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## Subcritical Water – a Perspective Reaction Media for Biomass Processing to Chemicals: Study on Cellulose Conversion as a Model for Biomass

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**Abstract:** Biomass and water are recognized as a key renewable feedstock in sustainable production of chemicals, fuels and energy. Subcritical water (SubCW), or commonly referred as hot compressed water (HCW), is the water above boiling and below critical point (CP; 374 °C, 22.1 MPa). It has gained great attention in the last few decades as a green, cheap, and nontoxic reagent for conversion of biomass into valuable chemicals. In this paper, hydrothermal reactions of cellulose, as the model biomass substance, with subcritical water at mild temperature and pressure regimes have been studied. The experiments were done in a batch reactor in the temperature range of 220 ° – 300 °C. The main products distributed in liquid, gaseous and solid phase were separated and quantified. The conversions to each group of products were found strongly dependent on the temperature and residence time.

*Key words:*

Biomass, cellulose, subcritical water (SubCW), hydrothermal conversion, bio-oils

### Introduction

Due to excessive reliance on nonrenewable resources and environmentally unacceptable production processes, the chemical industry is under increasing pressure and continuous improvement in performance, enabling more sustainable and safer production. The main technological challenge lies in “green chemical engineering” which comprises the selection of renewable raw materials, integration of material constraints, costs and safety, and increasing of energy and material efficiency in production and services.<sup>1</sup> In this context, biomass and water are recognized as key feedstock for a sustainable chemical industry, which provide entirely novel opportunities for production of chemicals, nowadays predominantly based on fossil resources. Integration of energy, fuels and chemicals produc-

tion through the concept of *biorefineries* is the most probable scenario in future.<sup>2</sup> Utilization of by-products and waste biomass for new or already known purposes leads to maximization of total value of biomass as raw material and increases the profitability, in comparison to the classical “one-product” approach.

Biomass, commonly referred to as lignocellulose, has a complex structure. It is constituted from three main structural components: cellulose, hemicelluloses and lignin. The most abundant components are cellulose and hemicelluloses, named carbohydrates, representing almost 75 % of biomass weight.<sup>2</sup> Cellulose is a linear polymer of glucose monomers linked via  $\beta$ -1-4-glycoside bonds in ribbon-like crystalline structure, resistant to low temperature water penetration/dissolution and enzyme attack. Cellulose fibers constitute cell walls, giving strength to biomass. Hemicellulose is a heterogeneous polymer composed of C5-sugars or pentoses

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(xylose and arabinose) and C6-sugars or hexoses (mannose, glucose, galactose), in different ratios, depending on feedstock. It is a branched polymer with amorphous structure and is relatively easily hydrolysable to its constituent sugars, unlike cellulose. Together, cellulose- and hemicellulose-sugars represent the most important green feedstock for conversion into chemicals and fuels.<sup>2</sup> The second most abundant chemical component is lignin (20–25 % of biomass weight). Lignin is a complex, highly aromatic polyphenolic material available in plants in different composition, molecular weight and amount. It has a complex, branched structure, mostly synthesized in enzyme polymerization of phenylpropane subunits of *trans-p*-coumaryl alcohol, *trans-p*-coniferyl alcohol and *trans-p*-synapyl alcohol (aromatic monomers).<sup>4</sup> It acts as a reinforcing agent, giving mechanical strength to biomass. Lignin does not have a regular structure like cellulose, but it is chemically and physically heterogeneous, even the chemical structure is unknown. However, it has great potential as a versatile building block within the biorefinery concept of biomass usage.<sup>5</sup> Also minor components of biomass such as proteins, fats and oils or extractives (tannins, lignans, stilbens, terpenes, etc.) have great potential as feedstock for many valuable chemicals.<sup>6</sup>

Methods for conversion of biomass into chemicals and fuels are divided into biochemical methods (e.g. enzymatic fermentation to ethanol,<sup>7</sup> anaerobic digestion to methane,<sup>8</sup> etc.) and thermochemical methods (pyrolysis, gasification and liquefaction).<sup>9</sup> Hydrothermal (HT) processes are defined as thermochemical reactions in water media at high temperatures (above 200 °C) and high pressures (high enough to keep water in liquid phase or supercritical state). They have gained increased attention in the last decades due to their several advantages over other biomass conversion methods, including the use of water as a cheap, environmentally friendly reaction medium with unique properties, and the ability to use wet heterogeneous biomass feedstock (waste, sewage sludge, etc.) without prior dewatering (drying) or other pretreatment process. Furthermore, HT reactions of complex biomass materials offer the possibility to produce versatile products, from solids, liquids to gases, through different HT processes (e.g. carbonization,<sup>10</sup> aqueous phase reforming,<sup>11</sup> liquefaction<sup>12</sup> and gasification<sup>13</sup>). The real advantage of HT processes lies in the unique properties of subcritical (SubCW) and supercritical water (SCW), significantly different compared to water at ambient conditions. The properties of SubCW and SCW as a solvent and reactant in reactions with biomass have been reviewed by G. Brunner<sup>14</sup> and A. Kruse and E. Dinjus<sup>15</sup>. The present article is focused on the properties and behavior

of subcritical water (SubCW) in reactions with cellulose as a model biomass compound.

