The study of model systems subjected to sub- and supercritical water hydrolysis for the production of fermentable sugars

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Bioenergy obtained from lignocellulosic biomass is considered the most efficient way to achieve sustainable development in the future. However, there still are challenges in the cellulose conversion to hexoses, which could be used as raw material for the bioenergy production. Sub- and supercritical water hydrolysis have been researched as emergent technologies to obtain simple sugars from lignocellulosic biomass; however, the reaction pathways and kinetics of the hydrolysis of cellulose into oligomers and monomers, and their degradation under sub- and supercritical conditions, are not completely understood yet. Thus, this review provides an overview of the state-of-the-art on hydrolysis with sub- and supercritical water of model systems, cellulose and starch, in the context of elucidating the reaction pathways and kinetic behavior of the biomass hydrolysis to produce suitable fermentation substrates for the production of second generation bioethanol and other biofuels.

Keywords: bioethanol; cellulose; starch; subcritical water hydrolysis; supercritical water hydrolysis

1. Introduction

The climate changes and the scarcity of natural resources are two of the main concerns of the population, reaching from the general public, through scientific community, up to the world political agenda. One of the major challenges is the increasing energy consumption and its associated dependence on fossil fuels (1, 2). The current energy system is unsustainable due to the limited availability of fossil fuels as well as economic and geopolitical concerns on environmental issues, that have implications far into the future (3).

Renewable energy is one of the most efficient ways to achieve sustainable development. One of the main options to provide a more sustainable base for the economy would be the transition to a bio-economy in which the importance of biotechnology and biomass-based production to generate economic output is significantly greater than today (1). Cellulose and lignocellulosic wastes are the most abundant and renewable biomass source in nature (4, 5). In general, biomass is composed of 34–50% cellulose, 16–34% hemicellulose, and 11–29% of lignin (6). The challenging step in the processing of cellulose is the production of hexoses that can be used as raw material in the production of chemicals, materials, and biofuels (7).

However, despite the fact that great technical developments have been achieved in this field, these technologies are still more expensive than that produced by nonrenewable sources (8). Thus, to make the transition from fossil to renewable sources of energy not only possible but also sustainable and attractive economically, new technologies and efficient use of biomass resources with good environmental performance in biorefineries are necessary (9).

Some studies have demonstrated that sub- and supercritical fluids have potential to be applied in biorefineries in order to convert lignocellulosic wastes to chemicals. One important route is obtaining fermentable sugars that can be converted into different types of energy (10–15). Sub- and supercritical water have attracted much attention because of their suitability as nontoxic, environmentally benign, and inexpensive media for chemical reactions (16). The
main reasons that make the hydrothermal medium a promising alternative for biomass processing are (11): (1) it is not necessary to reduce the water content in the raw material, thus avoiding energy losses; (2) the reaction medium permits the transformation of different biomass fractions; and (3) the mass transfer limitations are reduced or avoided, thus allowing faster reactions rates.

However, many engineering challenges remain for lignocellulosic processing by sub- and supercritical water. One of the most important is unknown or largely uncharacterized reaction pathways and kinetics of hydrolysis of cellulose into oligomers and monomers and their further degradation. To overcome it, the hydrolysis of model systems has been intensively investigated in the recent decades using both sub- and supercritical water. These studies provide the basic information about the mechanisms involved in the hydrolysis and in the degradation of the products, which are useful to understand the process and to properly preselect the operational conditions for applying the process to biomass.

2. Sub/supercritical water hydrolysis of model systems

A wide variety of fuels can be derived from lignocellulosic material via the biological or chemical synthesis of products from the breakdown of cellulose, hemicellulose, and lignin. However, the lignocellulosic complex is resistant to biological or chemical attack. Therefore, aggressive treatment is required to depolymerize it into fermentable sugars. The main purpose of hydrolysis is splitting the polymeric structure of cellulosic material into fermentable sugar monomers (Figure 1), which is usually achieved by high energy-consuming biochemical conversions. The cellulose hydrolysis stage can be carried out by chemical routes, using acidic or basic catalysts, by biological routes, using enzymatic catalysts or by thermochemical routes, using water at high temperature in an autocatalytic process (17, 18).

![Figure 1. The main reaction pathway of cellulose hydrolysis. Reprinted from Rostagno et al. (18). Subcritical and supercritical technology for the production of second generation bioethanol, Copyright 2013, with permission from Informa Healthcare.](image-url)
Sub/supercritical water hydrolysis (SCWH) is a thermochemical approach for the hydrolysis of cellulose. When compared with acidic, alkaline, and enzymatic catalysts, it presents several advantages: no need of pretreatment, shorter reaction time, less corrosion, lower residue generation, no use of toxic solvents, and lower formation of degradation products \((4, 19, 20)\). However, the technology is not yet fully developed such that it can be scaled up to the industrial level. Understanding the mechanisms taking place during hydrolysis is fundamental to better apply it to biomasses.

At high temperature and pressure the water shows singular physical properties including dynamic and kinematic viscosities, density, dielectric constant, and ionic product. As the temperature of water is increased by heating, the hydrogen bonding network weakens and permits the dissociation of water into hydronium ions \((\text{H}_3\text{O}^+)\) and hydroxide ions \((\text{HO}^-)\). At subcritical conditions (temperature between 100°C and 374.15°C and pressure sufficient to keep the water at liquid state), the ionization constant of water increases with temperature and is about three orders of magnitude higher than that of ambient water. On the other hand, the dielectric constant decreases drastically from 80 to 20, which improves the solubilization of organic compounds \((16, 18)\). In this way, subcritical water provides a sufficiently acidic medium for the hydrolysis of cellulose. Supercritical water (temperature above 374.15°C and pressure above 22.1 MPa) is compressible and its properties strongly depend on the pressure. Furthermore, it is miscible with light gases and small organic compounds, and its dielectric constant ranges from 3.70 to 19.72, which influences the rate of reactions with polar-activated complex. Employing supercritical water as reaction medium provides an opportunity to conduct chemical reactions in a homogeneous phase that would otherwise occur in a heterogeneous phase under more conventional conditions \((13)\).

There are several studies that were dedicated exclusively to elucidating degradation pathways of the monomers and oligomers using sub- (SbCWH) and supercritical water hydrolysis (SpCWH) \((21–26)\). However, the focus of this work is the hydrolysis for the depolymerization of cellulose and starch to form monosaccharides and oligosaccharides. Within this context, the state-of-the-art on SbCWh and SpCWH of model raw materials is presented in Table 1.

