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Pretreatment of Wheat Straw by Liquid Hot Water and Organosolv Processes

Felix Weinwurm*[a], Jenny Cunha[2], Anton Friedl[1]

[a]Vienna University of Technology, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria;
[b]University of Minho, Department of Biologic Engineering, Campus de Gualtar, 4710-057 Braga
felix.weinwurm@tuwien.ac.at

Wheat straw was subjected to liquid hot water (LHW) and ethanol organosolv (EOS) pretreatment in order to find optimum treatment conditions. The results were then used further to quantify the influence of the utilization of ethanol in the treatment liquor on the sugar and lignin yields.

The data was collected in two experimental works (the one LHW, the other EOS) which were carried out independently. Both were constructed as Central Composite experimental designs, which should cover most of the applicable treatment conditions. In the LHW experiments, residence time and temperature were varied, while in the EOS experiments the water-ethanol ratio was also varied. The resulting slurry fractions were analyzed for dry matter content, the liquid fractions were centrifuged and analysed for dry matter content, solubilized sugars and sugar degradation products. The amount of solubilised lignin was then estimated from these measurements under the assumption that the dry matter in the obtained liquor consisted of solubilised sugars, their degradation products, lignin and unspecified other residue.

Lignin solubilisation was between 6.2 % and 22.8 % of lignin present in the initial biomass in the LHW process, and between 9.2 % and 31.6 % in the EOS process. The EOS centerpoint combination of temperature and time was used in both experimental plans, (180°C, 60 min), so the influence of ethanol could be investigated. Statistics proved that significantly more lignin was solubilised by the EOS treatment (22.1 % opposed to 6.2 %).

On the other Hand, the average amount of sugars solubilised by the EOS treatment was only 0.9 % of the sugars in the biomass, opposed to 5.7 % solubilised by LHW treatment.

The results show that using a water-ethanol mixture improves selectivity in the pretreatment process. This could aid in downstream fractionation and production of value-added chemicals. Another observed advantage of the organosolv treatment is that apparently no sugars were degraded to Furfural or HMF, since these could not be detected in the liquors obtained in EOS experiments.

1. Introduction

The euopean commission points out in their General Report on the Activities of the European Union 2009 (Commission, 2010), that the effects of the climate change grow more and more noticeable globally, as well in europe. The EU has therefore set a number of goals for the year 2020 to approach the changing energy situation. It is planned, that the green house gas emissions should be lowered by 20 %, compared to the level of 1990. This goal should be accompanied with an increase of the share of renewable energy in the total energy consumption from 9 % to 20 % and a reduction of primary energy consumption by 20 %.

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To achieve these goals, lignocellulosic materials might be a promising resource. Their disadvantage is that their structure requires a chemical- respectively energy-intense pretreatment to make their components accessible for further steps, e.g. for bioethanol production, which could be used as a fuel substitute for fossile resources. However, the development and application of lignocellulosic biomass fractionation technologies that are technically and economically viable are not fully developed. Therefore this is a fundamental focus of the research in this area.

The aforementioned pretreatment step has therefore critical impact on the feasibility of the whole process. It not only directly influences the economic input through its resource demand, but also the efficiency of the process steps downstream.

Among the various pre-treatment methods currently being assessed is the organosolv process using different delignification agents (Araque, et al., 2007). This process has the potential to meet the objectives assigned to this stage, but still needs to be optimized. An effective organosolv pretreatment could significantly improve the performance of the enzymatic hydrolysis and fermentation, thus increasing the ethanol yield and finally allowing scaling up from demonstration stage to a mature commercial facility.

The complex structure of lignin, with a great variety of functional groups depends strongly on the original source and extraction method used. Organosolv methods facilitate the production of low molecular weight lignins that are soluble in many common solvents. Their structure presents relatively high amount of phenolic hydroxyl groups and oxidized groups that favour their incorporation into polymer formulations and their chemical modification (Garcia et al.2007).

