

Direct Precipitation of Organosolv Liquors Leading to Submicron Lignin Particles

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Micro- and nanosize lignin has recently gained interest due to improved properties compared to standard lignin available today. As the second most abundant biopolymer after cellulose, lignin is readily available but used for rather low-value applications. Applications for lignin in micro- to nanoscale, however, are ranging from improvement of mechanical properties of polymer nanocomposites, bactericidal and antioxidant properties and impregnations to hollow lignin drug carriers for hydrophobic and hydrophilic substances. This research represents an entire wheat straw biorefinery process chain and investigates the influence of Organosolv pretreatment conditions and precipitation parameters on particle size and morphology of nanolignin. A pretreatment temperature of 180 °C showed the best results in terms of morphology of the particles. Increasing addition flowrates of antisolvent to the Organosolv extract could decrease the particles size significantly to around 200 nm.

1. Introduction

Lignocellulosic biomass residues are estimated to exceed 2×10^{11} t/year worldwide and offers a vast source for lignin (Zhang et al., 2007). The major part of the lignin is used as an energy source. Considering a lignocellulose biorefinery producing bioethanol, only around 40 % of the produced lignin is needed to cover the thermal energy demand (Sannigrahi and Ragauskas, 2011). Hence, 60 % of the generated lignin is available to maximize valorisation in addition to the valorisation of the carbohydrate fractions. This increased valorisation is necessary to improve the utilization of the entire biomass and therefore to enhance the economics (Tuck et al., 2012).

Lignin is a highly irregularly branched polyphenolic polyether, consisting of the primary monolignols, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol, which are connected via aromatic and aliphatic ether bonds (Calvo-Flores and Dobado, 2010). Roughly three different types of lignins can be distinguished: softwood lignins are comprised almost solely of coniferyl alcohol, hardwood lignins of both coniferyl and sinapyl alcohol and grass lignins of all three types (Gellerstedt and Henriksson, 2008). The high complexity and inhomogeneity of the lignin structure is, in many cases, even further increased by currently applied pretreatment technologies and adds additional challenges for lignin's downstream processing and valorisation (Chandra et al., 2007). Compared to other pretreatment technologies, the Organosolv (OS) process, used in this work, 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).

An approach to overcome these issues of high complexity and inhomogeneity of lignin is the production and application of nanostructured lignin. Nanostructured materials, especially in the 1–100 nm range, offer unique properties due to their increased surface area (Xu et al., 2007), while their important chemical and physical interactions are governed by surface properties. Hence, a nanostructured material can have considerably different properties than a larger-dimensional material of the same composition (Hussain, 2006). Therefore, the preparation of lignin nanoparticles and other nanostructures has gained interest among researchers during the last years.

The application fields of lignin nano- and microparticles are ranging from improvement of mechanical properties of polymer nanocomposites, bactericidal and antioxidant properties and impregnations to drug carriers for hydrophobic and hydrophilic substances. Also, a carbonization of lignin nanostructures can lead to high-value

applications such as use in supercapacitors for energy storage (Beisl et al., 2017b). Also, first attempts for the upscaling of the production process are under investigation (Leskinen et al., 2017). However, most production methods published so far have a very high solvent consumption in common. Vast amounts of solvents are needed for purification of the lignin prior to precipitation, the precipitation itself and the downstream processing (Beisl et al., 2017c).

The present work also represents a concept for an integrated biorefinery and aims a direct precipitation of lignin in micro- to nanoscale from wheat straw OS pretreatment extracts. A similar process was already shown by Weinwurm et al. (Weinwurm et al., 2014) applying concentrated sulphuric acid as antisolvent. However, particle sizes and morphology were not investigated. The precipitation method used in this work combines the most commonly used methods solvent shifting and pH shifting and reduces the solubility of the lignin by decreasing the solvent concentration and lowering of the pH value via addition of diluted aqueous sulfuric acid (Beisl et al., 2017c). The focus of this work is the size and morphology depending on OS pretreatment and precipitation conditions in a batch precipitation setup after separation and drying of the particles.

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 5 mm mesh, before OS treatment. 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 M Ω /cm) and Ethanol (Merck, 96 %v/v, undenaturated) was used in the OS treatment and additionally sulphuric acid (Merck, 98 %) in the precipitation step.

