CHEMICAL ENGINEERING TRANSACTIONS

VOL. 52, 2016

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652063

Valorising of Wheat Straw by Applying Combined Liquid Hot Water and Ethanol Organosolv Pretreatment

Felix Weinwurm, Jürgen Denner, Teresa Turk, Anton Friedl*

Technische Universität Wien, Institute of Chemical Engineering, Getreidemarkt 9/166, 1060 Vienna, Austria
anton.friedl@tuwien.ac.at

The production of chemicals from renewable sources like lignocellulosic agricultural side products is widely seen as an important contribution to a sustainable future economy. Lignocellulosic biomass can be fractionated into its main components cellulose, hemicellulose, and lignin by Liquid Hot Water (LHW) or Ethanol Organosolv (EO) treatment. In order to optimize the biomass fractionation towards clean single components we investigated the sequential LHW and EO treatment of wheat straw. The release of carbohydrates and lignin was tracked over the treatment time. The experiments showed, that the treatment time should not exceed 30 min at 180 °C for each treatment. Furthermore, kinetic models for glucan and xylan fractionation during both treatments were created.

1. Introduction

Lignocellulose based biorefineries, analogous to conventional refineries, are aimed to produce value-added products from renewable lignocellulosic resources through a series of operations. These products are raw materials for the chemical industry, food and feedstuff production or biofuels. The lignocellulosic feedstock is often cheap and easily available as a byproduct from agriculture or forestry. There are different paths for utilizing the biomass. Some biorefineries use the whole biomass (e.g. for biogas or syngas production), others (product-driven biorefiernies) aim to deconstruct it and convert the resulting fragments to produce a variety of chemicals (Kamm and Kamm, 2004). Lignocellulosic biomass is made up of three major components – cellulose, hemicellulose, and lignin – which have to be separated in order to process them into specific products. The cellulose can be sold as fibers or, like the hemicellulose carbohydrates, processed further to platform and specialty chemicals through biological or chemical conversion. Lignin could be a precursor for phenolic platform chemicals, polymers or specialty chemicals.

There are different treatments available to fractionate the biomass. For example, it can be treated with pressurized water at temperatures from 160 to 240 °C (Liquid hot water treatment), or treated in acidic or alkaline conditions, or with organic solvents. Technologies, which include a sudden pressure release (e.g. steam explosion), also achieved good fractionation. The organosolv treatment, is a promising method to achieve high delignification of the biomass and to obtain relatively high purity lignin, and at the same time retain lower formation of sugar degradation products and cellulose cleavage. Yet, chemically diversified second generation biorefineries are rarely economically successful.

A number of preliminary studies, focused on finding optimum treatment conditions for liquid hot water (LHW) and ethanol organosolv (EO) treatment of wheat straw (Weinwurm et al., 2012), the impact of different EO liquor concentration methods on energy and chemicals demand for lignin precipitation (Weinwurm et al., 2014), and the performance of nanofiltration for concentration of EO liquors and separation of lignin (Weinwurm et al., 2016) were carried out previously. It was found, that the amounts of hemicellulose and cellulose derived sugars in the LHW liquors were maximized at medium temperatures and time (185 °C, 80 min total treatment time). The dissolved sugars were increasingly degraded at harsher conditions to furfural and 5-hydroxymethylfurufural (HMF). EO treatment led to a much lower amount of sugars removed (1.5 – 5 fold), lower amounts of degradation products, and achieves higher delignification at the same process conditions. Therefore, a sequential combination of LHW and EO treatment seems promising.

Please cite this article as: Weinwurm F., Denner J., Turk T., Friedl A., 2016, Valorising of wheat straw by applying combined liquid hot water and ethanol organosolv pretreatment, Chemical Engineering Transactions, 52, 373-378 DOI:10.3303/CET1652063

So far, only few authors have combined Liquid Hot Water prehydrolysis with subsequent organosolv treatment of wheat straw. The combination of both treatments was found to xylose recovery, production of cellulose-enriched solids (Ruiz et al., 2011) and improving enzymatic glucose yield, but may limit lignin recovery, depending on the treatment conditions (Huijgen et al., 2012). The aim of the presented work was to carry out the two treatments subsequently in order to track the release of carbohydrates and lignin into, and their degradation in, the respective liquid phases.

