9th International Conference on Applied Energy, ICAE2017, 21-24 August 2017, Cardiff, UK

Selective dissolution of woody biomass under hydrothermal conditions

Jesús D. Hernández O.[a], Khanh-Quang Tran[b], Thuat T. Trinh [c,d],*

[a]Enegy Department, Politecnico di Milano, 20156 Milano, Italy
[b]Department of Energy and Process Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway
[c]Computing and Design BioNanoChemisry Group, Faculty of Applied Science, Ton Duc Thang University, Ho Chi Minh city, Vietnam
[d]Department of Civil and Environmental Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway

Abstract

This study analyzes semi-continuous hydrothermal hydrolysis of lignocellulosic biomass operating between 200 °C and 300 °C with constant inlet water flow rate. Experiments were executed in a novel reactor system that offered a nearly linear temperature behavior during the heating period with heating rates between 40 °C/min and 60 °C/min and a nearly flat temperature profile during retention. Experimental results suggest that conversion efficiency improved at higher temperatures. After completion of the batch, solid and liquid products were collected and mass balance closures reached an average of 89%. It was discovered that, regardless of the temperature, a minimum of 90% of the total dissolution occurs within the first 15 minutes of the reaction. This work identifies various stages and conditions that favor the dissolution of certain components (hemicellulose, cellulose or lignin).

Keywords: Hydrothermal; Dissolution; Liquefaction; Woody Biomass.

1. Introduction

In recent years, hydrothermal technologies have arisen as very promising technologies to sustainably produce chemicals and fuels from biomass sources. However, state of the art research has shown that conversion efficiency and selectivity of the technology still need to be improved for it to be commercially viable [1]. The use of solid-biomass has also been identified as a hindrance to commercialization. Reactor loading, clogging, costs of feedstock

* Corresponding author. Tel.: +47 4038 5158; fax: +47-73-59-70-21
  E-mail address: trinhthanhthuat@tdt.edu.vn

handling and pumping limitations are all are major drawbacks of using solid biomass [2]. It has been suggested that a pretreatment dissolution step could solve most of the aforementioned problems [1-4].

Nomenclature

Eff_{dis}	percentage of total dissolved mass with respect to initial mass [%]
m_i	mass initial feedstock [g]
S_r	mass solid dried residues [g]
m_j	approximated mass of water soluble products during sampling period -*j*- [g]
T	sampling period [sec]
$m_{c(j-1)}$	collected mass in the previous sampling period [g]
$m_{c(j)}$	collected mass in the actual sampling period [g]
m_{twsp}	total mass of water soluble products [g]
X_{SR}	percentage of solid residues with respect to the initial mass [%]
X_{wsp}	percentage of water soluble products with respect to the initial mass [%]
X_{Lost}	percentage of not recovered mass with respect to the initial mass [%]

One such solution, hydrothermal dissolution (HTD), has been widely investigated in batch, semi-continuous and continuous conditions. The effects of temperature, holding time, and heat rates, on the total dissolution percentage have been studied for many diverse types of biomass [4-7]. Many studies have been conducted in batch settings at low heating rates and long residence time (over 10 mins). Dissolution efficiencies were found to reach up to 80% [5]. However, Hashaikeh *et al.* [4] have suggested that most of the dissolution process takes place during the heating period rather than during the holding time. This finding makes it difficult to draw conclusions about the real impact that temperature has over the dissolution process. This work seeks to further investigate the relationship between temperature and biomass dissolution.

In continuous conditions, researchers have utilized mixed, pressurized, pre-heated water slurries containing dissolved cellulose and other organic compounds to emulate the dissolution reaction of biomasses [7]. This technique reaches very high heating rates and enables the study of process kinetics. This strategy, however, has not been properly implemented in scenarios where relatively big (1mm³) lignocellulose material is used as the feedstock. The main problem in implementing such an experiment is that current pumping technology has difficulty in dealing with this type of material [2].

