CHAPTER 6

Processing of lignocellulosic biomass derived monomers with high-pressure CO_2 and CO_2-H_2O mixtures

Gianluca Gallina[a], Pierdomenico Biasi[b], Cristian M. Piqueras[c] and Juan García-Serna[a]*

[a] Department of Chemical Engineering and Environmental Technology, High Pressure Processes Group, University of Valladolid, Valladolid, ES-47011, Spain

[b] Process Chemistry Centre, Laboratory of Industrial Chemistry and Reaction Engineering, Åbo Akademi, Biskopsgatan 8, Turku/Åbo, FI-20500, Finland

[c] Planta Piloto de Ingeniería Química, PLAPIQUI-Universidad Nacional del Sur-CONICET, Camino La Carrindanga km 7-CC 717, (8000) Bahía Blanca, Argentina.

* e-mail: jgserna@iq.uva.es

Abstract

The degradation of monosaccharides, though often undesired in lignocellulosic pretreatment, often lead to the formation of products with a higher value than the same sugars. In this chapter, detailed information related to monomers-based lignocellulosic biomass decomposition towards value added products using both water alone and water/CO_2 mixture is showed. We will analyse the reaction mechanisms leading to the rupture of the oligomers into monosaccharaides, and then they breakage through dehydration reactions or aldol reactions. It will be demonstrated that CO_2 plays a determinant role in catalysis of hydrolytic reactions that take place in aqueous media.

The optimum conditions for obtaining different products will be discussed, also providing some indications on which configuration to adopt, for increasing the selectivity of some reactions with respect to others.

6.1 Introduction

The biorefinery concept is analogous to the concept of oil refinery, and assumes the production of fuel, chemicals and energy from different types of biomass. The choice of which type of biomass to treat can be influenced by economic, environmental or geographic factors; there is also a direct dependence between the raw material, the technology used for its conversion into a usable output and the range of products that can be obtained. Lignocellulosic biomass is considered the most promising feedstock for the production of bio-fuels and chemicals. Lignocellulosic materials belong to second-generation feedstocks, and can be obtained from various sources, such as wood residues, agricultural or municipal waste, not interfering with direct crops for human consumption. They are composed mainly of lignin, cellulose and hemicellulose, associated in a resistant structure, whose breakup requires a considerable amount of energy; however, thanks to their differentiated composition, allow to obtain multiple products, like high value chemicals and low value but high volume fuels.[1]

Figure 6.1 shows an outline of the concept of a lignocellulosic biorefinery. Lignocellulosic feed can be pre-treated and fractionated into cellulose, hemicellulose and lignin. Lignin phenolics can be used to produce materials like plastics or adhesives, glucose from cellulose can be converted to fuels or chemicals, while other chemicals, fuels, polymers and materials can be obtained from hemicellulose. Furthermore waste cellulose, hemicellulose and lignin can be used for cogeneration.

[Figure 6.1 near here]

Hydrothermal pre-treatments, as well as facilitate the enzymatic attack by reducing the recalcitrance of the biomass,[2] result in the production of different compounds, through the extraction and hydrolysis of the lignocellulosic biopolymers.

The monomeric sugars constituting cellulose and hemicellulose, under particular conditions of

temperature, acidity or residence time, can originate furfural, 5-hydroxymethylfurfural, glycolaldehyde, acetic acid, pyruvhaldehyde, lactic acid and other products resulting from their dehydration or through aldolic reactions.[3,4]

Although many of them are often considered undesirable by-products, as their presence inhibit a further enzymatic treatment,[5] often their commercial value exceeds that of sugars, or alcohols produced from their fermentation. For this reason, in some cases it is more correct to define these compounds as added-value products, rather than by-products. Among these chemicals, furfural, 5-hydroxymethylfurfural and lactic acid are of great economic interest: furfural can be the starting material for polymers such as nylon 6 and nylon 6,6; 5-HMF has the potential to replace terephthalic acid;[6-8] lactic acid can be used as a food preservative, flavouring agent and is also employed in pharmaceutical technology to produce water-soluble lactates.

A list of the top value added compounds from biomass is widely discussed in two volumes from NRE Laboratories,[9,10] identifying the products deriving from biomass, and the processes that would economically and technically support the production of fuels, power and chemicals in an integrated biorefinery. After a careful screening, 30 foundation chemicals were selected, which may be competitive with compounds deriving from the petrochemical industry. Some of these products, such as furfural and levulinic acid, can be directly produced via hydrothermal hydrolysis of biomasses, without the need for further processing. Other compounds such as formic acid, 5-hydroxymethylfurfural, acetic acid, glycolaldehyde, glyceraldehyde, pyruvaldehyde, lactic acid can be produced via saccharification and subsequent hydrolysis of cellulose and hemicellulose, using only water or mixtures of water and CO_2 as the only reagents, without the addition of any type of additives that presuppose a treatment and a detoxification of liquid effluents.[11,12]

In this chapter, different hydrothermal pre-treatments using subcritical and supercritical H_2O, and CO_2/H_2O mixture will be analysed, describing their incidence in the dehydration of

monomers towards value added compounds and their further transformations. The advantages and effectiveness of using supercritical CO_2 to separate compounds as furfural and acetic acid from aqueous effluents will be explained.

Moreover different types of reactors and setup will be illustrated, describing their characteristics and their effectiveness in the hydrolysis of biopolymers and real biomasses for the production of different lignocellulosic based compounds.

6.2 Cellulose and hemicellulose hydrolysis

Cellulose and hemicellulose, which together with lignin are the main components of lignocellulosic biomasses, are biopolymers with different structure, and require different operating conditions to be extracted.

