

Intensification of Cellulose Hydrolysis Process by Supercritical Water. Obtaining of Added Value Products



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Process developed: FastSugars

Summary

This thesis was focused in the development of a new process for converting cellulosic biomass into sugars using continuous ultra-fast micro reactors. This new process was called FastSugars due to the ability of the reactor to produce sugars selectively from cellulosic biomass in milliseconds. The developed process lies mainly in two factors: the **speed** of the reactions and the **control** over the reactions.

The *speed* of cellulose hydrolysis was extremely increased by working with supercritical water (SCW) as reaction medium, making it possible to completely hydrolyze cellulose in less than 100 ms. In addition, an effective *control* over the reactions by setting instantaneous heating and cooling methods allows the obtaining of high sugars yields. The other *control* key is the choice of reaction medium: SCW. This is highly important because it drives the hydrolysis reactions. In a SCW medium the reactions of glucose isomerization and dehydration are highly inhibited favoring the obtaining of high sugars yield and completely disfavoring the production of the undesired 5-hydroxymethylfurfural. A new reaction model was created and validated for cellulose and glucose hydrolysis elucidating the important factors to control the hydrolysis reactions: the ions concentration.

This improvement in the process makes possible to change the huge volume of the traditional hydrolysis reactors (enzymatic) to the small supercritical water micro reactor without losing selectivity and yield but increasing them. This change in the required volume is the key to develop the new philosophy of decentralized production of chemicals and fuels from renewable biomass. The FastSugars process allows obtaining sugars yields as high as 95% from cellulose hydrolysis and 75% from wheat bran hydrolysis. In addition high sugar content biomasses (Molasses and inulin) were employed to produce lactic acid. Near to 50% of the biomass was converted into lactic acid in 3 s of reaction time.

Finally, an energetic evaluation of the process was done in order to evaluate its applicability. The strategy was to link the cellulosic biomass hydrolysis process to the traditional methods of heat and power production by Combined Heat and Power Schemes. It was determined that the energy production per unit of fuel of the CHP schemes was increased in 10% by linking the process. In addition, using the residual heat and power from the CHP streams it is possible to completely hydrolyze the cellulosic biomass without the requirement of energy.

This PhD thesis is composed of 9 research articles published in International Journals like: ChemSusChem, Green Chemistry, Bioresource Technology (2), Chemical Engineering J., Catalysis Today and J. of Supercritical Fluids (3).

State of the Art

World Economy Context

In the last century, the production of chemical compounds has been founded on the availability of high amount of petroleum at low prices. These processes are developed in large chemicals plants that allow the reduction of the products prices. This production concept allowed the big development of the economy in the 20th century. Nowadays, new environmental friendly processes capable of producing chemicals from renewable and "inexhaustible" raw materials are searched. In addition, this new way of production look for a reduction in CO₂ emissions, a challenging goal that should be accomplish by the productive sector. The use of biomass as alternative carbon resource for the production of chemicals and fuels has been extensively studied in the last years. The use of biomass as raw material makes necessary to change the concept of big and centralized chemicals plants (petrochemical industry) into decentralized and efficient processes in small and versatile plants that can be placed near to the source of biomass[1]. The accomplishment of this goal was analyzed in this PhD Thesis by using supercritical water as reaction medium. This technology allows the process intensification of cellulose hydrolysis using low extremely reaction times, which will result in small (milli or micro) and easy scalable reactors.

