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Sequential Extrusion and Organosolv Pretreatment for Wheat Straw Valorization

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Lignocellulosic agricultural side products like wheat straw are widely seen as an important contribution to a sustainable future economy. However, the optimization of biorefinery processes, especially the pretreatment step, is crucial for a economical viable biorefinery. As an attempt to do so, wheat straw was subjected to a Liquid Hot Water (LHW) treatment in an extruder under 2 different conditions followed by an ethanol Organosolv (EOS) treatment in a batch reactor in order to investigate the influence of the extrusion on the extraction yields. Wheat straw extruded at two different extruder settings and non-extruded were included in a central composite experimental design in which the EOS treatment parameter time, temperature and the ratio of wheat straw/solvent were varied. Solid residues and extract were analyzed for lignin, carbohydrate and degradation product composition. The results showed minor influence on the lignin yield, slighty increased carbohydrate yields and increased acetic acid formation.

1. Introduction

Many petrochemicals are produced from crude oil-fed refineries, whereas in future, it is anticipated that many products and chemicals will be produced from biorefineries fed with lignocellulosic biomass such as residual wheat straw (Kamm and Kamm, 2004). Annually about 10^{10} t per year of wheat straw are available worldwide and is therefore, one of the favourable feedstocks for biorefineries (Sánchez and Cardona, 2008).
A biorefinery approach involves multi-step processes in which the first step, subsequent to the feedstock selection, typically involves treating the biomass to pre-separate the main components and to make it more amenable for further processing (FitzPatrick et al., 2010). This step is conventionally referred to as pretreatment and can account for up to 20-40% of the overall production cost (Yang and Wyman, 2008). Therefore, the first step to make a biorefinery more efficient is to optimize the pretreatment.
An effective pretreatment disrupts cell wall physical barriers and removes lignin so that hydrolytic enzymes can access the biomass macrostructure (Zhao et al., 2009). Both, extrusion and Organosolv pretreatment have unique advantages and a combination could lead to a significantly improved process. Extrusion, on one hand, exposes the biomass to shear stress and elevated but still relatively low temperatures which leads to physical and chemical changes in the structure of the lignocellulose and at the same time prevents by-product formation (Brudecki et al., 2013). The Organosolv process, on the other hand, extracts relatively pure, low-molecular-weight lignin from biomass. This lignin shows a minimum of carbohydrate and mineral impurities and facilitates lignin applications with higher value than heat and power generation (Huijgen et al., 2012)
In order to proof a reasonable sequential combination of extrusion and Organosolv treatment, an experimental plan was established which combines a Liquid Hot Water (LHW) treatment in an extruder and an Ethanol Organosolv (EOS) treatment in a batch reactor. The combination of LHW and EOS treatment in batch reactors was already investigated (Weinwurm et al., 2016) but the combination shearing forces in an extruder with an EOS was not investigated up to now.
Therefore, an experimental plan was established, which allows the comparison of the pretreatment performance of an EOS batch extraction of wheat straw, extruded under different conditions, with an EOS

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batch extraction of unextruded wheat straw regarding Lignin and Carbohydrate yield as well as the formation of degradation products including Acetic Acid, Hydroxymethylfurfural (HMF) and Furfural.

2. Experimental

2.1 Materials

The wheat straw used was harvested in 2015 in Lower Austria and stored under dry conditions until use. The particle size was reduced in a cutting mill, equipped with a 2 mm mesh, before extrusion. The composition of the straw was 16.1 %w/w Lignin and 63.1 %w/w Carbohydrates consisting of Arabinose, Glucose, Mannose, Xylose and Galactose. Ultra-pure water (18 MΩ/cm) and Ethanol (Merck, 96 %v/v, undenaturated) was used as solvent in the LHW and EOS treatment.