2. Materials and Methods

The effects of LHW treatment and subsequent EO treatment were tracked over time using five small (45 mL) reactors for later use in the creation of a kinetic model. The reactors were heated up simultaneously, but quenched individually after 0, 15, 30, 45, and 60 min. The feedstock for the EO treatment was LHW-pretreated in a larger 1 L reactor as shown in Figure 1. The treated straw was then used for EO experiments with the small reactors. EO treatment in the large reactor was performed earlier and is described elsewhere (Weinwurm et al., 2016). The raw material, wheat straw, was LHW and EO treated in the small reactors to track the yields of lignin, sugars, and degradation products over the treatment time. All liquid samples after treatment were analyzed for oligomeric and monomeric carbohydrates, their degradation products furfural and 5-hydroxymethylfurfural (HMF), acetic acid, and lignin by HPAEC-PAD, HPLC and UV/Vis methods.

2.1 Raw Material

Wheat straw was harvested in 2009 around the Lower Austrian town of Dürnkrut. The straw was stored as a bale in the laboratory at room temperature where it dried to a moisture content of 5 – 10 %. Prior to the individual experimental runs, portions of the straw were milled to the desired size and the moisture content of the samples was determined.

2.2 Large Batch LWH Pretreatment

A 1 L high pressure autoclave (HDA 9/16, Zirbus, Germany) was used to prepare the feedstock for the organosolv experiments by LHW treatment of wheat straw. It can withstand pressures up to 50 bar, is electrically heated, water cooled, stirred, and equipped with temperature and pressure measurement.

The autoclave was loaded with milled wheat straw and deminieralized water in a solid:liquid (S:L) ratio of 1:11 (by weight), sealed and the contents were heated to 180 °C in a timespan of 60 min, and then cooled down. After treatment, the contents were manually removed and the liquid was separated from the solids by vacuum filtration. The treated straw was washed multiple times with demineralized water by resuspension in a beaker (in total 330 g water) and dewatered by manual squeezing and vacuum filtration. The wash water was then combined with the treatment liquid for analysis. After separation of fine suspended solids by centrifugation, the combined liquids were analyzed for total solids, carbohydrates, byproducts, and lignin.

2.3 LWH and EO Kinetics Experiments

The small reactors were filled with the appropriate amounts of straw, water, and ethanol to achieve a S:L ratio of 1:11 and an ethanol content of 60 wt% in the liquor, sealed and inserted into the heating units. They were heated simultaneously, and reached the treatment temperature almost at the same time. Starting at this point, the reactors were removed from the heaters and cooled in a water bath in 15 min intervals. After cooling, the reactors were emptied into sealable plastic sample tubes for transport and storage. The solids and the liquids were separated by decantation and using a garlic press. The solids were washed with 60 wt% aqueous ethanol. The fine solids were separated again and the liquid combined with the treatment liquor. The combined liquids were analyzed for lignin, sugars, and degradation products.

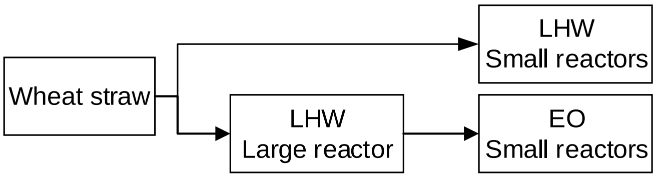

Figure 1: Overview of the treatments that were performed

2.4 Analytics

The lignin concentration in liquid samples was determined by UV/Vis spectrophotometry using a Shimadzu UV-1800 spectrophotometer. The samples were measured in glass cuvettes (Hellma, Germany) with a length of 1 cm against pure solvent (deionized water or aqueous ethanol, depending on the treatment) as a reference. The measurements were performed after appropriate dilution in duplicate. The contents of acetic acid, furfural and HMF were determined by HPLC with a HPLC system (LC-20A “prominence”, Shimadzu, Japan) using a Shodex SH1011 column at 40 °C, with 0.01 N H_2SO_4 as eluent. The content of monomeric sugars was analyzed with a Thermo Scientific ICS-5000 HPAEC-PAD system with deionized water as the eluent. To determine the total sugar concentration, the liquor samples were acid hydrolyzed at 120 °C for one hour to break up oligomeric carbohydrates into their monomer units. Sugar recovery standards were treated the same way to account for sugar losses during hydrolysis. After neutralization with $Ba(OH)_2$, the total sugar concentrations were analyzed by HPAEC-PAD as above.