BioEconomy Development by Supercritical Fluids

In the last years a general tendency has been developed towards a society supported in bioeconomy. This term refers to the sustainable production and conversion of biomass into a range of food, health products, fibers, industrial products and energy [2]. Biobased industries, based in the use of renewable materials and energy, still have to be developed in order to support a decentralized production as an alternative to the well supported centralized petrochemical production plants [1]. In order to accomplish this challenge, research must be focused on achieving the development of environmental compatible processes, the efficient handling of energy and reducing the equipment costs. Environmental friendly processes are characterized by high yield and high selectivity. This is achieved by simplifying the number of processes steps, by searching opportunities among new raw materials and by using clean solvents as water or carbon dioxide. Equipment cost reduction involves the development of compact apparatus with short operation times: changing the reaction time from minutes to milliseconds allows a reactor volume reduction from m³ to cm³. The use of pressurized fluids has been proposed as an environmentally compatible process to integrate the depolymerization-reaction-separation processes. Particularly, high-temperature pressurized water has proved to be a good solvent for clean, safe and environmentally benign organic reactions [1, 3-8]. Main advantages that make hydrothermal media a promising alternative for biomass processing are: (1) direct use of raw material regardless of its water content, which implies an important energy saving; (2) the same reaction medium can be used for the transformation of different biomass fractions; (3) mass transfer limitations can be reduced or avoided, thus reaction rates are faster [5, 8-10]. Furthermore, tunable properties of the reaction medium act as a control factor for the reaction selectivity, avoiding the generation of by-products. The change in the dielectric constant is proportional to the density and inversely proportional to the temperature. Hydrogen bonds behavior is analogous to that of the dielectric constant [3]. Another important property of the aqueous reaction media is the ionic product of water (K_w). The maximum value of the ionic product of water is presented at a temperature around 300°C (K_w = 10⁻¹¹). This creates a medium with high H⁺ and OH⁻ concentrations, favoring in this way acid/basis catalyzed reactions. Above the critical temperature of water (374°C), K_w decreases drastically (K_w = 10⁻²⁵) [11]. At higher pressures (P > 60 MPa) the K_w again presents values similar to those of ambient water.

Problem Addressed

Focus of the project

The aim of this PhD Thesis was to develop a process capable of converting cellulosic materials into valuable products such as chemicals and fuels using supercritical water as reaction medium. Specifically, the goal was the achievement of an efficient hydrolysis process of cellulosic materials in micro reactors. These micro reactors are compact and easily scalable which will allow a reliable production of a bio-based industry matrix in the countryside, where the biomass is produced (decentralized production).

Key Innovations, Applications, Implementations and Results

PhD Thesis layout

In order to reach the goal of this project, the research work was organized as follows. First, a review of the available technologies for biomass hydrolysis in sub- and supercritical water was done.

This review, was published in the Journal of Supercritical Fluids in the special issue *Workshop on Supercritical Fluids and Energy*.

 Danilo A Cantero, M Dolores Bermejo and M José Cocero. Biomass refining processes intensification by supercritical water. Journal of Supercritical Fluids. 96, 21-35, 2014. IF: 2.571.

Then, the thesis was structured in 5 pillars: (1) Technology development, (2) Kinetics study of model biomasses, (3) Production of chemicals, (4) Processing of natural biomass and (5) Energetic study of the technology.

1. Technology development

It was designed and built a novel facility able to continuously hydrolyze cellulosic biomass at temperatures between 250°C and 400°C, pressures of up to 30 MPa and reaction times of between 0.004 s and 40 s. The main advantage of the facility was its ability to start and end the reactions extremely fast, avoiding degradation and/or uncontrolled reactions. The heating method of the cellulosic stream was achieved by mixing with supercritical water. The cooling methods used to stop the reactions was a sudden expansion. The sudden depressurization provokes an instantaneous cooling of the fluid (Joule-Thomson effect). These methods showed to be very efficient for managing biomass hydrolysis in supercritical water allowing a strict control of reaction time and a concentration of the products by separating the produced vapor after flash it. In Figure 1 it is shown a schema of the designed experimental setup. This facility was used to study cellulose hydrolysis in pressurized water. It was observed that the glucose selectivity obtained from cellulose was improved by using ultra-fast reactions in which a selective medium was combined with an effective reaction time control. A selective production of glucose, fructose and cellobiose (50% w·w⁻¹) or total mono-oligo saccharides (>96% w·w⁻¹) was obtained from the cellulose in a reaction time of **0.03 s**. Total cellulose conversion was achieved with a 5-hydroxy-methyl-furfural (5-HMF) concentration lower than 5 ppm in a novel micro-reactor.

Reducing the reaction time from minutes to milliseconds opens the possibility of moving from the conventional m³ to cm³ reactor volumes. Controlling the hydrolysis reactions makes it possible to obtain selective products with high yields.

The development of this facility was published in the journal *Bioresource Technology*.

 Danilo A Cantero, M. Dolores Bermejo and M José Cocero. High glucose selectivity in pressurized water hydrolysis of cellulose using ultra-fast reactors. *Bioresource Technology*.135, 697-703, 2013. IF: 5.039.