### 2.1. Cellulose

Cellulose is a polysaccharide composed of units of glucose connected via \(\beta-(1/4)\)-glycosidic bonds (Figure 2), which allow for the formation of strong intra- and inter-molecular hydrogen bonds, making the polymer crystalline and resistant to swelling in water. Water at elevated temperatures and pressures can both break up the hydrogen-bound crystalline structure and hydrolyze the \(\beta-(1/4)\)-glycosidic bond, resulting in the production of glucose monomers \((11, 27)\). At room temperature, cellulose is insoluble in water, but at sub/supercritical conditions it is rapidly solubilized and hydrolyzed to its constituents.

As one of the main components in biomass, and the main source of glucose, cellulose is often studied as a model compound, and the conclusions obtained from these studies can be further applied as a first estimate for the behavior of more complex biomass materials. On the other hand, cellulose obtained from different biological sources has different properties, and both its physical (crystallinity) and chemical structure can affect its behavior. Therefore, there is considerable variation in the reported hydrolysis rates and sugar yields for cellulose.

The SbCWH (170–280°C) of cellulose in a batch system was studied by Kamio et al \((28, 29)\). The liquefaction of cellulose was little at 200°C and increased strongly at 240°C. Cellotetraose was detected from 200°C, with maximum concentration at 230°C. From 220°C, cellotriose and cellobiose were also detected, with maximum concentrations at 240°C and 260°C, respectively. Therefore, as temperature increases, the size of the oligomers decreases. Pavlovic et al \((30)\) performed the same type of experiment, and obtained maximum glucose yield of 32.5% at 250°C for 3 min.

Sakaki et al. \((31, 32)\) studied cellulose SCWH (305–405°C) in a batch system. The cellulose was converted to water-soluble compounds, which were in turn decomposed after reaching nearly 80% yield. The maximum water-soluble compounds occurred after 15 s at 355°C; at this condition, the glucose yield reached 40%. The filtrate of the hydrolysate obtained after 10 s at 330°C was subjected to fermentation by Saccharomyces cerevisiae IFO 0216. The fermentation of the hydrolysate was slower (140 h) than that of pure glucose (60 h), despite reaching the same ethanol yield (1.18 g ethanol/2.26 g glucose) \((31)\). The hydrolysate was then treated with activated carbon to remove the furfural and 5-HMF (hydroxymethylfurfural); their initial concentrations, of 0.6% and 1.4%, respectively, were reduced to zero. The fermentation time was shortened to 50 h. However, a significant percent of glucose was lost during the activated carbon treatment \((32)\). The same research group studied the semi-batch system \((33)\). The product that precipitated after cooling the hydrolysate was composed of oligosaccharides comprising 6–20 units. The decomposition rate of...
Table 1. Survey on the applications of sub/supercritical water for the hydrolysis of model systems.

