

# Chapter 4

## Hydrothermal Pretreatment of Lignocellulosic Biomass

Iwona Cybulska, Grzegorz Brudecki and Hanwu Lei

**Abstract** As global energy demands grow and as the environmental and economic issues of fossil fuel use arise, lignocellulosic biomass is starting to attract increased attention as a potential source of energy and chemicals. Being an abundant, accessible, and cost-effective feedstock for a wide variety of products, ranging from transportation fuels to pharmaceuticals, lignocellulose shows great promise for the future. However, in order to utilize its potential, an efficient pretreatment method has to be applied. Hydrothermal pretreatment is one of the most promising and environmentally friendly biomass pretreatment methods available to make the lignocellulosic biomass vulnerable to enzymatic breakdown. This chapter describes the principle of the hydrothermal pretreatments, as well as influence of temperature and time on the effectiveness of the pretreatment and the kinetic models of the process. Various configurations of systems employing hydrothermal pretreatments have also been presented (with examples of process conditions), including hot water, steam explosion, catalyzed hydrothermal treatment, and combination with other methods.

**Keywords** Hydrothermal pretreatment • Hot water • Steam explosion • Lignocellulosic biomass

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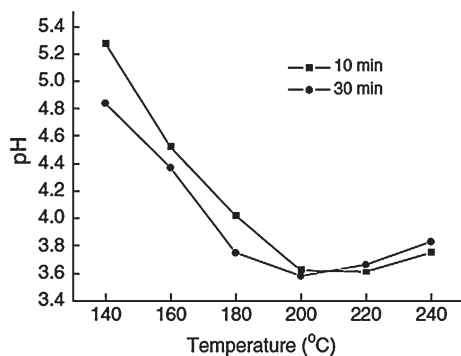
## 4.1 Introduction

Processing of lignocellulosic biomass requires breaking down the coherent structure in order to access all the needed components. The cellulose component needs to be hydrolyzed to fermentable glucose for the production of ethanol. Most of the cellulose is not accessible to enzymes because of its association with other lignocellulosic components. Non-treated lignocellulosic biomass usually produces glucose yields below 20 % (Zheng et al. 2009). Therefore, a suitable pretreatment has to be applied prior to hydrolysis in order to cleave the bonds among and within cellulose, hemicellulose, and lignin, as well as to increase its surface area and reduce the degree of polymerization (DP) and crystallinity.

The research performed to date shows that lignocellulosic biomass is potentially the most promising alternate source of energy and value-added products. It can be pretreated efficiently, cost-effectively, and in an environmentally friendly manner if the methods are correctly optimized. Ongoing research is focusing on optimizing and improving these technologies in order to reduce energy demands, the use of chemicals and the formation of by-products, and more importantly, to find applications for the coproducts produced during the lignocellulosic ethanol production process to create a complete and economically feasible biorefinery (Wyman 1996). A desired pretreatment method should be as simple as possible, applicable to a wide variety of feedstock, and should ensure purity of all products obtained (Chandra et al. 2007). Other important factors include catalyst use, catalyst recovery, and waste treatment (Zheng et al. 2009). Although currently there are no perfect pretreatment methods for lignocellulosic biomass, during the past decade advancements have been made in optimizing already discovered techniques and modifying old industrial processes for new applications (ethanol fermentation and lignin utilization). Based on many studies completed, one of the methods that show especially high potential in future research is hydrothermal pretreatment. Hydrothermal pretreatment uses no chemicals (or small amounts of mineral acids/alkali as catalysts), generates highly digestible cellulose, requires relatively short treatment time and moderate energy use, and has low equipment capital costs. All of these features suggest that hydrothermal pretreatment has low environmental impact and is highly effective in the improvement of lignocellulose's digestibility. It shows promise as a robust and effective biomass processing method to produce a wide range of biobased products. It can be designed as a green pretreatment method for on-farm or mobile applications.

## 4.2 Hydrothermal Pretreatment Influence on the Lignocellulosic Biomass

The principle of hydrothermal pretreatment is that high temperature causes auto-ionization of water, generates hydrogen ions, and thus reduces the pH significantly (Aita and Kim 2010). Water at high temperatures generates enough hydrogen ions



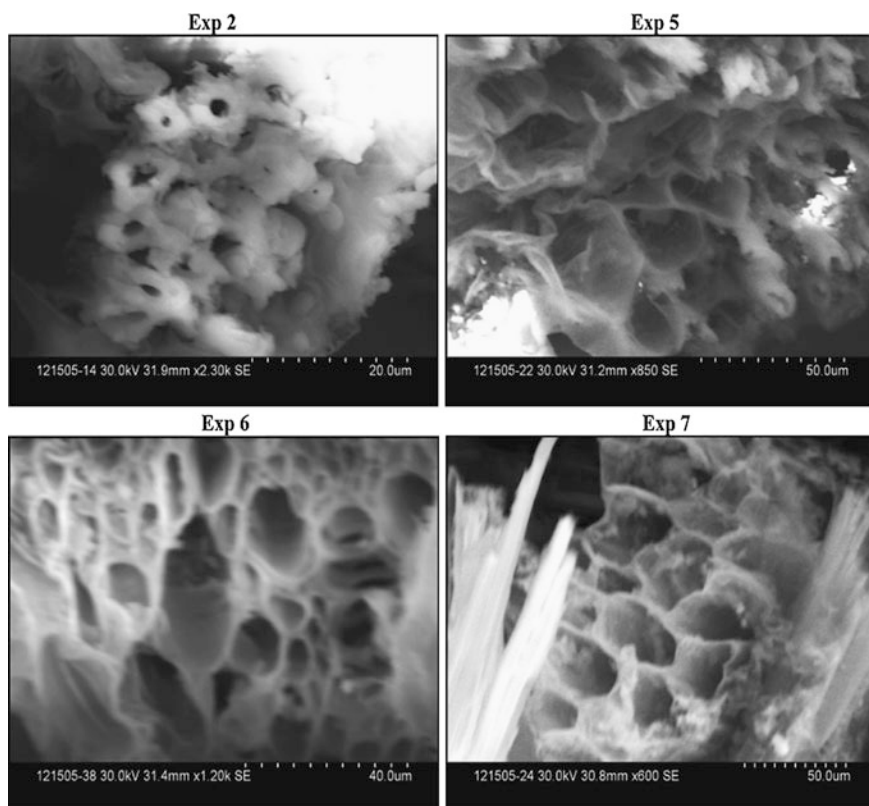
**Fig. 4.1** pH relationships with temperature in the liquid fraction of the hydrothermally pretreated rice straw indicate pressure (Reprinted from Applied Biochemistry and Biotechnology, 160/2, Pretreatment of Rice Straw by a Hot-Compressed Water Process for Enzymatic Hydrolysis, Guoce Yu, Copyright 2008, with permission from Springer)