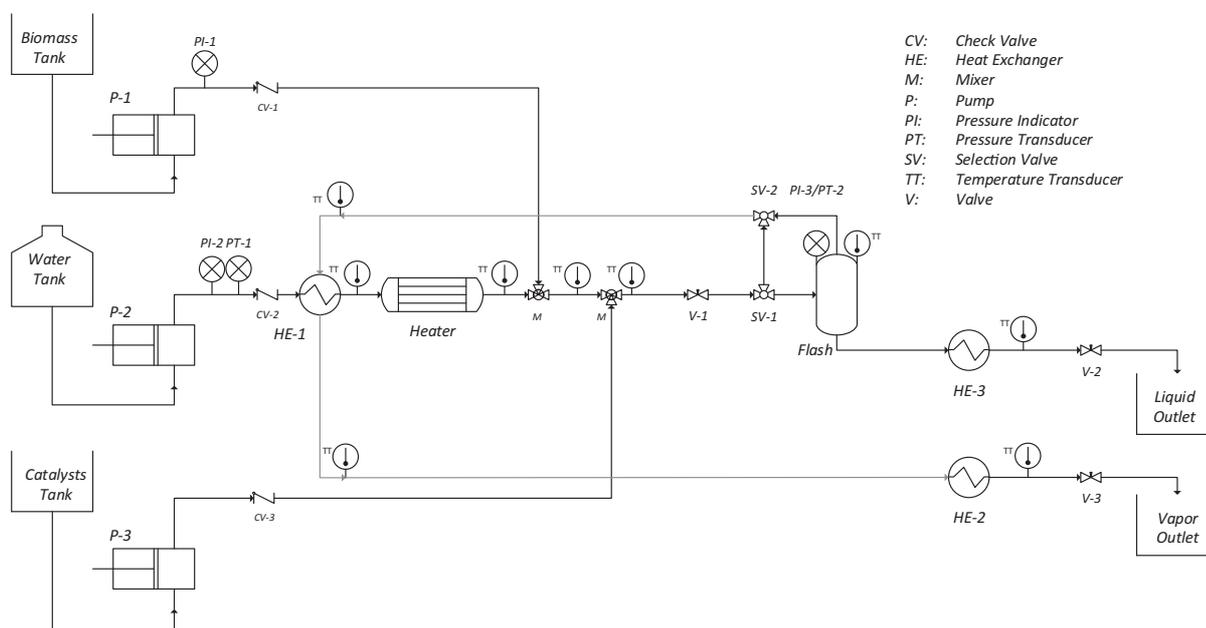


Figure 1. Designed and built Experimental Setup.

2. Kinetics study of model biomasses

Once the experimental setup was built it was employed to carry out several kinetic studies of cellulose hydrolysis. The main analyzed variable were: temperature, pressure, reaction medium and reaction time. To do so, a mathematical model was developed in order to predict the evolution of the cellulose concentration and its derivatives. A reaction schema was proposed, and kinetics parameters currently unavailable in literature were adjusted, using the experimental data obtained with the experimental device developed in the Thesis. The kinetics for cellulose hydrolysis showed a change around the critical point of water, being the activation energy $154.4 \pm 9.5 \text{ kJ}\cdot\text{mol}^{-1}$ and $430.3 \pm 6.3 \text{ kJ}\cdot\text{mol}^{-1}$ below and above the critical point, respectively. The activation energy for oligosaccharide hydrolysis was $135.2 \pm 9.2 \text{ kJ}\cdot\text{mol}^{-1}$ and $111.5 \pm 9.1 \text{ kJ}\cdot\text{mol}^{-1}$ for the glucose to fructose reaction. The kinetics of 5-hydroxymethylfurfural formation showed a drastic change at 330°C . The activation energy for 5-HMF formation is $285 \pm 34 \text{ kJ}\cdot\text{mol}^{-1}$ and $-61.3 \pm 15.7 \text{ kJ}\cdot\text{mol}^{-1}$ at temperatures below and above 330°C respectively. Above 330°C the low density and ionic product of the medium would disfavor the 5-HMF formation.

This kinetic study presented above was published in the *Journal of Supercritical Fluids*.