| Substrate          | Hydrolysis                                      | Main results                                                                 | Reference |
|--------------------|-------------------------------------------------|------------------------------------------------------------------------------|-----------|
| Cocero group, Spain | Microcrystalline cellulose                      | Liquefaction degree: 100% (400°C, 0.015 s; 350°C, 1 s)                      | (7)       |
|                    | Particle size: 20–137 µm                         | Total soluble sugars yield: 98%                                             |           |
|                    | Technique: SbCWH, SpCWH                          | Glucose + fructose + cellubiose yield: 47 (400°C, 0.03–0.07 s)             |           |
|                    | Design: continuous                               | 5-HMF yield: lower than 0.4%                                               |           |
|                    | Reactor volume: 0.05–8 mL                        | (400°C, up to 0.1 s)                                                       |           |
|                    | Temperature: 300–400°C                           |                                                                             |           |
|                    | Pressure: 25 MPa                                 |                                                                             |           |
|                    | Suspension flow rate: 17–24 mL/min              |                                                                             |           |
|                    | Water flow rate: 80–112 mL/min                   |                                                                             |           |
|                    | Residence time: 0.004–5 s                        |                                                                             |           |
|                    | S/F: 61.5 (w/w)                                  |                                                                             |           |
|                    | Liquefaction degree: 100% (400°C, 0.015 s; 350°C, 1 s) |                                                                             |           |
|                    | Oligosaccharides yield: 44% (375°C, 7.5 s, S/F of 244) |                                                                             | (4)       |
|                    | Hexoses yield: 2–6%                             |                                                                             |           |
| Zhao group, China  | Microcrystalline cellulose                      | Oligosaccharides yield: 44% (375°C, 7.5 s, S/F of 244)                     | (4)       |
|                    | Technique: SpCWH                                | Hexoses yield: 39.5% (batch, SbCWH, 280°C, 44 s); 31.5 (continuous, SpCWH, 380°C, 9.7 s, S/F of 283 + SbCWH, 240°C, 49 s) | (20)     |
|                    | Design: continuous                               |                                                                             |           |
|                    | Reactor volume: 10 mL                            |                                                                             |           |
|                    | Temperature: 375–390°C                           |                                                                             |           |
|                    | Pressure: 24–25 MPa                              |                                                                             |           |
|                    | Time: 6–16 s                                     |                                                                             |           |
|                    | S/F: 133–400 (v/w)                              |                                                                             |           |
|                    | Hexoses yield: 39.5% (batch, SpCWH, 380°C, 16 s, S/F of 41 + SbCWH, 280°C, 44 s); 31.5 (continuous, SpCWH, 380°C, 9.7 s, S/F of 283 + SbCWH, 240°C, 49 s) |           |
| Microcrystalline cellulose | Technique: SbCWH (SpCWH) + SbCWH (SbCWH) (continuous) | Hexoses yield: 39.5% (batch, SpCWH, 380°C, 16 s, S/F of 41 + SbCWH, 280°C, 44 s); 31.5 (continuous, SpCWH, 380°C, 9.7 s, S/F of 283 + SbCWH, 240°C, 49 s) | (20)     |
|                    | Design: batch, continuous                        |                                                                             |           |
|                    | Reactor volume: 5 mL (batch), 10 mL (SpCWH) + 50 mL (SbCWH) (continuous) |                                                                             |           |
|                    | Temperature: 380°C (SpCWH) + 280°C (SbCWH) (batch), 380°C (SpCWH) + 210–300°C (SbCWH) (continuous) |                                                                             |           |
|                    | Pressure: 24–25 MPa (SpCWH) + 8.5–9.0 MPa (SbCWH) |                                                                             |           |
|                    | Time: 16 s (SpCWH) + 44 s (SbCWH) (batch), 4.99–15.64 s (SpCWH) + 33.24–50.55 s (SbCWH) (continuous) | |           |
|                    | S/F: 42 (v/w) (batch), 158–581 (v/w) (continuous) |                                                                             |           |
|                    | Liquefaction degree: 87.4% (SpCWH, 380°C, 16 s) |                                                                             | (43)      |
|                    | Oligosaccharides yield: 8% (SpCWH, 380°C, 16 s + SbCWH, 280°C, 44 s) | |           |
|                    | Hexoses yield: 39.5% (SpCWH, 380°C, 16 s + SbCWH, 280°C, 44 s) | |           |
|                    | Glucose yield: 32.5% (SpCWH, 380°C, 16 s + SbCWH, 280°C, 44 s) | |           |
|                    | Fructose yield: 7.0% fructose (SpCWH, 380°C, 16 s + SbCWH, 280°C, 44 s) | |           |
|                    | Oligosaccharides + monosaccharides yield: 63% (380°C, 16 s) | |           |
|                    | 5-HMF yield: 1.0% (380°C, 16 s)                  |                                                                             |           |
|                    | Degradation products yield: 20.7% (380°C, 16 s) |                                                                             |           |
| Microcrystalline cellulose | Technique: SpCWH + SbCWH | Liquefaction degree: 100% (380°C, 20 s) | (5)       |
|                    | Design: batch                                    | Oligosaccharides yield: 40% (380°C, 16 s) |           |
|                    | Reactor volume: 5 mL                             | Glucose yield: 27.2% (378°C, 17 s) |           |
|                    | Temperature: 374–386°C                           | Fructose yield: 9.6% (378°C, 17 s) |           |
|                    | Pressure: 22 MPa                                 | Oligosaccharides + monosaccharides yield: 63% (380°C, 16 s) |           |
|                    | Time: 12–22 s                                    | 5-HMF yield: 1.0% (380°C, 16 s) |           |
|                    | S/F: 42 (v/w)                                    | Degradation products yield: 20.7% (380°C, 16 s) |           |
| Substrate                          | Hydrolysis                                      | Main results                                                                 | Reference |
|-----------------------------------|------------------------------------------------|-------------------------------------------------------------------------------|-----------|
| **Saka group, Japan**              |                                                |                                                                               |           |
| Microcrystalline cellulose        | Technique: SpCWH                                | Soluble oligosaccharides concentration in the hydrolysate: 2247 mg/L         | (39)      |
|                                   | Design: continuous                              | Insoluble oligosaccharides concentration in the hydrolysate: 3020 mg/L       |           |
|                                   | Reactor volume: 5 mL (batch)                    | Glucose concentration in the hydrolysate: 158 mg/L                           |           |
|                                   | Temperature: 380°C                              | Fructose concentration in the hydrolysate: 30.6 mg/L                         |           |
|                                   | Pressure: 40 MPa                                | 5-HMF concentration in the hydrolysate: 21 mg/L                               |           |
|                                   | Time: 0.12 s                                    | 5-HMF concentration in the hydrolysate after wood charcoal treatment: 0      |           |
|                                   | S/F: 490 (v/w)                                  |                                                                               |           |
| Microcrystalline cellulose        | Technique: SbCWH, SpCWH and SpCWH + SbCWH       | Liquefaction degree: 100% (400°C, 0.2 s)                                      | (40)      |
|                                   | Design: continuous                              | Oligosaccharides + monosaccharides yield: 66.8% (0.1 s SpCWH + 30 s SbCWH)    |           |
|                                   | Reactors volume: 0.25 mL and 137 mL (SpCWH); 280°C (SbCWH) | Glucose yield: 9.5% (0.1 s SpCWH + 30 s SbCWH); 29.2% (0.1 s SpCWH + 45 s SbCWH) |           |
|                                   | Temperature: 400°C (SpCWH); 280°C (SbCWH)       | 5-HMF yield: 1.0% (0.1 s SpCWH + 30 s SbCWH); 7.3% (0.1 s SpCWH + 45 s SbCWH) |           |
|                                   | Pressure: 40 MPa                                | Polymerization degree: 1–12 units (soluble fraction); 13–100 units (insoluble fraction) |           |
|                                   | Time: 0.1–0.3 s (SpCWH); 120–240 s (SbCWH); 0.1 s (SpCWH) + 15–45 s (SbCWH) |                                                                               |           |
|                                   | S/F: 25 (w/w)                                   |                                                                               |           |
| Microcrystalline cellulose        | Technique: SpCWH                                | Soluble oligosaccharides + monosaccharides yield: 50.5% (continuous, 25 MPa, 0.24 s); 31.3% (batch, 100 MPa, 5 s) | (41)      |
|                                   | Design: batch, continuous                       | Glucose yield: 8.9% (continuous, 40 MPa, 0.48 s); 23.3% (batch, 100 MPa, 5 s) |           |
|                                   | Reactor volume: 5 mL (batch)                    | 5-HMF yield: 1.8% (continuous, 25 MPa, 0.24 s); 9.5% (batch, 100 MPa, 5 s)   |           |
|                                   | Temperature: 380°C                              |                                                                               |           |
|                                   | Pressure: 100 MPa (batch); 25–40 MPa (continuous) |                                                                               |           |
|                                   | Time: 2–8 s (batch); 0.12–0.48 s (continuous)  |                                                                               |           |
|                                   | S/F: 33 (v/v) (batch); 300 (v/w) (continuous)  |                                                                               |           |
| Cellulose I, cellulose II and starch | Pretreatment: extracted with acetone and water | Cellulose I liquefaction degree: 95% (10 s)                                  | (42)      |
|                                   | Technique: SpCWH                                | Cellulose II liquefaction degree: 80% (15 s)                                 |           |
|                                   | Design: batch                                   | Starch liquefaction degree: 95% (5 s)                                         |           |
|                                   | Reactor volume: 10 mL                           | Cellulose I glucose yield: 32% (5 s)                                         |           |
|                                   | Temperature profile: 20–480°C                   | Cellulose II glucose yield: 48% (10 s)                                        |           |
|                                   | Pressure at room temperature: 35 MPa            | Starch glucose yield: 33% (5 s)                                               |           |
|                                   | Time: 15 s (heating up to 374°C) + 5–105 s (SpCWH) |                                                                               |           |
|                                   | Feed: 500 mg                                    |                                                                               |           |
| Sasaki group, Japan               |                                                | Liquefaction degree: 98% (400°C, 0.02 s)                                      | (36)      |
| Microcrystalline cellulose        | Technique: SbCWH, SpCWH                         | Soluble saccharides yield: 40% (320°C, 1.8 s)                                |           |
|                                   | Design: continuous                              |                                                                               |           |
|                                   | Reactor volume: 0.03–5.27 mL                    |                                                                               |           |
|                                   | Temperature: 380°C                              |                                                                               |           |
|                                   | Pressure: 100 MPa (batch); 25–40 MPa (continuous) |                                                                               |           |
|                                   | Time: 2–8 s (batch); 0.12–0.48 s (continuous)  |                                                                               |           |
|                                   | S/F: 33 (v/v) (batch); 300 (v/w) (continuous)  |                                                                               |           |