In this work, a semi-continuous process that enables the dissolution of large biomaterials in hot compressed water is developed. By means of injecting hot compressed water into a bed reactor full of biomass pieces, reaction temperatures were reached in 6 minutes. Diverse experiments were performed at different temperatures and flow rates. The results show that our system can selectively dissolve basic biomass components: lignin, hemicellulose and cellulose with an efficiency of up to 90%.

2. Materials and methods

2.1. Materialss

Lignocellulosic material (Norway spruce) in grain sizes of 2 mm was used as the feedstock with a composition of: 47% Cellulose, 30% Lignin and 23% Hemicellulose[8]. For all experiments, the wood chips were dried overnight in a bench oven at a temperature of 105 ºC. Distilled water with a purity of 98% was used as the reaction media.

2.2. Experimental Setup

High purity water is pumped through a heating furnace where it is brought to sub-critical conditions. The bed reactor with the biomass is connected in parallel to a bypass line that allows the hot-compressed water to pass through during the three hours that the system takes to reach its steady state. A detailed schematic of the pumping system is given in Fig. 1. The bed reactor is made up of a ½" diameter, 15 [cm] long SS 316 tube. A 1/16" SS 316 tube and a heating

band (Max temp. 300ºC) are coiled around the reactor. Finally, the whole reactor and process lines are insulated with Rockwool. Fig. 2 shows the detailed configuration of the custom-made bed reactor. This configuration has a huge amount of flexibility as the controlled variable (reaction temperature) can be influenced by 3 manipulated variables: temperature of the hot-compressed water flowing into the reactor, the rate of cold water pumped through the cooling line and the switching of the on-off state of the heating band.
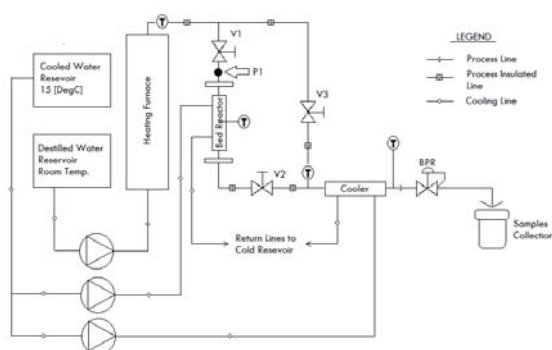

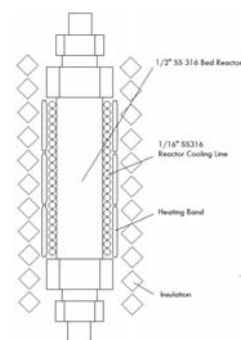Fig. 1. Detailed experimental Setup

Fig. 2. Detailed fixed bed reactor

A detailed explanation of the control philosophy of this configuration is out of the scope of this paper, however, we do outline the fact that the developed system offered an almost linear behavior during the heating period and reached heating rates of up to 60 ºC/min, one of the largest for this type of experiments. Fig. 3 shows the dynamic behavior of the system for different temperatures set-points of the heating furnace.
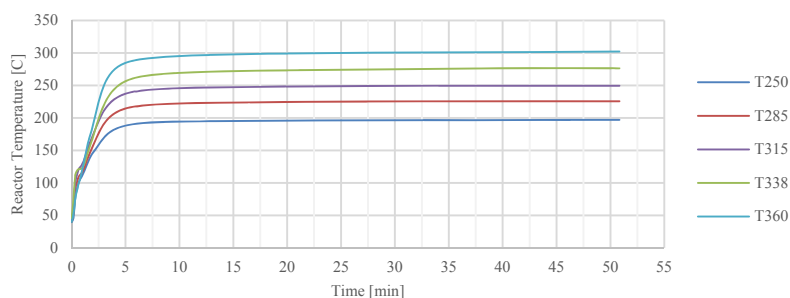

Fig. 3. Typical temperature profile at the bed reactor

2.3. Experimental Procedure

At the beginning of each hydrolysis experiment, a sample of 2.4g of biomass was loaded in the bed reactor. Ultrapure water was flushed through the system at 20 mL/min and atmospheric pressure until no air remained in the lines. Immediately after, the Back Pressure Regulator (BPR) was tightened until the pressure reached 100 Bar. The furnace was then switch-on, the system could reach its steady state and the control strategy of the bed reactor temperature was started. The sampling collection strategy was varied depending on the experiment as follows:

2.3.1. Total dissolution experiments
- Experiments were executed at either 225ºC or 275 ºC for 15, 30, 45 and 60 min.
- A 1L glass container was placed at the outlet of the for liquid products collection.
- At the end of the experiment, liquids collection was stopped and a fast reactor cooling procedure was initiated.
- Biomass solid residues were recovered, dried overnight at 105 ºC and further weighed.

