix 81 pH electrode (WTW) connected to an inoLab pH 720 meter (WTW). The pH meter was calibrated at three points. The accuracy of the measurement was 0.01 units.

3.4.2 HPLC analysis

The concentrations of cellobiose, glucose, xylose, 5-hydroxy-2-methylfurfural, levulinic acid, formic acid and furfural were analysed by High Performance Liquid Chromatography (HPLC). Fig. 7 shows a typical chromatogram from a refractive index detector for hydrolysis of microcrystalline cellulose in formic acid.

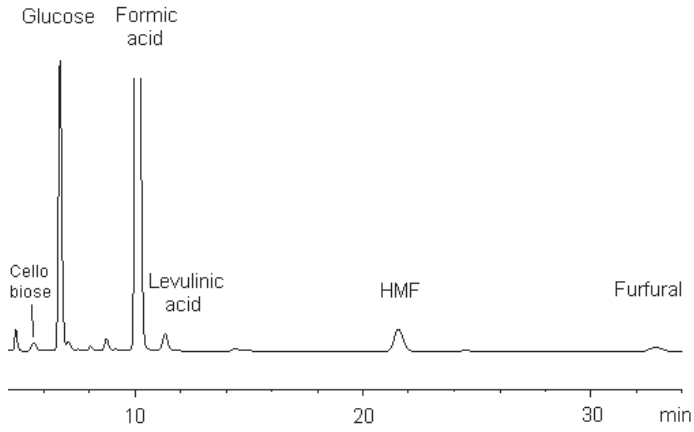

Fig. 7. Typical chromatogram from cellulose hydrolysis in formic acid.

The HPLC system included an ICSep ICE-Coregel 87H3 column (Transgenomic) operated at 60 °C, a diode array detector (Agilent Technology) and a refractive index detector (Agilent Technology). The mobile phase was 5 mM H_2SO_4 with a flow rate of 0.8 ml/min.

The calibration curves were based on four or five calibration points. Calibration verification standards were analysed to check the reliability of the calibration. The samples were filtered through a 0.2 μm filter.

Formic acid analysis was performed with the RI detector or with the DA detector with a wavelength of 210 nm. Small concentrations of HMF (< 0.4 g/l) and furfural (< 0.5 g/l) were analysed with the DA detector with a wavelength of 280 nm. Otherwise, the RI detector was used. The concentration of formic acid in samples from the catalyst decomposition tests was analysed at least in duplicate with a 100-fold dilution.

3.4.3 XRD analysis

The crystallinity of the cellulosic samples was measured using X-ray diffraction analysis. The analysis was performed with a Siemens D5000 X-Ray Diffractometer. The diffracted intensity of Cu Kα radiation generated at 40 kV and 40 mA was measured in a 2θ range between 5° and 30° or 50°.

Microcrystalline cellulose cakes were crushed in a mortar and pressed into pellets in order to prepare homogeneous samples for XRD measurements (Papers

II and V). The pulp cakes were pressed onto a KCl support material due to the small amounts of the samples (Paper V).

The crystallinity index, *CrI*, is determined using Segal's method (Bansal *et al.* 2010) as follows:

$$CrI = \frac{I_{22.5} - I_{18}}{I_{22.5}}, \tag{4}$$

where $I_{22.5}$ and I_{18} are the intensity at 2θ=22.5° and at 2θ=18°.

3.5 Parameter estimation and hydrogen ion calculations

In Papers I and II, the rate constants of the disappearance of glucose and cellulose respectively were calculated by fitting data to the analytically integrated first-order kinetic model with linear regression. In Papers III and IV, the kinetic parameters of the model including product formation were estimated in a Matlab 7.5.0, using a non-linear least square method that utilized the Levenberg-Marquardt algorithm. The differential and non-isothermal batch reactor model was solved with an ode15s solver. The rate constant equations were reparametrised for modelling. The model utilized the temperature data measured with respect to time.

For kinetic modelling, the cellulose concentration, C_c (mol/l), was calculated as glucose equivalents using a mass ratio of 0.9:

$$C_C = \frac{m_C}{0.9 \cdot V \cdot MW_g}, \tag{5}$$

where m_c is the mass of cellulose (g), MW_g is the molar mass of glucose (g/mol) and V is the volume of solution (0.03 l). The glucose yield is then defined per initial cellulose concentration as glucose equivalents. Glucose equivalents correspond to the maximum theoretical glucose obtained from cellulose.

In this thesis, hydrogen ion concentrations calculated at the reaction temperature are used instead of concentrations at room temperature. The relative differences between the pH values measured at room temperature before and after the experiments were 0–2% for glucose decomposition and below 1% for cellulose hydrolysis among the samples analysed in formic acid. In addition, the stability of the formic acid catalyst was studied within the reaction condition area

used (Papers I and II). Therefore, it was assumed that hydrogen ion concentration depends only on the temperature during the experiments.

The calculations are described in detail in Papers I and II. The calculation is based on estimating the temperature dependence of the dissociation constants. The dissociation constant of formic acid, $K_{a,FA}$, is calculated using Eq. 6 (Kim *et al.* 1996).

$$pK_{a,FA} = -57.528 + 2773.9 / T + 9.1232 \ln T \,, \tag{6}$$

where T is the reaction temperature in Kelvin. In Paper I, the dissociation constants of sulphuric acid, $K_{a,SA}$ and $K_{a,HSO}$, are calculated using Eq. 7 for the dissociation reaction of sulphuric acid, and using Eq. 8 for the dissociation reaction of the bisulphate ion (Oscarson *et al.* 1988).

$$\log K_{a,SA}' = -593089 / T + 8850.821 + 1.019062T - 3093.4566 \log T + 43593400 / T^2 \tag{7}$$

$$\log K_{a,HSO}' = -119452 / T + 1974.809 + 0.275677T - 703.8644 \log T + 7715600 / T^2 \,. \tag{8}$$

The dissociation constant is $K_{a,i} = 1/K_{a,i}'$, where i = SA or HSO. The first dissociation constant of sulphuric acid was 7.6–4.4 M at 180–220 °C. It was assumed that sulphuric acid dissociates completely.

In Paper II, the dissociation constant of the bisulphate ion was calculated using Eq. 9 (Marshall *et al.* 1966).

$$\log K_{a,HSO} = 56.889 - 19.8858 \log T - 2307.9 / T - 0.006473T \,. \tag{9}$$

In Papers I and III, the analytical solution for equations derived from the dissociation reactions were used, while in Papers II and IV a system of nonlinear equations was solved numerically in Matlab 7.5.0.

4 Results and discussion

Cellulose hydrolysis is considered in two ways. First, acid-catalysed phenomena are studied in formic and sulphuric acids for glucose decomposition and cellulose hydrolysis. Then a kinetic model including product formation is developed for glucose decomposition and cellulose hydrolysis catalysed by formic acid. In addition, the behaviour of biomass fibres is compared to that of microcrystalline cellulose.