 Danilo A Cantero, M Dolores Bermejo and M José Cocero. Kinetic analysis of cellulose depolymerization reactions in near critical water. *The Journal of Supercritical Fluids*. 75, 48-57, 2013. IF: 2.571.

After that, many efforts were done by author to determine the role of reaction medium in the hydrolysis selectivity. To do so, many hydrolysis experiments were done to optimize the reaction model. It was found that at extremely low reaction times (0.02 s), cellulose was hydrolyzed in supercritical water ($T=400^\circ\text{C}$ and $P=25 \text{ MPa}$) to obtain a sugar yield higher

than 95 wt %, whereas the 5-hydroxymethylfurfural (5-HMF) yield was lower than 0.01 wt %. If the reaction time was increased to 1 s, the main product was glycolaldehyde (60 wt %). Independently of the reaction time, the yield of 5-HMF was always lower than 0.01 wt %. To evaluate the reaction mechanism of biomass hydrolysis in pressurized water, several parameters (temperature, pressure, reaction time, and reaction medium) were studied for different biomasses (cellulose, glucose, fructose, and wheat bran). **It was found that the H^+ and OH^- ion concentration in the reaction medium as a result of water dissociation is the determining factor in the selectivity.** The reaction of glucose isomerization to fructose and the further dehydration to 5-HMF are highly dependent on the ion concentration. By an increase in the pOH/pH value, these reactions were minimized to allow control of 5-HMF production. Under these conditions, the retroaldol condensation pathway was enhanced, instead of the isomerization/dehydration pathway. The assumed reaction pathway is shown in Figure 2.

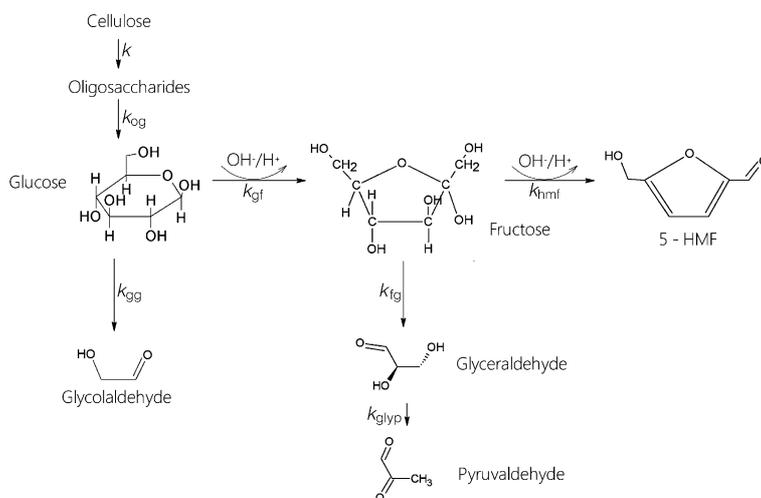


Figure 2. Cellulose hydrolysis pathway in pressurized water.

So, it can be concluded that cellulose hydrolysis in supercritical water will produce soluble sugars as main product if the reaction time is kept at extremely low values (between 0.03 to 0.2 s). On the other hand, if the reaction time is increased up to 1 s or higher, the main product will be glycolaldehyde because the reactions of 5-HMF are highly inhibited at supercritical conditions. This concept was schematized in Figure 3.

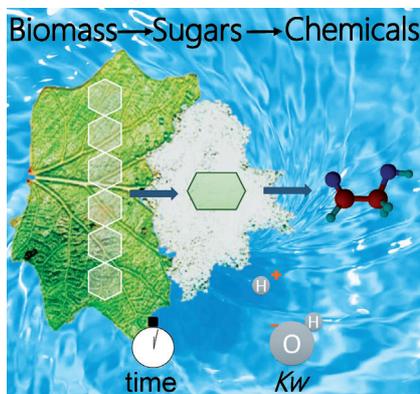


Figure 3. Key parameters in the selectivity of cellulose in supercritical water.

This study about the role of the reaction medium in the reactions of cellulose hydrolysis was published in the Journal ChemSusChem.

 Danilo A Cantero, M Dolores Bermejo and M José Cocero. Governing Chemistry of Cellulose Hydrolysis in Supercritical Water. ChemSusChem. 8, 1026-1033, 2015. IF: 7.117.