References:
(39), (40), (41), (42), (36)
Table 1 (Continued)

| Substrate                        | Hydrolysis                                                                 | Main results                                                                 | Reference |
|----------------------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------------|-----------|
| **Microcrystalline cellulose**   | Slurry flow rate: 5.0 mL/min                                              | Insoluble saccharides yield: 50%                                             | (37)      |
|                                  | Preheated water flow rate: 20.0 mL/min                                    | (400°C, 0.02 s)                                                             |           |
|                                  | Cooling water flow rate: 14.0 mL/min                                      |                                                                              |           |
|                                  | Temperature: 320–400°C                                                    |                                                                              |           |
|                                  | Pressure: 25 MPa                                                          |                                                                              |           |
|                                  | Time: 0.02–13.1 s                                                        |                                                                              |           |
|                                  | S/F: 10 (w/w), in the slurry                                              |                                                                              |           |
|                                  | Particle size: 20–100 µm                                                  | Liquefaction degree: 99% (320°C, 9.9 s; 350°C, 3.5 s; 400°C, 0.01 s)       |           |
|                                  | Technique: SbCWH, SpCWH                                                   | Oligosaccharides + monosaccharides yield: 76.5% (400°C, 0.05 s)             |           |
|                                  | Design: continuous                                                       | Glucose yield: 24.2% (400°C, 0.05 s)                                        |           |
|                                  |                                                                            | 5-HMF yield: 0.4% (400°C, 0.05 s)                                           |           |
|                                  |                                                                            | Polymerization degree: 1–6 units (400°C, soluble fraction)                   |           |
|                                  | Slurry flow rate: 5.0 mL/min                                              |                                                                              |           |
|                                  | Preheated water flow rate: 20.0 mL/min                                    |                                                                              |           |
|                                  | Cooling water flow rate: 8.0 mL/min                                       |                                                                              |           |
|                                  | Temperature: 320–400°C                                                    |                                                                              |           |
|                                  | Pressure: 25 MPa                                                          |                                                                              |           |
|                                  | Time: 0.01–10.0 s                                                        |                                                                              |           |
|                                  | S/F: 9 (w/w), in the slurry                                               | Liquefaction degree: 100% (320°C, 9.9 s; 350°C, 3.8 s; 400°C, 0.05 s)      | (38)      |
|                                  |                                                                            | Oligosaccharides + monosaccharides yield: ∼75% (SpCWH)                       |           |
| **Sakaki group, Japan cellulose**| Particle size: 100–120 µm                                                 |                                                                              | (33)      |
|                                  | Technique: SbCWH                                                          | Liquefaction degree: 100% (295°C, 10 min, 12.5 mL/min)                      |           |
|                                  | Design: semi-batch                                                        | Soluble saccharides: 81% (295°C, 12 min, 10 mL/min)                          |           |
|                                  | Reactor volume: 3.6 mL                                                    | Insoluble saccharides: 18% (295°C, 12 min, 10 mL/min)                        |           |
|                                  | Flow rate: 7.5–15.0 mL/min                                                | Polymerization degree: 1–5 units (soluble fraction), 6–20 units (insoluble fraction) |           |
|                                  | Pressure: 9.8 MPa                                                         |                                                                              |           |
|                                  | Temperature: 250–310°C                                                   |                                                                              |           |
|                                  | Time: 3–15 min                                                            |                                                                              |           |
|                                  | S/F: 30–120 (v/w)                                                        |                                                                              |           |
| Microcrystalline cellulose       | Slurry flow rate: 6.0 mL/min                                              |                                                                              |           |
|                                  | Preheated water flow rate: 12.0 mL/min                                    |                                                                              |           |
|                                  | Cooling water flow rate: 10.0 mL/min                                      |                                                                              |           |
|                                  | Temperature: 320–400°C                                                    |                                                                              |           |
|                                  | Pressure: 25 MPa                                                          |                                                                              |           |
|                                  | Time: 0.05–9.9 s                                                          |                                                                              |           |
|                                  | S/F: 10 (w/w), in the slurry                                              |                                                                              |           |
| **Sakaki group, Japan cellulose**| Particle size: 100–120 µm                                                 |                                                                              | (31)      |
|                                  | Technique: SbCWH                                                          | Glucose yield: 40% (355°C, 15 s)                                            |           |
|                                  | Design: batch                                                             | Cellobiose yield: 4% (355°C, 10 s)                                          |           |
|                                  | Reactor volume: 6 mL                                                      | Glucose concentration in the hydrolysate: 43% (330°C, 10 s)                 |           |
|                                  | Temperature: 305–405°C                                                   | Cellobiose concentration in the hydrolysate: 15% (330°C, 10 s)              |           |
|                                  | Pressure at room temperature: 0.1 MPa (with CO2)                         | Furfural concentration in the hydrolysate: 0.6% (330°C, 10 s)               |           |
|                                  | Time: 13–40 s                                                             | Furfural concentration in the hydrolysate: 1.4% (330°C, 10 s)               |           |
|                                  | S/F: 6 (w/w)                                                              | Furfural concentration in the hydrolysate after wood charcoal treatment: 0 |           |
|                                  |                                                                            | 5-HMF concentration in the hydrolysate after wood charcoal treatment: 0     |           |
|                                  |                                                                            | Fermentation time of the untreated hydrolysate: 150 h                       |           |
| Substrate                        | Hydrolysis                          | Main results                                                                 | Reference |
|---------------------------------|-------------------------------------|------------------------------------------------------------------------------|-----------|
| **Microcrystalline cellulose**  |                                     | Fermentation time of the treated hydrolysate: 50 h                          | (32)      |
|                                 |                                     | Glucose yield: 40% (355°C, 15 s)                                             |           |
|                                 |                                     | Fermentation time of the hydrolysate: 140 h                                 |           |
|                                 |                                     | Ethanol yield for fermentation: 1.18 g ethanol/2.26 g glucose                |           |
| **Wu group, Australia**         |                                     | Liquefaction degree: 100% (280°C, 20 min, 10–40 mL/min; 270°C, 40 min, 10–40 mL/min) | (14)      |
| **Microcrystalline cellulose**  |                                     | Polymerization degree: 1 to 23 units (230°C) to 28 units (270°C)             |           |
|                                 |                                     | Glucose + oligomers yield: 85% (on a carbon basis, 250°C, 40 mL/min)         |           |
|                                 |                                     | Lower sugars (C1-C5) yield: 34% (on a carbon basis, 250°C, 40 mL/min)        |           |
| **Gupta group, USA**            |                                     | Glucose concentration in the hydrolysate: 12.5 mg/L                          | (34)      |
| **Microcrystalline cellulose**  |                                     | Cellobiose concentration in the hydrolysate: 10 mg/L                         |           |
|                                 |                                     | Polymerization degree: up to 30 units                                        |           |
| **Okamura group, Japan**        |                                     | Liquefaction degree: 30% (300°C)                                            | (16)      |
| **Microcrystalline cellulose**  |                                     | pH of the hydrolysates: 3.3–6.4                                             |           |
|                                 |                                     | Oligosaccharides yield: 20.0% (315°C, 3.4 s)                                 |           |
|                                 |                                     | Cellobiose yield: 4.1% (315°C, 3.4 s)                                        |           |
|                                 |                                     | Glucose yield: 3.7% (315°C, 3.4 s)                                           |           |
|                                 |                                     | Fructose yield: 0.4% (315°C, 3.4 s)                                          |           |
|                                 |                                     | 5-HMF yield: 0.6% (315°C, 3.4 s)                                             |           |
|                                 |                                     | pH of the hydrolysates: 2.3–3.0                                              |           |
|                                 |                                     | Gasification: 43% (0.44% K₂CO₃ addition, 302°C)                              |           |
| **Microcrystalline cellulose**  |                                     | Liquefaction degree: 90% (330°C)                                            | (35)      |
|                                 |                                     | Oligosaccharides + monosaccharides yield: 66.7% (332°C, 4.8 s)               |           |
|                                 |                                     | Oligosaccharides yield: 18.0% (332°C, 4.8 s)                                 |           |
|                                 |                                     | Cellobiose yield: 6.2% (332°C, 4.8 s)                                        |           |
|                                 |                                     | Glucose yield: 37.6% (332°C, 4.8 s)                                          |           |
|                                 |                                     | Fructose yield: 4.9% (332°C, 4.8 s)                                          |           |
|                                 |                                     | Degradation products yield: 19.5% (332°C, 4.8 s)                           |           |
|                                 |                                     | pH of the hydrolysates: 2.3–3.0                                              |           |
|                                 |                                     | Gasification: 43% (0.44% K₂CO₃ addition, 302°C)                              |           |