While hemicellulose is a branched polymer consisting in short chains of about 500 to 3000 units of different monosaccharides, cellulose presents a crystalline structure, with linear molecules composed by 7000 to 15000 units of glucose.[13]

**6.2.1 The phenomena at a glance**

This type of reactions has a rich number chemical engineering steps. Thus, at a molecular level you will find the bonding of the sugars monomers and aromatic monomers forming the hemicellulose, cellulose and lignin, together with the extractives, starch, essential oils, etc. The real reaction takes place there. On the next level we find the polymers of a number of molecular weights that can be counted using population balances. Most of the polymers will be solid, crystalline or amorphous, and the oligomers will be soluble or non-soluble depending on the number of monomers that they have got, the acetyl groups, etc. Next, we find the particle level, the particles will be porous, with different shapes and sizes. They will create back-mixing due to hydrodynamics at millimetre scale. Finally, we find the reactor level, where the particles

distribute in slurry or in a fixed bed, there is heat transfer to the wall, etc. All these levels should be considered to determine the kinetics of the reactions and to model and scale up the process. In hot water media, the fractionation of lignocellulosic biomass takes place in solid phase, where cellulose and hemicellulose start to break into oligomers, with a decrease of their molecular weight. When a certain molecular weight is reached, they became water-soluble and the hydrolysis proceeds both in liquid and in solid phase.[14,15] Depending on the temperature and on the residence time, the oligomers extracted undergo a fractionation process: they are depolymerised into monomers, which are subsequently decomposed in a broad range of products.

Due to the differences in structure, whereas temperatures between 140 and 190 ºC are sufficient for the extraction of hemicellulose, the depolymerisation of cellulose requires temperatures above 230 ºC.[16-18]

6.2.2 Simple mathematical models to describe hydrolysis

There are mainly two models to study the depolymerisation of the polymers: the first model considers a direct hydrolysis of cellulose or hemicellulose to the respective monomers, the second model considers the rupture of the polymers to intermediate oligomers, which are subsequently hydrolysed to monomers;[19] since, in general, it is difficult to experimentally quantify the production of oligomers, the first model is the most extended. It assumes that the kinetics of decomposition of cellulose and hemicellulose can be summarised by two second order reactions, where k_1 represent the dissociation constant of polymers to monomers, and k_2 the reaction rate from monomers to dehydrated products.[20,21] This model, proposed by Saeman[15] for cellulose can be extended also to hemicellulose depolymerization, and does not consider any intermediate oligomer.

$$\text{Polymers} \xrightarrow{k_1} \text{Monomers} \xrightarrow{k_2} \text{Decomposition Products}$$
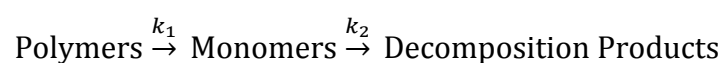
The concentration of monomers can be calculated analytically by integrating the two

differential equations with initial value[22] $M = M_0 e^{-k_2 t} + P_0 \frac{k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right)$, where M

indicates the concentration of monomers, P the concentration of polymers, t the reaction time

and the index 0 the initial values. Kinetic constants can be related to the operation temperature

by Arrhenius equation[22]: $k_i = k_{i0} e^{-\frac{Ea}{RT}}$, where Ea is the activation energy, R is the gas constant,

T the temperature and i the kinetic coefficient (1 or 2). Typical values of k_1 and k_2 constants are

represented in Table 6.1.

[Table 6.1 near here]

Kinetic studies carried out so far are aimed at maximising the yield of monomers, avoiding their

degradation products, there are not therefore many studies that investigate deeply the formation

of single degradation compounds from raw biomass;[23] there is however a greater number of

studies dealing with the formation of degradation products from pure monosaccharides.[24-26]

6.2.3 Main reactions of the monomers in water: tautomerisation, dehydration and aldol

reactions

The main reactions that involve the monomers of cellulose and hemicellulose in hot pressurised

water are: tautomerisations, dehydrations and aldol reactions.[8]

Dehydration reaction is the chemical reaction that involves the loss of a water molecule from

the reacting molecule. The hydroxyl group (-OH) is a leaving group with poor efficacy, a

Brønsted acid often act as a catalyst, helping to protonate the hydroxyl group, producing the

leaving group, $-OH_2^+$. An example of dehydration is shown in Scheme 6.1.

[Scheme 6.1 near here]

Tautomerisation is the chemical reaction happening when two constitutional isomers of organic

compounds readily interconvert with each other. Isomers are substances with the same

molecular mass and the same composition percentage of atoms, but different physical properties

and often also different chemical behaviour. Many isomers have the same (or very similar) bond energy, so they easily interconvert. An example of tautomerisation is shown in Scheme 6.2.

[Scheme 6.2 near here]

The aldol reaction is a reaction in which two molecules of an aldehyde or of a ketone, which have at least one hydrogen atom in α position to the carbonyl group ($C = O$), combine with each other to form a β-hydroxyaldehyde or a β-hydroxyketone. Furthermore, the formed product, commonly called aldol, being very unstable, can be dehydrated and converted to the corresponding unsaturated conjugate compound. Scheme 6.3 shows an example of aldol reaction.

[Scheme 6.3 near here]

The hydrolysis of hemicellulose in water begins at temperatures around 100 °C, the two principal reactions are represented in Scheme 6.4 for xylans[27]:

- Acetyl groups bonded to oligomers are cleaved and reduced to acetic acid, catalysing the autohydrolysis of the oligomers.

- The oligomer chain is hydrolysed to obtain monomeric sugars, which are dehydrated to furfural at harsher conditions.