2.2 Extrusion and Organosolv treatment

The experimental set up consisted of the extrusion and the EOS treatment with a subsequent analysis of carbohydrates, lignin and degradation products (see Figure 1).
The extruder used was a conical, counter-rotating twin-screw extruder CM45-F, Cincinnati Milacron, Austria. The general screw geometry was length 1,000 mm, diameter from 90 to 45 mm, channel depth 8.5 mm, calender gap 0.5 mm, and flight gap 0.2 mm. A screw configuration with five convenient sections and three drossel zones SK-1552-300, Cincinnati Milacron, Austria was used in this study. The nozzle used was equipped with 8 holes á 4 mm diameter and a total nozzle area of 100.48 mm^2. The wheat straw was added dry to the extruder and a certain amount of water was added with a plunger pump in order to achieve a final water content of roughly 40 %w/w. The screw speed was 40 rpm and 81 rpm while the wheat straw feed flow was held constant at 0.1 kg/rpm screw speed. The average residence time at 40 rpm and 81 rpm was 3.5 min and 8 min, respectively. The barrel was not heated and cooled which lead to an average barrel temperature of 115 °C for both revolution speeds. The extruded straw was stored at -18 °C until the EOS experiments were conducted.
The EOS experiments were conducted in 45 ml pressure vessels (PARR, Model 4716) in electrical heating jackets. Certain amounts of Ethanol, water and wheat straw were added to the pressure vessels in order to achieve a 60 %w/w Ethanol content in the solvent mixture as well as the desired solvent/wheat straw ratio of 8.30 %w/w, 14.15 %w/w and 20.00 %w/w. The filled pressure vessels were rapidly heated to temperatures of 120 °C, 170 °C and 220 °C and held at this temperatures for the desired time of 0, 30 and 60 min. Afterwards, the pressure vessels were immersed in a water bath in order to achieve fast cooling of the vessel content. The solid and liquid phase was then separated and the solid phase was washed with 25.3 g of 60 %w/w Ethanol mixture. Afterwards, the liquid phase was centrifuged at 14,000 rpm for 20 min. The washed solid residues of the first separation were used for the lignin determination and the supernatant for the determination of carbohydrate and degradation product concentrations.

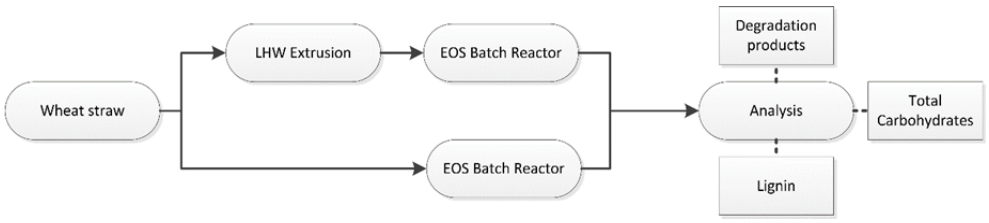

Figure 1: Schematic experimental plan

2.3 Analytical Methods

The lignin concentration of the washed solids after the EOS treatment was determined following the Laboratory Analytical Procedure (LAP) of the National Renewable Energy Laboratory (NREL) (Sluiter et al., 2012). The concentration of the degradation products acetic acid, HMF and furfural were determined with a Shimadzu LC-20A “prominence” HPLC system and a Shodex SH1011 column at 40 °C, with 0.005 M H_2SO_4 as eluent. The Carbohydrate content of the liquid sample was determined by the sample preparation following the NREL LAP (Sluiter et al., 2008) but no neutralization of the samples after hydrolysis was conducted and a Thermo Scientific ICS-5000 HPAEC-PAD system with deionized water as the eluent was used for the determination. Yields of lignin and carbohydrates were reported following equation 1 where Y_i is the extraction yield in %w/w, m_r the mass of the component in the raw material and m_s the mass of the solved component

after extraction. The yield of degradation products (equation 2) is based on the dry mass of wheat straw (m_{rm}) where m_{dp} is the mass of degradation products formed during the pretreatment step.

$$Y_i, \quad \% = \frac{m_s}{m_r} \cdot 100 \tag{1}$$

$$Y_{dp}, \quad \% = \frac{m_{dp}}{m_{rm}} \cdot 100 \tag{2}$$

2.4 Design of experiment and statistical evaluation

Three different starting materials, non-extruded straw and extruded straw with two different extrusion parameters, were used for the EOS treatment. The first setting, referred to as extrusion setting 1 used a water content of 37.7 %w/w H_2O and a feed rate of 8 kg dry straw/h at 81 rpm. The second extrusion setting used a water content of 41.9 %w/w at 40 rpm with a feed rate of 4 kg dry straw/h.
For each of the 3 settings, a face-centred central composite design with 3 centre points (170 °C, 30 min and 14.15 %w/w solvent/wheat straw ratio) and one full repetition (2 complete runs) was set up. The varied factors in EOS treatment were the wheat straw/solvent ratio (8.30, 14.15, 20.00 %w/w), treatment time (0, 30, 60 min) and temperature (120, 170, 220 °C). Therefore, 3x34 experiments were conducted.
The statistical software Statgraphics Centurion XVII (Statpoint Technologies Inc., USA) was used for regression and graphical analysis of the data obtained. The initial model was based on a model equation including all linear interactions of the independent variables and the extrusion setting as categorial factor. Categorial factors have two coefficients with two indicator variables. The first variable equals 1 when the extrusion setting is 0, -1 when the extrusion setting is 2 and 0 when the setting is 1. The second variable equals 1 when the extrusion setting is 1, -1 when the setting is 2 and 0 when the setting is 0. Therefore, all factors containing the extrusion setting have two coefficients.
Statistically not significant factors (significance level α=0.05) were stepwise removed from the model and led to the final model. Therefore, only coefficients of statistically significant factors are shown in Table 1.