2.5 Severity Factor

To compare the results at different treatment conditions and between the large and small reactors, the severity factor R_0 (Overend et al., 1987) was used. It is a characteristic number which represents the combined effect of temperature and time on the biomass during acid catalyzed hydrolysis processes. A discretized version, shown in Eq(1), was used.

$$R_0 = \sum_i \exp\left(\frac{\bar{\vartheta}_i - 100°C}{14.75}\right)\Delta t_i \qquad (1)$$

With R_0 … Severity factor

Δt_i … Time interval

$\bar{\vartheta}_i$ … Average temperature in the interval Δt_i

3. Results and Discussion

3.1 Large reactor LHW

The feedstock for later EO treatment in the small reactors was prepared by Liquid Hot Water treatment of wheat straw with a target temperature of 180 °C in the described 1 L stirred reactor. The desired temperature was reached after 60 min, and the treatment was stopped. These conditions led to a R_0 of 4713. Temperature and severity factor are plotted versus time in Figure 2. After the treatment, 31 % of the hemicellulose sugars, 5 % of the cellulose, and 21 % of the lignin were found dissolved in the liquor. The total (sum of cellulose and hemicellulose derived monomers and oligomers) carbohydrate yields were 17 % after LHW treatment in the large reactor. The xylan yield was rather low compared to literature values. For example, Huijgen et al. (2012) found 44 % of xylan dissolved after LHW treatment of wheat straw at 175 °C for 30 min. The difference could be caused by the acid catalyst used in their case, and the holding period at treatment temperature.

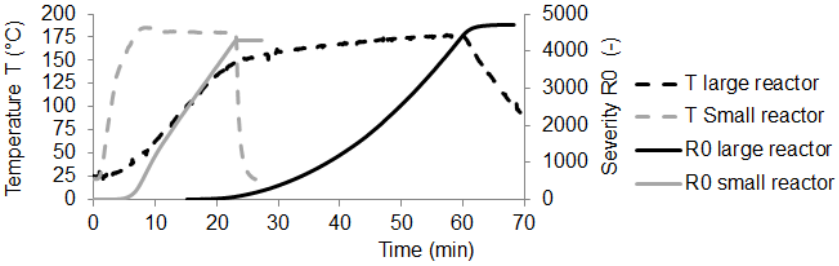

Figure 2: Temperature profiles and R_0 values during LHW and EO treatment in small reactors and large reactors. The treatment temperature of 180 °C was reached after 6, and held for 15 minutes with the small reactor, and reached after 60 minutes with the larger vessel without holding time

3.2 Small reactors LHW

The temperature profile during LHW treatment in the small reactors and the corresponding severity factors, depending on the treatment time, are also shown in Figure 2. A R_0 value of 4,713 was reached after 60 min in the treatment in the large reactor. The same value was reached with the small reactors after approximately 17 min at 180 °C. The closest holding period at 180 °C was 15 min with the small reactors, which corresponded to a R_0 of 4,295, at which point the total carbohydrate yields were 11.0 %, somewhat lower than the yields with the large reactor.

The higher carbohydrate yields in the large reactor could be explained through longer residence time and thus higher severity, so the use of R_0 remains a valid way to compare the treatments in the two reactor systems, and a fitting tool for upscaling the process.

Figure 3 (left) shows the developement of sugar and lignin yields during LHW treatment in the small reactors over time. Mainly oligomeric carbohydrates were released from the straw, which were then broken down to monomers and further degraded to furfural and HMF. The yield of cellulose-derived oligomers increases during the treatment to a maximum of 5 % after 45 min, while the yield of cellulose-derived monomers stays below 0.5 % all the time. The yields of monomers from hemicellulose increase steadily over the whole time to a maximum of approx. 7.5 %. Hemicellulose-derived oligomers form the largest sugar fraction in the liquor, with yields of up to almost 40 %. Lignin yields apparently increase steadily over the whole time to a maximum of approx. 60 %.