As stated above, for temperatures above 100 °C hydrolysis of hemicellulose begins and can be more or less intense, depending on the composition of the treated biomass. Xylans from hardwood contain greater amounts of acetyl groups respect to softwoods and herbaceous plants. Approximately 60% of the units of xylose, carry an acetyl group attached to position C-2 or C-3.[28] For this reason, auto-hydrolytic capacity in hemicellulose from hardwood is much more intense compared to that of other species. The dehydration of xylose to furfural begins around 160ºC, and gradually becomes more pronounced as the temperature of the water increase.[29]

Kinetic studies show that the xylose, before the dehydration to furfural, passes through an isomerization process, forming xylulose.[30,31]

[Scheme 6.4 near here]

As mentioned previously, cellulose structure presents a crystalline domain; strong intra-chain hydrogen bonds result in a stable and linear configuration of the fibrils[19] that require high temperatures for the depolymerization to glucose units. Once formed, among the glucose molecules, reactions of isomerization and dehydration take place at temperatures above 200 ºC.[32]

Glucose undergoes isomerization to fructose, the reverse reaction (fructose to glucose) is almost inhibited. Fructose dehydration leads to the formation of 5-hydroxymethylfurfural and the HMF formation is directly proportional to the temperature rise of the medium until about 350ºC. 5-HMF can follow principally two pathways: it can be decomposed into furfural and formaldehyde, or can be hydrated to form levulinic acid and formic acid. Reaction pathways are proposed in Scheme 6.5.

[Scheme 6.5 near here]

In addition to the reactions listed above, the glucose molecule is also subject to aldol reactions, producing one molecule of two carbons and one molecule of four carbons; fructose produces two molecules of three carbons (like glyceraldehyde).[33]

Glucose, through an aldol reaction, can lead to the production of erythrose and glycolaldehyde. Fructose, through a first aldol reaction can produce glyceraldehyde and its isomer dihydroxyacetone. Another aldol reaction and subsequent dehydration can convert the glyceraldehyde into pyruvaldehyde, which can be further converted into lactic acid, with the loss of another water molecule. Dehydration as well as isomerisation reactions are favoured in

acidic media,[33] while aldol reactions are promoted in neutral media.[34] Principal aldol reactions involving glucose and fructose monomers are represented in Scheme 6.6.

[Scheme 6.6 near here]

Also xylose can participate in aldol reactions inside a hydrothermal medium, producing a molecule with three atoms of carbon and a molecule with two atoms of carbon (Scheme 6.7). Glyceraldehyde, consequently, through another aldolic reaction can lead to the production of glycolaldehyde and formaldehyde, or can be isomerised into dihydroxyacetone.

[Scheme 6.7 near here]

Scheme 6.8 shows schematically a simplified pathway for compounds resulting from the depolymerisation of cellulose and hemicellulose oligomers and decomposition of the monomers (xylose oligomers were chosen as representatives of hemicellulose oligomers).[4,12,25,31,35-37]

[Scheme 6.8 near here]

6.3 Reaction medium and operational conditions

As mentioned, there are not many studies with the main objective to carry out pre-treatments for lignocellulosic biomass to maximise the conversion of carbohydrate to form dehydration products, since often the main purpose is to avoid the so-called "degradation"; however, there are conditions that promote the formation of these chemicals.

What are the main factors influencing the reactions of depolymerization and hydrolysis of lignocellulosic biomass in aqueous media?

- Temperature

- Residence/reaction time of the compounds inside the reaction medium

- pH at which the reaction takes place (i.e. proton concentration)

The different properties that the pressurised water may assume varying these conditions, can be used to control the selectivity of the reactions, in other words, to tune the reaction. According to the idea of thermohydrolysis reactions performed using pure water, without addition of mineral acids or other chemical additives that presuppose a subsequent disposal or neutralization of the sludge, two kind of aqueous media can be considered: subcritical water (high polarity, medium temperature) and supercritical water (low polarity, high to very high temperature). By choosing the appropriate temperature and pressure it is therefore possible to obtain a solvent with distinct and peculiar characteristics, which can promote some reactions than other. The addition of carbon dioxide to the aqueous medium allows more possibilities to influence the kinetics of the reactions, by increasing the conversion of oligosaccharides and modifying the selectivity towards certain products.

In this section we will study the aqueous reaction media mentioned above; we will see which conditions to adopt, in order to achieve high selectivity towards value-added products from lignocellulosic biomasses.

6.3.1 Subcritical water and carbonated subcritical water

It was verified that the addition of CO_2 in hot pressurised water enhances the hydrolysis of lignocellulosic materials[38,39] due to the decrease in pH, by the formation and the dissociation of carbonic acid in the aqueous mixture.[21] When formation of carbonic acid occurs, an increase in hydronium ion concentration is observed due to the dissociation of the unstable acid, thus promoting acid-catalysed dissolution of the biomass[40] and leading to reduce the temperature and the reaction time of the reactions.

By controlling the amount of CO_2 dissolved in water, which is dependent on the temperature and the pressure of the mixture, the pH of the solution mixture can be controlled. Over the

temperature range 25 to 70 °C and pressure range 70 to 200 bar, pH may decrease to values down to 2.8 or 2.95.[41]

Figure 6.2 shows the variation of solubility of CO_2 in water at different temperatures and pressure according to experimental data.[42]

[Figure 6.2 near here]

Unlike the pre-treatments with acids, the addition of CO_2 does not require a subsequent neutralisation processes, because the CO_2 removal can be accomplished by the reduction in pressure and CO_2 desorption.

In an aqueous pre-treatment, the combination of temperature and reaction time define the severity of the reaction,[43] according to the experimental equation[44] $R_0 = t * \exp[(T - 100)/14.75]$, where t is the reaction time (min), and T is the temperature (°C) (Figure 6.3).