4.1 Phenomena in formic and sulphuric acids

4.1.1 Glucose decomposition in formic and sulphuric acid

The effect of the hydrogen ion concentration on glucose decomposition was investigated in formic and sulphuric acids (Paper I). Kinetic experiments were carried out by varying the temperature, time, catalyst and catalyst concentration. Data was fitted to the analytically integrated first-order kinetic model using linear regression analysis. Kinetic parameters for the specific acid catalysis model are shown in Table 3.

It was found that the rate of glucose decomposition is directly proportional to the hydrogen ion concentration at reaction temperature regardless of acid type when formic and sulphuric acids are the catalysts (Paper I). Fig. 8 shows the rate constant as a function of hydrogen ion concentration calculated at 200 °C. The result is consistent with the concept of specific acid catalysis, but contrary to earlier findings by Mosier *et al.* (2002) in organic acids. The contradiction can be explained by the different temperature dependence of the dissociation constants of organic and sulphuric acids, which was systematically taken into account in this thesis but not in the previous studies. The findings of this thesis illustrate the importance of hydrogen ion concentration calculations: if the temperature dependence of the dissociation constants is not taken into consideration, the effect of different acids on glucose decomposition can be interpreted incorrectly. Fig. 9 shows that when the rate constants are plotted as a function of hydrogen ion concentration measured at room temperature, a difference between the rate constants is observed.

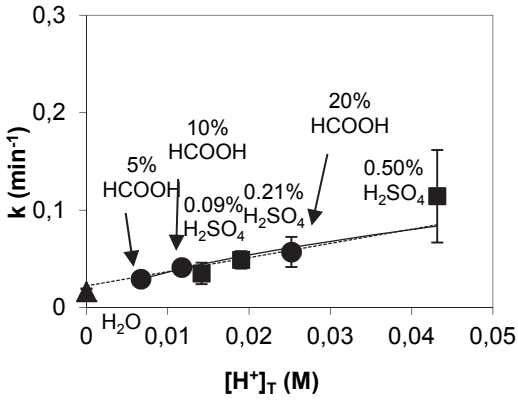

Fig. 8. Experimental rate constants of glucose decomposition as a function of hydrogen ion concentration calculated at 200°C. Symbols: acid-catalysis model (dashed line), modified Saeman's equation (solid line), ■ sulphuric acid, ● formic acid, ▲water. Error bars represent a 95% confidence interval. (Paper I © ACS)

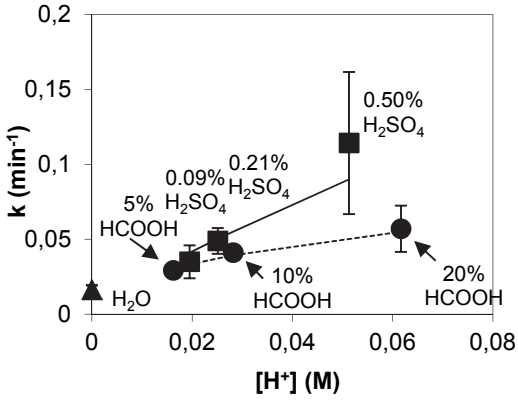

Fig. 9. Experimental rate constants of glucose decomposition as a function of hydrogen ion concentration measured at room temperature and Saeman's equation for sulphuric acid (solid line) and formic acid (dashed line). Symbols: ■ sulphuric acid, ● formic acid, ▲water. Error bars represent a 95% confidence interval. (Paper I © ACS)

As can be seen in Figs. 8–9, the conventional Saeman's model predicts the rate constant of glucose decomposition equally as well as the specific acid catalysis model in a narrow hydrogen ion concentration range. However, Gurgel *et al.* (2012) and Xiang *et al.* (2004) have observed that Saeman's model cannot predict glucose decomposition under extremely low sulphuric acid conditions (0.07%

H_2SO_4). This is in fact quite reasonable: when the hydrogen ion concentration approaches that of pure water, Saeman's model predicts a lower reaction rate for glucose decomposition than the reality, because it does not take into account the effect of the solvent. In fact, glucose decomposition takes place in pure water with a significant reaction rate at elevated temperatures (Paper I). In contrast, the specific acid catalysis model can successfully predict the rate constants both at low and high hydrogen ion concentrations. The benefits of the specific acid catalysis model are shown later in Section 4.2.1, and the limitations are discussed in Section 4.2.3.

4.1.2 Cellulose hydrolysis in formic and sulphuric acid

The effect of hydrogen ion concentration on cellulose hydrolysis was investigated in formic and sulphuric acids (Paper II). A significant difference was found between the reaction rates of cellulose hydrolysis in formic and sulphuric acids despite the same hydrogen ion concentration at the reaction temperature (Paper II). Fig. 10 shows that the rate constant of cellulose hydrolysis is higher in sulphuric acid than in formic acid at the same hydrogen ion concentration, and that the difference increases with temperature. This is not consistent with the proposed mechanism of acid-catalysed cellulose hydrolysis, which assumes that the hydrolysis rate depends only on hydrogen ions. Hydrogen ion concentrations lower those calculated in formic acid would explain the difference between the reaction rates, but there is no evidence of this kind of reduction. For example, it was evaluated that formic acid is stable enough and that esterification of formic acid with cellulose is unlikely under the reaction conditions studied (Papers I-II). Surprisingly, the inconsistency between the mechanism and experimental observations cannot be explained by the crystallinity of cellulose either. As shown in Table 2, the crystallinity indexes of cellulose decrease during acid-catalysed hydrolysis both in formic and sulphuric acids, indicating that the physical state of cellulose, i.e. crystallinity, is changed similarly in both acids. Thus, there is not a difference in the crystallinity that could explain the higher hydrolysis rate in sulphuric acid. In addition, cellulose hydrolysis follows the first-order kinetics nicely within the whole time range, both in formic and sulphuric acids (Paper II), implying that the effects of intraparticle diffusion are negligible with respect to the overall hydrolysis rate in both acids.

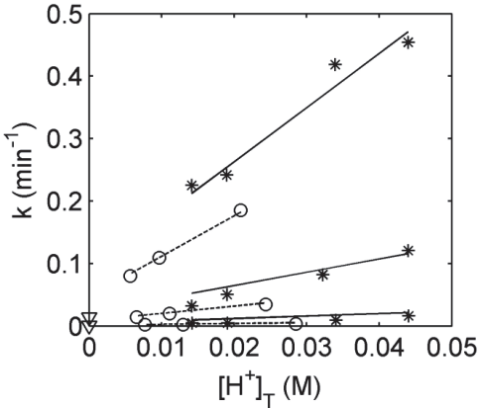

Fig. 10. Rate constant for cellulose hydrolysis in HCOOH (o) and H_2SO_4 (*) at 180–218°C and in H_2O (∇) at 180°C and 220°C and the specific acid catalysis model (---/—). (Paper II © ACS)

Table 2. Crystallinity index of microcrystalline cellulose. (Paper II © ACS).