to drop the pH to acidic levels. At 200 °C the pH of water was found to be below 5 (Wyman et al. 2005). This process induces hemicellulose solubilization and hydrolysis of the acetyl groups. Acetic acid is a by-product of this reaction, which further catalyzes the hydrolysis. Hydronium ions generated from acetic acid are considered even more important than those of water origin (Garrote et al. 1999). Therefore, another name for the hydrothermal treatment is autohydrolysis (Aita and Kim 2010). The pH relationship with temperature in the liquid fraction of the hydrothermally pretreated rice straw can be found in Fig. 4.1 (Yu et al. 2010). This treatment has been proven to work especially well when applied to herbaceous materials and hardwoods, but was not efficient for softwoods due to the low content of acetyl groups in the softwood hemicellulose (Alvira et al. 2010).

Generally, hydrothermal pretreatment does not require size reduction prior to the process, especially when applied on a large scale, thus resulting in a large cost reduction (Taherzadeh and Karimi 2008). However, according to Hosseini and Shah (2009), 50 % increase in energy efficiency can be achieved when the size of wood chips is reduced. Hydrothermal pretreatment removes only small amounts of lignin (the acid soluble fraction), but it does change lignin structure by melting, coagulation, and its subsequent repolymerization on cellulose fibers. Therefore, it is not possible to extract lignin in its functional form from hydrothermally pretreated solids (Aita and Kim 2010). Changing the lignin structure results in cleavage of the linkages between lignin and carbohydrates. This opens the cellulose fibrils to the actions of enzymes. Syringil units in lignin were found to be most susceptible to degradation during hydrothermal pretreatment. Repolymerized lignin, referred to as “pseudolignin”, contains residual xylans as well as hemicellulose degradation products, and is acid insoluble, thus resulting in false Klason lignin measurements of the solid fraction. Sugar degradation products tend to react with precipitating lignin, following the condensation route (Garrote et al. 1999; Young 1998). Repolymerization counteracts depolymerization and lignin removal, and although

the ether bonds are being cleaved, delignification rates can be found close to zero (Li et al. 2007). Furthermore, as depicted in Li et al. (2007), the molecular weight of lignin measured in the pretreated material increases with the increasing severity factor, thus suggesting lignin's repolymerization.

Hydrothermal pretreatment greatly increases surface area of cellulose (by nonchemical swelling), which significantly enhances possible enzyme access (Chang et al. 1981; Sun and Cheng 2002) (Fig. 4.2). Due to its high severity of process conditions, this treatment is one of the methods creating high concentrations of sugar degradation products. These include furfural (from dehydration of pentoses) and 5-hydroxyl-methyl-furfural (from dehydration of hexoses). Both degradation products and acetic acid (along with small amounts of other organic acids, such as levulinic and formic acids) formed during the treatment inhibit yeast and other fermenting microorganisms when present in high concentrations.



**Fig. 4.2** Scanning electron microscopy (SEM) photographs of prairie cordgrass pretreated under various conditions: 210 °C/10 min (*Experiment 2*), 162 °C/15 min (*Experiment 5*), 218 °C/15 min (*Experiment 6*), and 190 °C/15 min (*Experiment 7*). (Reprinted with permission from Energy Fuels, Hydrothermal Pretreatment and Enzymatic Hydrolysis of Prairie Cord Grass, Iwona Cybulska, Hanwu Lei, and James Julson, Copyright 2010, American Chemical Society)

Other by-products can include lignin degradation products, which are generally organic acids of phenylpropane origin (e.g., coumarilic acid, ferulic acid) (Aita and Kim 2010; Garrote et al. 1999). Hexose degradation to by-products become more favorable at temperatures above 210–220 °C (Garrote et al. 1999). There are methods for detoxification that could be applied in order to remove the inhibitory compounds, but it should be avoided due to the additional costs (Alvira et al. 2010). Instead, a simple filtration following the cooking step, would remove most of the by-products. Also, controlling pH during the process by addition of a base was found to reduce degradation of pentoses and therefore the formation of by-products (Taherzadeh and Karimi 2008). Steam explosion can also be part of hydrothermal pretreatment treatment with high-pressure saturated steam. The steam explosion process causes hemicelluloses degradation and lignin transformation due to high temperature (Sun and Cheng 2002). Limitations of steam explosion were reported, such as destruction of a portion of the xylan fraction, incomplete disruption of the lignin-carbohydrate matrix, and generation of compounds that might be inhibitory to microorganisms used in downstream processes (Mackie et al. 1985). Steam pretreated biomass needs to be washed with water to remove the inhibitory materials along with water soluble hemicellulose (McMillan 1994).