**Note:** CO₂ denotes carbon dioxide.
| Substrate | Hydrolysis | Main results | Reference |
|-----------|------------|--------------|-----------|
| Microcrystalline cellulose | Reactor volume: 97 mL  
Temperature: 170–280°C  
Pressure at room temperature: 1 MPa (with N₂)  
Time: 330 min  
S/F: 99 (w/w)  
Particle size: 20–100 µm  
Technique: SbCWH  
Design: batch | Cellobiose concentration in the hydrolysate: 1.0 mol/m³ (270°C)  
Cellotriose concentration in the hydrolysate: 0.25 mol/m³ (240°C)  
Cellotetraose concentration in the hydrolysate: 0.25 mol/m³ (220°C)  
Cellulose concentration in the hydrolysate: 0.24 mol/m³ (230°C); 0.03 mol/m³ (270°C)  
Cellulobiase concentration in the hydrolysate: 1.3 mol/m³ (260°C)  
Cellotriose concentration in the hydrolysate: 0.2 mol/m³ (240°C)  
Cellotetraose concentration in the hydrolysate: 0.15 mol/m³ (230°C) | (28) |
| Škerget group, Slovenia  
Microcrystalline cellulose | Technique: SpCWH  
Design: batch  
Reactor volume: 60 mL  
Temperature: 220–300°C  
Time: 0–60 min  
S/F: 10 (v/w) | Liquefaction degree: 87.7% (250°C, 5 min)  
Water soluble fraction yield: 51.4% (250°C, 5 min)  
Bio-oil yield: 21.1% (250°C, 60 min)  
Glucose yield: 32.5% (250°C, 3 min)  
Cellulobiase concentration in the hydrolysate: 0.5% (250°C, 3 min)  
Lactose yield: 1.5% (250°C, 3 min)  
Gasification: 68% (300°C, 60 min) | (30) |
| Zhu group, China  
Microcrystalline cellulose | Technique: SbCWH  
Design: batch  
Reactor volume: 200 mL  
Temperature: 240–260°C  
Time: 1–10 min  
S/F: 10 (v/w) | Total reducing sugars yield: 46.05% (260°C, 2 min) | (51) |
| Suzuki group, Japan  
Microcrystalline cellulose and filter paper | Technique: SbCWH  
Design: batch  
Temperature: 198–300°C  
Pressure at room temperature: 10 MPa  
Time: 20–33 min  
S/F: 10 (v/w) | Liquefaction degree: 97% (260°C, 20 min); 99% (300°C)  
No effect of the shape/size of cellulose | (52) |
| Aurand group, USA  
Microcrystalline cellulose and starch | Technique: SbCWH, SpCWH  
Design: continuous  
Reactor volume: 0.09–2.13 mL  
Temperature: 200–400°C  
Pressure: 34.5 MPa  
Slurry flow rate: 5–10 mL/min  
Preheated water flow rate: 5–10 mL/min  
Cooling water flow rate: 10 mL/min  
Residence time: 0.445–23 s  
S/F: 100 (w/w) | Cellulose  
Liquefaction degree: 100% (320°C, 0.725 s)  
Glucose yield: 36.7% (250°C, 5 mL/min)  
Cellobiose yield: 2.9% (230°C, 5 mL/min)  
Fructose yield: 6.7% (250°C, 5 mL/min)  
Frufural yield: 6% (300°C, 10 mL/min)  
5-HMF yield: 5% (300°C, 10 mL/min)  
Starch  
Glucose yield: 35% (250°C, 5 mL/min) | (27) |
| Substrate | Hydrolysis | Main results | Reference |
|-----------|------------|--------------|-----------|
| Macaskie group, UK | Technique: SbCWH | Fructose yield: 5.3% (250°C, 5 mL/min) Maltose yield: 7.6% (230°C, 5 mL/min) | (47) |
| Starch from potato powder | Design: batch | Liquefaction degree: ~ 100% (all conditions) pH of the hydrolysates: 2.8–3.7 Glucose yield: 628 g /kg starch carbon (200°C, S/F of 5) 5-HMF yield: 100 g/kg starch carbon (200°C) 5-HMF yield for the hydrolysate treated with activated carbon: 0 Fermentation of the hydrolysate detoxified with activated carbon: 70% more hydrogen production | |
| Brunner group, Germany | Technique: SbCWH | Cellulose Liquefaction degree: 95% (severity of 6.0) Glucose yield: 13% (severity of 5.3) Starch Glucose yield: 95% (severity of 4.7, 153% CO2) | (10) |
| Microcrystalline cellulose and starch | Design: continuous | | |
| Funazukuri group, Japan | Technique: SbCWH | Liquefaction degree: > 90% (290°C, 2.5 min) Oligosaccharides yield: 80% (carbon basis, 240°C, 5 g/min) Glucose yield: 43.8% (carbon basis, plug-flow reactor, 270°C, 3.64 min, 5 g/min) Fructose yield: 3.1% (290°C, 5 g/min) 5-HMF yield: 5.1% (290°C, 5 g/min) | (46) |
| Starch from sweet potato | Design: semi-batch + plug-flow reactor | Starch Glucose yield: 53.0% (0.32 g CO2, 200°C, 15 min) Oligosaccharides: 90.5% (no CO2, 200°C, 15 min) Oligosaccharides + monosaccharides yield: 94.7% (no CO2, 200°C, 15 min) 5-HMF: 0.9% (no CO2, 200°C, 15 min) Glucose yield: 20.3% (10 mM AcOH) Glucose yield: 60.0% (10 mM HCl) Agar Monosaccharides yield: 24% (0.2 g CO2, 160°C, 30 min) Guar gum Monosaccharides yield: 10% (0.2 g CO2, 200°C, 15 min) Xylan | (45) |
| Starch from sweet potato, xylan from birchwood, agar, guar gum | Design: batch | | |