Subcritical water (SubCW) is pressurized water at temperatures above its boiling point at ambient pressure and below critical point ( $T_c=374$  °C,  $p_c=22.1$  MPa,  $\rho_c=320$  kgm<sup>-3</sup>). Within a region close to critical conditions (near-critical or subcritical), water properties become more sensitive to pressure and temperature changes. Above the critical point, water is called supercritical water (SCW) and its properties vary between liquid-like and gas-like with changing temperatures and pressures without any phase transition. The most relevant properties of SubCW as a reaction media are miscibility, dielectric constant, ionic product, electrolytic solvent power, transport properties (viscosity, diffusion coefficients and ion mobility), hydrogen bonding, etc. These properties are strongly influenced by the temperature and water density so they could be manipulated as parameters to enhance reaction selectivity to desired products. The dielectric constant decreases by temperature due to lowering of hydrogen bonds number, making SubCW more similar to hydrocarbon solvents. For this reason, the solubility of hydrophobic organic compounds and light gases in subcritical water is increased and thus they can be extracted and subsequently easily separated from reaction mixture upon cooling. The ionic product of subcritical water ( $K_w = [H^+][OH^-]$ ) increases with temperature and is greater by 1 to 2 orders of magnitude than at ambient temperatures, so SubCW has an important role in acid- and base-catalyzed reactions (e.g. biomass hydrolysis). Furthermore, good transport properties (high diffusion coefficient and thermal conductivity, and low viscosity) make SubCW more similar to a gas than a liquid, and enable high reaction rates.<sup>16</sup> All these properties of SubCW greatly impact biomass decomposition, mainly through reactions of solvolysis, depolymerisation and further decomposition of monomers by cleavage, dehydration, decarboxylation, deamination and rearrangements of reactive fragments.<sup>12,16</sup>

The present work is focused on uncatalyzed hydrothermal transformations of microcrystalline cellulose as a representative model biomass, in subcritical water at mild temperatures and autogenous pressure. Biomass conversion rate and a yield of each group of products are strongly influenced by many factors such as reaction temperatures, water properties, reactor system, catalysts implied, heating rate, biomass properties, etc.<sup>17</sup> The influence of reaction temperature (220 °C – 300 °C) and residence time (3–60 minutes) in batch reactor were examined in relation to overall conversion and conversion to various products (solid, liquid and gaseous).

## Materials and methods

### Materials

Microcrystalline cellulose powder was obtained from Merck (Germany). Deionized water having resistivity of  $18 \text{ M}\Omega \text{ cm}^{-1}$  was obtained by water purification apparatus (ELGA, Veolia). Sugar standards (glucose, cellobiose, fructose, galactose, ribose, etc.) and other high-purity reagents for HPLC analysis were purchased from Sigma-Aldrich (Germany).

### Experimental methods

Experiments of the microcrystalline cellulose conversions were carried out in stirred batch reactor made from HT/HP 1.4980 steel tube (volume capacity = 60 ml) in temperature range from  $220^\circ$  –  $300^\circ \text{C}$  and equivalent autogenous pressure. The suspensions of 3.0 g cellulose in 30 ml deionized water were prepared, pre-mixed on magnetic stirrer and charged in the reactor. The reactor was heated by electrical wire-heater to the desired temperature. The heating rate was  $8\text{--}10^\circ \text{C min}^{-1}$ . Reaction mixture was mixed by magnetic stirrer at 600 rpm. The reaction temperature and pressure were measured by K-type thermocouple and pressure sensor connected to reactor interior, respectively. The reaction time was measured from the moment the set temperature was reached. After a defined reaction time, the reactor was quickly immersed in an ice bath to stop the reaction immediately. The reaction mixture was cooled to room temperature and the final temperature and pressure were recorded. In case gas formation was detected (elevated final pressure at room temperature), the gaseous phase was collected in sampling bags. The liquid and solid contents in the reactor were separately collected as water-soluble (WS), acetone-soluble (AS) and acetone-insoluble or solid residue (SR) fractions.

The reactor content was filtered using a pre-weighed standard filter-paper (Whatman, USA, Grade one  $>11 \mu\text{m}$ ). The total volume of filtrate, i.e. WS fraction, was measured and stored in freezer until analysis on HPLC. The aliquot of WS fraction was evaporated under reduced pressure at  $60^\circ \text{C}$  in rotary evaporator and the content of dry matter in WS phase was determined gravimetrically, and the conversion to WS products was calculated. The water-insoluble fraction as well as reactor walls were washed three-times with acetone, filtered through pre-weighed filter-paper, and acetone soluble (AS) and acetone insoluble or solid residue (SR) fractions were obtained. The aliquot of AS fraction was evaporated under reduced pressure in rotary evaporator at  $40^\circ \text{C}$  and the dry matter of AS fraction was determined. Solid residue (SR) was

dried overnight in oven at  $105^\circ \text{C}$  and weighed. The total conversions and yield of WS, AS and gas fractions, all expressed in %, were calculated relative to initial amount of dry cellulose according to following equations:

$$\begin{aligned} \text{overall conversion (wt\%)} &= \\ &= 100 - \frac{m_{\text{SR}}}{m(\text{initial cellulose})} \times 100 \end{aligned} \quad (1)$$

$$\begin{aligned} \text{yield of products (wt\%)} &= \\ &= \frac{m(\text{WS or AS})}{m(\text{initial cellulose})} \times 100 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{yield of gases and loses (wt\%)} &= \\ &= 100 - \left( \frac{m_{\text{WS}} + m_{\text{AS}} + m_{\text{SR}}}{m_{\text{initial cellulose}}} \right) \times 100 \end{aligned} \quad (3)$$

Similarly, the weight fraction of SR was calculated as:

$$w(\text{SR}) (\text{wt\%}) = \frac{m(\text{SR})}{m(\text{initial cellulose})} \times 100 \quad (4)$$

where  $m$  denotes measured weight of dry matter of SR, WS or AS fraction. The experiments at each condition were done in duplicate and average value was calculated.