Acid	Time (min)	Temperature (°C)	Conversion (%)	CrI
Original MC			0	0.75–0.72
20% HCOOH	3.25	219	17	0.70
	7	217	60	0.62
0.21% H2SO4	3.25	220	19	0.75
	7.25	217	69	0.72
0.50% H2SO4	3.25	219	34	0.70
	7	219	88	0.46

Despite the difference between the reaction rates in formic and sulphuric acids, cellulose hydrolysis is directly proportional to the hydrogen ion concentration at reaction temperature when cellulose hydrolysis is considered separately in formic acid or in sulphuric acid. This implies that, after all, a reaction similar to specific-acid catalysis takes place in the system, but there are some extra factors in addition to hydrogen ions that accelerate the hydrolysis rate, especially in sulphuric acid. Charmot & Katz (2010) reported recently on the catalytic effect of phosphate salt on cellobiose hydrolysis. If the hydrolysis of glycosidic bonds in a homogeneous system is catalysed by anions, they may also influence the hydrolysis of cellulose. On the other hand, Torget *et al.* (2000) discussed the phenomena that may take place in the cellulose and liquid interface. They proposed, based on results from flow and batch reactors, that the hydrolysis (and

the glucose release) is affected by a boundary layer. However, in this case, the main distinction between the systems is the acid, and more specifically, the anion.

The effects of sulphate ions on cellulose have been studied previously in the literature. For example, it has been found that sulphate esters on the surface of cellulose can change cellulose properties such as viscosity (Araki *et al.* 1999), or that an increase in sulphate groups on cellulose leads to the increasing thermal degradation of cellulose (Roman *et al.* 2004, Wang *et al.* 2007). Cellulose formates were not studied in this context. Cellulose formates are unstable, since formyl groups can be easily removed by hot water or heat (Heuser 1994), and are formed in highly concentrated formic acid conditions (98%) during long reaction times (Fujimoto *et al.* 1986).

Table 3 shows the estimated kinetic parameters for cellulose hydrolysis (Paper II) and glucose decomposition (Paper I) in formic and sulphuric acids. In the case of cellulose hydrolysis, the data for sulphuric acid can only be fitted satisfactorily to the model based on specific acid catalysis. The confidence intervals of the kinetic parameters are large with sulphuric acid, and the R^2 value is worse than with formic acid. The data with sulphuric acid was fitted a slightly more accurately to the model that consisted of two parts: an additional, promoting factor for the bisulphate ion and the specific acid catalysis part based on the parameters from cellulose hydrolysis in formic acid (Paper II).

Table 3. Kinetic parameters for cellulose hydrolysis and glucose decomposition (95% confidence interval, t distribution). (Modified Paper II © ACS).

Reaction	Acid	k_0[a] (min^{-1})	k_{H+}[a] ($M^{-1}min^{-1}$)	E_a (kJ/mol)	R^2
Cellulose hydrolysis	5–10% HCOOH	0.009 ± 0.003	1.2 ± 0.3	183 ± 25	99.6
Cellulose hydrolysis	0.09–0.5% H_2SO_4	0.02 ± 0.02	2.1 ± 0.9	150 ± 35	97.9
Glucose decomposition	HCOOH or H_2SO_4	0.022	1.45	115	

[a] The values are at the reference temperature of 200 °C.

4.1.3 Discussion

It has been stated that at a certain hydrogen ion concentration 1) cellulose is hydrolysed slower in formic acid than in sulphuric acid and 2) glucose decomposition takes place at a similar rate in formic and sulphuric acids. If it is assumed that cellulose is hydrolysed directly to glucose, this should result in a lower glucose yield in formic acid than in sulphuric acid at the same hydrogen ion concentration. However, a difference between glucose yields from the hydrolysis

of microcrystalline cellulose in formic and sulphuric acids was not detected. Figs. 11–12 show that experimental glucose concentrations are almost identical from cellulose hydrolysis in formic and sulphuric acids under similar hydrogen ion concentrations, whereas the model combined from Papers I and II (the kinetic parameters shown in Table 3) predicts higher glucose concentrations in sulphuric acid. Although the uncertainty of the model can be seen with respect to sulphuric acid at 180 °C, some conclusions can be made from these findings. First, the findings indicate that the simple serial reaction scheme is not sufficiently accurate for acid-catalysed cellulose hydrolysis under the reaction conditions studied in this thesis. Not all the cellulose that has reacted will end up as glucose; instead there is an additional side-reaction from cellulose to unidentified, soluble products. This is consistent with the results in Mok *et al.* (1992), who found substantial amounts of non-hydrolysable oligomers from cellulose hydrolysis in water. The findings could also be explained by the reaction step via oligomers: if the reaction rate from hydrolysable oligomers to glucose was lower than the formation rate of oligomers, then glucose yield would be decreased. In hot-compressed water conditions, oligomers have a significant role in cellulose hydrolysis (see e.g. Yu & Wu 2010), but in acidic conditions they are hydrolysed quickly to glucose. Thus, it is likely that an additional side-reaction to non-hydrolysable oligomers exists (or that hydrolysable oligomers are converted to non-glucose products).

Secondly, since experimental glucose concentrations are similar in both acids, glucose is formed more selectively from cellulose in formic acid than in sulphuric acid. The findings can be explained by a different “mechanism” of cellulose hydrolysis in formic and sulphuric acids. If non-hydrolysable oligomers are formed with different reaction rates depending on the acid catalyst, glucose yield can be influenced in the way described above. However, there are too few experimental data points at similar hydrogen ion concentrations for this to be confirmed.

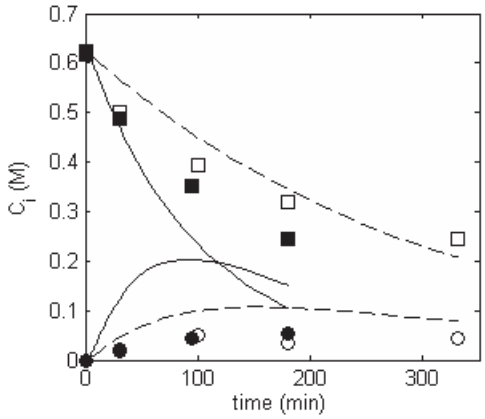

Fig. 11. Cellulose hydrolysis (squares) and glucose formation (circles) in 10% formic acid (white) and 0.09% sulphuric acid (black) in hydrogen ion concentrations at 180 °C. Formic acid model (--) and sulphuric acid model (–) from Papers I and II, non-isothermal system.