Once the reaction pathway and reaction mechanism were elucidated, the model was used to calculate the parameters that relates the effect of temperature and pressure on cellulose and glucose hydrolysis in a hydrothermal media. To do so, cellulose hydrolysis experiments were carried out at temperature between 300°C and 400°C and pressures between 10 MPa and 27 MPa. The main products of cellulose hydrolysis were oligosaccharides, cellobiose, glucose and fructose. The concentration profiles of each component followed a similar behavior at a fixed temperature changing pressure. Nevertheless, glucose and fructose hydrolysis reaction to give dehydration of retro aldol condensation products were strongly affected by pressure and temperature. When increasing temperature in the studied range, the reaction of glucose isomerization to fructose and the production of 5-hydroxymethylfurfural (5-HMF) obtained through fructose dehydration were inhibited. On the other hand, 5-HMF production was favored by high proton concentrations due to water dissociation. Thus, at a constant temperature, the production of 5-HMF was increased by rising the ionic product of water (increasing pressure). The production of glycolaldehyde (retro-aldol condensation of glucose) was increased by rising temperature and pressure. The kinetic constants of the cellulose hydrolysis reactions were determined at the experimented conditions using the experimental results. The kinetic constants were plotted against temperature and pressure (surface) to determine the activation energy and the activation volume for each reaction, respectively. Pressure seems to have no effect on the cellulose hydrolysis kinetic to simple sugars. However, at supercritical water temperatures the increment in pressure disfavored the glucose isomerization and dehydration reactions.

This study about the pressure dependence of the kinetics was published in the Chemical Engineering Journal.

 Danilo A Cantero, Ángel Sanchez, M Dolores Bermejo and M José Cocero. Pressure and temperature effect on cellulose hydrolysis in pressurized water. Chemical Engineering Journal. DOI: 10.1016/j.cej.2015.04.076. IF: 4.058.

3. Production of chemicals

The process developed in this Thesis was also tested as alternative for the production of added value products from sugars like fructose and glucose. The reactions of fructose in sub- and supercritical water were analyzed changing the chemical properties of the reaction medium (K_w , ϵ , pH and free radical kidnapers). The reactions were performed in a continuous reactor at 260°C, 330°C and 400°C, at 23 MPa and 27 MPa using water as reaction medium. The pH of the medium was modified using oxalic acid and sodium hydroxide. Also, scavengers (TEMPO and BHT) were tested in order to determine its influences in the radical reactions. The main product of fructose hydrolysis in supercritical water was pyruvaldehyde (>80%, w·w⁻¹) at 400°C and 23 MPa with a reaction time of 0.7 s. Furthermore, the reactions of fructose were analyzed in combination with glucose. It was determined that different retro-aldol condensation products can be obtained depending on the starting material. Fructose produced mainly C-3 molecules (pyruvaldehyde) and glucose produced mainly C-2 molecules (glycolaldehyde). The isomerization of fructose to glucose was negligible and so was the production of C-2 when the starting material was fructose. The yield of 5-HMF was negligible when the starting material was glucose. Three different biomass enriched in fructose (sugar cane molasses, beet molasses and inulin) were tested as

starting material for the hydrolysis process. **It was determined that lactic acid (50%, w·w⁻¹) was the main product of molasses and inulin hydrolysis in a supercritical water medium modified with basic catalysts.**

This study about fructose valorization in supercritical water was published in the Journal Catalysis Today.

 Danilo A Cantero, Luis Vaquerizo, M Dolores Bermejo and M José Cocero. Selective Transformation of Fructose into Pyruvaldehyde in Supercritical Water. Reaction Pathway Development. Catalysis Today. DOI: 10.1016/j.cattod.2014.11.013. IF: 3.309.