### Analysis

The sugars were determined by HPLC system (Agilent Technologies 1200 Series) equipped with ELSD detector (Agilent Technologies 1200 Series), according to modified method reported by F. A. Agblevor *et al.*<sup>18</sup> An Agilent Carbohydrate column ( $250 \times 4.6 \text{ mm}$ ) packed with  $5 \mu\text{m}$  spherical polymer beads coated with proprietary bonding material was used together with Eclipse XDB-C18 pre-column (Agilent,  $150 \times 4.6 \text{ mm}$  cartridge,  $5 \mu\text{m}$ ) at  $30^\circ \text{C}$ . The mobile phase consisted of A: water, and B: acetonitrile. To analyze the mixture of monomers and dimers, the chromatograph was initially run with flow rate of  $1.2 \text{ ml min}^{-1}$  in the isocratic mode (acetonitrile:water, 85/15 v/v) for 25 min, and then it was shifted to gradient mode at the flow rate of  $1 \text{ ml min}^{-1}$ . The water content was increased from 15 % to 35 % in 10 minutes, and then reduced to 15 % in 10 minutes. The total run time was 45 minutes, with 10 minutes of post run. The ELSD was operated at  $40^\circ \text{C}$ , 0.35 MPa and nitrogen was used as the nebulizing gas.

Gaseous samples were analyzed by gas chromatography (Shimadzu) to measure vol% of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$ . GC was equipped with 2 m long  $\times$  1 mm diameter Restec ShinCarbon 100/120 col-

umn and thermal conductivity detector ( $T=100\text{ }^{\circ}\text{C}$ ). Helium as the carrier gas was used. The column oven temperature program:  $40\text{ }^{\circ}\text{C}$  (hold 3 minutes), raised to  $160\text{ }^{\circ}\text{C}$  ( $8.0\text{ }^{\circ}\text{C min}^{-1}$ , hold for 30 minutes), split ratio = 1:3.

The AS fraction and solid residue spectra were recorded using a Shimadzu Instrument IR-8000 spectrophotometer within the range of  $4000\text{--}400\text{ cm}^{-1}$  by standard KBr pelletization method.<sup>19</sup>

## Results and discussion

### Effect of reaction temperature and residence time on cellulose conversion

Fig.1. shows the influence of residence time (0–60 minutes) and temperature ( $220^{\circ}$ ,  $250^{\circ}$  and  $300\text{ }^{\circ}\text{C}$ ) on overall conversion determined by Eq. 1. It is evident, roughly, that decomposition of cellulose increases with increasing reaction temperature from  $220\text{ }^{\circ}\text{C}$  to  $300\text{ }^{\circ}\text{C}$ . At low-temperature HT conversion at  $220\text{ }^{\circ}\text{C}$ , conversion increases almost linearly with increasing of residence time and achieves a value of 63.7 % at 60 minutes, with evident tendency to continue to rise with further increasing of residence time. At middle – temperature HT reactions at  $250\text{ }^{\circ}\text{C}$  cellulose starts to decompose very quickly, achieving overall conversion of 87.7 % in only 5 minutes, but after that, it drastically decreases (to 53.2 % at 60 minutes). At temperature  $300\text{ }^{\circ}\text{C}$ , maximal overall conversion 78.5 % has been achieved in only 3 minutes. Further increase in reaction time has no effect on it.

The phenomenon for HT conversion of cellulose, observed at temperatures of  $250\text{ }^{\circ}\text{C}$  and higher, is a result of competition of the two general groups of reactions: dissolution and hydrolysis of cellulose to primary hydrolysis products on the one side, and

their further repolymerization, condensation and pyrolysis to form char, gases and oils on the other side, occurring in parallel in the reaction system of cellulose with subcritical water.<sup>20,21</sup> In general, the cellulose in subcritical water is subjected firstly to depolymerization into oligosaccharides ( $\text{DPs} = 2\text{--}6$ ) and monosaccharides (glucose) and then to hydrolysis and rearrangement/decomposition of glucose and other monomer sugars to various products: fructose, 5-hydroxymethylfurfural (5-HMF), furfural, pyruvaldehyde, dihydroxyacetone, glyceraldehydes, glycolaldehyde, erythrose. At higher temperatures and/or longer reaction time, occurs isomerization, fragmentation and repolymerization of these small compounds into liquid oils, gases and char.<sup>21,22</sup> Similar results were presented by T. Minowa *et al.*<sup>23</sup> for cellulose conversions in catalyst-free hot-compressed water at temperature range  $200\text{ }^{\circ}\text{C}$  –  $350\text{ }^{\circ}\text{C}$  in batch reactor. They demonstrated that cellulose undergoes too quick decomposition at  $T > 240\text{ }^{\circ}\text{C}$  and almost immediate decomposition at  $T > 300\text{ }^{\circ}\text{C}$ . According to product distribution analysis, they reported that cellulose decomposes at temperatures below  $240\text{ }^{\circ}\text{C}$  only to water-soluble products (glucose, cellobiose). By increasing the temperature above  $240\text{ }^{\circ}\text{C}$ , bio-oils and tar were obtained, indicating secondary decomposition and rearrangement of water-soluble sugars to oils and further to gases and char. To discuss more detailed reaction mechanism of biomass conversion in subcritical water, in this work the product distribution in samples obtained from cellulose reactions with subcritical water at  $220\text{ }^{\circ}\text{C}$ ,  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$  at residence time 3–60 min has been determined.