### Notes
- **SbCWH** refers to the Sulfite-based Cellulosic Hydrolysis process.
- **Severity** is a measure of the reaction conditions, calculated as S/F ∙ exp(-Δp/1000) ∙ exp(T/200) ∙ exp(V/1000) ∙ exp(T/1000), where S/F is the solid-to-liquid ratio (v/w), Δp is the pressure drop, T is the temperature, and V is the reactor volume.
- **Oligosaccharides** include fructose, glucose, and other low-molecular-weight carbohydrates.
- **5-HMF** (5-hydroxymethylfurfural) is a byproduct of the hydrolysis process.
- **pH of the hydrolysates** is important for subsequent processing steps.
- **Glucose yield** is calculated by dividing the mass of glucose produced by the mass of starch used.
- **AcOH** refers to acetic acid.
cellulose was not affected by the flow rate (7.5–15.0 mL/min), but the depolymerization of the products was suppressed as the flow rate increased due to the shorter residence time.

Studying SbCWH in a semi-batch system, Yu and Wu (14, 34) were able to completely solubilize cellulose at 280°C for 20 min or 270°C for 40 min. The monomer + oligomer yield was very high (~80% on a carbon basis). The total yield of lower sugars (C1–C5) was 31–34%. The mean concentrations of glucose and cellobiose in the hydrolysate were 12.5 mg/L and 10 mg/L, respectively. The hydrolysate contained a wide range of glucose oligomers, with degrees of polymerization of up to 30 units, and monomers derivatives. The glucose oligomers with degrees of polymerization higher than five units precipitated quickly during the 8 h immediately following the process; the precipitation leveled off as the precipitation time further increased and was completed after 120 h. Therefore, at room temperature, only cellobiose, cellotriose, cellotetraose, and cellopentaose are soluble in water. The oligomers with higher degree of polymerization will precipitate.

Kumar et al. (16, 35) studied the SCWH (200–405°C) of cellulose in a continuous system. The liquefaction degree increased from 10% at 200–275°C to over 90% above 330°C. The highest yield of oligomers and monomers (18.0% oligomers, 6.2% cellobiose, 37.6% glucose, and 4.9% fructose) was obtained at 320°C for 4.8 s. For this condition, approximately 65% of the cellulose was liquefied and the yield of degradation products was 19.5%. The pH of the hydrolysates was 2.3–3.0 for all conditions due to a high concentration of organic acids, derivative from monomers degradation. The addition of 0.44% of the alkaline catalyst K$_2$CO$_3$ increased the gasification of cellulose to 43% at 302°C. Therefore, when the objective is to obtain fermentable sugars, the severity of the process should be decreased to prevent glucose degradation, especially when considering that the degradation products are fermentation inhibitors. Moreover, the continuous process used in these studies showed better results in terms of decreasing processing time when compared to batch and semi-batch systems.