2.2 Process

The biorefinery process chain consists of three different parts shown in Figure 1: Pretreatment/Extraction, Precipitation and Downstream Processing.

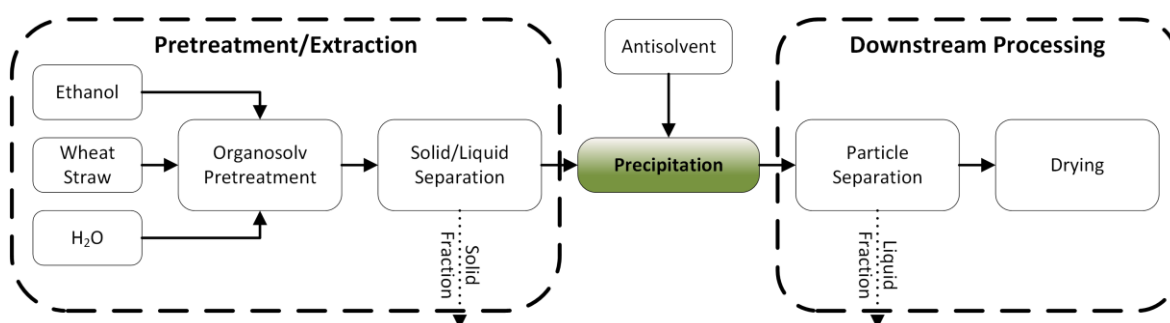


Figure 1: Schematic representation of the investigated biorefinery process chain.

Pretreatment/Extraction

The OS treatment was conducted in a 1 l stirred autoclave (Zirbus, HAD 9/16) using a 60 %w/w aqueous ethanol mixture as solvent under consideration of the water content in the straw. The wheat straw content in the reactor based on dry straw was 8.3 %w/w. The reactor was heated to the desired temperature within 45 min and held at this temperature for 15 min. After these 60 min of treatment, the reactor was cooled to room temperature. The solid and liquid fractions were separated using a hydraulic press (Hapa, HPH 2.5) at 200 bar and a centrifuge (Sorvall, RC 6+) at 30,074 g for 20 min. The supernatants were stored at 5 °C until the precipitation experiments were performed.

Precipitation and Downstream Processing

The precipitation setup consists of a temperature controlled 250 ml beaker with a magnetic stirrer and a syringe pump for addition of the antisolvent via an anti-diffusion tip. The antisolvent used was ultra-pure water set to the desired pH-value with sulphuric acid. The cooling jacket and antisolvent temperature were kept constant at 25 °C. The OS extract was placed in the beaker and antisolvent was added with the desired flowrate incrementally through the immersed anti-diffusion tip until a pH-value of approximately 2.2 was reached. The stirrer speed was kept constant at 625 rpm. Lignin particles were separated using a centrifuge (Sorvall, RC 6+) at 30,074 g for 20 min. The precipitate was dried in a climate chamber at 40 °C and a dew point of 0 °C.

2.3 Analytics

The molecular weight was measured via High Performance Size Exclusion Chromatography (HPSEC) using a Agilent 1200 HPLC system equipped with a UV-Detector. The lignin samples were dissolved in 10 mM NaOH and compared with sodium-polystyrene-sulfonate standards ranging from 210 Da to 77 kDa. The particle size and shape were investigated in a Scanning Electron Microscope (SEM) (Fei, Quanta 200 FEGSEM). The samples were sputter coated with 4 nm Au/Pd (60 %w/w / 40 %w/w) before analysis. The particle sizes were manually analysed using the software imageJ. More than 200 particles were measured for each particle size distribution. The total yield is defined as the ratio of the lignin amount in the utilized volume of wheat straw to the mass of precipitate after drying in the climatic chamber.

3. Results and Discussion

To investigate the influence of the pretreatment temperature on the final particle size and morphology, temperatures were varied between 160 °C and 220 °C. Figure 2 shows the molecular mass of the lignin resulting from different pretreatment temperatures and their corresponding SEM images for precipitation with pH 2 antisolvent, and an addition flowrate of 4 ml/min. The weight based average molecular mass is significantly decreasing with increasing pretreatment temperature. The SEM images indicate, in terms of morphology, the most uniform spherical particles for 180 °C pretreatment temperature. Particles from a 160 °C pretreatment show smaller particles. When increased temperatures are applied, the final particles seem to fuse together.