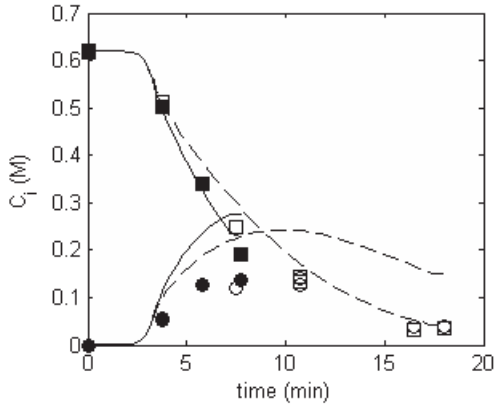

Fig. 12. Cellulose hydrolysis (squares) and glucose formation (circles) in 20% formic acid (white) and 0.21% sulphuric acid (black) in hydrogen ion concentrations at 220 °C. Formic acid model (--) and sulphuric acid model (–) from Papers I and II, non-isothermal system.

4.2 Kinetics in formic acid

This chapter summarises the main results in developing the kinetic model for cellulose hydrolysis and glucose formation in formic acid. The advantages and limitations of the kinetic model are also discussed.

4.2.1 Kinetic model for glucose decomposition and product formation in formic acid

A kinetic model was developed for glucose decomposition and product formation in formic acid (Paper III). It was assumed that the rate constant according to specific acid catalysis is valid for every reaction step and that every reaction step follows first-order kinetics. The reaction scheme that represented the data best is presented in Fig. 13 and the best fit of the kinetic parameters is summarised in Table 4 (reaction steps 3–7). The relative standard errors of the kinetic parameters were between 0.44 - 3.2% and the R^2 value was 98.7%.

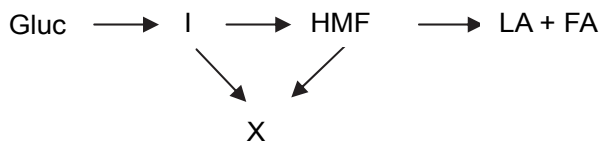

Fig. 13. Reaction scheme for glucose decomposition in formic acid. (Paper III © Elsevier)

The kinetic model predicts glucose decomposition well in a broad range of reaction conditions. It was stated earlier that the specific acid catalysis model can successfully predict glucose decomposition at low and higher hydrogen ion concentrations and that glucose decomposition takes place similarly in formic and sulphuric acids despite the hydrogen ion source. As a consequence, kinetic parameters from formic acid catalysed glucose decomposition can be used directly to predict glucose decomposition in sulphuric acid and water. Moreover, the model also predicts the formation of HMF and LA very well. Figs. 14–16 show glucose decomposition and product formation in formic acid, water and sulphuric acid as well as the prediction by the kinetic model based on formic acid. As shown in Fig. 16c, the model is even able to extrapolate glucose decomposition in 0.50% H_2SO_4 at 180 °C. However, the model is inaccurate under reaction conditions of 0.50% H_2SO_4 at 200–220 °C, in which the reaction rates are high.

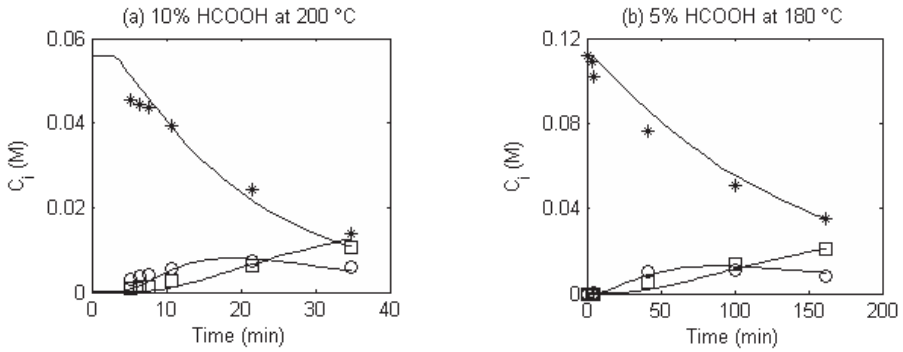

Fig. 14. Glucose decomposition in formic acid. Symbols: * glucose, o HMF, □ LA, – formic acid model (Modified Paper III © Elsevier)

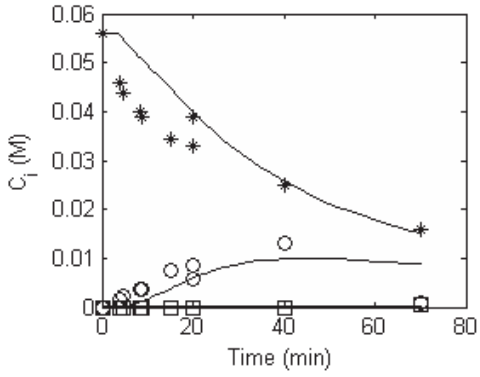

Fig. 15. Experimental glucose decomposition in water and prediction by the model based on formic acid at 200 °C. Symbols: * glucose, o HMF, □ LA, – formic acid model. (Paper III © Elsevier)

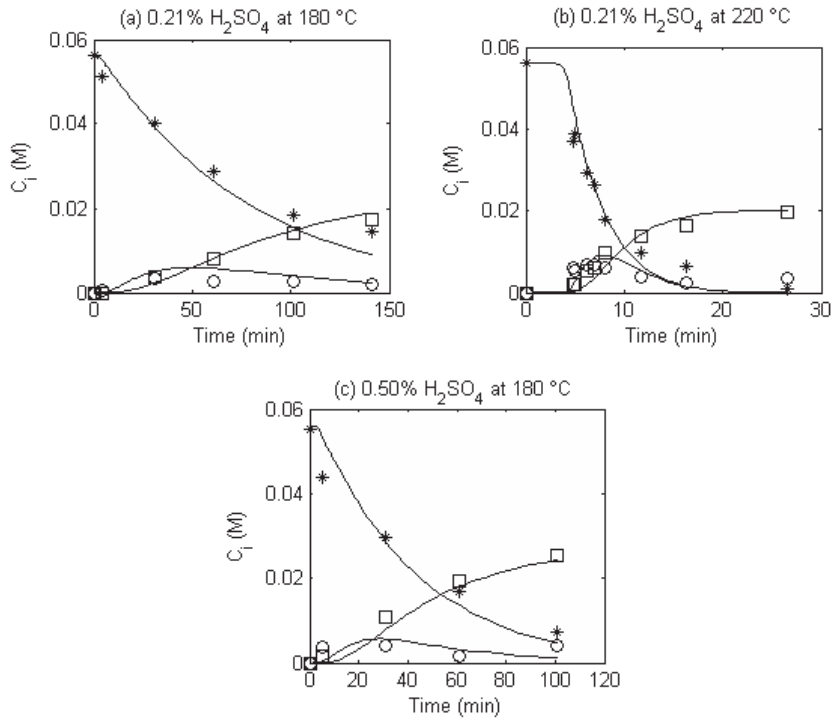

Fig. 16. Experimental glucose decomposition in sulphuric acid and prediction by the model based on formic acid. Symbols: * glucose, o HMF, □ LA, –formic acid model.