### 4.3 Kinetics of Hydrothermal Pretreatment (Time and Temperature Effects)

Generally, there are two models used for describing the kinetics of hydrothermal pretreatment: pseudohomogeneous first-order model and severity factor model (Garrote et al. 1999). The first model uses similar simplifications as the model of acid hydrolysis (the same mechanism of reaction) (Rodrigues Rde et al. 2010; Yat et al. 2008), and assumes that the polysaccharides hydrolysis follows irreversible and pseudohomogeneous first-order kinetics, with apparent coefficients following the Arrhenius equation for temperature dependence, and that hemicellulose degradation is independent of other processes occurring in the treatment. This model also neglects time, particle size, and pH effects (Saeman 1945). However, this model does not include the subsequent steps of the hydrothermal pretreatment, which are: diffusion of the hydronium ions into biomass structure, protonation of ether bonds, cleavage of ether bonds, and diffusion of the reaction products into the liquid phase (Garrote et al. 1999).

Severity factor is defined by an empirical equation, which is related to the most important factors of the treatment—time and temperature (Eq. 4.1) (Aita and Kim 2010; Hendriks and Zeeman 2009):

$$R_0 = t e^{(T-100)/14.75} \quad (4.1)$$

$T$ —temperature, °C

$t$ —time, min

$R_0$ —severity factor

Its logarithmic form has been used by other authors (Eq. 4.2) (Galbe and Zacchi 2007; Hendriks and Zeeman 2009):

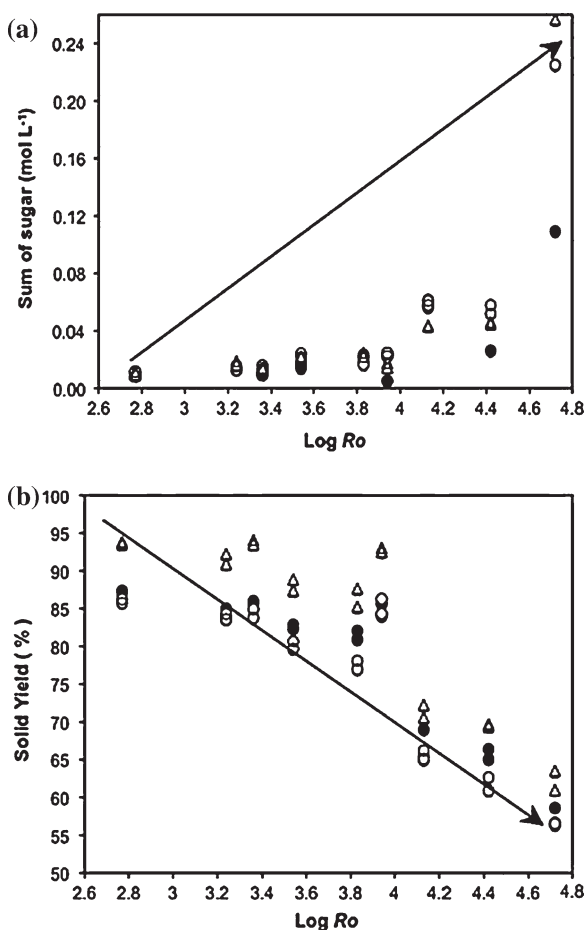
$$\text{Log}(R_0) = \log\left(t \exp\left(\frac{T - 100}{14.75}\right)\right) \quad (4.2)$$

The pH influence can be also included in the equation (Eq. 4.3) (Galbe and Zacchi 2007):

$$\text{CS (combined severity)} = \text{log}(R_0) - \text{pH} \quad (4.3)$$

The optimal value of the severity factor for maximum enzymatic hydrolysis yield should be contained between 3.0 and 4.5 (Aita and Kim 2010). The relationship between the severity factor and sugar removal to the liquid fraction (biomass solubilization) can be found in Fig. 4.3a, while Fig. 4.3b presents the severity factor influence on the solid fraction yield remaining after the pretreatment (Ruiz et al. 2011).

**Fig. 4.3** Severity factor versus solubilized sugar concentration (a) and solid fraction yield (b) for wheat straw. Different dots represent various particle sizes of wheat straw blends: 0.488 mm, 0.330 mm, and 0.435 mm (Reprinted from Journal of Chemical Technology & Biotechnology, Hector A. Ruiz, Denise S. Ruzene, Daniel P. Silva, Mafalda A.C. Quintas, Antonio A. Vicente, Jose A. Teixeira, 88-94, Copyright 2010, with permission from Springer Science + Business Media)



Severity factor equation can be used for each of the subsequent steps of the pretreatment process. Since hydrothermal treatment removes most of the hemicellulose, describing its kinetics can be based on the xylan removal from biomass using a following differential equation (Eq. 4.4) (which assumes first-order relation):

$$\frac{d(PX)}{dR_0} = -K(PX) \quad (4.4)$$

where:

PX—percent of xylan remaining in the solid, %

$R_0$ —severity factor

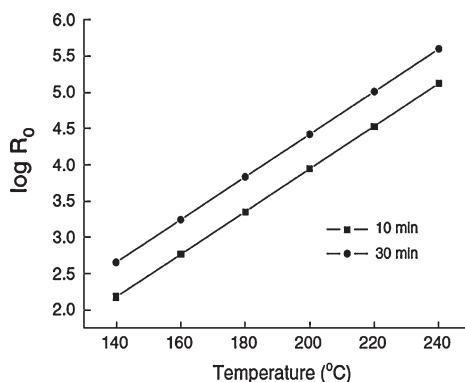
K—kinetic constant independent from the severity of the process,  $\text{min}^{-1}$

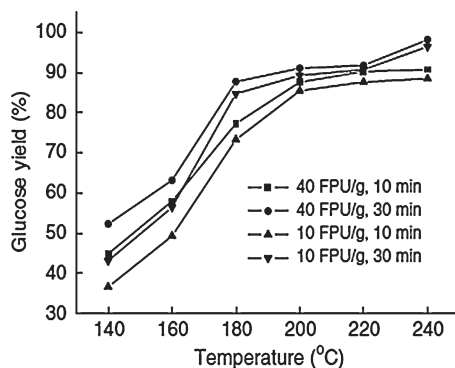
### 4.3.1 Influence of the Temperature Parameter

According to many studies performed to date, temperature has a major influence on the hydrothermal pretreatment efficiency and it determines the severity of the treatment more than the time factor (being in the exponent of the severity factor equation). The relationship between severity factor and temperature has been presented in Fig. 4.4 (Yu et al. 2010).

