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Potential of a short rotation coppice poplar as a feedstock for platform chemicals and lignin-based building blocks

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ABSTRACT

In the context of a biorefinery, the potential of the short rotation coppice "poplar with bark" as a feedstock for the acid-catalyzed ethanol-water Organosolv process and furthermore for possible applications of the biomass components was investigated aiming at optimal separation of the non-standardized woody biomass. The study was supported and evaluated by an experimental design (Box-Behnken). The statistical analysis showed an increase in lignin yield with rising process intensity with an optimum for precipitated lignin yield of 42%. A change in downstream processing from lignin precipitation by simple dilution of the reaction water to stripping of the ethanol provided a 10% higher lignin yield. Molecular weight distribution of the lignin samples as well as the number of aliphatic OH-groups within the lignin molecules decreased with intensified conditions whereas the phenolic group content increased. The cellulose content in the fibre fraction is hardly influenced by the pulping conditions, lignin and hemicellulose removal lead to a raising cellulose recovery.

1. Introduction

In a developing bioeconomy there is a growing demand for non-food biomass in order to produce bioenergy and biofuels as well as biobased materials and chemicals (Scarlat et al., 2015). The biomass should be produced in sufficient quantities and in a sustainable way. In this context, lignocellulosic perennial crops (LPCs) are often cited as a sustainable biomass source (Monti et al., 2009; Wagner and Lewandowski, 2017). LPCs have, especially in comparison to conventional annual biomass crops, several environmental advantages. These environmental advantages are the ability to grow on contaminated and marginal land (no competition with feed and food crops) (Gelfand et al., 2013), significantly lower nitrate leaching, reduced soil erosion and a higher species richness as well as abundance compared to annual crops (Rowe et al., 2009). Additionally an increase in soil organic carbon (Harris et al., 2015), as well as an improved soil quality (Milà i Canals et al., 2007) and lower greenhouse gas emission are reached through cultivation and utilization of LPCs.

Examples for LPCs are perennial grasses (e.g. *Miscanthus*, switchgrass) and woody perennials like short rotation coppice (SRC trees: *Salix* ssp. (willow), *Populus* L. (poplar), *Alnus* spp. (alder) or *Robinia pseudoacacia* (black locust)). These trees have the ability to regrow from rootstock and can thus be harvested every 3–5 years (Kauter et al., 2003). In Northern Europe, e.g. Sweden, mostly willow is grown, whereas in Central and Southern Europe poplar is predominantly cultivated due to its higher productivity under the prevailing climatic conditions (Aylott et al., 2008; Spinelli et al., 2008). Poplar is a low-input crop which only needs little amounts of fertilizer (Boehmel et al., 2008). In a commercial plantation under well-managed conditions dry matter biomass yields of between 8.0 and 12.0 tonnes per hectare and year are achievable (Mitchell et al., 1999).

Poplar biomass can be utilised in several different conversion pathways. There are various studies investigating the utilisation of SRC biomass as a resource for biofuel and bioenergy (Kauter et al., 2003, 2001; Roedl, 2010). Ray et al. for example investigated the accessibility of cell wall glucose of short rotation willows as a factor for its biofuel potential (Ray et al., 2012). Another study of I. Dimitriiou demonstrated the effect of waste water and sewage sludge applied on SRC plantations on the subsequent bioenergy production (Dimitriou and Rosenqvist, 2011). However, less research was done in the field of

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utilising the biomass as feedstock for a lignocellulose biorefinery in a primary refining module. This implies the conversion of renewable resources into the value-added platform molecules (cellulose, lignin, hemicellulose) and products for material applications (Aylott et al., 2008; Bauen et al., 2010; Michels and Wagemann, 2010). Poplar is a promising feedstock for such conversion and material usage due to its favourable biomass composition (Sannigrahi et al., 2010).

Lignocellulose biomass such as poplar mainly consists of the two most abundant natural biopolymers cellulose and lignin and a third polymer, called hemicellulose, composed of hexoses and pentoses (Mondal, 2015; Sun et al., 2012). In common, lignin consists of three major building blocks. Based on the structural differences within the numbers of methoxy groups located on the C_6 aromatic side, these monomer units will also be called hydroxy phenyl (H), methoxyphenyl (G: guaiacyl) and 2,6-dimethoxyphenol (S: syringyl). The building blocks are linked through ether and carbon-carbon bonds (e.g. α-***O***-4, β-***O***-4, 4-***O***-5, β-1, β-β, 5-5 etc.) and form a three dimensional amorphous network (Dorrestijn et al., 2000; Sjöström, 1993). The ratio and number of the different building blocks in the lignin molecule depend on the origin and type of the lignocellulosic biomass (Gellerstedt and Henriksson, 2008). Moreover structural and functional features are also affected by the choice of pulping process that is used to separate and extract the three main components (Rinaldi et al., 2016). The functionality of the lignin, and particular OH-number, is important for the development of strategies within the generation of so called low emission, bio-based building blocks for material applications.