4.2.2 Kinetic model for cellulose hydrolysis and product formation in formic acid

Finally, the whole cellulose hydrolysis system is considered, based on Paper IV. This combines the separate study of glucose decomposition in formic acid (Paper III) with cellulose hydrolysis and also provides more knowledge of the reactions of cellulose hydrolysis.

A kinetic model was developed for microcrystalline cellulose hydrolysis and product formation in formic acid using the specific acid catalysis model for the rate constants. The reaction scheme is presented in Fig. 17, and Table 4 shows the best estimates of the kinetic parameters (reaction steps 1–2). Kinetic parameters from individual glucose decomposition experiments (Paper III) were successfully applied in the modelling of the whole cellulose hydrolysis system. Therefore, it can be concluded that there are no major interactions between microcrystalline cellulose, glucose, HMF and LA.

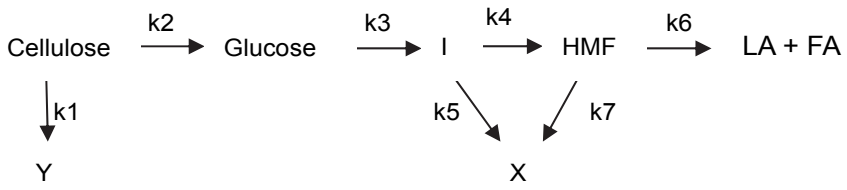

Fig. 17. Reaction scheme for cellulose hydrolysis in formic acid.

Table 4. The kinetic parameters of cellulose hydrolysis and glucose formation in formic acid (confidence interval of 95%, n-distribution). (Papers III and IV).

Reaction i	k_{H2O}[a] (min^{-1})	k_{H+}[a] ($M^{-1}min^{-1}$)	E_a (kJ/mol)
1	0.0047 ± 0.0006	0.63 ± 0.07	161 ± 9
2	0.0026 ± 0.0004	0.74 ± 0.06	201 ± 9
3	0.018 ± 0.000	2.6 ± 0.0	153 ± 2
4	0.109 ± 0.001	8.6 ± 0.1	110 ± 5
5	0.058 ± 0.002	2.9 ± 0.1	117 ± 4
6	0	5.5 ± 0.2	107 ± 5
7	0.031 ± 0.005	2.5 ± 0.2	127 ± 9

[a] The values are at the reference temperature of 200 °C.

Figs. 18–19 illustrate cellulose hydrolysis, product formation and the prediction by the kinetic model at 220 °C. The model predicts cellulose hydrolysis and production of glucose, HMF and LA well. As shown in Fig. 18, in prolonged reaction times cellulose concentration seems to increase suddenly. However, the increase is due to the formation of humins from glucose decomposition reactions, and the data points are erroneous. The prolonged reaction times were necessary before the glucose maximum was reached in a serial reaction.

At 220 °C, the model is inaccurate in predicting levulinic acid formation at higher formic acid concentrations. It was assumed for the modelling that levulinic acid does not undergo further reactions in the reaction conditions studied. When sulphuric acid is used, levulinic acid is stable at 141 °C (Girisuta *et al.* 2006a). According to Fig. 16b, it is unlikely that dramatic LA degradation would take place in sulphuric acid. One may conclude that this is true also for formic acid. However, due to possible anion effects, which are discussed more later on, the possibility of further reactions of levulinic acid cannot be excluded in formic acid.

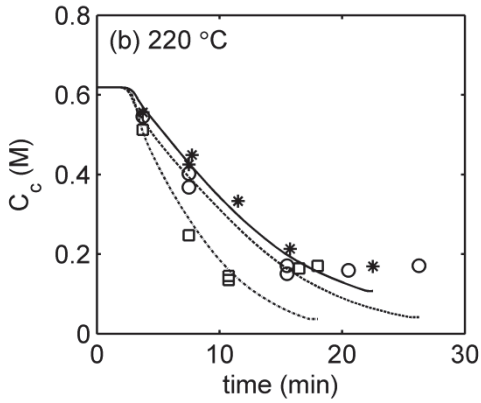

Fig. 18. Cellulose hydrolysis in formic acid and the model prediction. Symbols: (*) 5%, (○) 10%, (□) 20% HCOOH.

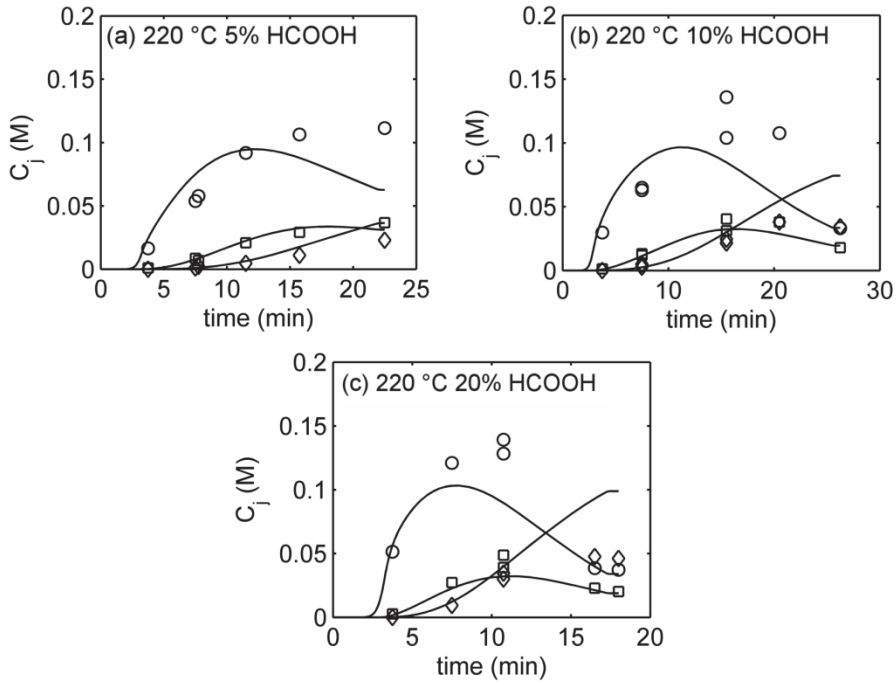

Fig. 19. Product formation in formic acid and the model prediction. Symbols: (o) Glucose (□) HMF (◊) LA.