Furthermore, oligomers and monomers hydrolyzed from the hemicelluloses as well as the degraded hemicellulosic polymers could be used as a variety of chemicals for industry.

2. Materials and Methods

2.1 Materials

The wheat straw was harvested in lower austria and then dried at room temperature to moisture content of roughly 10%. Prior to use in the experiments it was cut by hand into pieces of 1-2cm of length. Raw material analysis was as provided: Lignin 22.6 %, Xylan 21.6 %, Cellulose (Glucan) 33.1 %, Arabinan 3.4 %, Extractives 4.3 %, Ash 5.5 %, Protein 3.2 %, Acetyl groups approx. 2 %. Ethanol 96% and sulfuric acid 98% were acquired from Merck, Germany. Analytic grade sugars were acquired from Sigma-Aldrich, Germany.

2.2 Treatment Methods

LHW Treatment

30 grams of wheat straw and 330 grams of ultrapure water were put into the autoclave. Wetting of the straw was ensured by pressing the straw under the liquid surface with a steel plate. The reactor was then sealed and heated to the desired temperature under constant stirring. After reaching the target temperature and time, the autoclave was cooled to room temperature. The liquor and pretreated straw were first separated by decantation. Dry matter of both fractions was determined by drying at 105C. The liquid fraction was centrifuged at 5100 rpm in a Sigma 4K15 for 30 minutes, and the supernatant taken for determination of dry matter at 105C and further analysis by HPLC (Weinwurm et al., 2010).

EOS Treatment

30 grams of wheat straw and 330 grams of a ethanol-water mixture water were put into the autoclave. Wetting of the straw was ensured by pressing the straw under the liquid surface with a steel plate. The reactor was then sealed and heated to the desired temperature under constant stirring. After reaching the target temperature and time, the autoclave was cooled to room temperature. The liquor and pretreated straw were first separated by decantation. After decantation, the solid fraction was then washed with water to remove any residual liquor prior to analysis, and liquid phases were combined. The resulting liquid fraction centrifuged for 30 min at 5100. The supernatant was collected and reserved for subsequent analysis (Cunha et al., 2011).

Analysis for sugars, by- and degradation productst

A small amount of the liquor was filtered through a 0.2µm filter into an autosampler vial, and then the vial was sealed and labeled. Acetic acid, 5- HMF and furfural and ethanol were measured by a Shimadzu HPLC system with a Shodex SH1011 column, at a flow rate of 0.6ml/min at 50ºC, with 0.005M H2SO4 as mobile phase and an injection volume of 5µl.

For monomeric sugar contents determination, 10ml of liquor were taken, and neutralized to pH 7 by addition of barium hydroxide. The concentration of monomeric sugars (xylose, glucose, galactose, arabinose and mannose) and cellobiose was analyzed in the same HPLC system, with a Shodex SP0810 column at 80ºC, and an injection volume of 5µl. The flow rate was set to 0.6 ml/min with deionized water as eluent.

To determine the total sugar content, a 10ml of the liquor was transferred to a pressure tube and brought to 4% sulfuric acid by addition of 1ml acid-water solution. At the same time, 10ml of Sugar recovery standards (SRS) were transferred to a pressure tube and brought to 4% H2SO4. Both samples and SRS were autoclaved in duplicate for 1h at 120ºC.

The resulting solution was neutralized with Ba(OH)2 and filtered through a 0.2 µm filter into autosampler vials and injected into HPLC at the same conditions as used for determination of monomeric sugars concentration.

Lignin Estimation

Lignin was not measured at the time directly, but was estimated as “lignin + rest” as the difference between the dry matter content of the centrifuged process liquids and the total content of sugars and sugar degradation- and byproducts present therein (data not shown). This value is further related to as “lignin”.

3. Results and Discussion

A summary of the sugars and lignin found in the process liquids is shown in Tables 1 and 2.