In addition, the chemical transformation of glucose into added value products (lactic acid and 5- hydroxymethylfurfural) was analyzed using the developed experimental facility. The reactions of glucose in hot pressurized water were analyzed at 300°C, 350°C, 385°C and 400°C; the pressure was fixed at 23 MPa and 27 MPa for the experiments. No lactic acid was found at those conditions. High yield of glycolaldehyde (80%, w·w⁻¹) was found operating at 400°C and 27 MPa with reaction times of 20 s. Two additives (H₂O₂ and NaOH) were added in different experiments to improve the lactic acid production. The maximum yield of lactic acid was 57% (w·w⁻¹) carbon basis using NaOH (0.5 M) as catalyst at 27 MPa and 400°C with 20 s of residence time. **It was observed that the pH of the medium plays an important role in the selectivity of the process.**

This study about glucose valorization in supercritical water was published in the Journal of Supercritical Fluids.

 Danilo A Cantero, Ana Alvarez, M Dolores Bermejo and M José Cocero. Transformation of glucose into added value compounds in a hydrothermal reaction media. The Journal of Supercritical Fluids, 98, 204-210, 2015. IF: 2.571.

4. Processing of natural biomass

In the aforementioned work, it was demonstrated that Supercritical water (SCW) is an excellent solvent and reaction medium to improve the cellulose hydrolysis selectivity by controlling the reaction time. Then, the conversion of wheat bran into soluble saccharides such as glucose, xylose and arabinose was analyzed at 400 °C and 25 MPa with reaction times between 0.2 and 1 s. The process yield was evaluated for two different products: C-6 (glucose derived from cellulose) and C-5 sugars (saccharide derived from hemicellulose hydrolysis). The production of glycolaldehyde, furfural and 5-hydroxymethylfural (5-HMF) was analyzed as byproduct formation. Operation under supercritical conditions allows a biomass liquefaction of 84% w·w⁻¹ at 0.3 s of reaction time. The obtained solid after the hydrolysis was composed of mainly lignin (86% w·w⁻¹). The highest recovery of cellulose (C-6) and hemicellulose (C-5) as soluble sugars (73% w·w⁻¹) was achieved at 0.19 s of reaction time. An increase in the reaction time decreased the yield of C-6 and C-5. A total recovery of C-5 was achieved at 0.19 s. On the other hand, the highest yield (65% w·w⁻¹) of C-6 was achieved at 0.22 s of reaction time. The main hydrolysis product of C-6 and C-5 was glycolaldehyde, yielding 20% w·w⁻¹ at 0.22 s of reaction time. Furfural and 5-HMF production was highly inhibited under the experimental conditions, obtaining yields lower than 0.5% w/w.

This study about wheat bran hydrolysis in supercritical water was published in the Journal of Green Chemistry.

 Danilo A Cantero, Celia Martínez Fajardo, M Dolores Bermejo and M José Cocero. Simultaneous and Selective Recovery of Cellulose and Hemicellulose Fractions from Wheat Bran by Supercritical Water Hydrolysis. 17, 610-618, 2015. IF: 6.852.

5. Energetic study of the technology.

The topics 1, 2, 3 and 4 of the thesis research demonstrated that cellulosic biomass hydrolysis can be performed in supercritical water with a high selectivity of soluble sugars. In order to complete the study, the energetic aspect were analyzed. The FastSugars process produces high-pressure steam that can be integrated, from an energy point of view, with the whole biomass treating process. This work investigated the integration of biomass hydrolysis reactors with commercial combined heat and power (CHP) schemes, with special attention to reactor outlet streams. The innovation developed in this work allows adequate energy integration possibilities for heating and compression by using high temperature of the flue gases and direct shaft work from the turbine as it is schematized in Figure 4. The integration of biomass hydrolysis with a CHP process allows the selective conversion of biomass into sugars with low heat requirements. **Integrating these two processes, the CHP scheme yield is enhanced around 10% by injecting water in the gas turbine. Furthermore, the hydrolysis reactor can be held at 400 °C and 23 MPa using only the gas turbine outlet streams.**

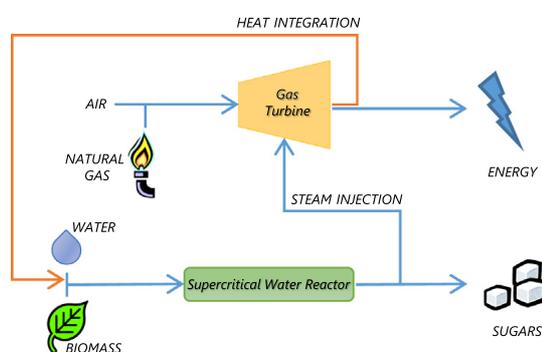


Figure 4. Integration of FastSugars process with the CHP schemes.