The kinetic model was applied to evaluate the cellulose hydrolysis phenomena. Fig. 20 shows the product distribution from formic acid catalysed cellulose hydrolysis. The model predicts that a significant amount of cellulose is lost in a side-reaction to soluble non-glucose products (Y), even at the high temperature and short reaction times in which glucose yield is maximized. Therefore, it is concluded that the main reason for low glucose yields from acid catalysed cellulose hydrolysis is the side-reaction and not the glucose decomposition reaction.

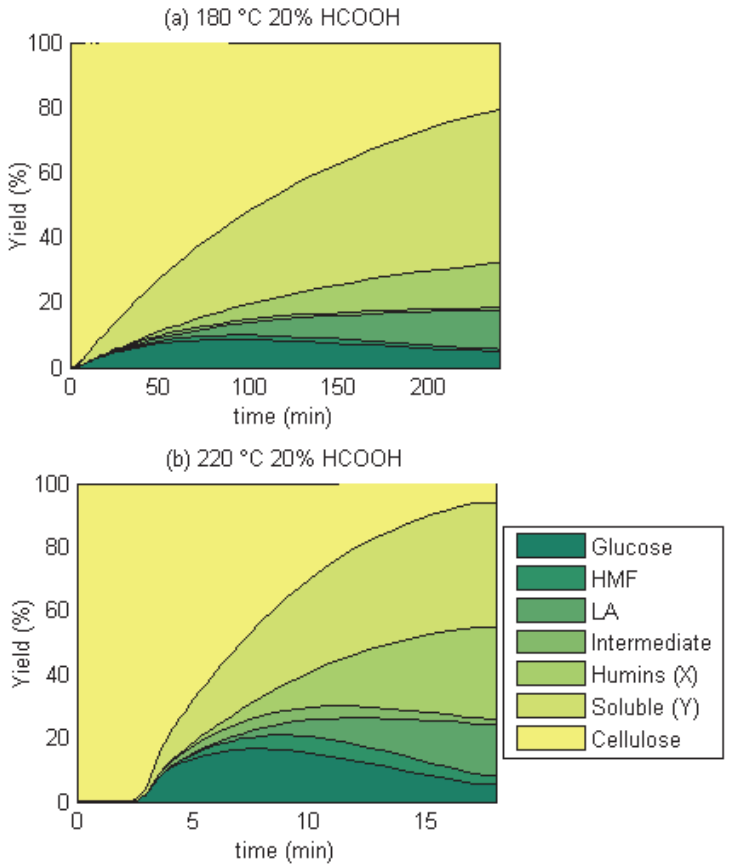

Fig. 20. Product distribution of cellulose hydrolysis in formic acid predicted by the non-isothermal model.

4.2.3 Discussion

The parity plot showed good agreement between the experimental and predicted values (Papers III-IV). This can be also seen from Figs. 14, 18 and 19, where the model predicts glucose decomposition well, along with product formation and cellulose hydrolysis in formic acid. The kinetic model proposed in this thesis differs from the previous models often used in cellulose hydrolysis. First of all, the reaction scheme includes an intermediate compound between glucose and HMF and a side reaction from cellulose to unidentified non-glucose products. This study confirms the importance of an intermediate compound for the kinetic modelling of glucose decomposition: without an intermediate compound, the model was unable to represent the experimental results (Paper III). McKibbins *et al.* (1962) concluded on the basis of their experimental results that there has to be an intermediate compound between glucose and HMF. Kuster & Baan (1977) modelled the kinetics using an intermediate compound, but this was done for fructose decomposition in HCl. Moreover, Girisuta *et al.* (2007) included a side reaction in their kinetic model of cellulose hydrolysis. Secondly, the concept of specific acid catalysis is utilised instead of Saeman's equation. By combining specific acid catalysis with the calculation of hydrogen ion concentration at reaction temperature, the kinetic model can be used to predict glucose decomposition in sulphuric acid.

Specific acid catalysis has not been widely applied in the field of cellulose hydrolysis. From the mechanistic point of view, specific acid catalysis is related to the reactions in which the proton transfer to the reactant is rapid (Laidler 1987, Ault 2007). It has been presented that protonation of both glucose (Bienkowski *et al.* 1987) and glycosidic oxygen in cellulose (Fan *et al.* 1987) takes place rapidly. On the other hand, it has been suggested, based on the method of molecular dynamics simulations, that the rate-determining step in glucose decomposition is protonation of the hydroxyl groups on the sugar ring (Qian *et al.* 2005), which refers to general acid catalysis (Panchenkov & Lebedev 1976). However, this kind of general catalysis can be verified experimentally only at a constant pH in different buffer solutions (Ault 2007), and therefore association of species other than hydrogen ions with cellulose hydrolysis and glucose decomposition cannot be ruled out based on this study. In fact, Baugh & McCarty (1988) have found that glucose decomposition is hydroxyl ion catalysed, i.e. base catalysed, at pH values above 3, when a buffer solution consisted of butyric and phosphoric acids. Kuster & Temmink (1977) have shown that the formate ion, i.e. a weak base, has

an accelerating influence on fructose decomposition at pH 3 compared to the chloride ion. Formate could also affect glucose decomposition. Fig. 21 illustrates how anions affected glucose decomposition in the reaction conditions used in this thesis. Selectivity to HMF was enhanced when a formate anion was present rather than a sulphate anion. Therefore, formate and sulphate ions have a different effect on some mechanistic step of glucose decomposition reactions. Thus, as already speculated in the case of cellulose that anions may participate in the hydrolysis reaction, anions may also take part in glucose decomposition reactions as a base catalyst. However, although the assumption of specific acid catalysis may not be valid for every reaction step due to possible anion effects, the concept of specific acid catalysis can be applied successfully under acidic conditions and even at low hydrogen ion concentrations in order to evaluate cellulose hydrolysis and glucose decomposition.

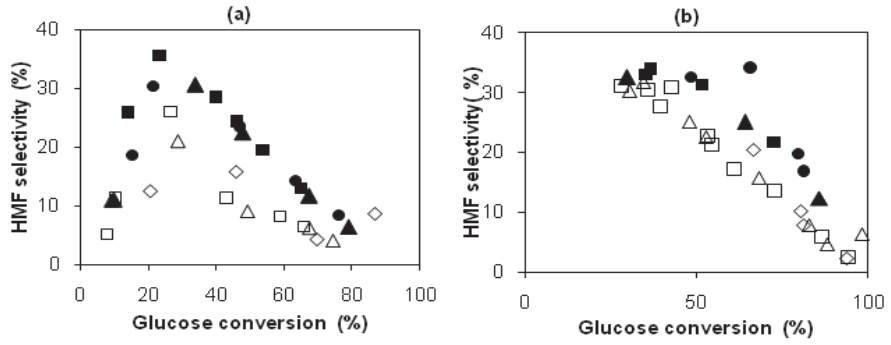

Fig. 21. Effect of catalyst type on HMF selectivity from glucose at (a) 180 °C and (b) 220 °C. Symbols: □ 0.09% Δ 0.21% ◊ 0.50% H_2SO_4 and ■ 5%, ▲10%, ● 20% HCOOH.