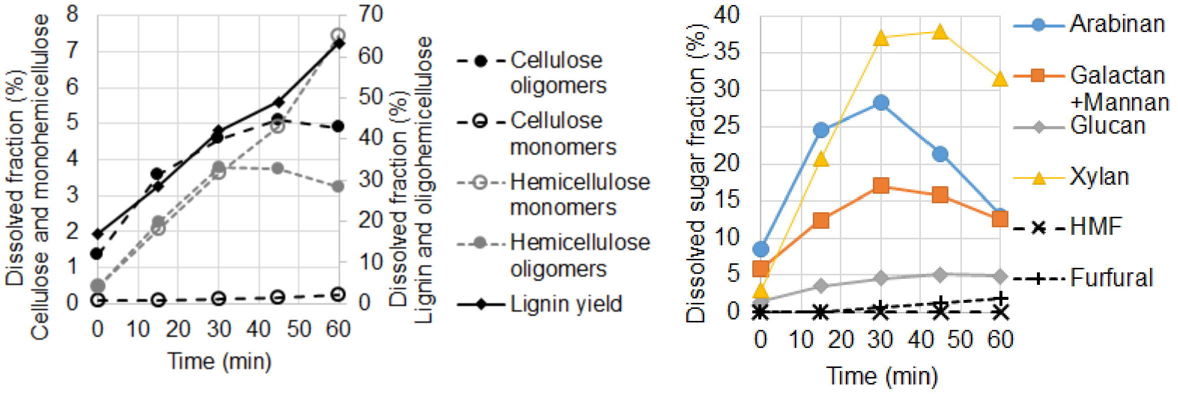

Figure 3: Progression of yields from LHW liquors. Left: oligomers, monomers and lignin. Right: Total yields of individual sugar species.The total sugar (oligomers and monomers) yields of the individual analyzed species (Arabinose, Galactose, Xylose, and Mannose) are also shown in Figure 3 (right). All species seemed to reach a yield peak at 30 min, and react further afterwards, except glucan, which reached its peak at 45 min

3.3 Small reactor EO after large reactor LHW prehydrolysis

When the LHW treated straw from the large reactor was subjected to EO treatment, the sugar yields were much lower, although they increased almost steadily with the treatment time. Of the initial hemicelluloses, less than 1.4 % were dissolved as monomers and less than 8 % as oligomers. Of the initial cellulose, less than 0.06 % were dissolved as oligomers, and less than 0.02 % as monomers. The dissolved fractions of sugars and lignin over the treatment time are shown in Figure 4.

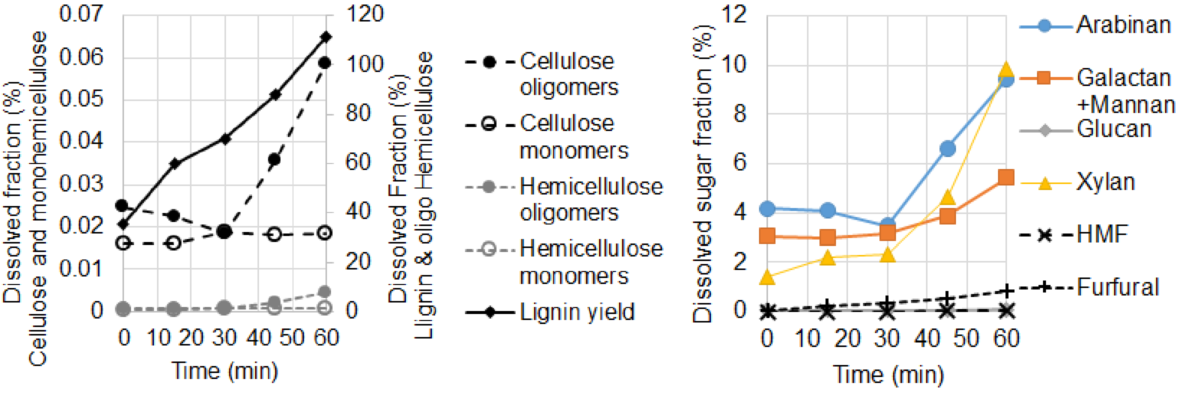

Figure 4: Progression of yields from EO liquors. Left: Oligomers, monomers and lignin. Right: Total yields of individual sugar species

The total yields of the individual sugars were between 2 and 10 %. Compared to the LHW treatment in the small reactors (up to 38 %) and in the large reactors (17 %), these values are rather low, as it is usual for ethanol organosolv treatment (Sun et al., 2016). The measured yields present snapshots of the sugar concentrations at the moment, meaning that the carbohydrate fraction which was dissolved earlier and reacted to other compounds before the measurement is not included in the yields. In large parts, the removed carbohydrate fraction could correspond to the “fast reacting” fraction reported in literature (Shatalov and Pereira, 2005). During the LHW pretreatment, large parts of the fast reacting carbohydrate fractions were presumably removed, and mostly the slow reacting fractions remained, causing lower yields in the EO treatment.