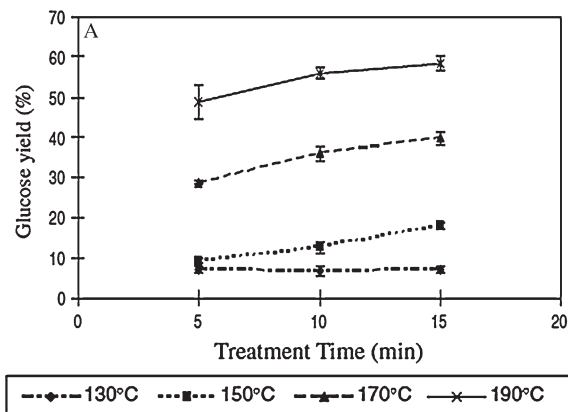
Temperatures below 180 °C were found to give low enzymatic hydrolysis glucose yields when applied to rice straw as a feedstock according to Yu et al. (2010) and Zhang et al. (2011). However, according to Cybulska et al. (2009), temperatures above 200 °C were found to produce high enzymatic hydrolysis glucose yields when hydrothermal pretreatment was applied to prairie cordgrass. These trends are presented in Figs. 4.5, 4.6, and 4.7 (Cybulska et al. 2009; Yu et al. 2010; Zhang et al. 2011). One of the reasons for an increased cellulose digestibility with increased pretreatment temperature is reduced DP of the cellulose fibers in samples treated at higher temperatures (Fig. 4.8). Generally, xylose yield rapidly decreases after a pretreatment at a temperature higher than 170 °C,

**Fig. 4.4** Severity factor versus temperature of the hydrothermal pretreatment (based on severity factor model in Eq. (4.2) (Reprinted from Applied Biochemistry and Biotechnology, 160/2, Pretreatment of Rice Straw by a Hot-Compressed Water Process for Enzymatic Hydrolysis, Guoce Yu, Copyright 2008, with permission from Springer)





**Fig. 4.5** Temperature influence on the enzymatic hydrolysis glucose yield of the solid fraction obtained after hydrothermal pretreatment of rice straw. (Reprinted from *Applied Biochemistry and Biotechnology*, 160/2, Pretreatment of Rice Straw by a Hot-Compressed Water Process for Enzymatic Hydrolysis, Guoce Yu, Copyright 2008, with permission from Springer)



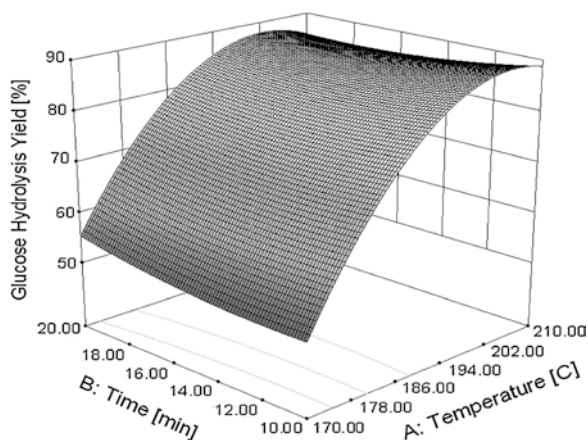
**Fig. 4.6** Temperature influence on the enzymatic hydrolysis glucose yield of the solid fraction obtained after hydrothermal pretreatment of cattails. (Reprinted from *Journal of Industrial Microbiology and Biotechnology*, 38/7, Hot water pretreatment of cattails for extractions of Cellulose, Bo Zhang, Copyright 2010, with permission from Springer)

as the degradation of pentoses becomes favorable. This relationship has been presented in Figs. 4.9, 4.10, and 4.11 (Cybulska et al. 2009; Yu et al. 2010; Zhang et al. 2011).

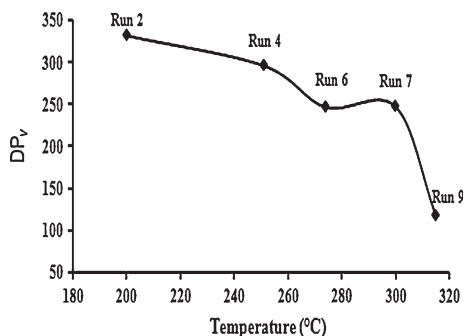
### 4.3.2 Influence of the Time Parameter

Based on the severity factor theory of hydrothermal pretreatment, time has a much lower influence on the pretreatment's effectiveness in improving cellulose digestibility than temperature. This fact has been proven by many experimental data, in



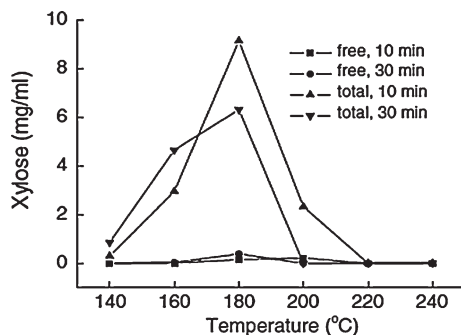


**Fig. 4.7** Temperature versus time versus glucose hydrolysis yield for hot water pretreatment of prairie cordgrass. (Reprinted with permission from *Energy Fuels*, Hydrothermal Pretreatment and Enzymatic Hydrolysis of Prairie Cord Grass, Iwona Cybulska, Hanwu Lei, and James Julson, Copyright 2010, American Chemical Society)