Table1: Sugars and Lignin in the liquid phase after LHW treatment

Temperature	Residence time	Sugars solubilized			Lignin solubilized	Sugars converted to byproducts	
		Glucose	Xylose	Arabinose		Xylose and Arabinose	Glucose
°C	min	%	%	%	%	%	%
160	81	1.6	3.6	9.5	10.5	n.d.	n.d.
165	66	0.9	2.5	8.0	10.6	n.d.	n.d.
165	96	1.5	9.6	14.0	9.5	0.16	2.72E-04
180	60	1.5	10.0	12.3	6.2	0.06	6.08E-05
180	81	1.3	12.5	8.0	10.3	0.22	7.80E-04
180	81	1.5	12.7	8.7	15.9	n.d.	n.d.
180	81	1.6	12.0	8.7	22.7	n.d.	n.d.
180	81	2.6	11.9	7.1	11.4	0.28	2.18E-04
180	81	1.5	11.1	5.8	15.7	0.31	3.09E-04
180	102	1.9	12.2	4.4	12.9	0.74	1.84E-03
195	66	2.0	12.2	8.0	12.0	0.28	n.d.
195	96	1.5	2.7	0.6	22.8	2.10	5.42E-03
200	81	1.0	2.0	0.7	18.1	2.29	5.40E-03

3.1 Sugar removal

During LHW treatment, an average of 1.6 % of the cellulose, 8.8 % of the xylan, and 7.4 % of the arabinan were solubilized from the straw into the process liquid. Cellulose solubilization ranged from 0.9 to 2.6 %, xylan solubilization from 2 to 12.7 %, and arabinan solubilization from 0.6 to 14.0 %.

While the maximum of cellulose and xylan was removed from the raw material at centerpoint conditions (180 ºC, 81 minutes), the most arabinan was removed at the low temperature, and short reaction time (165 ºC, 66 minutes). On the other hand, the minimum removal of cellulose occurred at low temperature and time (165 ºC, 81 minutes), the lowest amount of C-5 sugars in the process liquid was found at higher temperature (195 ºC, 200 ºC) and reaction times (81 and 96 minutes). This behaviour could indicate that the C-5 sugars are favourably solubilized at rather moderate treatment conditions, and are further degraded as the conditions get rather severe.

During EOS treatment, an average of 0.4 % of the cellulose, 1.7 % of the xylan, and 2.7 % of the arabinan were solubilized from the straw into the process liquid. Cellulose solubilization ranged from 0.1 to 1.1 %, xylan solubilization from 0.1 to 7.9 %, and arabinan solubilization from 0.7 to 7.4 %. The highest concentrations of cellulose, xylose and arabinose in the liquid were found at high temperature, high reaction time and high ethanol concentration (200 ºC, 90 minutes and 60 %w). At center temperature, center time and highest ethanol concentration, the lowest amount of cellulose was found in the liquid. Xylose and arabinose were least present in the liquid at low temperature, low reaction time and low ethanol concentration (160 ºC, 30 minutes and 40 %w).

Table2: Sugars and Lignin in the liquid phase after EOS treatment

Temperature	Residence time	Ethanol fraction	Sugars solubilised			Lignin solubilized	Sugars converted to byproducts
			Glucose	Xylose	Arabinose		
°C	min		%	%	%	%	
146	60	0.5	0.1	0.1	1.2	16.5	n.d.
160	30	0.4	0.1	0.1	0.7	18.3	
160	30	0.6	0.1	0.3	1.2	24.0	
160	90	0.4	0.4	3.8	3.5	18.9	
160	90	0.6	0.7	1.4	3.3	15.9	
180	30	0.5	0.9	2.0	7.2	9.2	
180	60	0.34	0.8	4.4	2.8	17.8	
180	60	0.5	0.3	0.5	1.5	29.5	
180	60	0.5	0.1	0.4	3.6	26.3	
180	60	0.5	0.1	0.3	1.6	18.7	
180	60	0.5	0.3	0.5	1.6	18.7	
180	60	0.5	0.4	0.3	2.2	23.5	
180	60	0.5	0.6	1.0	4.1	23.9	
180	60	0.67	0.1	0.1	0.7	17.9	
180	110	0.5	0.6	1.5	2.2	31.6	
200	30	0.4	0.9	4.0	3.8	31.6	
200	30	0.4	0.2	1.0	2.0	30.2	
200	90	0.6	0.2	3.1	1.3	25.6	
200	90	0.6	1.1	7.9	7.4	27.4	
214	60	0.5	0.5	1.8	1.7	30.4	