The lignin yield, which was already high during LHW treatment exceeds a value of 100 %. Values this large could be explained through the formation of soluble degradation products from carbohydrates or lignin, which inflated the measurements at 280 nm. Due to this reason, the lignin values were not investigated further for the matter of this publication. In their organosolv step, Huijgen et al. (2012) found ca. 50 % of lignin, and approx. 4.5 % of hemicellulose dissolved after EO treatment at 175 °C for 30 min. Considering the inflated lignin values due to the formation of degradation products, the achieved lignin yield could be in the same range.

3.4 Optimization of the combined LHW and EO treatment

The purpose of the combined treatment is to produce three clean products: First, a cellulose-rich solid residue, second, a liquor, containing the dissolved hemicelluloses, and third, an organosolv lignin fraction. To design such a process in any scale, the optimum conditions and processing times are of high importance. The goal of the LHW treatment is to remove as much hemicelluloses as possible while keeping the damage to the cellulose and the formation of degradation products as low as possible. The LHW experiments showed, that the released carbohydrates peak at 30 to 45 min after the treatment temperature of 180 °C was reached The amount of monomeric sugars still increases at this point, suggesting ongoing conversion of oligomeric to monomeric sugars. Simultaneously, the degradation products, mostly furfural, are produced increasingly after this treatment duration. Therefore, performing LHW treatment longer than 30 min at 180 °C seems not advisable. As determined with our equipment, this conditions correspond to a R_0 of approximately 7,800, which should not be exceeded. During the subsequent EO treatment, a large number of other byproducts are produced, as suggested by the lignin measurements. Additionally, the amounts of cellulose- and hemicellulose-derived sugars, as well as their degradation products, in the liquor start to increase distinctly after 30 min treatment time. For the EO treatment it is therefore also recommended to keep the residence time below 30 min.

3.5 Kinetic modelling of hydrolysis reactions during LHW and EO treatment.

Plotting the dissolved fractions of initial carbohydrates F_i found during LHW and EOS experiments in the small reactors versus time enables the calculation of a regression curve, representing the momentary amounts of sugars and degradation products in the liquors over the whole experiment. The derivatives of the regression curves represent the net reaction rates in the system of reaction equations Eqs(2-6) (Sidiras and Koukios, 2004). For this purpose, only glucan and xylan, the two major carbohydrates of cellulose and hemicellulose, and their derivatives were considered.

$$-dF_{Polymer}/dt = r_{Polymer} \quad (2)$$

$$dF_{Oligomer}/dt = r_{Polymer} - r_{Oligomer} \quad (3)$$

$$dF_{Monomer}/dt = r_{Oligomer} - r_{Degradation} \quad (4)$$

$$dF_{Degradationproduct}/dt = r_{Degradation} \quad (5)$$

$$\text{with } r_j = -kj \cdot C_i^n \quad (6)$$

This system of reaction equations, covering the release of oligomers into the liquor, the conversion of oligomers to monomers, and the conversion of monomeric sugars to degradation products (HMF and furfural), can be solved sequentially by starting from the end. The calculated parameters k and n can be used to calculate the different fractions (Figure 5a-d) at any point during the treatments.

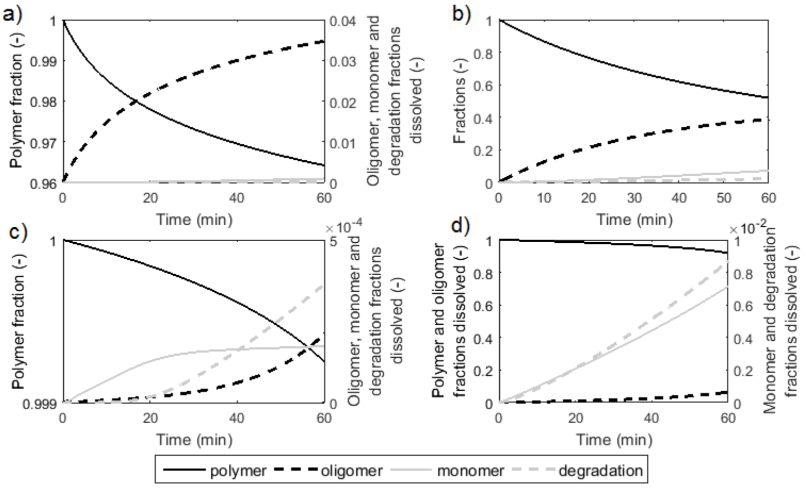

Figure 5: Models of glucan and xylan removal during LHW (a) glucan, b) xylan) and EO (c) glucan, d) xylan) treatment

The models mostly meet the expectations. The glucan is relatively hard to fractionate, resulting in low amounts of dissolved products (oligomers, monomers and HMF), while large portions of the xylose are dissolved and degraded to some amount. During EO treatment of LHW treated straw, the model predicts extremely little amounts of dissolved glucan products, and some xylose products. Again, much less carbohydrate products are released during the EO treatment.