[Figure 6.3 near here]

If carbon dioxide is added to water, the pH variation changes the severity of the reaction; it is therefore necessary to modify the factor taking into account of this influence. Van Walsum et al. defined a combined severity factor for binary systems with water and CO_2 in the temperature range of 100–250 °C and partial pressure of CO_2 up to 151.9 bar, suggesting the equation[45]:

$CS_{P_{CO_2}} = \log(R_O) - 8.00 * 10^{-6} * T^2 + 0.00209 * T - 0.216 * \ln(p_{CO_2}) + 3.92$, in which $CS_{P_{CO_2}}$ is the severity due to the presence of CO_2, R_O is the severity factor calculated as above, p_{CO_2} is the partial pressure of CO_2 (atm) and T is the temperature (°C). This combined equation includes all the most important parameters affecting the hydrolysis of oligomers to monomers, and to dehydration products.

Some of the early experiments in which carbon dioxide was added to the aqueous medium to improve the efficiency of hydrothermal pre-treatments were carried out by Van Walsum et al.

As well as studying the production of monosaccharaides, they investigated the formation of degradation products in lignocellulosic pre-treatment with mixture of water and CO_2.[46] They analysed the composition of the extraction liquors from experiments in a batch reactor, at 180 °C, after a cooking time of 16 min; comparing the data obtained using only water as a solvent and water with 55 bar of CO_2. Two biomasses were tested: corn stover and aspen wood, Figure 6.4 shows the differences in concentration between the experiments without CO_2 and with CO_2 for both the biomasses and for the different compounds.

[Figure 6.4 near here]

The two biomasses have a different behaviour: while in aspen wood the addition of CO_2 results in an increase of all the products analysed (despite the weak analytical reproducibility), in corn stover it leads to the increase in the concentration of some products and to the decrease of others. Acetic acid concentration increases in both biomasses, confirming the capacity of CO_2 to hydrolyse xylan oligomers, even if in the case of aspen wood the yield of xylose monomers does not seem to show relevant differences if compared with experiments with only water.[47] In corn stover, furfural and formic acid concentrations decrease when adding CO_2 while in aspen wood seem to increase. This behaviour should indicate that in aspen wood, the auto-hydrolytic capacity of the raw material in water is sufficient to break the hemicellulose oligomers into xylose, and the acidification of the aqueous medium due to the presence of CO_2 leads to the degradation of the monomers.[47] In the case of corn stover, the autocatalytic capacity is less strong, and CO_2, with its capacity of penetrating small pores of recalcitrant lignocellulosic structure, favours the extraction of hemicellulose oligomers from the wooden matrix and with its acidifying effect, leads to the hydrolysis of the oligomers into monosaccharaides, more than the degradation of the lasts.[38] The hydrolysing power of carbonic acid, therefore, seems to exert a different effect depending on the type of pre-treated biomass.

Aside from the considerations made so far, the hydrolysing effect due to CO_2 in aqueous media, appears to depend very much on the partial pressure of the gas, the temperature of the system and thus the solubility of CO_2 in water. Figure 6.2 indicates that the solubility of CO_2 in water increases with increasing pressure, in addition, with the operating conditions tested in the experiments, the solubility of CO_2 increases at increasing the temperature. To have catalytic effect due to the presence of carbon dioxide in the hydrolysis of lignocellulosic compounds, it is therefore necessary to operate with sufficiently high pressures.

In the hydrothermal pre-treatment of wheat straw with a temperature of 210 ℃, Magalhães da Silva et al., found an increase in the production of furfural from a concentration of 0.1 g/L to 5.4 g/l when adding CO_2 at 60 bars to the aqueous medium;[48,49] with the same raw material, increasing the temperature at 225 ℃, the same group noticed only a small difference between the amount of furfural when increasing the initial pressure of CO_2 (Figure 6.5).[45,50]

[Figure 6.5 near here]

Of great interest are the results obtained by the experiments carried out by Rogalinski et al.[51] and King et al.[52] The two groups studied the hydrolysis of similar biomass (rye straw and switchgrass respectively) in mixtures of water under subcritical conditions with the addition of carbon dioxide at different pressures. Pressure of carbon dioxide was 0 and 100 bar in the experiments of the first group, whereas ranged from 150 to 550 bar in the experiments of the second group. While no significant differences were reflected between experiments performed with pure water and those made with carbonated water at 100 bar, an increased catalytic effect was recognised with increasing the pressure: the yield of xylose increased approximately 2 wt.%, by increasing the pressure from 350 bar to 450 bar at constant temperature of 170 ℃, a value only slightly smaller than that obtained using dilute sulfuric acid hydrolysis. Moreover, at these conditions, the hydrolysis of switchgrass resulted in a production of a larger amount of

HMF and furfural respect to those produced using dilute acid pre-treatment. An enhance in the hydrolysis of cellulose by means of carbon dioxide under high pressure was also confirmed by other experiments carried out by the group of Brunner.[53]

The addition of carbon dioxide to water, if carried out at sufficiently high pressures, seems to have a catalytic effect in the hydrolysis of oligosaccharides and in the decomposition of monosaccharaides; it is necessary to analyse which is the combined effect of the temperature change and the carbonation, and which prevails over the other.

Dhamdere et al.[54] tested the hydrolysis of switchgrass at different temperatures (220, 250, 280, 310 ºC) in a semi-continuous batch flow system, with and without the addition of CO_2 with a pressure of 68 bars. Results indicated that at temperatures between 220 ºC and 280 ºC, the production of furfural was higher in the water/CO_2 mixture than in pure water; when the temperature was increased to 310 ºC the difference in the yield between the two media was only minimal, indicating that at that temperature there was no catalytic activity due to the carbonated water.[54] A maximum yield of 1.3 wt.% was obtained at 310 ºC.