There are also some limitations in this study. The reactant concentrations used limit the applicability of the kinetic model, and the accuracy of the kinetic model may suffer in a certain range of reaction conditions. In most of the studies, like in this thesis, first-order kinetics is used for cellulose hydrolysis and glucose decomposition (Saeman 1945, Fagan *et al.* 1971, Malester *et al.* 1992, Gurgel *et al.* 2010). However, although the apparent reaction order for the overall reactions is clearly one (Papers I and II), the initial cellulose concentration affects the glucose yield and selectivity. Fig. 22 shows that selectivity to glucose from cellulose is slightly increased with a decreasing initial cellulose concentration. The effect of cellulose concentration on glucose selectivity is small, and therefore

this kind of behaviour cannot be observed in a narrow cellulose concentration range. Girisuta *et al.* (2007) found that levulinic acid yield is enhanced by decreasing the cellulose concentration. Furthermore, the reversion reactions of glucose have been excluded from the model. However, the significance of reversion products increases with increasing glucose concentration.

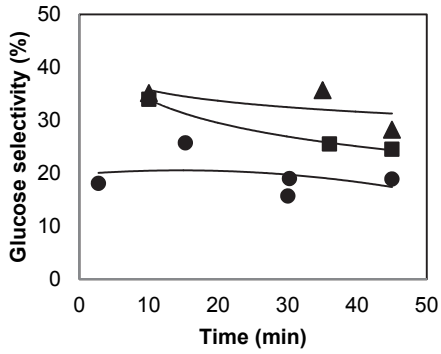

Fig. 22. Effect of initial cellulose concentration on glucose selectivity in 10% HCOOH at 200 °C. Symbols: ● 100 g/l, ■ 39 g/l, ▲10 g/l, – trend line.

4.3 Hydrolysis of wheat straw pulp in formic acid

The behaviour of biomass pulp was investigated in Paper V. Wheat straw pulp delignified by the formicodeli^{TM} method was hydrolysed in formic acid and compared to microcrystalline cellulose, the model component often used in cellulose hydrolysis studies.

Wheat straw pulp can surprisingly be hydrolysed more selectively to glucose than microcrystalline cellulose. This leads to a better glucose yield and a better combined product yield of glucose, HMF and LA from biomass fibres than from microcrystalline cellulose particles. Fig. 23 shows that a two-fold increase in the glucose yield was achieved at 220 °C. The difference between the yields increases with conversion.

It was evaluated that the large difference in yield cannot be explained by particle size, initial raw material concentration or crystallinity. The particle size experiments were performed using the pulp fractions shown in Fig. 24. The results from these experiments indicated that the particle size had no significant effect on the hydrolysis rate of pulp (Paper V). Moreover, although the particle size of microcrystalline cellulose (90 μm) was beyond the particle size of wheat

straw pulp (from <35 mesh to unsieved material) resulting in a higher external surface area available for hydrolysis, microcrystalline cellulose was hydrolysed slower than wheat straw pulp in kinetic experiments. In fact, conversions were slightly higher from wheat straw pulp than from microcrystalline cellulose under similar reaction conditions. This was caused by the rapid removal of hemicellulose, ash and bounded acids from wheat straw pulp, and the conversion of cellulose in pulp approached the conversion of microcrystalline cellulose.

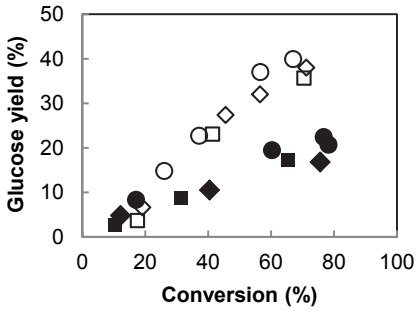

Fig. 23. Glucose yield from pulp (white) and microcrystalline cellulose (black) at 220 °C in 5% (square), 10% (diamond) and 20% (circle) HCOOH (39 g dry pulp/l or 100 g MC/l). (Modified Paper V © Elsevier)

Fig. 24. Wheat straw pulp fractions: (a) > 16 mesh, (b) 16–32 mesh, (c) < 35 mesh.

Experiments with varying initial raw material concentrations showed that conversion is reduced by increasing the initial concentration of pulp and MC. Simultaneously, the glucose yield is also decreased, as shown in Table 5. As discussed earlier, the initial cellulose concentration has an effect on glucose selectivity (and yield). However, although different initial raw material concentrations can slightly affect the results, the large difference in glucose yields from pulp and microcrystalline cellulose cannot be caused solely by the initial raw material concentration. For example, when the cellulose concentration is 36–39 g/l, glucose yield is more than 1.5-fold higher from pulp than from microcrystalline cellulose, despite the similar concentration range.

Table 5. The effect of initial concentration on the hydrolysis of wet pulp and microcrystalline cellulose at 200 °C in 10% HCOOH within 45 min. (Paper V © Elsevier).

C_o (g/l)	Conversion (%)	Glucose yield (%)
Pulp (cellulose in pulp)		
19 (14)	70	29
39 (29)	69	28
49 (36)	62	27
68 (50)	60	26
MC		
20	67	14
39	65	16
101	59	11

The crystallinity indexes were 0.65 and 0.72 for pulp and microcrystalline cellulose, respectively. Thus, cellulose in pulp has a slightly less crystalline structure than microcrystalline cellulose. However, the difference was small. In addition, the crystallinity decreased in both pulp and microcrystalline cellulose during formic acid hydrolysis. For example, the crystallinity index was 0.59 for pulp hydrolysed for 10 min at 220 °C in 10% HCOOH and 0.62 for microcrystalline cellulose hydrolysed for 7 min at 220 °C in 20% HCOOH.

Fig. 25 illustrates the product distribution from cellulose in pulp and from microcrystalline cellulose under the mildest and harshest reaction conditions used in this study. Reaction conditions have a strong influence on the product distribution. Decreasing the temperature and increasing the formic acid concentration enhance the yield of LA, leading to a maximum LA yield of 21% (molar basis) from cellulose in pulp, while increasing the temperature enhances the yield of glucose. The maximum glucose yields from pulp and MC were 40% and 22%, respectively. The maximum LA yield from microcrystalline cellulose was 12%. The product distributions from pulp and MC are quite similar, which implies that glucose decomposition takes place in the same way despite the different liquid matrix.