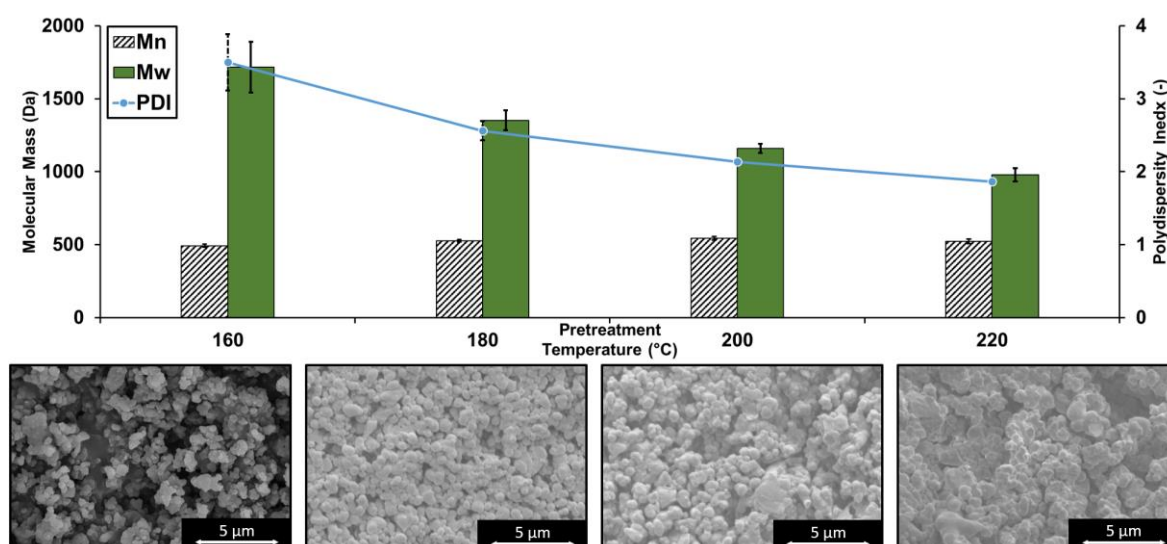


Figure 2: Molecular mass of lignins from pretreatment temperatures ranging from 160 °C to 220 °C and the corresponding SEM images for precipitation with pH 2 antisolvent and an addition flowrate of 4 ml/min.

The particle size distributions and median diameters given in Figure 3 show smaller particle sizes for a pretreatment temperature of 160 °C compared to higher pretreatment temperatures. However, particles from the 220 °C pretreatment seem to be very clustered and might not be separated in dispersion. Further investigation in liquid suspension is necessary in order to investigate the particle behaviour and size further.