At all the temperatures tested, the production of 5-HMF was enhanced in carbonated water mixtures, as 5-HMF is a product deriving from the dehydration of glucose, and thus from cellulose, its production is favoured at high temperatures. Yield of 5-HMF was similar at 280 ºC and at 310 ºC, indicating that most of the formation occurs at 280 ºC. A maximum yield of 1.8 wt.% was obtained at optimum conditions.

The main operating condition that controls the hydrolysis of lignocellulosic biomass is therefore the temperature. Hemicellulose and cellulose polymers are extracted from biomass and fractionated into oligomers for effect of temperature, carbon dioxide is proven to have a slight additional role in this phase, by swelling the plant material, and favouring the breakage.[55] The rupture of the oligomers is always influenced for the most part on the temperature, however,

the addition of carbon dioxide with sufficiently high pressures, can play a significant supporting role.

Temperature is also the main responsible for the decomposition of the monomers: the increase of temperature leads to a higher conversion of xylose and glucose to furfural and HMF, and their subsequent processing in the other products depicted in Scheme 6.8. The addition of carbon dioxide has a catalytic effect in the production of furfural at temperatures below 300 °C, at higher temperatures its incidence is negligible. The dehydration of glucose to HMF is catalysed by carbon dioxide up to temperatures above 310 °C.

Summarising what has been said so far, carbon dioxide at high pressures can be used in conjunction with pressurised hot water to enhance the hydrolysis of lignocellulosic oligomers to obtain monomers, and to catalyse the dehydration of monosaccharaides to obtain added values of products.

Experiments conducted starting from pure xylose as a raw material, indicate that a conversion of 97 % is achieved in water at 230 °C with CO_2 at 12 MPa; with a yield of 68% to production of furfural. Lower pressures lead to lower yields of furfural, while higher pressures did not show significant changes.[24] The initial concentration of xylose in the reaction influences the production of furfural; optimal concentrations of monomer to obtain a high selectivity, are around 4%, higher concentrations lead to lower yields.

Carbon dioxide, in addition to favour the production of monosaccharaides dehydration compounds, can also facilitate the removal from the aqueous phase and recovery, in particular that of furfural. The use of supercritical CO_2 for extracting low concentration of furfural (around 1 wt.%) from aqueous solutions, is a good alternative to organic solvents.[56] A 48.1% of produced furfural can be extracted with CO_2 at 8 MPa from an aqueous mixture with a temperature of 230 °C; higher temperatures decrease the extraction solubility, as furfural solubility in CO_2 decrease with increasing the temperature. The increase in the concentration

of xylose in the reactor is proportional to the concentration of furfural extract; depending on whether the goal is to recover furfural or increase the yield, different concentrations of initial xylose can be selected.[24,56]

6.3.2 Reactions in supercritical water

Water is under supercritical conditions at temperatures higher than 374ºC and pressures higher than 22.1 MPa. The intermolecular structure of water, at these conditions, varies significantly as hydrogen bonds are significantly reduced in number, giving both gas-like properties (like high diffusivity and low viscosity) and liquid-like properties like high density.

The dielectric constant is subject to significant variations, reaching at supercritical conditions values inside the common range of most organic solvents. At normal conditions of 25 °C and pressure of 1 bar, water has a dielectric constant of about 78.[57] Figure 6.6 shows that at a pressure of 25 MPa bar and temperature of 375 °C the dielectric constant of water is around 12, and decrease rapidly at increasing the temperature. A range between 2 and 30 is typical for most organic solvents for dissolving organic macromolecules such as cellulose.

Another property which varies significantly at supercritical conditions is the ionic product of water (K_w). At ambient conditions, the value of K_w, represented as the product of H^+ and OH^- concentrations, is 10^{-13}, at temperatures around 300 ºC it reaches its maximum value (10^{-11}), which creates a medium with high ions concentration, favouring acid/basis catalysed reactions. Under supercritical conditions, K_w decreases drastically to 10^{-25},[58] promoting non-ionic reactions.[57,59]

[Figure 6.6 near here]

The combination of these properties and the high temperature that allows high reaction rates makes supercritical water an effective solvent and an excellent reaction medium in the

hydrolysis processes of lignocellulosic materials. At near critical conditions, therefore, the drastic changes in the ionic product and in the density of water influences the reaction of degradation of monosaccharaides. In the case of xylose, while at subcritical temperatures, the main product of degradation is furfural, with a maximum production between 300 and 350ºC, at supercritical conditions aldolic reactions are favoured, with an increase in the formation of glycolaldehyde and glyceraldehyde. A maximum yield of retro-aldol products of around 45 wt.% obtained at 400ºC and 100 MPa [30,31].

Similarly, with glucose as base monomer, the dehydration reaction leading to the formation of 5-hydroxymethylfurfural is promoted at subcritical conditions with a maximum at around 350 °C, while retro-aldol condensations are favoured at higher temperatures, with water uncer supercritical conditions; glycolaldehyde is the main product deriving from glucose, and at 450ºC and 35 MPa, yields as high as 70 wt.% can be reached.[60]

Also the pressure can influence the dehydration reactions, as low densities favour aldolic reactions, while high densities and high ionic products enhance the formation of furfural and 5-HMF. As stated by Aida et.al, higher yields of 5-HMF from glucose (8 wt.%) were obtained at 350º C and 80 MPa, compared to other experiments conducted at the same temperature and lower pressures; also the furfural yield reaches the maximum value at the maximum pressure tested, of 80 MPa.[8,26] Higher pressures than 100 bar, under supercritical conditions (400ºC) promote also the formation of lactic acid, showing a decrease of the yield of glyceraldehyde, dihydroxyacetone and pyruvaldehyde.