### Effect of reaction temperature and time on water-soluble (WS) products yield

Fig 2. shows the yield of WS fraction at  $220\text{ }^{\circ}\text{C}$ ,  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$ , as a function of residence time. The yield of WS fraction at  $220\text{ }^{\circ}\text{C}$  ranges from 4.3 % at 3 minutes to 33.6 % at 60 minutes, indicating slow conversion of cellulose to WS products at this temperature. By increasing the temperature to  $250\text{ }^{\circ}\text{C}$ , yield of WS product increases significantly. The yield reaches maximum at 5 minutes (51.4 %) and after that it constantly decreases to only 11.0 % at 60 minutes. By further increasing the temperature, WS yield drastically decreases. At  $300\text{ }^{\circ}\text{C}$ , the yield reaches maximal value of only 10.0 % at in 3 minutes, and after that it starts to decrease slightly to 3 % at 60 minutes.

It is evident that WS compounds are the major liquid products of cellulose liquefaction at  $220\text{ }^{\circ}\text{C}$  because yield of AS compounds at this temperature is very low (Figure 3). This result suggests that conversion of cellulose at low temperature ( $T \leq 220\text{ }^{\circ}\text{C}$ ) occurs only through reactions of dissolu-

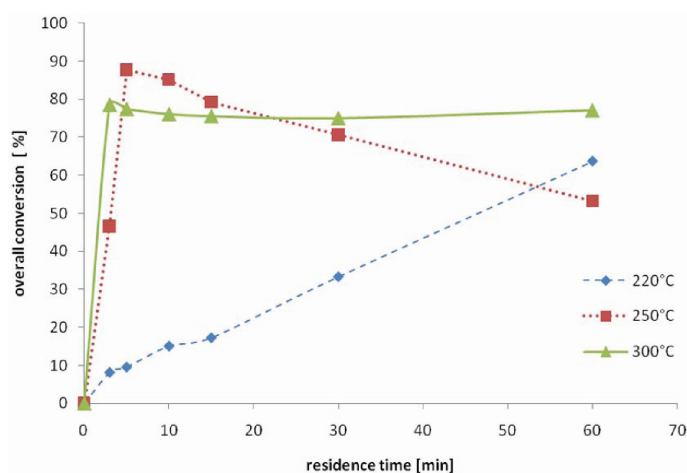


Fig. 1 – Effect of residence time on overall conversion of microcrystalline cellulose at temperatures  $220\text{ }^{\circ}\text{C}$ ,  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$

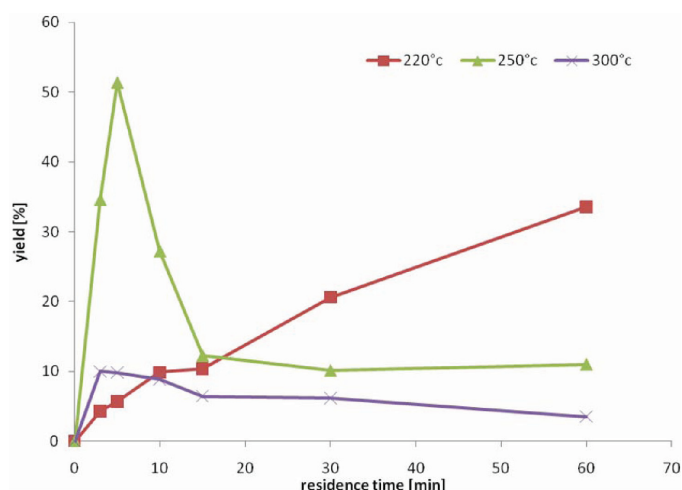


Fig. 2 – Effect of temperature (220 °C, 250 °C and 300 °C) and residence time on WS yield

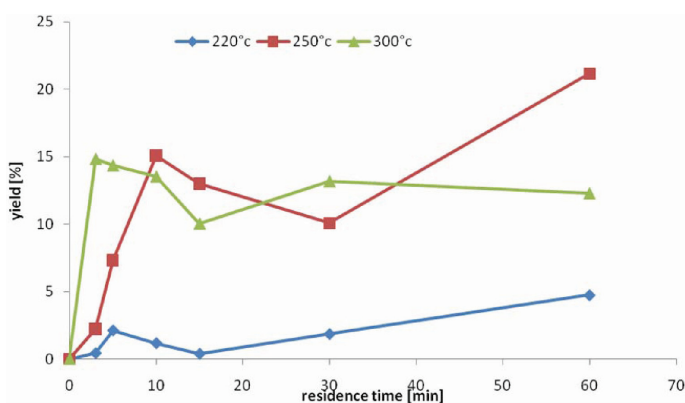


Fig. 3 – Effect of temperature (220 °C, 250 °C and 300 °C) and residence time on AS yield

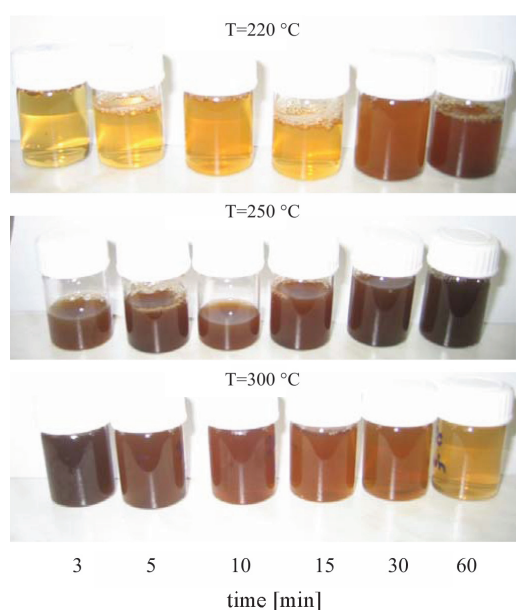


Fig. 4 – Color changes of WS products obtained at various temperature (220 °C, 250 °C and 300 °C) and reaction times (3 to 60 minutes)

tion and hydrolysis to water-soluble sugars (oligomers and monomers) and further products of their dehydration to carboxylic acids, aldehydes and ketones. Secondary reactions to bio-oil (AS phase), gases or char could be neglected at this temperature, even at high residence time. Secondary reactions of WS primary products start at 250 °C and are more obvious at 300 °C. Even at higher temperatures or/and long residence time they undergo accelerated decomposition/conversion to water-insoluble, long-chain carboxylic acids/esters and hydrocarbons, referred to as bio-oils (here AS fraction). The similar conclusions were presented by T. Minowa *et al.*<sup>23</sup> and E. Kamio *et al.*<sup>24</sup>