The SCWH in continuous mode was also studied by Sasaki et al. (36–38). The cellulose was 99% liquefied after 9.9 s at 320°C, 3.5 s at 350°C, or 0.01 s at 400°C. For SbCWH, the water-soluble saccharide yield increased with time, reaching 40% at 320°C for 1.8 s, but mostly degradation products were obtained, leading to a low pH. By increasing the residence time in SbCWH, the saccharide yield decreased while the degradation product yield increased. For SpCWH (400°C, 0.05 s), the hydrolysate was primarily composed of monomers and oligomers comprising up to six units (76.5%), and presented higher pH.

Nakata et al. (39) studied the SpCWH (380°C) of cellulose in a continuous system. The hydrolysate contained 2247 mg/L oligosaccharides, 158 mg/L glucose, and 21 mg/L 5-HMF. The glucose obtained by SpCWH followed by enzymatic hydrolysis could be converted to ethanol by fermentation, and inhibition could be reduced by alkaline or wood charcoal treatments.

Cantero et al. (7) optimized the SpCWH of cellulose using a continuous micro-reactor that allowed precise control of the residence time. At 400°C, 98% of the mass was recovered as sugars (monomers and oligomers), while less than 0.4% of 5-HMF was obtained. A maximum of 47% of glucose + fructose + cellobiose was obtained at 400°C for 0.03–0.07 s. The authors have suggested that this short
residence time could allow for the reduction of the size of an industrial reactor from m³ to cm³.

Ehara and Saka (40, 41) studied the SpCWH of cellulose in batch and continuous systems and the combination of SpCWH followed by SbCWH in a continuous system. For SpCWH in the batch system, all sugars were degraded after 45 s, but it minimized the pyrolyzed products and shortened the heating, reaction, and cooling times compared to the batch system (42). On the other hand, the batch system resulted in a higher yield of glucose (23.3% vs. 8.9%), but the highest yield of soluble oligosaccharides + monosaccharides was 50.5% in the continuous system (380°C, 25 MPa, 0.24 s) and 31.3% in the batch system (380°C, 100 MPa, 5 s) (41). In the combined treatment (0.1 s at 400°C + 30 s at 280°C), the yield of monosaccharides and oligosaccharides increased to 66.8% (40).

Zhao et al. (20, 43) focused on SpCWH to achieve a high yield of oligosaccharides, which was followed by SbCWH to further hydrolyze the oligosaccharides to monosaccharides. In the batch system, the cellulose was completely liquefied above 380°C. In SpCWH, the maximum yield of the monosaccharides was 27.2% at 378°C for 17 s, but the maximum yield of the total saccharides (24% monosaccharides and 40% oligomers) was obtained at 380°C for 16 s. The saccharides were completely decomposed at higher temperatures and/or longer reaction times. Hence, 380°C and 16 s were considered as the optimum conditions to obtain oligosaccharides (43). Cellulose hydrolysis in a combined process using supercritical water followed by subcritical water in a batch system was both rapid and effective. The highest yield of monosaccharides (39.5%), containing 32.5% glucose and 7.0% fructose, was obtained under the conditions of 380°C and 22 MPa for 16 s (SpCWH) followed by 280°C and 10 MPa for 44 s (SbCWH). The process was then adapted to a continuous system. The maximum yield of monosaccharides (31.5%) was obtained using a combination of SpCWH (S/F of 283, 380°C, 9.7 s) and SbCWH (240°C, 49 s). Compared to the batch system, the continuous system yielded a reasonable amount of monosaccharides and proved to be promising for practical applications (20). After further optimizing the continuous supercritical step of the process, the maximum oligosaccharide yield at 375°C was 44% (S/F of 244 and 7.5 s) (4). Long reaction times caused a decrease in the oligosaccharide yields due to depolymerization, but shorter reaction times resulted in low hydrolysis rate due to low residence time.

From the data gathered, it is possible to notice that SCWH is able to liquefy 100% of cellulose. However, not all the mass can be recovered as glucose. The best results for cellulose SCWH have been recently found by Cantero et al. (7) using a continuous reactor at 400°C, S/F of 61.5, and 0.015 s. These authors recovered 98% of cellulose as monosaccharides + oligosaccharides, from which 46% were glucose + fructose + cellobiose. Zhao et al. (4, 20, 43) obtained a maximum oligosaccharides yield of 44% for SpCWH at 375°C for 7.5 s in a continuous system using S/F of 244 (4). The maximum hexoses yield obtained was 39.5% (32.5% of glucose) for SpCWH at 380°C for 16 s using S/F of 41 followed by SbCWH at 280°C for 44 s in a batch system using S/F of 41 (20, 43). Kumar and Gupta (35) and Sakaki et al. (31, 32) obtained even higher glucose yield, 37.6% and 40%, for SbCWH in a continuous system at 332°C for 4.8 s and SbCWH at 355°C for 15 s in a batch system, respectively. Yu and Wu (14) also found high oligomers + monomers yield (85%) when conducting SbCWH at 250°C for 60 min in a semi-batch system and Sasaki et al (38) recovered 75% oligomers + monomers for SpCWH in continuous system. However, in all these studies, furfural, 5-HMF, and other degradation products were detected. Moreover, the batch process is not feasible at industrial scale, but for continuous processes the S/F necessary is too high. Therefore, there is still much to be improved in the SCWH process.

The studies of SCWH with model systems indicate that the most important parameter that affects the monosaccharides yield is the combination of temperature and time of process. While high temperature is necessary for the depolymerization of cellulose, exposing it to high temperature for a long time leads to the formation of degradation compounds. Hence, a strict control of these parameters is important to successfully develop the SCWH process. Another parameter that can contribute to the SCWH process is the addition of catalysts. Although it is not indispensable for the process, the addition of catalyst can improve the monosaccharides yield and also inhibit the formation of degradation compounds. Therefore, an analysis of cost × benefit is important to define about the addition of catalysts.

2.2. Starch

Cellulose and starch (Figure 2) are two polysaccharides that are identical in chemical composition based on the monomer glucose, but that have different chemical structures and physical properties. Starch consists of glucose monomers bound with α-(1/4) and α-(1/6) bonds and is characterized by a more amorphous structure than cellulose (11, 13). Because of its weaker structure compared to cellulose, starch is
hydrolyzed faster and at lower temperatures than cellulose in \textit{SCWH}, producing higher sugar yield due to less severe operation conditions used, which prevent the degradation of glucose \cite{10, 12, 42}.