Even if 5-HMF and furfural achieve the maximum production at subcritical conditions, the use of supercritical water as reaction medium allows the intensification of the process by reducing the required residence time of the reactions. Typical residence times of glucose and fructose reactions in water at near critical and supercritical conditions are between 20 ms and 5 s. These residence times are three orders of magnitude lower than those required at low temperature

catalysed processes and up to five orders of magnitude lower than those needed in microorganism processes [34]. At 400ºC and 100 MPa, glycolaldehyde can be produced from xylose with residence times of 0.5 s with a yield of 40 %, and; lactic acid from glucose at 400ºC requires residence times between 10 s and 20 s to be produced,[34] while at reaction temperatures around 300ºC will require residence times of 60 s [61].

6.4 Reaction configuration

Thus raise the question what is the best reaction technology for each case study? When facing the question of what type of equipment will be the best option to study a subcritical or supercritical biomass fractionation or hydrolysis there are several guidelines that might help.

#1. Subcritical or supercritical? How much time do I need?

The products from the hydrolysis will highly depend on the residence time that we use, provided the residence time will depend on temperature too. If we are using subcritical water (e.g. typically between 160ºC and 250ºC) hemicellulose usually takes from 10 to 20 min to hydrolyse, while cellulose takes from 40 to 60 min at least. In that case the use of a batch reactor is feasible, although heating-up takes 10 to 20 min and cooling down might take 5 min, and temperature-time profile must be considered in kinetics calculation. The use of a semi-continuous reactor is also valid as the real residence time of the liquid phase is usually less than 1 min, although the solid rests in the reactor until it is opened.

When supercritical water is used the temperature goes over 374ºC, but even operating at 300ºC (not supercritical) accelerates the hydrolysis so much that the produced sugars degrade quite easily and sometimes even re-polymerise. In such cases, using batch is not recommended. Semi-continuous at high flowrate it is an option, but some degradation might appear. The perfect system will be the continuous reactor, but for this milling under 200-300 um is usually needed,

as a slurry needs to be pumped at high pressure. To assure low residence times (e.g. 20 to 40 ms, less than 1 s always) an effective system for heating-up and quenching is required.

#2. How much sample do I need to analyse? How much power do I need?

Analysing the products from biomass hydrolysis is expensive and time consuming, as it normally requires further hydrolysis, e.g. using NREL procedures. The question is, is my system reliable? Biomass exhibit great differences and it is important to be sure having a representative for the experiment. Common subcritical batch reactors are between 25 mL and 1 L (not many cases of 5 or 20 L), supercritical batch are normally below 250 mL. You can considered to fill the reactor 50-60% with water and a water/biomass mass ratio of 20:1, this means treating 6.25g of biomass in a typical 250 mL (e.g. Autoclave, Parr, etc). For that case, you should expect 40-50% sugars yield, so a total of 2 to 3 grams of sugars (pentoses and hexoses).

For the continuous reactor the mass of solid obtained depend on the flowrate and the time you collect sample. It is typical a 10% solid concentration at the inlet. Regarding the flowrate take into account your electric power, as you will need approx. 65 W per mL/min of flowrate (e.g. 20 mL/min of liquid inlet will require 1.3 kW. This will be acute for a supercritical continuous reactor that requires high flowrates to reduce the residence times.

In the case of semi-continuous the case can be similar to the batch in terms of solid handled and similar to the continuous in terms of power needed.

3#. Do I need to mill?

Batch and semi-continuous do not require extensive milling, if you need to keep the particle as it is, e.g. beans, chips, pellets, etc. batch and semi-continuous can be the option. You will only need a filter to hold the particle bed.

On the other hand, continuous operation requires very fine particles. At lab scale equipment (e.g. pipes of 1/8", 1/4", etc.) pumps like HPLC pumps, or membrane pumps can handle some

solids (not always, check with your provider) under 100 microns. The bottleneck is normally the checkvalves of the pump. At a higher scale, i.e. pilot or demo, there are pumps that can even handle 1 mm particles in slurry.

#4. Can or should I recycle the CO_2?

If you have used CO_2 to enhance the reactivity and hydrolysis, as explained in the book, you will probably need to recover it to improve your economic balance. At laboratory scale recovering it is probably not recommended and not needed, but at pilot scale (e.g. a 5 L reactor) it starts being required. It will require basically a high pressure vapour-liquid separator to split the two phases and a condenser to recover CO2 as a liquid for easier pumping. There are many examples of these options in the reference books for supercritical fluid extraction, like the one from G. Brunner.

6.5 Conclusions

In this chapter it has been shown that temperature is the main operating variable to manipulate for modifying the kinetics of the reactions that lead to the rupture of oligosaccharides, and to the formation of degradation products in aqueous media. The addition of carbon dioxide at high pressures, in water at subcritical conditions, enhances the hydrolysis of lignocellulosic compounds, through the formation of carbonic acid and its subsequent dissociation. The decompression of the carbon dioxide at the end of the extraction process, moreover, facilitates the removal and recuperation of compounds such as furfural from the aqueous mixture.

The pre-treatment with mixtures of water and CO_2 constitute therefore an effective way to produce value added products from lignocellulosic biomass.