2.3.2. Dynamic dissolution experiments

- Experiments were carried out for five different Temperatures: 200, 225, 250, 275 and 300 °C.
- Samples of 10 [mL] of products were collected in small glass containers of 25 mL capacity.
- The Sampling period for all cases was 75 seconds for the initial 20 minutes. Afterwards, it was doubled every two samples up to 40 minutes when the experiment ended.
- Collected liquid samples were individually weighted and dried for 5 days in a big bench furnace at 80 °C.
- After drying, liquid-free samples were re-weighted and the total mass of water soluble products calculated.
- At the end of the biomass solid residues were recovered, dried overnight at105 °C and further weighed.

2.4. Data Quantification

Dissolution efficiency, instantaneous mass of water soluble products, cumulative mass, and mass balances (solids, water soluble products and mass not recovered) were calculated according to (1) – (6), respectively.

$$Eff_{dis} = \frac{m_i - S_r}{m_i} * 100\% \qquad (1)$$

$$m_j = \frac{T}{60} * \left(m_{c(j-1)} + m_{c(j)}\right), \quad j = 1 \dots 20 \qquad (2)$$

$$m_{twsp} = \sum_{j=1}^{20} m_j \qquad (3)$$

$$x_{SR} = \frac{S_r}{m_i} * 100\% \qquad (4)$$

$$x_{WSP} = \frac{m_{twsp}}{m_i} * 100\% \qquad (5)$$

$$x_{Lost} = (1 - x_{SR} - x_{WSP}) * 100\% \qquad (6)$$

3. Results and discussions

3.1. Total dissolution experiments

The results obtained from this set of experiments, eight runs in total, are summarized in the Tables 1 and 2.

Table 1. Total dissolved mass at 225 °C.

T = 225 °C			
Time [min]	Initial mass [gm]	Final mass [gm]	Diss. Efficiency [%]
15	1.52	0.858	43.55
30	1.543	0.865	43.94
45	1.563	0.827	46.09
60	1.42	0.768	46.1

Table 2. Total dissolved mass at 275 °C.

T = 275 °C			
Time [min]	Initial mass [gm]	Final mass [gm]	Diss. Efficiency [%]
15	1.513	0.293	80.63
30	1.562	0.166	89.37
45	1.505	0.137	90.90
60	1.578	0.128	91.89

The results suggest that temperature has a direct impact on the total dissolved biomass, showing larger efficiencies at higher temperatures. Additionally, it was also found that regardless of the temperature, the majority of the dissolution took place in the initial 15 minutes of reaction. These quantitative findings are in agreement with the observations of the physical properties of the liquids and solid collected during the experiments. While yellow solutions were obtained at the beginning of the process, after a peak in colour around 7 minutes, color intensity decreased continuously. For the experiment at 275 °C, the water turned almost completely clear after 20 mins, while for 225 °C a subtle yellow tone was always observed. Strong changes in the color of the solid residues was observed for the 225 °C experiment but not at 275 °C. Interestingly, the volume occupied by the solid residues of both experiments 225 and 275 °C after 60 mins where the same. Even though chip size variations were invisible to the naked eye, their mass varied considerably. This is therefore an indicator that at elevated temperatures, biomass is not only dissolving in the exterior surface of the chip, but also at its core.
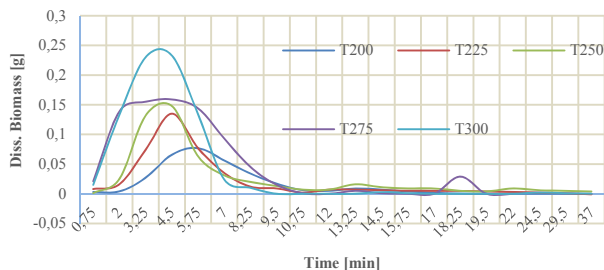
3.2. Dynamic dissolution experiments