4. Conclusions

Uncatalyzed Liquid Hot Water prehydrolysis and subsequent organosolv treatment were carried out successfully and the behaviour of the dissolved components over time was recorded.

The combination of LHW and EO treatment is not a completely new concept, which was demonstrated earlier by Huijgen et al. (2012). In addition to their study, we investigated the treatments with smaller reactors, which were able to heat up fast and hold the treatment temperature rather constantly over extended periods of time. By logging the treatment temperature over time, the severity factor R_0 was calculated. Using this parameter, the process conditions may be varied, to accommodate reactor-specific heating rates for example. As long as the same – equipment independent – R_0 value is reached, at least comparable treatment results can be achieved.

The validity of using the severity factor was checked by performing LHW experiments in two different reactor systems. Similar results were obtained, which can be reasonably attributed to slightly different severities.

With the combination of LHW and EO treatment, the clean removal of carbohydrates would be possible by LHW before the lignin is extracted using EO treatment. Optimum treatment times were 30 min for both treatments at a temperature of 180 °C, which corresponds to a severity R0 of approximately 7800.

Using the results from the experiments, a kinetic model of carbohydrate fractionation was established. Kinetic parameters for glucan and xylan fractionation during LHW and, for the first time to our knowledge, EO treatment of LHW treated straw were calculated. In continuation of this work, this model will be refined and expanded to include other carbohydrates, validated against analyses of the treated material, and can be applied for scale-up of the processes in combination with the severity factor.

Acknowledgments

The authors thank Charles Trey Sides for implementing the system of differential equations and producing the plots of the models in Matlab®.

References

Huijgen W., Smit A., de Wild P., den Uil H., 2012, Fractionation of wheat straw by prehydrolysis, organosolv delignification and enzymatic hydrolysis for production of sugars and lignin, Bioresource Technology, 114, 389-398, DOI:10.1016/j.biortech.2012.02.143.

Kamm B., Kamm M., 2004. Principles of biorefineries. Applied Microbiology and Biotechnoly, 64, 137-145. DOI:10.1007/s00253-003-1537-7.

Overend R.P., Chornet E., Gascoigne J.A., 1987, Fractionation of Lignocellulosics by Steam-Aqueous Pretreatments [and Discussion], Philosophical Transactions of the Royal Society of London. Series A, Mathematical and Physical Sciences, 321, 523-536.

Ruiz H., Ruzene D., Silv, D. P., da Silva F. F. M., António A., Vicent, A.A., Teixeira J.A., 2011, Development and Characterization of an Environmentally Friendly Process Sequence (Autohydrolysis and Organosolv) for Wheat Straw Delignification, Appl Biochem Biotechnol, 164, 629–641.

Shatalov A.A., Pereira H., 2005, Kinetics of organosolv delignification of fibre crop *Arundo donax L*., Industrial Crops and Products, 21, 203-210, DOI:10.1016/j.indcrop.2004.04.010.

Sidiras D., Koukios E., 2004, Simulation of acid-catalysed organosolv fractionation of wheat straw, Bioresource Technology, 94, 91-98, DOI:10.1016/j.biortech.2003.10.029.

Sun S., Sun S., Cao X., Sun R., 2016, The role of pretreatment in improving the enzymatic hydrolysis of lignocellulosic materials , Bioresource Technology, 199, 49-58, DOI:10.1016/j.biortech.2015.08.061.

Weinwurm F., Cunha J., Friedl A., 2012, Pretreatment of wheat straw by liquid hot water and organosolv processes, Chemical Engineering Transactions, 29, 541-546, DOI:10.3303/CET1229091.

Weinwurm F., Drljo A., Silva T.L.S., Friedl A., 2014, Principles of ethanol organosolv lignin precipitation: process simulation and energy demand, Chemical Engineering Transactions, 39, 583-588.

Weinwurm F., Drljo A., Waldmüller W., Fiala B., Niedermayer J., Friedl A., 2016, Lignin concentration and fractionation from ethanol organosolv liquors by ultra- and nanofiltration, Journal of Cleaner Production, 136 (B), 62-71, DOI:10.1016/j.jclepro.2016.04.048.