To gain better insight into the reaction mechanism of cellulose transformation in subcritical water, a more detailed analysis of WS products was done. Even changes in color of WS fractions obtained at different temperatures and reaction times indicated different composition (Figure 4).

Considering that cellulose undergoes decomposition to oligomers and monomers sugars, the determination of most relevant carbohydrate sugars (cellobiose, sucrose, glucose, fructose, ribose, xylose, arabinose, mannose, galactose, maltose and lactose) in WS fraction was done on HPLC. Fig. 5a-b presents yields of mainly detected sugars as a function of residence time at 220 °C and 250 °C. Only three compounds were detected in all samples: glucose, cellobiose and lactose. At 220 °C the glucose concentration slowly increased with reaction time from 11.2 % at 3 minutes to maximal 57.2 % at 30 minutes.

This is a result of slow hydrolysis of cellulose. Small quantities of cellobiose were obtained only at short reaction time (up to 10 minutes), after that, by prolongation of reaction all cellobiose depolymerized to glucose. At 250 °C, content of glucose reached maximum 63.3 % in only 3 minutes, after that it decreased rapidly and at 15 minutes only 2.8 % of glucose remained. Cellobiose was detected only in samples obtained at 3 and 5 minutes of reaction time, indicating rapid cellobiose conversion to glucose at these temperatures. In all samples obtained at 300 °C, no sugars were detected, confirming that at these temperatures depolymerization of cellulose and further glucose conversion to other products occurs in a few seconds. This confirms that conversions at this temperature are very rapid.<sup>23,26</sup> A similar effect was detected by S. Kumar and R. B Gupta during the research of hydrolysis of microcrystalline cellulose in subcritical and supercritical water (temperature range of 302–405 °C, pressure of 27.6 MPa, residence time 2.5–8.1s), showing that 66.8 % of crystalline cellulose can be converted to hydrolysis products (oligomers and glucose) at 335 °C and 27.6 MPa in only 4.7 s.<sup>20</sup>

According to these results and considering that glucose is the most important bio-based platform feedstock for production of commodity chemicals, such as sugar alcohols, levulinic acid, succinic acid and others,<sup>26</sup> it is very important to optimize process conditions to maximize glucose yield as intermediate precursor in chemicals production.

Besides the temperature (and water properties), the results suggest that residence time also affect product distribution (and reaction mechanism). In batch reactor, residence time of mixture is long, enabling the secondary reactions of the hydrolysis products and increased yield of oil and char, and low yield of sugars. The comparative study of reactions of cellulose in batch and flow-type of reactor systems showed that in flow-type reactor systems, the cellulose hydrolyzes to minimal contents of condensation/pyrolysis products, whereas in batch-type higher yields of these products were detected.<sup>12,22</sup> Therefore, it is very important to investigate the fundamental reactions of biomass degradation in appropriate reactor systems and conditions, to avoid secondary reactions of primary products.

#### Effect of reaction temperature and time on acetone-soluble (AS) products yield

The effect of temperature and reaction time on the conversion of cellulose to acetone-soluble (AS) compounds is demonstrated in Fig.3. It is clear that AS fraction yield at 220 °C is very low. At 3 minutes, the AS fraction yield was only 0.4 % and reached maximal value of 4.7 % after 60 minutes. As temperature increases to 250 °C, bio-oils (AS) formation increases from 2.2 % at 3 minutes to maximal 21.1 % at 60 minutes. With the further increase in temperature to 300 °C, the yield of AS products was in the range of 10.1 % to 14.9 %, and stayed almost constant at all reaction times. At the same time, yield of gases and char drastically increased (Figs. 7 and 8). This implies that at higher temperatures (300 °C and higher), condensation and cracking reactions of AS compounds (resulting in formation of carbonaceous solid product, referred to as hydrochar, and gases) are obviously dominant over the dehydration of WS products and formation of bio-oils. So, to further increase bio-oil yield, this side-reaction must be depressed. This could be done by using various catalysts, mostly alkaline salts, such as  $\text{Na}_2\text{CO}_3$ ,  $\text{KOH}$ ,  $\text{K}_2\text{CO}_3$ , etc.<sup>26,27,28</sup>