For starch SbCWH in a batch system, Nagamori and Funazukuri \cite{44} obtained over 90\% liquefaction at 180\°C. After 5 min at 200\°C, glucose was not recovered, but the starch was degraded into a wide range of oligosaccharides; at more severe conditions, the oligosaccharides with high degrees of polymerization were no longer present. Gaseous compounds resulting from decomposition were formed at 240\°C and 10 min. The maximum glucose yield was approximately 62\% at either 200\°C and 30 min or 220\°C and 10 min.

In another study, \(\text{CO}_2\) was added to the system \cite{45}. The glucose yield increased linearly with the amount of added \(\text{CO}_2\); the addition of 0.32 g \(\text{CO}_2\) resulted in a glucose yield of 53.0\%, a 14-fold increase over the glucose yield obtained by SbCWH with pure water. Furthermore, the degree of polymerization of the oligosaccharides decreased with \(\text{CO}_2\) addition. The yield of monomers + oligomers was 88.0\%. Schacht et al. \cite{10} also found higher glucose yield from starch in SbCWH when \(\text{CO}_2\) was added. Miyazawa and Funazukuri \cite{45} compared the addition of small amounts of hydrochloric acid (HCl) and acetic acid (AcOH) to \(\text{CO}_2\). The glucose yield was 20.3\% for the 10 mM AcOH aqueous solution and 60.0\% for the 10 mM HCl aqueous solution. For the addition of \(\text{CO}_2\) and AcOH, the glucose yield was similar (60.4\%) but the degradation products were lower (4.5\%) than for HCl alone.

The SbCWH of starch was later studied in a semibatch system \cite{46}. At 290\°C, over 90\% of the starch was hydrolyzed within 2.5 min. The maximum glucose yield, obtained at 270\°C, was 16.1\%. Fructose and 5-HMF were formed at temperatures of 220\°C and above, and their yields gradually increased with temperature up to 3.1\% and 5.1\%, respectively, at 290\°C. The yield of oligosaccharides increased and that of monosaccharides decreased as the flow rate increased due to the shorter residence time in the reactor; the production of aldehydes (degradation products) decreased at higher flow rates due to the same reason. By installing a plug-flow reactor at the exit of the first reactor to increase and precisely control the residence time, the maximum glucose yield (43.8\%) was obtained after 3.64 min at a flow rate of 5 g/min and 240\°C. Adjusting the residence time was the most effective method to increase the glucose yield and suppress its degradation.

In the SbCWH of starch in a batch system, Orozco et al. \cite{47} obtained 100\% liquefaction at 180\°C. The pH decreased with temperature due to the accumulation of organic acids. The yield of glucose increased with temperature, reaching its maximum value (548 g /kg starch carbon) at 200\°C, and then decreased, reaching the minimal value at 235\°C. The hydrolysates were detoxified with activated carbon by removing 5-HMF and organic acids. This procedure resulted in 70\% more hydrogen production by \textit{E. coli} when compared to the untreated hydrolysates. The dilution also improved the fermentability of the hydrolysate.

From Table 1 it can be noticed that starch yields more glucose than cellulose under less aggressive operation conditions. The best results found for starch SCWH are glucose yield of 95\% for SbCWH in a continuous system at severity of 4.7 and using \(\text{CO}_2\) as additive \cite{10}. However, starchy raw materials are usually considered to have applications in the food industry, and should therefore be avoided as energy sources. That is why lignocellulosic raw materials are always preferred when it comes to producing second generation bioethanol. Nevertheless, understanding the mechanisms that take place during SCWH is fundamental so that it can be applied to more complex biomass.

### 3. Future perspectives

By the data gathered from literature on SCWH of cellulose and starch, it is possible to notice that although up to 100\% of liquefaction of cellulose and
starch have been achieved, not all the mass can be recovered as monosaccharides. Moreover, in all the studies cited it was detected the presence of degradation products as furfural and 5-HMF, that are considered undesirable because they can act as fermentation inhibitors.

Despite the fact that there is no consensus about the best process to hydrolyze cellulose and starch, the studies agree that it is necessary a strict control of the process to avoid the formation of degradation products (7, 40, 41, 35). Therefore, the key factors to minimize the formation of degradation products are setting the conditions of the media to favor dehydrolysis reactions and disfavor the degradation reactions; and an effective control of the residence time (7).

In studies of cellulose SCWH it was observed that in the subcritical region (under 376°C), the glucose and oligomer conversion rates were much faster than the hydrolysis rate of cellulose. Therefore, even if the
hydrolysis products, such as glucose or oligomers, are formed, their further decomposition rapidly takes place and thus high yields of hydrolysis products cannot be obtained. However, around the critical point, the hydrolysis rate jumps to more than one order of magnitude higher level and becomes faster than the glucose or oligomer decomposition rate (37, 38). On the other hand, for starch hydrolysis, as the temperature increases, the decomposition products yield increases and, correspondingly, the glucose yield decreases. Moreover, as the temperatures used in SCWH are high, it is necessary to apply extremely low residence times in order to achieve an efficient energy balance. Therefore, there should be more studies in this field in the next years.

The biomass hydrolysis is a complex and extremely substrate-dependent process and, consequently, it becomes necessary to study the real systems behavior due to its diverse composition (12). The data obtained from model systems provide a good basis to understand the behavior of biomass hydrolysis. However, they do not rule out the careful investigation of the hydrolysis of real biomass, since each raw material has a particular composition and hence the processing conditions for an effective hydrolysis process with high monosaccharides yield and low degradation products content should be optimized for each one of them. Figure 3 shows the variety of residues generated in Brazil during 2009/2010 and demonstrates that many products can be obtained through the SCWH processing of these residues. Nowadays, there are applications of SCWH on biomasses, especially for sugarcane bagasse, different types of corn residues, and rice bran (4, 48–50). The applications of SCWH to biomass tends to increase in the next years, as it is the main goal of studying the hydrolysis of cellulosic and starchy materials.

4. Conclusions

The studies of hydrolysis of model systems using sub- and/or supercritical water demonstrate that this technology is very promising to obtain monosaccharides from cellulose and starch. They show that hydrolysates with high monosaccharides yield and low degradation products content can be obtained in extremely short time, less than one second, although it is necessary to optimize the process conditions for each raw material. Further studies in the development of this technology can lead to sustainable processing of biomass to produce biofuels, as long as it is technically, environmentally, and economically feasible.

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