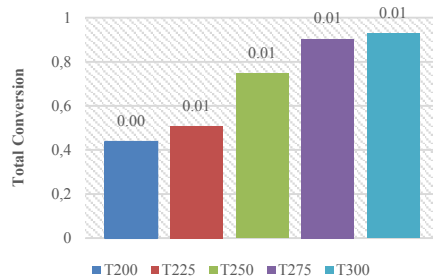Fig. 4. Dynamic collected mass during the experiment.

Fig. 5. Total mass dissolved after 40 mins at different temperatures.

Fig.4. shows the mass collected from every sample at each of the different temperature conditions. For all temperatures, the dissolution profile has a bell shape that peaks between 3:30 and 5 minutes, and the dissolution rate increases with temperature. For medium temperatures (225, 250, 275 °C) total dissolved mass peaked at 0.15g, for 200 and 300 °C the peaks were 0.1g and 0.24g respectively. Fig. 5. summarizes the results obtained from the calculations of total dissolved masses. These results agree with those obtained in Section 3.1. and display a trend in accordance with the composition of the Spruce. At 200 and 225 °C, dissolved mass reached a maximum of 51%, which we believe are the lignin and hemicellulose components of the Spruce. Interestingly, our dissolution efficiency of 75% at 250 °C indicated that dissolution of cellulose is possible at such a low temperature.
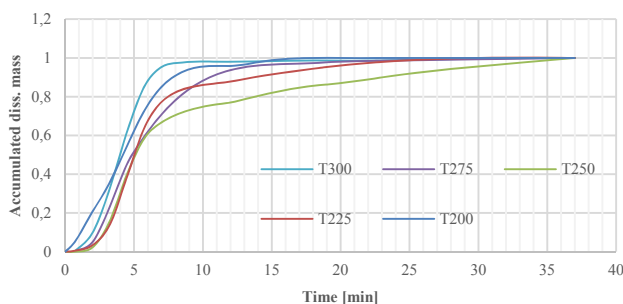

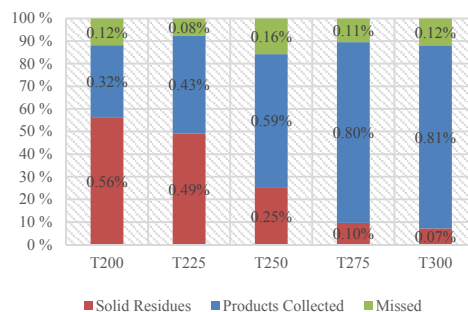Fig. 6. Normalized total collected mass during the experiments

Fig. 7. Mass balances

In Fig 6. the normalized accumulated mass of water soluble products is presented. These curves demonstrate that the hydrothermal dissolution of biomass is a very fast process that reaches more than 80% of the total yield during the first 10 mins. By comparing Fig. 4 and Fig 6, it is possible to conclude that regardless of the temperature, 50% of the total yield of dissolved products is achieved during the initial 4 minutes of reaction. Moreover, the combination of: instantaneous dissolution maximums in Fig. 4., reaction temperatures in Fig. 3. and total dissolved masses Fig. 6., all suggests that:

- At low peaks, 200 °C, only hemicellulose is dissolved.
- At the medium peaks, 225, 250, 275 °C, dissolution of hemicellulose and lignin takes place.
- At high peaks, 300 °C, dissolution of all cellulose, hemicellulose and lignin occurs.

After the initial 4 minutes, it is noticeable that the curves at 200 and 275°C exhibit the slowest decay until the 10-th minute. As for the initial stage of the reaction, by analyzing Fig. 3, Fig. 4. and Fig. 6., it is possible to hypothesize for this second stage of the reaction, minutes 5 to 10, that:

- At 275 °C most of the cellulose dissolution occurs during this period.
- At 200 °C most of the lignin dissolution occurs.