3. Results and discussion

3.1 Model data

Coefficients and p-values of the different component models are shown in Table 1 where empty cells indicate insufficient statistical significance of these factors and therefore, the removal out of initial model.

Table 1: Coefficients and p-values of the 5 different component models

	Lignin		Carbohydrates		Acetic Acid		HMF		Furfural	
Factor	p-value	Coef	p-value	Coef	p-value	Coef	p-value	Coef	p-value	Coeff
Intercept	-	$-3.99*10^{5}$	-	$-8.75*10^{-1}$	-	-1.33	-	$1.59*10^{-3}$	-	$-7.58*10^{-2}$
ES	-	-	-	-	-	-	-	-	-	-
T	<0.000	$2.93*10^{-1}$	<0.000	$1.04*10^{-2}$	<0.000	$1.61*10^{-2}$	-	-	0.008	$4.80*10^{-4}$
Ti	<0.000	$-9.18*10^{-1}$	-	-	-	-	-	-	-	-
SS	-	-	-	-	-	-	-	-	-	-
ES*T	-	-	-	-	-	-	-	-	-	-
ES*Ti	-	-	-	-	-	-	-	-	-	-
ES*SS	-	-	-	-	-	-	-	-	-	-
T*Ti	<0.000	$8.22*10^{-3}$	<0.000	$1.11*10^{-4}$	<0.000	$8.17*10^{-5}$	-	-	-	-
T*SS	-	-	0.007	$1.31*10^{-4}$	-	-	-	-	-	-
Ti*SS	0.033	$3.43*10^{-2}$	<0.000	$1.52*10^{-3}$	-	-	<0.000	$-1.04*10^{-4}$	<0.000	$-2.82*10^{-4}$
ES**Ti	-	-	-	-	-	-	-	-	-	-
ES*T*SS	-	- -	0.011	$2.68*10^{-6}$ $-6.06*10^{-5}$	-	- -	-	- -	-	- -
ES*Ti*SS	<0.000	$-5.15*10^{-3}$ $2.99*10^{-2}$	-	- -	-	- -	-	- -	-	- -
T*Ti*SS	0.002	$-2.81*10^{-4}$	<0.000	$-1.67*10^{-5}$	-	-	<0.000	$7.85*10^{-7}$	<0.000	$2.23*10^{-6}$
ES*T*Ti*SS	<0.000	$4.28*10^{-5}$ $-2.37*10^{-4}$	0.007	$7.73*10^{-7}$ $1.10*10^{-6}$	-	- -	-	- -	-	- -
R^2	0.87		0.76		0.79		0.74		0.71	

ES-Extrusion setting; T-EOS Temperature; Ti-Treatment time; SS-Straw/Solvent ratio

3.2 Lignin

The global model for the lignin extraction yield shows a relatively high coefficient of determination with a value of 0.87. The Box-Plot in Figure 2 shows the centre points of each treatment setting in comparison. The arithmetic average of the centre points shows a slightly increased lignin yield of the extruded samples in comparison to the non-extruded experiments. However, the difference is not significant and the global model shows a decreasing lignin yield for extrusion setting 1 and 2 in comparison to the setting 0. The comparison of all 34 experimental points in each setting shows an average lignin extraction yield of 22.3, 19.1 and 14.7 %w/w for extrusion setting 0, 1 and 2, respectively. The highest Lignin yield of over 70 % could be achieved for non-extruded straw at 220 °C after 60 min (see Figure 2).