References

1. D. King, O. Inderwildi, A. Williams and A. Hagan, The future of industrial biorefineries, World Economic Forum, Geneva, Switzerland, 2010.
2. Y. Pu, F. Hu, F. Huang, B. Davison and A. Ragauskas, *Biotechnol. Biofuels*, 2013, **6**, 15.
3. F. Cherubini, *Energ. Convers. Manage.*, 2010, **51**, 1412-1421.
4. P. Mäki-Arvela, B. Holmbom, T. Salmi and D. Y. Murzin, *Catal. Rev.*, 2007, **49**, 197-340.
5. M. S. Moreno, F. E. Andersen and M. S. Díaz, *Ind. Eng. Chem. Res.*, 2013, **52**, 4146-4160.
6. F. W. Lichtenthaler and S. Peters, *C. R. Chim.*, 2004, **7**, 65-90.
7. C. Moreau, M. N. Belgacem and A. Gandini, *Top. Catal.*, 2004, **27**, 11-30.
8. T. M. Aida, Y. Sato, M. Watanabe, K. Tajima, T. Nonaka, H. Hattori and K. Arai, *J. Supercrit. Fluid.*, 2007, **40**, 381-388.
9. T. Werpy and G. R. Petersen, *Top Value Added Chemicals From Biomass - Volume I: Results of Screening for Potential Candidates from Sugars and Synthesis Gas* the Pacific Northwest National Laboratory (PNNL) and the National Renewable Energy Laboratory (NREL), http://www.nrel.gov/docs/fy04osti/35523.pdf, 2004.
10. J. E. Holladay, J. J. Bozell, J. F. White and D. Johnson, *DOE Report PNNL-16983 (website: http://chembioprocess.pnl.gov/staff/staff_info.asp)*, 2007.
11. P. Mäki-Arvela, T. Salmi, B. Holmbom, S. Willför and D. Y. Murzin, *Chem. Rev.*, 2011, **111**, 5638-5666.
12. D. A. Cantero, M. D. Bermejo and M. J. Cocero, *J. Supercrit. Fluid.*, 2013, **75**, 48-57.
13. L. J. Gibson, *J. R. Soc. Interface*, 2012, 1-18.
14. A. Cabeza, C. Piqueras, F. Sobrón and J. García-Serna, *Bioresource Technol.*, 2016, **200**, 90-102.
15. G. Gallina, Á. Cabeza, P. Biasi and J. García-Serna, *Fuel Process. Technol.*, 2016, **148**, 350-360.
16. D. A. Cantero, M. D. Bermejo and M. J. Cocero, *J. Supercrit. Fluid.*, 2015, **96**, 21-35.
17. A. Romaní, G. Garrote, F. López and J. C. Parajó, *Bioresource Technol.*, 2011, **102**, 5896-5904.
18. O. Bobleter, *Prog. Polym. Sci.*, 1994, **19**, 797-841.
19. L. Negahdar, I. Delidovich and R. Palkovits, *Appl. Catal. B-Environ.*, 2016, **184**, 285-298.
20. J. F. Saeman, *Ind. Eng. Chem.*, 1945, **37**, 43-52.
21. C. Schacht, C. Zetzl and G. Brunner, *J. Supercrit. Fluid.*, 2008, **46**, 299-321.
22. R. Aguilar, J. Ramırez, G. Garrote and M. Vázquez, *J. Food Eng.*, 2002, **55**, 309-318.
23. S. Rivas, M. J. González-Muñoz, V. Santos and J. C. Parajó, *Bioresource Technol.*, 2014, **162**, 192-199.
24. K. Gairola and I. Smirnova, *Bioresource Technol.*, 2012, **123**, 592-598.
25. B. M. Kabyemela, T. Adschiri, R. M. Malaluan and K. Arai, *Ind. Eng. Chem. Res.*, 1999, **38**, 2888-2895.
26. T. M. Aida, K. Tajima, M. Watanabe, Y. Saito, K. Kuroda, T. Nonaka, H. Hattori, R. L. Smith and K. Arai, *J. Supercrit. Fluid.*, 2007, **42**, 110-119.
27. G. Garrote, H. Dominguez and J. C. Parajo, *J. Chem. Technol. Biotechnol.*, 1999, **74**, 1101-1109.
28. A. Teleman, M. Nordström, M. Tenkanen, A. Jacobs and O. Dahlman, *Carbohydr. Res.*, 2003, **338**, 525-534.
29. S. Noguki, R. Uehara, M. Sasaki and M. Goto, Thermal stability of monosaccharides in subcritical water, in 8th International Symposium on Supercritical Fluids Kyoto, Japan, 2006.
30. N. Paksung and Y. Matsumura, *Ind. Eng. Chem. Res.*, 2015, **54**, 7604-7613.
31. T. M. Aida, N. Shiraishi, M. Kubo, M. Watanabe and R. L. Smith, *J. Supercrit. Fluid.*, 2010, **55**, 208-216.
32. T. Zhang, Glucose production from cellulose in subcritical and supercritical water, University of Iowa, 2008.
33. R. S. Assary, T. Kim, J. J. Low, J. Greeley and L. A. Curtiss, *Phys. Chem. Chem. Phys.*, 2012, **14**, 16603-16611.
34. D. A. Cantero, Intensification of cellulose hydrolysis process by supercritical water: Obtaining of added value products, University of Valladolid, 2014.