Although the qualitative results are similar from cellulose in pulp and microcrystalline cellulose under different reaction conditions, the results indicate that findings from the hydrolysis of microcrystalline cellulose should be taken with caution and not applied directly to actual biomass. The mechanisms behind the better glucose yield from pulp can only be speculated on. Obviously, the presence of hemicellulose and lignin did not have a negative effect on acid hydrolysis in this case. It is possible that pretreatment prior to hydrolysis had

modified the state of the fibres to enable the selective production of glucose. However, what happens between cellulose and glucose remains an open question.

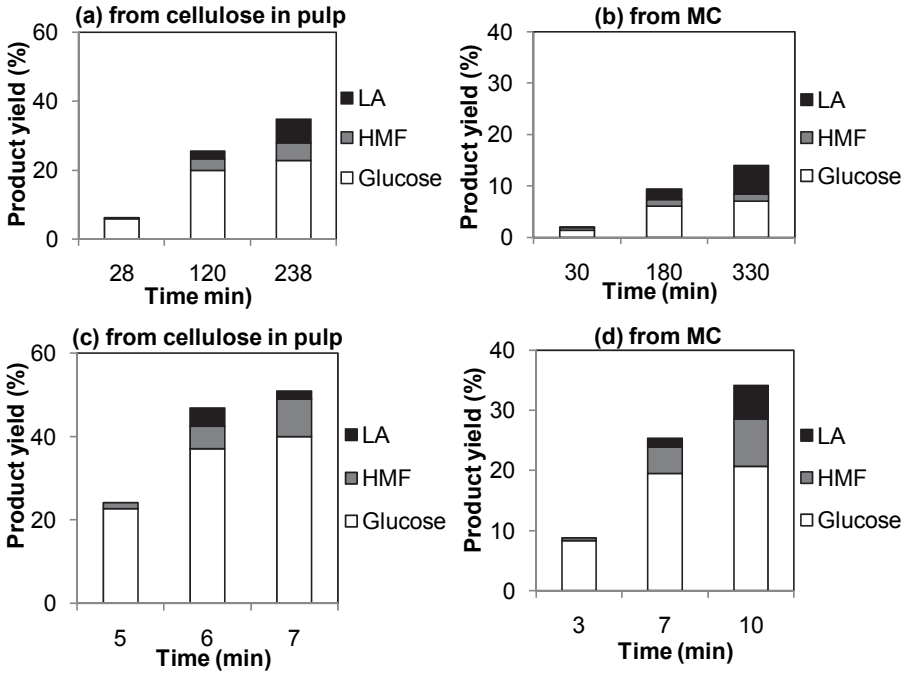

Fig. 25. Product distribution in 5% HCOOH at 180 °C (a-b) and in 20% HCOOH at 220 °C (c-d). (Modified Paper V © Elsevier)

4.4 Results summary

Cellulose hydrolysis and glucose decomposition take place through a complicated mechanism involving several steps. Empirical kinetic models make sense due to the complexity of cellulose hydrolysis systems. However, if mechanistic-like features could be brought into the models, their reliability and extrapolation ability, i.e. their usability, would be enhanced. The kinetic model presented here for glucose decomposition has features that enable us to extrapolate glucose decomposition outside the hydrogen ion concentration range used for developing the model. The predictability arises from the calculation of hydrogen ion concentrations at the reaction temperature and the use of a specific acid catalysis

model. Specific acid catalysis was also used successfully for cellulose hydrolysis in formic acid. Despite the limitations, the kinetic model presented here is a powerful engineering tool for evaluating heterogeneous cellulose hydrolysis and glucose decomposition reactions.

The model predicts only a 30% yield of valuable products from microcrystalline cellulose when 20% formic acid is used as a catalyst. Sulphuric acid was shown to catalyse cellulose hydrolysis more, but this did not result in significantly better glucose yields. However, wheat straw pulp was able to hydrolyse more selectively to glucose, resulting in about a 2-fold increase in glucose yield. Formic acid is therefore a promising catalyst for cellulose hydrolysis.

5 Conclusions and recommendations for future research

The aim of the thesis was to increase our knowledge of the phenomena that take place in acid-catalysed cellulose hydrolysis. The main findings of this thesis were:

1. Glucose decomposition is directly proportional to the hydrogen ion concentration at reaction temperature with no difference between the catalytic powers of formic and sulphuric acid. In contrast, cellulose is hydrolysed faster in sulphuric acid than in formic acid. This is most likely due to the distinct effect of the anions on cellulose hydrolysis.
2. A kinetic model based on specific acid catalysis was developed for cellulose hydrolysis and glucose decomposition in formic acid. The model predicts a significant yield of non-glucose products from cellulose, implying that a side-reaction from cellulose has a significant role in cellulose hydrolysis. The formic acid based specific acid catalysis model can be used successfully to predict glucose decomposition in sulphuric acid and even in pure water.
3. Wheat straw pulp can be hydrolysed in formic acid more selectively to glucose than microcrystalline cellulose, resulting in a better glucose yield from pulp. The crystallinity of cellulose in pulp diminishes during formic acid-catalysed hydrolysis, but this also occurs with microcrystalline cellulose.

In summary, formic acid is a potential catalyst for cellulose hydrolysis. About 50% of the cellulose in wheat straw pulp was converted to valuable products. It is recommended that the temperature dependence of the acid dissociation constant be taken into account in the kinetic modelling of cellulose hydrolysis and glucose decomposition, especially when comparing acids of different types.

This thesis gave rise to the need for further research. More knowledge is required about the anion effects on cellulose hydrolysis and glucose decomposition. This could lead to more selective routes for the production of hydroxymethylfurfural and levulinic acid, which are also valuable chemicals. The mechanism behind the yield difference between pulp and microcrystalline cellulose should be elucidated. Furthermore, it would be very useful and interesting to investigate the feasibility of the kinetic model of glucose decomposition in formic acid for acidic catalysts other than sulphuric acid. Generally speaking, the phenomena related to cellulose hydrolysis and glucose decomposition in formic acid should be studied specifically under reaction conditions of high temperatures and short reaction times. These conditions also

require that possible formic acid decomposition reactions are investigated more profoundly.

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I Kupiainen L, Ahola J & Tanskanen J (2010) Comparison of formic and sulfuric acids as a glucose decomposition catalyst. Industrial & Engineering Chemistry Research 49(18): 8444–8449.

II Kupiainen L, Ahola J & Tanskanen J (2012) Distinct effect of formic and sulfuric acids on cellulose hydrolysis at high temperature. Industrial & Engineering Chemistry Research 51(8): 3295–3300.

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