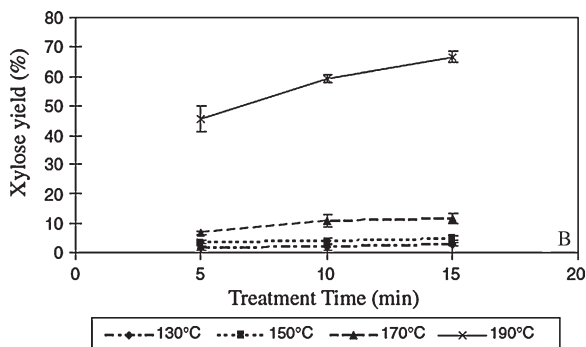


**Fig. 4.8** Degree of polymerization of cellulose versus pretreatment temperature (Reprinted from *Bioresource Technology*, 101/4, Cellulose pretreatment in subcritical water: Effect of temperature on molecular structure and enzymatic reactivity, Sandeep Kumar, Rajesh Gupta, Y.Y. Lee, Ram B. Gupta, 1337-1347, Copyright 2010, with permission from Elsevier)

which time is mostly a factor of low significance in modeling of the sugar yields responses. The trend has been presented in Figs. 4.5, 4.6, 4.7, and 4.12 for the enzymatic hydrolysis glucose yield for different biomasses. Furthermore, the same trend was observed for xylose yields in both enzymatic hydrolysis and pretreatment liquid fraction (Figs. 4.9, 4.10, and 4.11). Similarly, experimental data show that inhibitory by-products formation does not depend strongly on the processing time, which is depicted in Fig. 4.13.



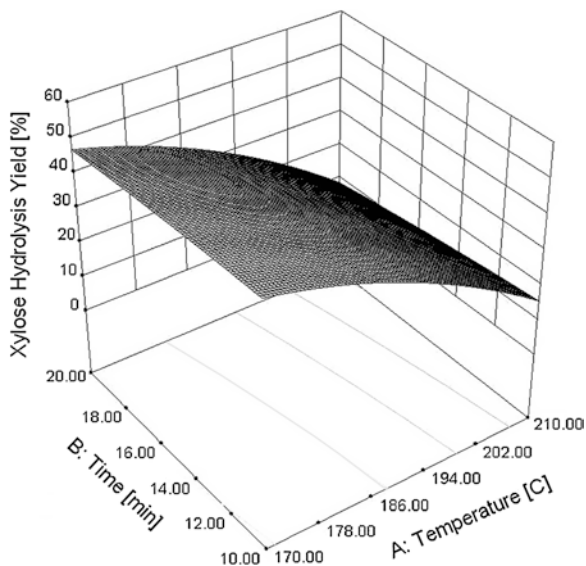
**Fig. 4.9** Temperature influence on the xylose yield extracted to the liquid fraction (free means xylose in monomeric form; total includes both monomeric and oligosaccharide forms) of the hydrothermally pretreated rice straw. (Reprinted from Applied Biochemistry and Biotechnology, 160/2, Pretreatment of Rice Straw by a Hot-Compressed Water Process for Enzymatic Hydrolysis, Guoce Yu, Copyright 2008, with permission from Springer)



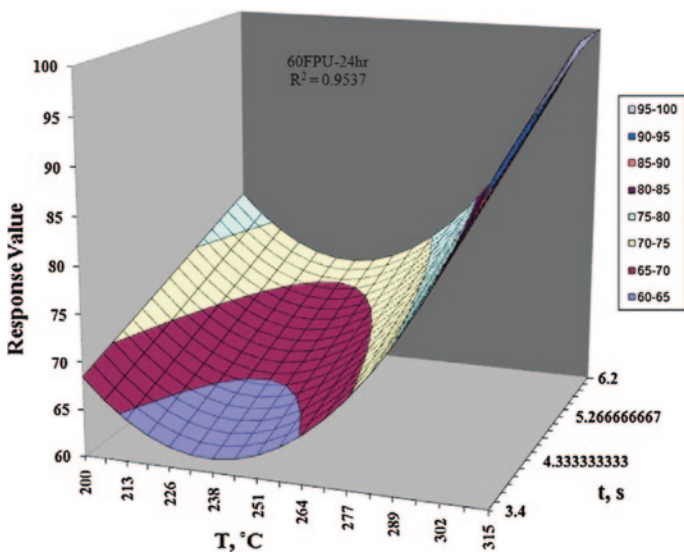
**Fig. 4.10** Temperature influence on the enzymatic hydrolysis xylose yield of the solid fraction obtained after hydrothermal pretreatment of cattails. (Reprinted from Journal of Industrial Microbiology and Biotechnology, 38/7, Hot water pretreatment of cattails for extractions of Cellulose, Bo Zhang, Copyright 2010, with permission from Springer)

### 4.3.3 Influence of Other Factors (Biomass Loading and Pressure)

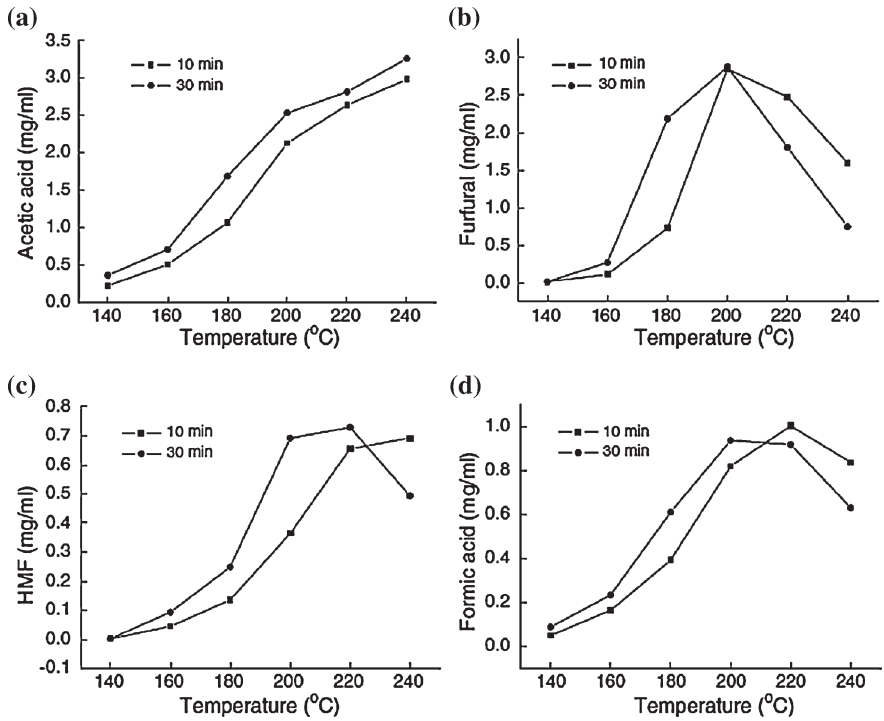
According to Taherzadeh and Karimi (2008) solids loading for the process ranges from 1 to 8 %. However, most of the industrial process conditions include solids loading of 10 % (liquor to solids ratio (LSR) is equal to 10) (Garrote et al. 1999). Pressure influence is directly related to the processing temperature used, and thus the relationship is similar (based on vapor pressure of water related to temperature). Enzymatic hydrolysis yield of the pretreated lignocellulosic materials tends to increase in the range between 0.5 and 2 MPa, then drastically decreases