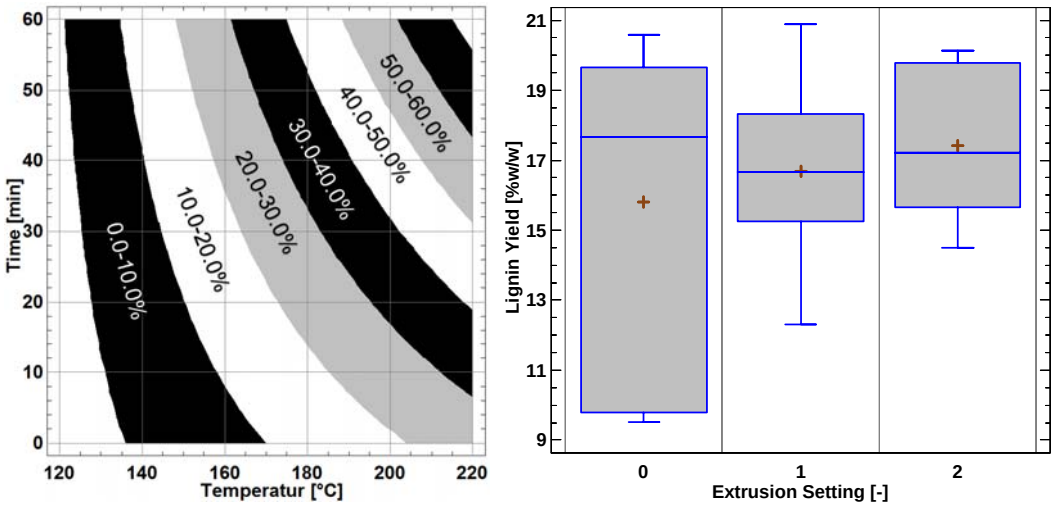

Figure 2: (a) Contour plot of the lignin yield for non-extruded straw at a straw/solvent ratio of 8 %w/w; (b) Box-Plot of the 3x2 centre points at each extrusion setting

3.3 Total carbohydrates

The yields of carbohydrates show relatively low values of less than 3 %w/w at the maximum as expected for EOS treatments regarding previous investigations by Weinwurm et al. (2012). The Box-Plot in Figure 3 as well as the global model show significant dependencies on the extrusion setting for linear combination factors. For the central point parameters, the high screw speed in extrusion setting 1 seems to increase the average yield to 1.42 % in comparison to setting 0 and 2 with yields of 1.15 and 1.18 %w/w, respectively.

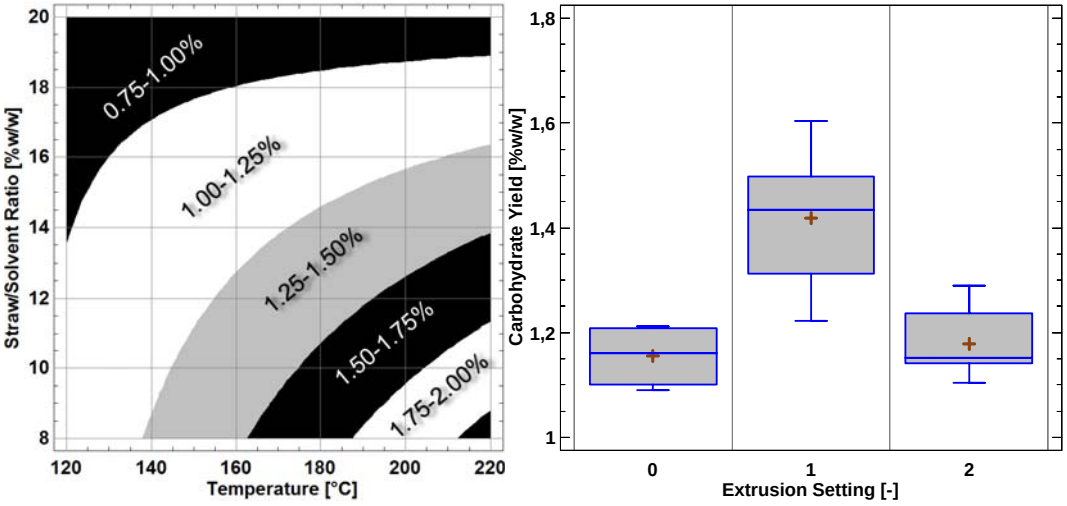

Figure 3: (a) Contour plot of the carbohydrate yield for straw extruded at setting 2 after 60 min EOS treatment time; (b) Box-Plot of the 3x2 centre points at each extrusion setting

The sugar yield is increasing with increasing temperature, extrusion and decreasing treatment time. The highest yields were achieved for the extrusion settings 1 and 2. In terms of selectivity, the average ratio of the lignin/carbohydrate concentrations in the extract were 5.1, 3.4 and 2.5 for extrusion setting 0, 1 and 2, respectively. Therefore, it can be stated that the LHW extrusion treatment is decreasing the extraction selectivity of lignin in comparison to the carbohydrates based on the concentrations in the extract.