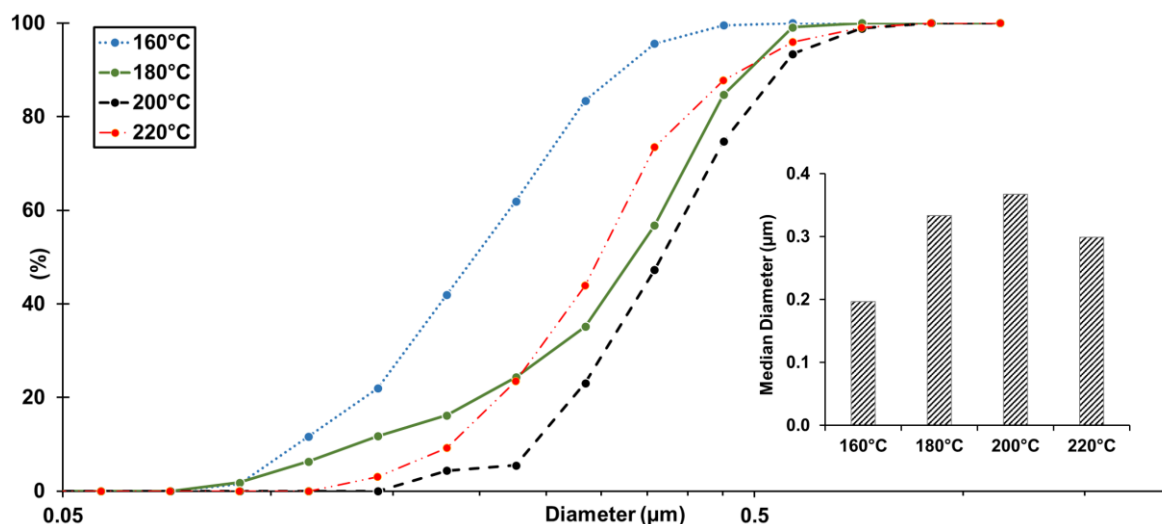


Figure 3: Cumulative distributions of lignin particles from pretreatment temperatures ranging from 160 °C to 220 °C and the corresponding median diameters for precipitation with pH 2 antisolvent and an addition flowrate of 4 ml/min.

Furthermore, an overall higher concentration of lignin, carbohydrates and degradation products is expected in the resulting OS extracts for increasing pretreatment temperatures (Beisl et al., 2017a) and is confirmed by the total process yields shown in Figure 4. The yields reach up to 47 %w/w total yield based on the lignin content in the wheat straw. The carbohydrates and degradation products, however must be considered as impurities in the precipitation process and might influence the resulting particle size and morphology. The influence of impurities on the particle formation, however, must be further investigated.

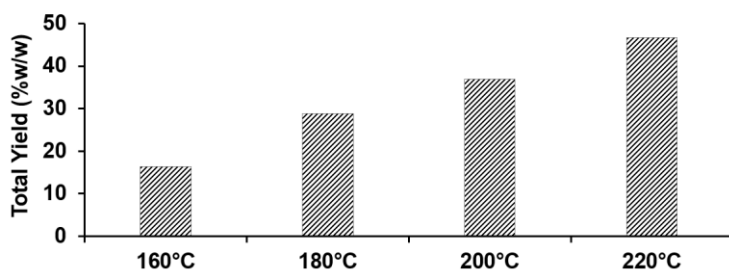


Figure 4: Total Yields of the process covering pretreatment and precipitation for precipitation with pH 2 antisolvent and an addition flowrate of 4 ml/min.

The influence of the pH value of the antisolvent is shown in Figure 5 where a precipitation with pH 1 and pH 2 antisolvent are compared with otherwise identical conditions. The particle size distributions show only minor differences while in terms of morphology slightly better results and more uniform spherical particles can be seen for pH 2 compared to pH 1. The median diameters of the particles are 415 nm and 385 nm for the pH 1 and pH 2 precipitation, respectively. A ratio of antisolvent to extract of 6.3 ml/g was needed for pH 2 antisolvent and 0.4 ml/g for pH 1 antisolvent to reach the final pH value of 2.2. The ethanol concentration of the suspension after precipitation is 43 %w/w and 8 %w/w for the precipitation with pH 1 and pH 2 antisolvent, respectively. The fact of different ethanol concentrations is causing significant changes in terms of the yield. The precipitation applying pH 1 antisolvent reaches only a yield of 45 % compared to the yield reached by the pH 2 precipitation indicating that the solubility of lignin is higher in the pH 1 precipitation due to its higher ethanol concentration.