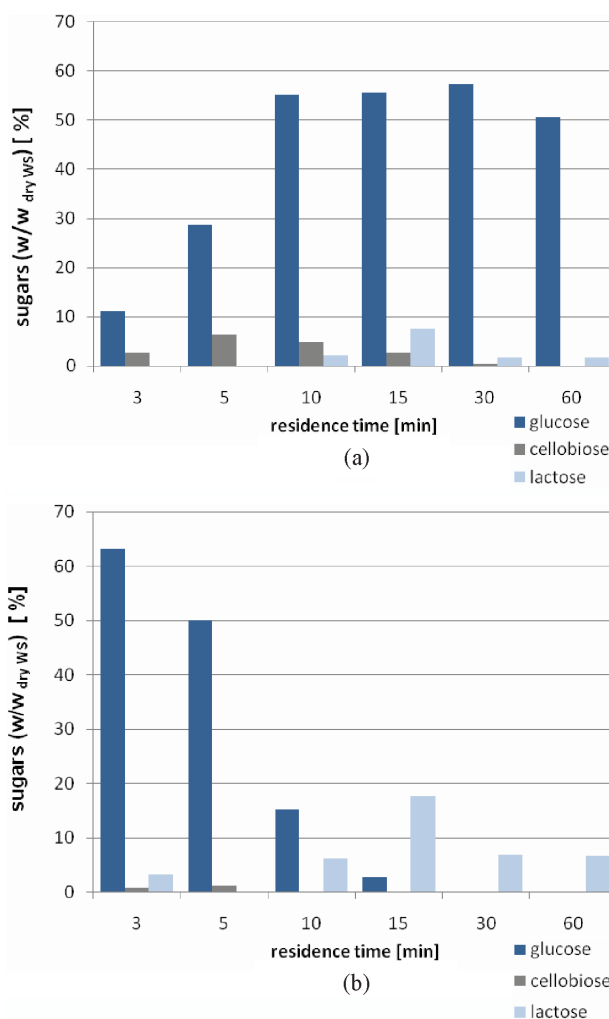


Fig. 5 – Mass percentage of detected sugars in WS products (on the base of dry WS matter) in dependence on residence time at (a) 220 °C and (b) 250 °C

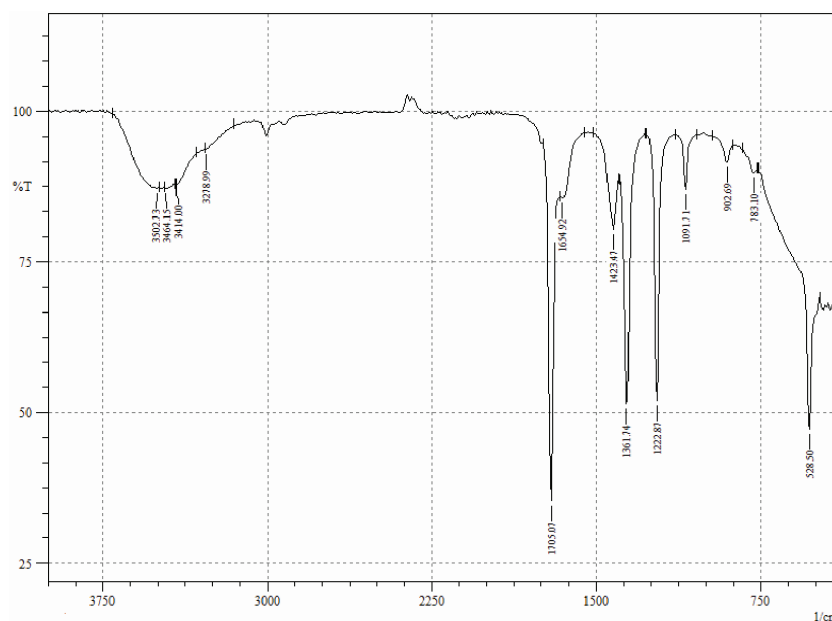


Fig. 6 – FTIR spectra of AS sample (experimental conditions: 250 °C, residence time 15 min)

The compositional structure of AS fraction was analyzed using FTIR spectroscopy in the mid-infrared region ( $200\text{--}4000\text{ cm}^{-1}$ ). In Fig. 6, the FTIR spectra of typical AS sample can be seen. It was obtained at  $250\text{ }^{\circ}\text{C}$  and 15 minutes. All other samples have similar functional groups. The spectra shows that the main absorbance bands were attributed to alcohols ( $3500\text{--}3450\text{ cm}^{-1}$ ), carboxylic acids (O–H stretch at  $3000\text{ cm}^{-1}$  and  $1430\text{--}1370\text{ cm}^{-1}$ ), ketones (very strong C=O vibration at  $1705\text{ cm}^{-1}$ ), primary, secondary and tertiary alcohols, phenols, esters (C–O stretching at  $1250\text{--}900\text{ cm}^{-1}$ ). Therefore, it could be concluded that the AS fraction consists mostly of a mixture of carboxylic acids, alcohols, phenols, esters, etc., commonly referred to in literature as biocrude or bio-oil. Similar observations for bio oil produced from model and real biomass could be found elsewhere.<sup>29,30</sup>

### Effect of reaction temperature and time on gaseous and solid product formation

Although gaseous and solid products (hydrochar/tar) could be considered primarily as side-products in the HT liquefaction process, highlighting the mechanism of their formation is a very important step for further optimization of the liquefaction process. During the research, at  $220\text{ }^{\circ}\text{C}$  the gas production was not evident (no elevated pressure was detected in reactor after cooling down). Therefore, it can be concluded that the yield of gas and losses expressed according to Eq. 3, at residence time 3–30 minutes, represents only experimental losses of volatile compounds during separation of water and acetone by rotary evaporator, eventual uncompleted extraction of acetone-soluble products from solid residue (which could evaporate during oven-drying at  $105\text{ }^{\circ}\text{C}$ ), as same as losses due to the deposition of insoluble char/tar on the reactor wall. At residence time of 3–30 minutes, where the amount of gas phase is negligible (Fig. 7) and no deposition of insoluble char on reactor wall was observed, total dry mass recovery regarding initial cellulose weight is  $89.5\%$ , which indicates that losses during experiments were generally approximately  $10\%$ .