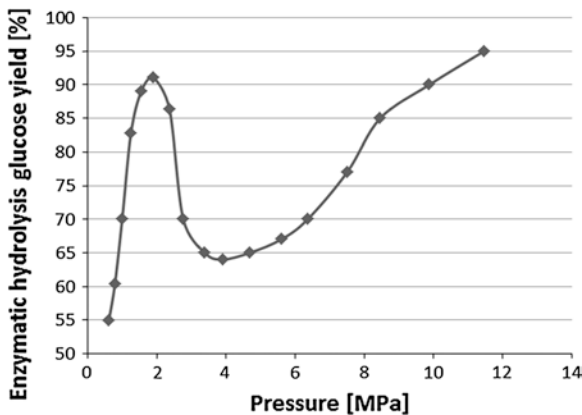
**Fig. 4.11** Temperature and time influence on the enzymatic hydrolysis xylose yield from prairie cordgrass. (Reprinted with permission from Energy Fuels, Hydrothermal Pretreatment and Enzymatic Hydrolysis of Prairie Cord Grass, Iwona Cybulska, Hanwu Lei, and James Julson, Copyright 2010, American Chemical Society)



**Fig. 4.12** Enzymatic hydrolysis glucose yield percentage (*response value*) after subcritical water pretreatment of cellulose (Reprinted from Bioresource Technology, 101/4, Cellulose pretreatment in subcritical water: Effect of temperature on molecular structure and enzymatic reactivity, Sandeep Kumar, Rajesh Gupta, Y.Y. Lee, Ram B. Gupta, 11 pages, Copyright 2010, with permission from Elsevier)



**Fig. 4.13** Formation of inhibitory by-products in liquid fraction during hydrothermal pretreatment of rice straw. (Reprinted from Applied Biochemistry and Biotechnology, 160/2, Pretreatment of Rice Straw by a Hot-Compressed Water Process for Enzymatic Hydrolysis, Guoce Yu, Copyright 2008, with permission from Springer)



**Fig. 4.14** Pressure influence on the enzymatic hydrolysis glucose yield of the lignocellulosic feedstock (combined data from pretreatment of Avicel cellulose and prairie cordgrass) (Cybulska et al. 2009; Geankoplis 2003; Kumar et al. 2010)

between 2 and 4 MPa, to eventually increase beyond 4 MPa (entering subcritical region for water). An exemplary graph combining two pressure regions from two research studies is presented in Fig. 4.14.

## 4.4 Characteristics of Hydrothermal Pretreatment and Examples of Applications

### 4.4.1 Hot Water Pretreatment

It has been established that hydrothermal pretreatment does not have to involve explosion, but the reactor is slowly heated and then cooled after the process (can be referred to as hot water treatment or liquid hot water cooking). The process is gaining interest as a pretreatment method for the ethanol industry since it does not require any chemicals and is simple in operation. It has been implemented on a pilot scale at DONG Energy facility in Skærbek, Denmark. Hot water pretreatment has been applied in a screw-conveying reactor. A particle pump prevents the biomass from splashing due to pressure release while exiting the reactor. Splashing is a common problem occurring at the location of biomass removal from the reactor (in either continuous or batch mode) (Petersen et al. 2009). The process schematic is presented in Fig. 4.15. Hot water pretreatment may be followed by a liquid and solid fractionation separation step, or the effluent can be fed into the next step in the form of a slurry (Wyman 1996). Hot water pretreatment can be applied to almost any type of lignocellulosic biomass. A study using olive tree residues revealed that the highest

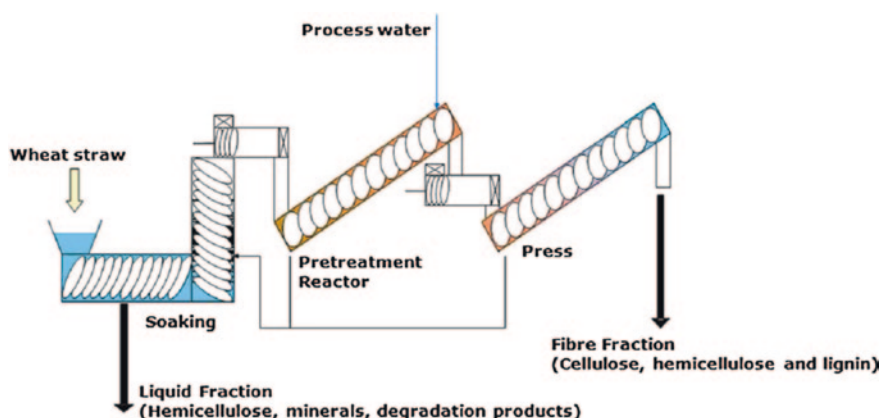


Fig. 4.15 Flow sheet a hydrothermal pretreatment process. (Reprinted from Biomass and Bioenergy, 33/5, Optimization of hydrothermal pretreatment of wheat straw for production of bioethanol at low water consumption without addition of chemicals, Mai Østergaard Petersen, Jan Larsen, Metter Hedegaard Thomsen, 834-840, Copyright 2009, with permission from Elsevier)

glucose yields obtained in enzymatic hydrolysis using the pretreatment temperatures between 200 and 210 °C are the most efficient, while the highest xylose recovery occurred at lower temperatures (~170 °C) (Cara et al. 2007). Glucose yield of 90 % occurred during enzymatic hydrolysis of hydrothermally pretreated (at 240 °C) yellow poplar sawdust. However, the inhibitory compounds formed during the treatment resulted in a low ethanol yield (50 %) (Weil et al. 1997).