3.4 Degradation products

The comparison of the acetic acid formation for the different extrusion settings as the major degradation product is shown in Figure 4 right. The Box-Plot shows a comparison of the centre points and therefore equal EOS treatment conditions for all samples, which shows a significant increase of the acetic acid formation in the extruded samples with a p-value of 0.0050 by using an F-Test. However, the global model does not include an extrusion setting term which leads to the conclusion that the extrusion has no major influence to the acetic acid formation. The global model shows that the main influencing factors of the acetic acid formation are EOS treatment time and temperature. Whereas the ratio between wheat straw and solvent does not influence the formation. EOS treatments at 220 °C showed that over 3 % of the applied wheat straw was present as acetic acid after 60 min.

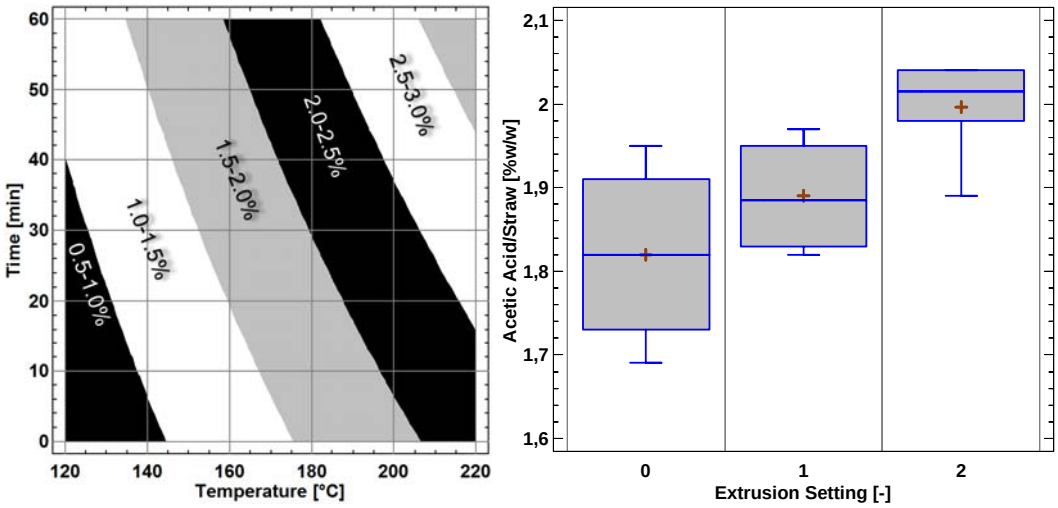

Figure 4: (a) Contour plot of the acetic acid yield in %w/w based on dry weight of straw extruded at setting 2 at a straw/solvent ratio of 14.15 %w/w; (b) Box-Plot of the 3x2 centre points at each extrusion setting

HMF formation shows dependencies on treatment time, temperature and the wheat straw/solvent ratio whereas the extrusion treatment shows no significant influence. Reason for this behaviour could be the relatively low temperature of 115 °C during the extrusion step which is not sufficient for the HMF formation reaction (de Souza et al., 2012). The results show that neither of the examined settings led to a considerable HMF amount greater than 0.01% below treatment temperatures of 140 °C. However, treatment conditions of 220 °C, 60 min and a straw/solvent ratio of 20 % showed HMF conversion of over 0.8 %.
The degradation of carbohydrates to Furfural shows the lowest yields of the three investigated degradation products with a maximum straw conversion of only 0.25 % obtained at a treatment temperature of 220 °C and a straw/solvent ration of 20 % after 60 min. The treatment temperature shows the highest influence followed by the treatment time and straw/solvent ratio. The regression model shows the beginning of Furfural degradation reactions at temperatures over 130 °C.

3.5 Energy demand

The energy required for the operation of the extruder has to be considered if compared with other pretreatment methods. In this investigation, the EOS treatment conditions were varied in the same range for all extrusion settings. Therefore, only energy demand of the extrusion was taken into account. The extrusion setting 1 and setting 2 had an energy demand of 557 and 627 kJ per kg of throughput (straw plus water), respectively. These values have to be taken into account if both, the extrusion and EOS treatment are combined especially since these values do not include the non-load power of the extruder.

4. Conclusion

The EOS batch extraction performance of LHW extruded and non-extruded straw was compared in terms of lignin and carbohydrate yields as well as degradation product formation. The experimental results show that the LHW extrusion has only a minor effect on the yields of lignin, carbohydrates and the formation of degradation products. However, the macrostructural disruption caused by the extrusion is expected to lead to improved enzymatic accessibility and therefore to an increased enzymatic hydrolysis yield which is crucial for a following fermentation step. Therefore, a final conclusion about the influence of the extrusion needs to be based on further results of enzymatic hydrolysis yields, which is the aim of future work of the authors.

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