- 250 ºC shows a fast dissolution behavior of lignin and hemicellulose after and before the peak. However, after minute 8 the reaction slows down and steadily dissolves cellulose in small quantities.

In the late stage of the reaction, minutes 11-15, most of the experiments at each of the temperatures have reached over 90% of the total yield they produce, with the least effective experiment (250ºC) reaching only 83%. Lastly, during the final stage of the reaction, all experiments have reached their completion except the reaction carried out at 250 ºC. Our findings showing the effects that temperature has on both speed and selectivity of the process are summarized in Table 3.

Table 3. Dissolution process classification by stage and type of dissolved mass.

Velocity of Reaction – Type of biomass dissolved				
Temperature	Early Stage	Second Stage	Late Stage	Final Stage
[ºC]	[0-4 mins]	[5-10 mins]	[11-15 mins]	[16-40 mins]
200	F – Hmc	S – Hmc / S – Lig	Reaction Finished	Reaction Finished
225	F – Hmc	S – Hmc / S – Lig	S – Lig	Reaction Finished
250	F – Hmc / S – Lig	S – Hmc / S – Lig / S – Cel	S – Cel	S – Cel
275	UF – Hmc / UF – Lig	F – Cel	S – Cel	Reaction Finished
300	UF – Hmc / UF – Lig	UF – Cel	Reaction Finished	Reaction Finished

UF: Ultra-Fast; F: Fast; S: Slow; Hmc: Hemicellulose; Lig: Lignin; Cel: Cellulose.

4. Conclusions

Dissolution of woody biomass in a novel semi-continuous reactor was studied in this work. It was found that the constitutive elements of the feed-stock could be selectively dissolved by targeting specific reaction temperatures and heating rates. Additionally, the total yield of obtained products is heavily influenced by the temperature. A maximum dissolution efficiency of 93% was reached at a reaction temperature of 300ºC without the need for intermediate steps contrary to what has been previously suggested by other authors [4]. When compared to other experiments reported in literature [5], the reactor system studied in this work obtained one of the largest yields of water soluble products and one of the smallest percentage of solid residues for process temperatures under 300 ºC.

References

[1] Shijie Liu, Houfang Lu, Ruofei Hu, Alan Shupe, Lu Lin, Bin Liang, A sustainable woody biomass biorefinery, Biotechnology Advances 30 (2012) 785–810.
[2] Douglas C. Elliotta, Patrick Billerb, Andrew B. Rossb, Andrew J. Schmidta, Susanne B. Jonesa, Review: Hydrothermal liquefaction of biomass: Developments from batch to continuous process, Bioresource Technology 178 (2015) 147–156.
[3] Yukihiko Matsumuraa, Tomoaki Minowab, Biljana Poticc, Sascha R.A. Kerstenc, Wolter Prinsc, Willibrordus P.M. van Swaaijc, Bert van de Beldd, Douglas C, Biomass gasification in near- and super-critical water: Status and prospects, Biomass and Bioenergy 29 (2005) 269–292.
[4] R. Hashaikeh, Z. Fang, I.S. Butler, J. Hawari, J.A. Kozinski, Hydrothermal dissolution of willow in hot compressed water as a model for biomass conversion, Fuel 86 (2007) 1614–1622.
[5] M. Mosteiro-Romero, F.Vogel, A.Wokaun, Liquefaction of wood in hot compressed water. Part1 — Experimental results, Chemical Engineering Science 109(2014)111–122.
[6] Xin Lu, ShiroSaka, Hydrolysis of Japanese beech by batch and semi-flow water under subcritical temperatures and pressures, Biomass and bioenergy 34(2010)1089–1097.
[7] Danilo A. Cantero, M. Dolores Bermejoa, M. José Cocero, Kinetic analysis of cellulose depolymerization reactions in near critical water, J. of Supercritical Fluids 75 (2013) 48– 57.
[8] Frederique Bertaud, Bjarne Holmbom, Chemical composition of earlywood and latewood in Norway spruce heartwood, sapwood and transition zone Wood. Wood Sci Technol (2004) 38: 245–256