According to Mok and Antal (1992), the efficiency of the treatment does not depend on the reaction conditions, but mainly on the feedstock type, especially when woody and herbaceous materials are being compared. However, the variability among the feedstock types was not found to be significant. It was also observed that compressed hot water percolation can remove 76–100 % of hemicellulose (depending on the material type) and up to 60 % of lignin at a severity parameter ( $\log R_0$ ) of 4.1 (at 230 °C for 2 min). Fermentation of the pretreated samples was not performed (Mok and Antal 1992). Good hemicellulose solubility (64 %) was also achieved in a study using hydrothermally treated wheat straw (with severity factor equal to 3.96, corresponding to 215 °C). Hemicellulose removal resulted in enriching the solids in cellulose up to 61 %. The amount of inhibitors generated was acceptable (Carvalho et al. 2009).

The most beneficial configuration for the hot water pretreatment reactor would be a continuous flow-through. This would ensure constant removal of hemicellulose from the material (Alvira et al. 2010). Other configurations include cocurrent and countercurrent flow reactors (Mosier et al. 2005b).

Hydrothermal pretreatment possesses some desirable features for bioethanol production. It is usually short (minutes), does not require any chemicals, and produces good hydrolysis and fermentation results. It cleaves the bonds between lignin and carbohydrates, and alters lignin structure to the point where it does not interfere with the enzymes. Moderate energy demand and water usage are also favorable characteristics of this green pretreatment method.

#### **4.4.2 Steam Explosion**

Steam explosion is a type of hydrothermal pretreatment and one of the most common and efficient methods of lignocellulosic biomass pretreatment. In this process, steam is injected into a reactor along with biomass feedstock, resulting in swelling of the lignocellulosic structure. Steam temperature, which also generates high pressure is usually in the range of 180–260 °C (corresponding pressure, 0.69–4.83 MPa). After a specified reaction time, usually between 5 and 30 min, the steam is released suddenly through a release valve, causing the biomass structure to explode. The explosion rapidly disrupts the linkages between cellulose, lignin, and hemicellulose.

During steam explosion, some of the hexoses and pentoses from hemicellulose fraction are degraded to aldehydes and organic acids due to high temperature and pressure, which are inhibitory to fermenting microorganisms (Kosarie et al. 2001). The treatment does not involve any chemicals and has a moderate energy demand (Chandra et al. 2007). Steam explosion efficiency is affected by particle size of the feedstock (Zheng et al. 2009). For example, a steam explosion at 210 °C and 4 min

residence time applied to poplar resulted in a 60 % glucose enzymatic hydrolysis yield, 60 % ethanol yield obtained during the simultaneous saccharification and fermentation (SSF), and 41 % xylose recovery in the liquid fraction (Negro et al. 2003). This pretreatment method is one of the few that have been demonstrated on both a pilot scale and a commercial scale (Wyman 1996; Zheng et al. 2009).

One of the industrial demonstration-scale steam explosion facilities is operated by Iogen Corporation in Canada. Its production capacity is 340 L of ethanol per ton of fiber (Zheng et al. 2009). Another example of the industrial-scale steam explosion pretreatment is the Masonite batch process used for production of fiber-board and other products in the early twentieth century (Mosier et al. 2005b). This pretreatment was applied to wood chips and used steam at pressures up to 90 atm and residence time between 1 and 10 min. A continuous mode of the Masonite process, called Stake II, uses an extruder as the reactor. Another example of a continuous industrial-scale process is the Rapid Steam Hydrolysis (RASH). In this process, the liquid fraction is continuously drained from the reactor, which reduces generation of inhibitory by-products (Garrote et al. 1999; Young 1998). A summary of hydrothermal pretreatment results for various biomass feedstocks is presented in Table 4.1.

### 4.4.3 Catalyzed Hydrothermal Pretreatment

#### 4.4.3.1 Sulfur dioxide Catalyzed Hydrothermal Treatment

When compared to sulfuric acid impregnation, sulfur dioxide application creates less corrosion concerns, reduces gypsum formation, and produces higher xylose

**Table 4.1** Exemplary hydrothermal pretreatment results for various biomass feedstocks

Biomass	Type of pretreatment	Optimal temperature (°C)/ time (min)/ pressure (MPa)	Enzymatic hydrolysis glucose yield (%)	Reference
Yellow poplar sawdust	Hot water cooking	230/<1/2.8	90	Weil et al. (1997)
Prairie cordgrass	Hot water cooking	210/10/1.9	95	Cybulska et al. (2009)
Olive tree	Hot water cooking	210/60/1.9	76	Cara et al. (2007)
Wheat straw	Hot water cooking	195/6-12/1.4	93-94	Petersen et al. (2009)
Corn fiber	Hot water cooking	260/0.17/4.7	100	Weil et al. (1998)
Corn stover	Hot water cooking	190/15/1.3	90	Mosier et al. (2005a)
Poplar	Steam explosion	210/4/1.9	60	Negro et al. (2003)
Wheat straw	Steam explosion	200/10	75	Ballesteros et al. (2006)

yields (Aita and Kim 2010; Wyman 1996). As an example, SO<sub>2</sub> can be applied at the concentration of 1–4 % w/w biomass at typical steam explosion temperature and time (Taherzadeh and Karimi 2008). Catalyst application in hydrothermal treatment generally reduces the temperature and time needed for the autohydrolysis of lignocellulose, and also partially hydrolyzes cellulose (Aita and Kim 2010; Chandra et al. 2007). It is especially effective when applied to softwoods (Alvira et al. 2010).