The Organosolv process, first described in 1931 by Kleinert and Tayenthal (1931) is an environmental friendly way (Ferraz et al., 2000) to fractionate lignocellulosic biomass into cellulose, hemicellulose and a high-quality lignin which is sulfur-free, has a narrow molecular weight distribution and is well suited for high-value application (Robles et al., 2018). Besides that the hemicellulose fraction is isolated more efficiently than with conventional processes and the conversion of pretreated cellulose into sugars by enzymatic hydrolysis is improved. An additional advantage is the utilization of organic solvents which enable a simple recovery of the pulping medium. Despite a lot of available studies on ethanol-water Organosolv pulping the optimum process parameters need to be adapted for every biomass regarding the desired target composition of extracted lignin, solid or saccharified cellulose and the amount of converted hemicellulose depending on the planned usage of the different fractions (Zhang et al., 2016).

In industrial scale pulping processes generally standard wood chips size from debarked soft wood and hard wood are processed. However, from SRC plantations such a standardized debarked wood chip material is not available. Only bark containing wood chips with smaller dimensions and inhomogeneously particle size distribution can be economically produced due to the stem thickness of the 3–5 year old plants. It is advantageous to utilise the biomass including the bark, as the bark accounts for up to 34% dry matter content of the harvested biomass in a short rotation coppice system (Guidi et al., 2008). In addition, usually a larger part of the lignin is located in the bark in comparison to the wood, whereas the ash content is up to 5% higher in the bark compared to wood of willow and poplar plants (Feng et al., 2013; Klasnja et al., 2002). To our knowledge no data concerning a catalyzed ethanol-water Organosolv process applied to a short rotation poplar are available.

In the present work a sulfuric-acid catalyzed ethanol-water Organosolv process is adapted to the non-standardized lignocellulosic biomass “poplar with bark” to consider the potential of the short rotation coppice as a feedstock for a conceptual biorefinery.

The process was investigated regarding the effect of process parameters on yield and structural features of the lignin (molecular weight and number of hydroxy groups). Another focus was on the evaluation of yield, composition and quality of the polysaccharide fractions (cellulose, hemicellulose/-hydrolysate) including the enzymatic hydrolyzability of the generated raw fibres. The study was supported by a design of experiments (Box-Behnken-model) (Box and Behnken, 1960) to screen the effects of the individual process parameters on the one hand and on the other hand to optimize the parameter combination with regard to lignin yield and structural properties.

2. Materials and methods

2.1. Materials

The poplar plants were harvested after three years of growing on a short rotation trials field of the University of Hohenheim (Germany). The air-dried biomass was milled in an ALPINA cutting mill into particle sizes less than 2 mm and subsequently extracted three times with acetone in a circulation reactor at 50 °C for 60 min to eliminate lipophilic materials in the bark that might disturb the pulping process. The solvent was recovered by vacuum rotation evaporation and the air dried biomass was used as feedstock for the Organosolv process without additional treatment.

All chemical reagents in this study were purchased from VWR or Sigma-Aldrich and used as received without further purification.

2.2. Analytical characterization of biomass and Organosolv fractions

The pre-extracted biomass as well as all solid products of the pulping process was analyzed according to the NREL/TP-510-42618 procedure (Sluiter et al., 2008). Extractives in the biomass were analytically characterized using the NREL/TP-510-42619 method (Sluiter et al., 2005). Sugars, byproducts and degradation products in the liquid fractions were determined according to the NREL/TP-510-42623 procedure using a HPLC series 1200 device by Agilent Technologies (Germany) with a 125-0129 precolumn and an Aminex 87H, 300 × 7.8 mm (by Bio RAD, Germany). As mobile phase sulfuric acid (0.005 mol/l) was used with a flow rate of 0.6 ml/min, column temperature was 50 °C and temperature of RID was 40 °C (Sluiter et al., 2006).

For all solid fractions ash and moisture content were determined and elemental analysis (CHON) was performed with an Electron Flash EA 1112 device by THERMO. The lignin samples were additionally analyzed by gel permeation chromatography (GPC) in THF after acetylation with pyridine and acetic anhydride (2:1) with a concentration of 2–3 g/l to determine the molar average molecular weight (M_w), the number average molecular weight (M_n) and the polydispersity index ($D = M_w/M_n$). The measurements were performed on an HPLC series 1100 device by Agilent Technologies (Germany) with a PSS SDV precolumn (5 µm particle size), 3 PSS SDV columns (100 Å, 1000 Å, 10^5 Å) and a Diode Array Detector. THF was used as mobile phase with a flow rate of 1 ml/min. The column temperature was 35 °C and polystyrene standards in a range of 682–66000 g/mol were used for calibration.

2.2.1. ^{31}P-NMR of lignin

P-NMR analysis was performed on a Bruker Avance III wide bore 300 MHz spectrometer using a BBO 5 mm probe head. 15 mg of the generated lignin samples were phosphitylated with 50 µl 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane in 400 µl $CDCl_3$ and pyridine (1.6:1 v/v). Cylohexanol (4.58 mg/ml) as an internal standard and Cr(III)acetylacetonate (3.59 mg/ml) as relaxation reagent in 150 µl Pyridin/$CDCl_3$ are added. The detailed procedure is described and published by Granata and Argyropoulos (1995). Data was analyzed using TopSpin 3.5pl7 and the hydroxy group content was calculated based on the OH-group content of the internal standard in mmol/g.

2.3. The ethanol-water Organosolv process

The catalyzed ethanol-water Organosolv process was performed in a 500 ml batch reactor supplied from Berghof Company (Eningen, Germany). The dry biomass to pulping solution (ethanol/water/sulfuric