3.2 Lignin removal

The estimated lignin removal in the LHW experiments ranges from 6.2 % to 22.8 % with an average of 13.7 %. The minimum lies at 180 °C and a reaction time of 60 minutes, while the maximum occurs at 195 °C and 96 minutes. The distribution of the values suggests, that elevated temperature and time facilitate the removal of lignin to the liquid phase. But as one can see from the centerpoint data (180 °C, 81 minutes) the variation in lignin removal data is rather large, so estimates on lignin removal based on them should be questioned.

In the EOS experiments, the lignin removal ranges from 9.2 % to 31.6 % with an average of 22.6 %. The minimum lies at 180 °C, a reaction time of 60 minutes, and a ethanol concentration of 50%w, while the maximum values lie at 180 °C, 110 minutes, 50%w ethanol, and at 200 °C, 30minutes and 40%w ethanol. The distribution of the values suggests, that elevated temperature and time facilitate the removal of lignin to the liquid phase. The outer values of the ethanol concentration correspond to lower amounts of removed lignin at the same temperature (180 °C).Lignin was not measured at the time directly, but was estimated as “lignin + rest” as the difference between the dry matter content of the centrifuged process liquids and the total content of sugars and sugar degradation- and byproducts present therein (data not shown). This value is further related to as “lignin”.

When the same combination of temperature and residence time was used (180 °C and 60 minutes) as well in the LHW and EOS experiments, the effect of ethanol could be evaluated.

The amount of lignin from the raw material, which was found in the process liquid is illustrated in Figure 1. When only water was used as the process liquid, 6.2 % of the lignin were released. Increasing the ethanol mass fraction to a third resulted in 17.8 % of the lignin being found in the liquid phase. In the centeroint experiments, where a mixture of 50:50 water-ethanol mixture was used, the resulting solubilization varied between 18.7 and 29.5 %. With a mixture of two thirds of ethanol, 17.9 % of lignin were found in the liquid phase. It seems as the most lignin could be removed from the straw with a 50 %w ethanol solution, there is a lot of variation in the data though.