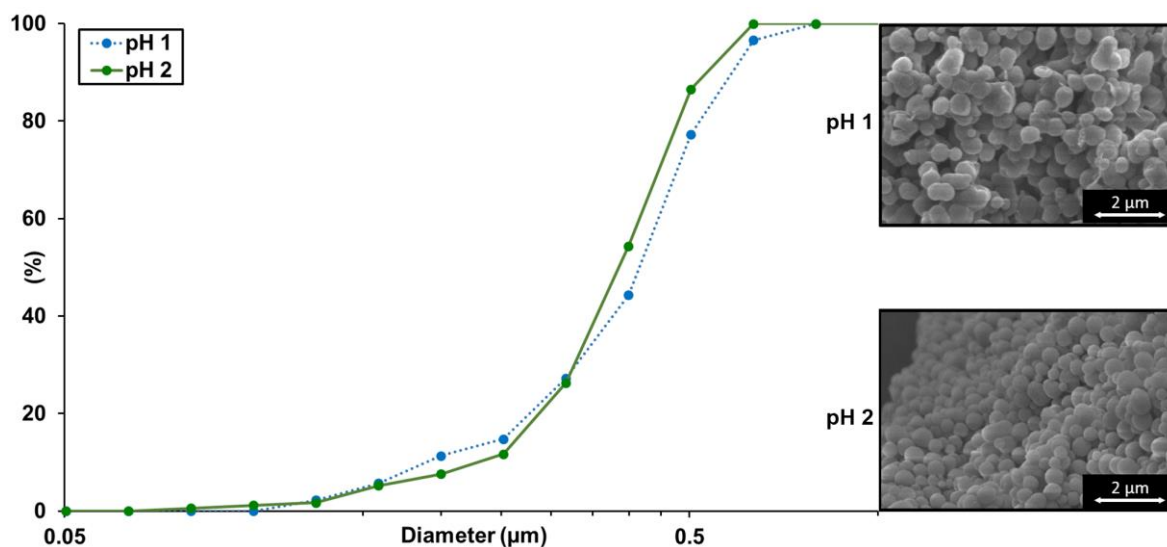


Figure 5: Particle size distributions and SEM images of particles from precipitations with pH 1 and pH 2 antisolvents, and an addition flowrate of 3 ml/min.

The addition speed of antisolvent to the extract is a crucial precipitation parameter since it controls the degree of lignin supersaturation, Supersaturation in turn has significant influence on the precipitation mechanisms and particularly on the nucleation (Lewis et al., 2015). Therefore, the particle size varies with varying supersaturation and addition speed of antisolvent. Figure 6 shows particle size distributions of precipitation with addition flowrates ranging from 3 to 50.9 ml/min. A significantly reduced particle size distribution can be seen for the highest addition flowrate whereas the particle size distributions for addition flowrates of 3 and 4 ml/min show only minor differences. The median diameters of the reveal values of 400 nm, 372 nm and 193 nm for addition flowrates of 3 ml/min, 4 ml/min and 50.9 ml/min, respectively. The tendency of this findings is consistent with the results of Li et al. (Li et al., 2016) where particle sizes decreased from around 300 nm to around 110 nm by increasing the addition speed of water into a dioxane Kraft lignin solution from 0.33 to 6.9 ml/min.

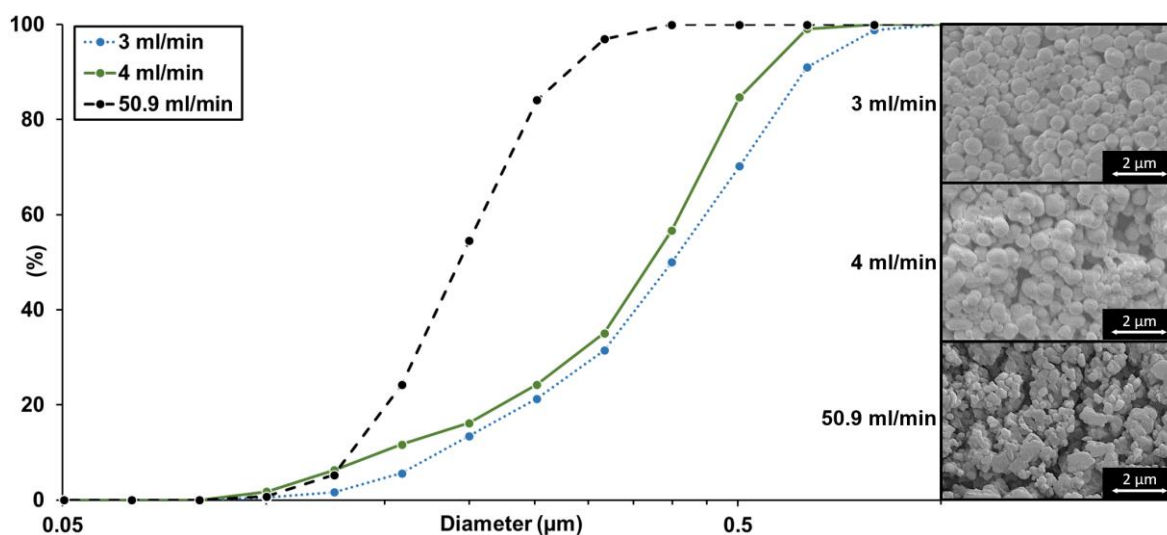


Figure 6: Cumulative particle size distributions and SEM images of particles from precipitations with addition flowrates of 3, 4 and 50.9 ml/min, and pH 2 antisolvent.