A study with a two-step process of SO<sub>2</sub>-catalyzed steam explosion applied to softwood showed high cellulose digestibility and ethanol yield (higher than a one-step process), achieving glucose yield of 80 % and ethanol yield of 69 % (Söderström et al. 2002). This process has also been practiced as a pretreatment method applied to agricultural residues with high efficiencies. Complete glucose to ethanol conversion and xylose to ethanol conversion was achieved by sugarcane bagasse pretreated by SO<sub>2</sub>-impregnated steam explosion, utilizing recombinant yeast strains (Rudolf et al. 2008). High enzymatic hydrolysis glucose yields (~90 %) were also obtained from sweet sorghum bagasse treated by SO<sub>2</sub>-impregnated steam explosion at ~200 °C for a short time (5–10 min) (Sipos et al. 2009). However, sulfur dioxide presents a health and safety hazard, and therefore the necessary precautions must be taken. There have been pilot-scale trials reported utilizing sulfur dioxide catalyzed steam explosion process (Wyman 1996; Zheng et al. 2009).

#### 4.4.3.2 Carbon dioxide Catalyzed Hydrothermal Treatment

In this treatment, carbon dioxide under high pressure penetrates into the lignocellulosic structure, where it converts into carbonic acid, catalyzing the hydrolysis of hemicellulose. The studies using carbon dioxide include trials with supercritical carbon dioxide (Aita and Kim 2010). Supercritical carbon dioxide is in the form of a gas that has been compressed above the critical temperature and critical pressure, and therefore has some properties of a liquid. It is called a supercritical fluid. It possesses mass transfer properties of a gas and solvating power of a liquid. Carbon dioxide has been found to be a good lignin solvent, because it is nontoxic, non-flammable, and easy to recover (Alvira et al. 2010; Taherzadeh and Karimi 2008). There are several studies reporting application of carbon dioxide as a catalyst in the steam explosion process, most of them less efficient than Ammonia Fiber Explosion (AFEX) or the sulfur dioxide catalyzed process (Wyman 1996). However, according to Aita and Kim (2010), carbon dioxide use was found to be more economically feasible than AFEX when applied to agricultural and industrial residues.

Using supercritical carbon dioxide, which is a green solvent without the need for waste treatment, simultaneously with enzymes to hydrolyze lignocellulosic feedstock has been reported to result in high glucose yield (up to 100 %). Applying supercritical fluid during the hydrolysis can significantly increase the kinetic constants of the process, enabling the retention time to be shortened (Taherzadeh and Karimi 2008). Usage of different catalysts in the hydrothermal pretreatment process applied to various biomass feedstocks are presented in Table 4.2.



**Table 4.2** Examples of catalyst uses for various types of biomass feedstocks

Biomass	Catalyst type	Enzymatic hydrolysis glucose yield (%)	Reference
Softwood	Sulfur dioxide	80	Söderström et al. (2002)
Sweet sorghum bagasse	Sulfur dioxide	90	Sipos et al. (2009)
Switchgrass	Carbon dioxide	81	Luterbacher et al. (2010)
Corn stover	Carbon dioxide	85	Luterbacher et al. (2010)

#### ***4.4.4 Hydrothermal Pretreatment Integrated with Other Methods***

Due to drawbacks of individual pretreatment methods examined to date, many researchers have tried combining two or more pretreatment methods in series in order to enhance the overall performance. This includes combinations within the categories as well as between them. Generally, it has been found that integration of the treatment methods is more effective and selective than application of a single method; however, adding an extra step is usually associated with additional costs (Wyman 1996).

An example of an integrated process is the combination of steam explosion and alkaline/hydrogen peroxide post-treatment. It was found that while steam explosion removes most of the hemicellulose component, the oxidative treatment that follows remove up to 80 % of the remaining lignin (Taherzadeh and Karimi 2008). Another example of an integrated biomass processing is an organosolv treatment followed by a hydrothermal post-treatment (Cybulska et al. 2012). The first step removes relatively pure lignin, which can be used as a value-added coproduct, while the hydrothermal post-treatment produces highly fermentable cellulose. It has been found that as much as 51 % of lignin can be recovered from prairie cordgrass and up to 67 % from corn stover, producing 79 and 90 % of enzymatic hydrolysis glucose yields for prairie cordgrass and corn stover, respectively (Cybulska et al. 2012).

### **4.5 Conclusion**

Hydrothermal pretreatment is one of the most effective and environmentally friendly pretreatment methods available. It has been optimized for a wide variety of feedstocks and has been tested extensively throughout the years. The disadvantage of using high temperatures (and thus the need for pressure reactors and energy demand) is balanced with the advantages of no requirement of chemical additives and a short processing time. Excluding chemicals from the process reduces its environmental impact and eliminates the costs in the pretreatment and product recovery, making the hydrothermal pretreatment a rather “green” process.

Although high temperatures used during the hydrothermal processing favor formation of small amounts of organic acids and furans, these by-products can be converted into value-added products and used as an additional source of profit, or (especially in the case of acetic acid) recycled and utilized as an external catalyst of the lignocellulosic bonds cleavage.

As explained in this chapter, due to years of research, there are multiple versions of the hydrothermal pretreatment, thus there is a vast range of possibilities suitable for various settings. Depending on the biomass feedstock used, available resources, or application of the end product, the proper configuration of this process can be employed. It is one of the pretreatment methods that can be deployed on a farm or on a mobile platform without the need for on-site waste treatment.

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