As can be seen from Fig. 7, at  $250\text{ }^{\circ}\text{C}$  the yield of gases reached maximum  $55.7\%$  at 15 minutes and after that slightly decreased to  $31.6\%$  at 60 minutes. By further increasing temperature to  $300\text{ }^{\circ}\text{C}$ , significant gas formation was evident through elevated final pressure in reactor after cooling down to room temperature. The yield reached the value of  $52.3\%$  very quickly (in only 3 minutes) and increased slightly to  $68\%$  at 60 minutes, indicating enhanced secondary reactions of AS compounds to gaseous and solids at this temperature. A more significant presence of gas phase has been evidenced

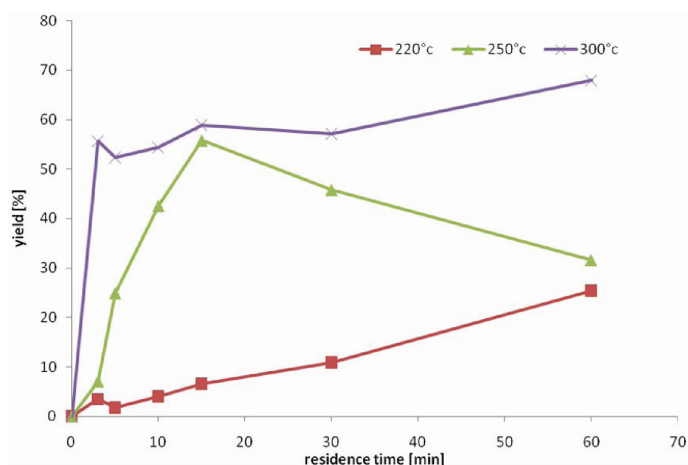


Fig. 7 – Effect of temperature ( $220\text{ }^{\circ}\text{C}$ ,  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$ ) and residence time on “gases and losses” yield

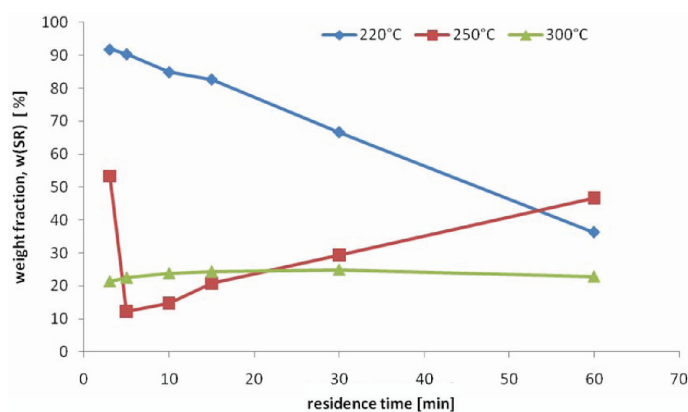


Fig. 8 – Effect of temperature ( $220\text{ }^{\circ}\text{C}$ ,  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$ ) and residence time on solid residue (SR) weight fraction

at  $250\text{ }^{\circ}\text{C}$  at 10 minutes of residence time. A gas-phase analysis of samples at  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$  shows that main gases at  $250\text{ }^{\circ}\text{C}$  were  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2$  (max.  $29.7\text{ vol}\%$  at 5 min). This is a result of reversible water-gas shift reaction at lower temperature in which  $\text{H}_2$  is formed. With increasing the temperature to  $300\text{ }^{\circ}\text{C}$ ,  $\text{vol}\%$  of  $\text{CO}_2$  is decreased and at the same time,  $\text{vol}\%$  of  $\text{CO}$  and  $\text{CH}_4$  is increased, due to another reversible reaction of methanation.<sup>31</sup>

Fig. 8 presents the weight fraction of SR, remaining after reactions, vs. reaction time at  $220\text{ }^{\circ}\text{C}$ ,  $250\text{ }^{\circ}\text{C}$  and  $300\text{ }^{\circ}\text{C}$ . From declining curve of SR with residence time at  $220\text{ }^{\circ}\text{C}$  and from light color of residual cellulose observed after reaction, it is evident that SR represents remained cellulose, not char. Char formation could be detected at  $250\text{ }^{\circ}\text{C}$  and residence times of 10 minutes and higher. By increasing the reaction time, the amount of SR started to increase. WS and AS fractions started to decrease at this moment, indicating char formation by condensation and re-polymerization of these liq-

uid products. At 300 °C, also one part of SR was gasified, resulting in lower and almost constant weight fraction of SR at this temperature.

To confirm the proposed reaction pathway, SR samples were analyzed also by a FTIR spectrophotometer. Characteristic cellulose absorption peaks

are at 3400  $\text{cm}^{-1}$  (O-H stretching vibration), 2900  $\text{cm}^{-1}$  (saturated aliphatic C-H stretching vibration), 1370  $\text{cm}^{-1}$  (-CH<sub>3</sub> bending vibration) and 1100  $\text{cm}^{-1}$  (O-H bending vibration).<sup>29</sup> More significant structural changes, comparing it with raw cellulose, started at 250 °C and 60 minutes and became more evident at 300 °C. As can be seen from Fig. 9, sharp absorption at 3348  $\text{cm}^{-1}$ , 2924  $\text{cm}^{-1}$  and 1423  $\text{cm}^{-1}$  of the SR started to decline at 250 °C and 60 minutes, indicating more significant cellulose decomposition. Peaks from 1033  $\text{cm}^{-1}$  to 1203  $\text{cm}^{-1}$  totally disappeared at 250 °C and 60 minutes, indicating strong dehydration. Furthermore, SR at this and higher temperatures, has carbonyl (C=O) absorption peaks around 1700  $\text{cm}^{-1}$ , which suggests formation of ketones, aldehydes and other carbonyl products. Also, the appearance of the peak at 798  $\text{cm}^{-1}$  in SR, suggests aromatization (aromatic C-H out-of-plane bending vibrations).<sup>29</sup> All these observations correspond to predicted reactions at three different temperature regimes mentioned above. In Table 1, the main reaction pathways at different temperature regimes are proposed.