4. Conclusion

Direct precipitation of submicron lignin particles from wheat straw OS extracts applying diluted sulphuric acid as antisolvent was shown. Pretreatment temperatures were investigated ranging from 180 °C to 220 °C which showed increasing yields with increased temperatures. However, a temperature of 180 °C showed the best results in terms of the morphology of the particles. The pH value of the antisolvent showed only minor influence on the particle size distribution of the dried particles when lowered from pH 2 to pH 1. Furthermore, increasing addition flowrates of antisolvent into the extract can significantly decrease the resulting particle sizes to around 200 nm.

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References

- Beisl, S., Biermair, F., Friedl, A., Mundigler, N., Miltner, A., 2017a, Sequential Extrusion and Organosolv Pretreatment for Wheat Straw Valorization, *Chemical Engineering Transactions*, 61, 853–858.
- Beisl, S., Friedl, A., Miltner, A., 2017b, Lignin from Micro- to Nanosize: Applications, *International Journal of Molecular Sciences*, 18, 2367.
- Beisl, S., Miltner, A., Friedl, A., 2017c, Lignin from Micro- to Nanosize: Production Methods, *International Journal of Molecular Sciences*, 18, 1244.
- Calvo-Flores, F.G., Dobado, J.A., 2010, Lignin as Renewable Raw Material, *ChemSusChem* 3, 1227–1235.
- Chandra, R.P., Bura, R., Mabee, W.E., Berlin, A., Pan, X., Saddler, J.N., 2007, Substrate Pretreatment: The Key to Effective Enzymatic Hydrolysis of Lignocellulosics? Chapter in: *Biofuels*, Springer, Berlin, Heidelberg, 67–93.
- Gellerstedt, G., Henriksson, G., 2008, Lignins: Major Sources, Structure and Properties, Chapter in: *Monomers, Polymers and Composites from Renewable Resources*, Elsevier, Amsterdam, 201–224.
- Huijgen, W.J.J., Smit, A.T., de Wild, P.J., 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.
- Hussain, F., 2006, Polymer-matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview, *Journal of Composite Materials*, 40, 1511–1575.
- Leskinen, T., Smyth, M., Xiao, Y., Lintinen, K., Mattinen, M., Kostianen, M.A., Oinas, P., Österberg, M., 2017, Scaling Up Production of Colloidal Lignin Particles, *Nordic Pulp & Paper Research Journal*, 32, 586–596.
- Lewis, A., Seckler, M.M., Kramer, H., van Rosmalen, G., 2015, Precipitation and anti-solvent crystallization, Chapter in: *Industrial Crystallization*, Cambridge University Press, Cambridge, UK, 234–260.
- Li, H., Deng, Y., Wu, H., Ren, Y., Qiu, X., Zheng, D., Li, C., 2016, Self-assembly of kraft lignin into nanospheres in dioxane-water mixtures, *Holzforschung* 70, 725–731.
- Sannigrahi, P., Ragauskas, A.J., 2011, Characterization of Fermentation Residues from the Production of Bio-Ethanol from Lignocellulosic Feedstocks, *Journal of Biobased Materials and Bioenergy*, 5, 514–519.
- Tuck, C.O., Perez, E., Horvath, I.T., Sheldon, R.A., Poliakoff, M., 2012, Valorization of Biomass: Deriving More Value from Waste, *Science*, 337, 695–699.
- Weinwurm, F., Driljo, 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.
- Xu, T., Zhang, N., Nichols, H.L., Shi, D., Wen, X., 2007, Modification of nanostructured materials for biomedical applications, *Materials Science and Engineering: C*, 27, 579–594.
- Zhang, M.L., Fan, Y.T., Xing, Y., Pan, C.M., Zhang, G.S., Lay, J.J., 2007, Enhanced biohydrogen production from cornstalk wastes with acidification pretreatment by mixed anaerobic cultures, *Biomass and Bioenergy*, 31, 250–254.