35. B. M. Kabyemela, T. Adschiri, R. Malaluan and K. Arai, *Ind. Eng. Chem. Res.*, 1997, **36**, 2025-2030.
36. N. Akiya and P. E. Savage, *Chem. Rev.*, 2002, **102**, 2725-2750.
37. H. Rasmussen, H. R. Sorensen and A. S. Meyer, *Carbohydr. Res.*, 2014, **385**, 45-57.
38. G. P. van Walsum and H. Shi, *Bioresource Technol.*, 2004, **93**, 217-226.
39. J. S. Luterbacher, Q. Chew, Y. Li, J. W. Tester and L. P. Walker, *Energ. Environ. Sci.*, 2012, **5**, 6990-7000.
40. A. R. C. Morais, A. M. da Costa Lopes and R. Bogel-Lukasik, *Chem. Rev.*, 2015, **115**, 3-27.
41. K. L. Toews, R. M. Shroll, C. M. Wai and N. G. Smart, *Anal. Chem.*, 1995, **67**, 4040-4043.
42. S. Takenouchi and G. C. Kennedy, *Am. J. Sci.*, 1964, **262**, 1055-1074.
43. R. P. Overend, E. Chornet and J. A. Gascoigne, *Philos. Trans. R. Soc. London, A*, 1987, **321**, 523-536.
44. H. L. Chum, D. K. Johnson, S. K. Black and R. P. Overend, *Appl. Biochem. Biotechnol.*, 1990, **24-5**, 1-14.
45. G. P. van Walsum, *Appl. Biochem. Biotechnol.*, 2001, **91-3**, 317-329.
46. G. P. Van Walsum, M. Garcia-Gil, S.-F. Chen and K. Chambliss, *Appl. Biochem. Biotechnol.*, 2007, 301-311.
47. R. C. McWilliams and G. P. van Walsum, *Appl. Biochem. Biotechnol.*, 2002, **98**, 109-121.
48. F. Carvalheiro, T. Silva-Fernandes, L. C. Duarte and F. M. Gírio, *Appl. Biochem. Biotechnol.*, 2009, **153**, 84-93.
49. S. P. Magalhães da Silva, A. R. C. Morais and R. Bogel-Lukasik, *Green Chem.*, 2014, **16**, 238-246.
50. A. R. C. Morais, A. C. Mata and R. Bogel-Lukasik, *Green Chem.*, 2014, **16**, 4312-4322.
51. T. Rogalinski, T. Ingram and G. Brunner, *J. Supercrit. Fluid.*, 2008, **47**, 54-63.
52. J. W. King, K. Srinivas, O. Guevara, Y. W. Lu, D. F. Zhang and Y. J. Wang, *J. Supercrit. Fluid.*, 2012, **66**, 221-231.
53. G. Brunner, *J. Supercrit. Fluid.*, 2009, **47**, 373-381.
54. R. T. Dhamdere, K. Srinivas and J. W. King, Carbochemicals Production from Switchgrass using Carbonated Subcritical Water at High Temperatures, in 10th International Symposium on Supercritical Fluids, San Francisco, 2012.
55. M. Stamenic, I. Zizovic, R. Eggers, P. Jaeger, H. Heinrich, E. Roj, J. Ivanovic and D. Skala, *J. Supercrit. Fluid.*, 2010, **52**, 125-133.
56. T. Gamse, R. Marr, F. Froschl and M. Siebenhofer, *Sep. Sci. Technol.*, 1997, **32**, 355-371.
57. K. B. Olanrewaju, Reaction kinetics of cellulose hydrolysis in subcritical and supercritical water, University of Iowa, 2012.
58. H. L. Clever, *J. Chem. Educ.*, 1968, **45**, 231.
59. D. A. Cantero, M. D. Bermejo and M. J. Cocero, *Bioresource Technol.*, 2013, **135**, 697-703.
60. M. Sasaki, K. Goto, K. Tajima, T. Adschiri and K. Arai, *Green Chem.*, 2002, **4**, 285-287.
61. X. Yan, F. Jin, K. Tohji, T. Moriya and H. Enomoto, *J. Mater. Sci.*, 2007, **42**, 9995-9999.
62. W. L. Marshall and E. Franck, *J. Phys. Chem. Ref. Data*, 1981, **10**, 295-304.
63. M. Uematsu and E. Frank, *J. Phys. Chem. Ref. Data*, 1980, **9**, 1291-1306.
64. H. Pińkowska, P. Wolak and A. Złocińska, *Biomass Bioenerg.*, 2011, **35**, 3902-3912.
65. F. M. Relvas, A. R. C. Morais and R. Bogel-Lukasik, *J. Supercrit. Fluid.*, 2015, **99**, 95-102.

Caption of figures and schemes

Figure 6.1 Lignocellulosic biorefinery concept.

Figure 6.2 Solubility of CO_2 in water at different temperatures and pressures.[43, 44]

Figure 6.3 Values of $Log(R_O)$ varying temperature and residence time

Figure 6.4 Concentration differences between experiments with water/ CO_2 mixtures and only water. Data obtained from Van Walsum et al.[46]

Figure 6.5 Concentration of furfural and HMF in water mixtures with different pressures of CO_2. Data obtained from Morais et al.[50]

Figure 6.6 Properties of water at subcritical and supercritical at 25 MPa.[59,62,63]

Scheme 6.1 Example of dehydration reaction for alcohols.

Scheme 6.2 Example of tautomerization reaction.

Scheme 6.3 Example of aldol reaction.

Scheme 6.4 Hydrolysis of xylans and dehydration to furfural.

Scheme 6.5 Hydrolysis of glucose oligomers, formation and decomposition of 5-hydroxymethylfurfural.

Scheme 6.6 Aldol reactions involving glucose and fructose.

Scheme 6.7 Aldol reactions involving xylose.

Scheme 6.8 Reaction pathway for hydrolysis of xylose and glucose oligomers.

TABLES CAPTIONS

Table 6.1 K_1 and K_2 constants at different temperatures and pressure of CO_2

T (° C)	K_1 (min^{-1})	K_2 (min^{-1})	p_{CO2} (bar)	Ref.
220	0.076	0.044	0	[64]
235	0.116	0.052	0	[64]
180	0.093	0.041	0	[65]
180	0.127	0.064	20	[65]
180	0.109	0.065	35	[65]
180	0.073	0.068	50	[65]
				[65]