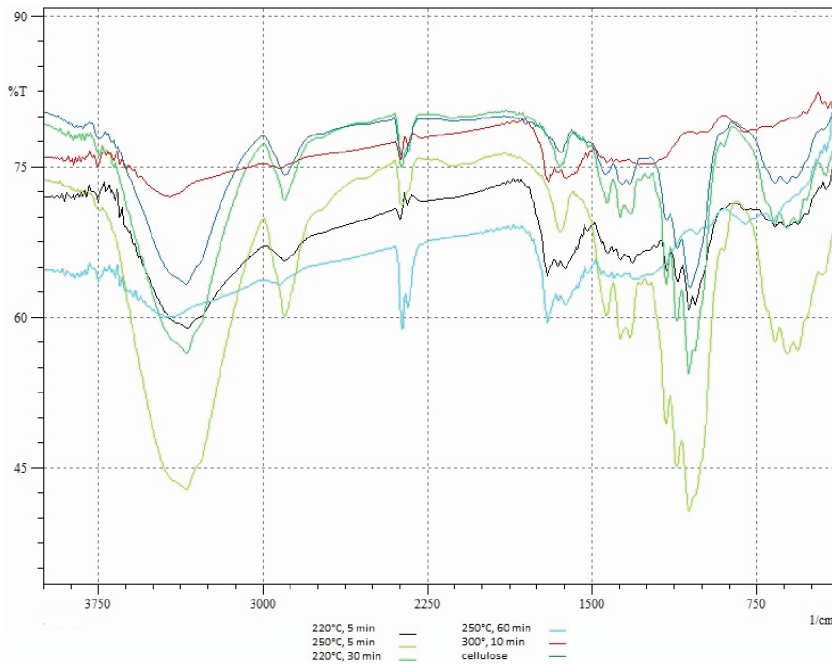


Fig. 9 – Differences in FTIR spectra of raw cellulose and SR samples obtained at various experimental conditions

Table 1 – Reaction regimes and proposed mechanisms for cellulose HT conversion to valuable products in subcritical water (SubCW)

Temperature regimes	Most favorable reaction	Main products
220 °C	Cellulose → oligomers/glucose → <b>aqueous soluble products</b>  <i>Slow reactions!</i> <i>(τ = several minutes)</i>	Levulinic acid, formic acid, acetic acid, oxalic acid, 5-HMF, furfural, glycolaldehyde, glyceraldehydes
250 °C	Cellulose → oligomers/glucose → <b>acetone-soluble products (bio-oil)</b>	Bio-oil (mixture of water insoluble carboxylic acids/esters, ketones, aldehydes, alcohols, alkanes, etc.)
	↓ Short residence time → <b>aqueous soluble products</b> ↓ Long residence time gases and hydrochar	
300 °C	Cellulose → intermediates (aqueous products) → <b>gases</b> hydrochar  <i>Rapid reactions!</i> <i>(τ = few minutes)</i>	Gases (CO, CO <sub>2</sub> , H <sub>2</sub> , CH <sub>4</sub> )
	↓ Short residence time → acetone soluble oils  <i>Very rapid reactions!</i> <i>(τ = few seconds)</i>	



## Conclusions

Conversion of cellulose, a biomass model substance, in subcritical water at mild temperature conditions (220 °C – 300 °C) and autogenous pressure was studied, and the results presented. The aim was to highlight the potential of subcritical water as a unique media for biomass transformation to valuable products. The results show that various products could be obtained. The liquid products were separated regarding their solubility in water and acetone. A water-soluble phase (WS) represents mostly cellulose decomposition products, such as sugar monomers and monomer degradation products (organic acids, 5-HMF, aldehydes etc.). Acetone-soluble phase, referred to also as bio-oil, mainly consists of hydrophobic phenols and its derivatives, ketones, carboxylic acids, long-chain alkanes, etc. Significant gaseous phase was observed only at 300 °C, indicating that non-catalytic gasification of biomass occurs only at temperatures above 300 °C.

In summary, at the three investigated temperatures, different product distribution has been detected. The maximal yield (51.4 %) of WS products was obtained at 250 °C and 5 minutes. Maximal yields of bio-oils were obtained at 250 °C and 60 minutes (21.1 %). Gas yield was maximal (68 %) at 300 °C and 60 minutes, and solid residue (SR) or char formation was the most intensive at 250 °C and 60 minutes. This confirms that targeted control of process conditions (and properties of SubCW), allows for manipulation with selectivity of reactions to desired products. All four main types of products obtained, possess great potential for further synthesis of commodity chemicals, so selection of proper reaction conditions is necessary to optimize selectivity to desired products and minimize undesirable products. More detailed insight into the reaction mechanism to products from real biomass samples is planned in future work.

## List of symbols and abbreviations

$T_c$	– critical temperature, °C
$p_c$	– critical pressure, MPa
$K_W$	– ion product, mol <sup>2</sup> L <sup>-2</sup>
$C_p$	– heat capacity, J g <sup>-1</sup> K <sup>-1</sup>
$\eta$	– viscosity, $\mu\text{Pa s}$
SubCW	– subcritical water
HCW	– hot compressed water
CP	– critical point
SCW	– supercritical water
HT	– hydrothermal

DP	– degree of polymerization
WS	– water-soluble fraction of products
AS	– acetone-soluble fraction of products
SR	– solid residue
FTIR	– Fourier transforms infrared spectrophotometry

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