This study about energy studies and integration of cellulosic biomass hydrolysis in supercritical water was published in the Journal of Bioresource Technology.

 Danilo A Cantero, Luis Vaquerizo, Fidel Mato, M Dolores Bermejo and M José Cocero. Energetic Approach of Biomass Hydrolysis in Supercritical Water. Bioresource Technology. 179,136-143, 2015. IF: 5.039.

Conclusions of the Thesis

The process of cellulose hydrolysis was intensively studied in near critical water. **A new concept of reactors for reactions in supercritical water was developed.** The used experimental setup is able to operate up to 425°C, 30 MPa with reaction times between 0.004 and 50 s. The used method to start and finish the reaction is achieved by applying sudden changes in temperature, obtaining an isothermal reactor. In this kind of reactor is easy to determine the reaction time of the reagents in the reactor, which will drive to precise results. The continuous operation mode of the reactors and the use of supercritical water as reaction medium showed to be adequate for the selective hydrolysis of biomass. The hydrolysis selectivity obtained in this PhD Thesis was higher than the process selectivity presented in literature for batch, semi-continuous and continuous reactors.

Cellulose hydrolysis was studied at temperatures between 275°C and 400°C and pressures between 10 MPa and 27 MPa. **It was observed that cellulose hydrolysis kinetic is much accelerated by rising temperature than glucose hydrolysis does.** This difference is accentuated at temperatures above the critical point of water, however, both reactions are

enhanced. From this phenomenon it can be taken benefit if an adequate control on reaction time is applied. The total conversion of cellulose at 400°C and 25 MPa takes 0.013 s, if the reaction is stopped at reaction times between 0.013 s and 0.03 s the yield of sugars will be higher than 96% w·w⁻¹. The pressure effect on the kinetics of cellulose is less marked than temperature and reaction time effects. Nevertheless, it plays an important role in the composition of the hydrolysis products. An increment in pressure will produce sugars of higher molecular weights.

The variation of temperature and pressure together allows the modification of the chemical and physical properties of water, thus, the reaction medium. The main properties of water which will affect the kinetics of the process are density and ionic product. It was observed that ***the hydroxide ion and proton concentration in the medium is a driving factor in the reactions in which glucose is converted. At low ion concentrations, the reactions of glucose-fructose isomerization and dehydration are diminished while retro-aldol condensation reactions are benefited.*** The kinetics of cellulose hydrolysis as well as glucose and fructose hydrolysis were studied and the Arrhenius parameters were calculated for each one. Also, the kinetics were analyzed with pressure, obtaining the activation volume of the reaction kinetics.

The reactions of fructose and glucose hydrolysis were studied and the main reaction pathways were developed. Firstly, ***it was found that the main reaction at supercritical conditions is retro-aldol condensation. This reaction produces two-carbon or three-carbon molecules when glucose or fructose is converted respectively.*** The main product of glucose hydrolysis at 400°C, 27 MPa and 20 s of reaction time was glycolaldehyde (>80% w·w⁻¹). On the other hand, when fructose was hydrolyzed at the same conditions, the main product was pyruvaldehyde. The reaction of the glucose and fructose mixture produced a combination of glycolaldehyde and pyruvaldehyde as main products.

The effect of homogeneous catalyst was tested in glucose conversion. It was observed that ***sodium hydroxide favors the reaction of glucose isomerization to fructose as well as the reaction of pyruvaldehyde conversion into lactic acid.***

The developed reactor was tested for the hydrolysis of natural biomass, wheat bran. It was observed that ***the designed experimental setup is capable of recovering the 77% w·w⁻¹ of the wheat bran sugars as soluble sugars in 0.19 s of reaction time.*** The obtained solid particles after hydrolysis were composed of 85% w·w⁻¹ lignin.

Finally, three energetic alternatives have been analyzed for the biomass hydrolysis in supercritical water. According to the thermodynamic calculations, ***the biomass hydrolysis process could be carried out without extra requirements of heat and work if the process is integrated to a plant of heat and power production.*** In addition, the vapor phase produced after the reactor can be used to improve the global yield of the combined heat and power production plants.

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