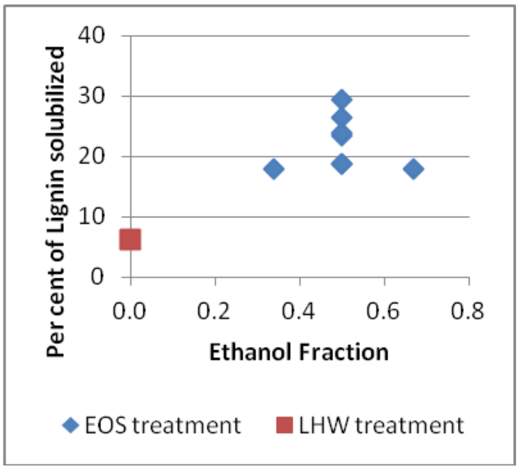

Figure 1: Influence of ethanol on Lignin solubilization

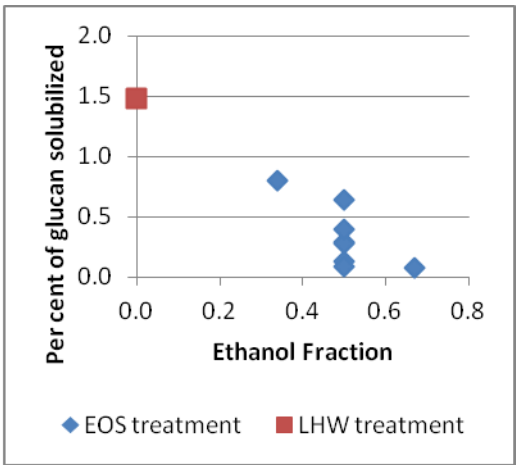

Figure 2: Influence of ethanol on glucan solubilization

In Figures 2 to 3, the influence of ethanol in the process liquor is illustrated. Increasing the ethanol content of the process liquid seems to drastically lower the amount of sugars that is released into the liquid phase. Since there is a lot of variation in the repeated experiments, this trend cannot be sufficiently explained with the existing data. By increasing ethanol content, the amount of glucose found in the liquid phase decreases from 1.5 % when only water was used, to 0.1 % with a solution consisting of two thirds ethanol. Xylan solubilisation was decreased from 10 % to 0.1 %, and Arabinan solubilisation from 12.3 % to 0.7 %, using the same process liquid compositions.

When the samples from LHW were analyzed for sugar by- and degradation products, a maximum of 2.29 % of xylan and arabinan, in the raw materials were found as furfural in the liquid phase. The conversion of cellulose to 5-HMF was observed in a negligible scale. In the EOS samples, no Furfural or HMF could be detected.

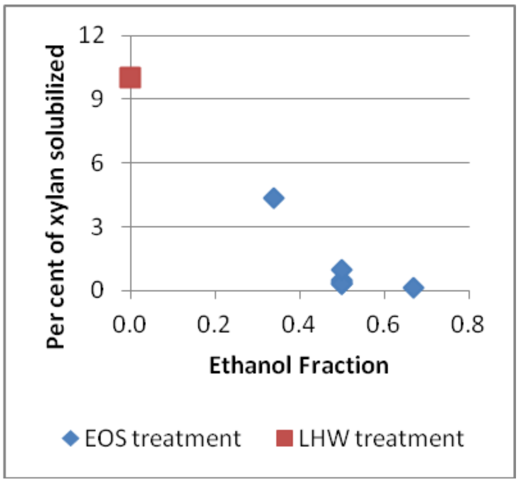

Figure 3: Influence of ethanol on xylan solubilisation

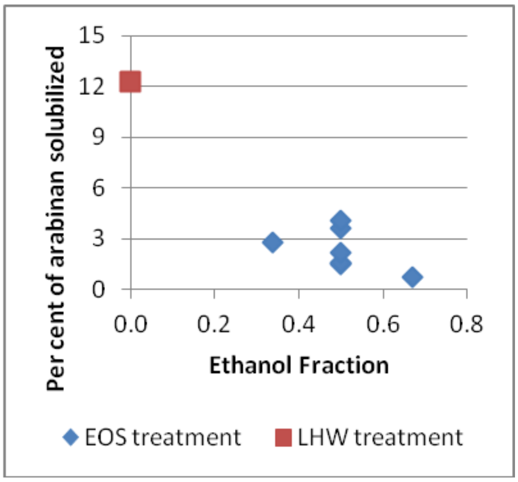

Figure 4: Influence of ethanol on arabinan solubilisation

4. Conclusions

In the presented work, ethanol organosolv treatment was compared to a liquid hot water treatment. Since the two treatments were studied independently, only a small portion of the single experiments could be compared. It was found, that the use of ethanol in the process liquid had three major effects. First, the amount of lignin removed from the raw material was increased, whereas the maximum was achieved when using a solution of 50 % ethanol (by weight). Second, the amount of sugars released into the process liquid was greatly reduced with increasing ethanol content. And third, formation of fermentation inhibitors as Furfural or 5-HMF could not be observed in the organosolv treatment.

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