

Effect of steam explosion treatment on chemical composition and characteristic of organosolv fescue lignin



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ABSTRACT

Tall fescue, a grass currently grown as forage, presents a good potential as a feedstock in the development of biorefining. In this study, combination of steam explosion and an acetic/formic acid “organosolv” pretreatments are applied on raw fescue to optimize lignin extraction yields and obtain specific products. In a first step, fescue is pretreated by steam explosion under severity factors from 1.4 to 4.2. These treatments allow hemicelluloses solubilization and open the lignocellulosic structure. Steam exploded solid residues are then treated with an acetic acid (50%)/formic acid (30%)/water (20%) mixture. Extracted lignins are precipitated and characterized by size exclusion chromatography (SEC), ³¹P NMR and HSQC NMR. Results show that acetic and formic acids extracted lignins present G, H and S units with ferulate and *p*-coumarate. Lignin typical linkages identified are of β -O-4 and spirodienone substructures. Combination of steam explosion and acetic and formic acid pretreatments increases extraction yields from 30% to 100%. Moreover, an increase of the steam explosion treatment intensity induces chemical modifications in lignin structure such β -O-4 and spirodienone substructure degradations, increase of free COOH and phenolic OH bonds, decrease of aliphatic OH ferulate and *p*-coumarate bonds and changes in G/H/S units proportions. Steam explosion intensity affects also lignin molecular weights.

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1. Introduction

Tall fescue, a pluriannual *Poaceae* family plant, is currently used for animal feed and presents a good potential for the second-generation biorefining development. Fescue grows typically in Northern Europe from March to October with a productivity of six to fifteen tons of dry matter by ha. This crop possesses a long vegetation season, a ground cover in winter and an easy culture and harvest which requires less of plant protection agents (Besnard et al., 2013).

Lignin is the second most abundant natural polymer in the world behind cellulose. Its occurrence and relative amount in biomass depends mainly on plant species. Currently, lignin interest increase in Europe as high-added value materials for specific applications and formulations (Azadi et al., 2013; Rochez et al., 2013; Thakur and Thakur, 2015).

Lignin is formed by oxidative biopolymerization of three alcohol-containing monomers (called monolignols): synapyl alcohol, *p*-coumaryl alcohol and hydroxyphenyl alcohol which account respectively syringyl units (S), guaiacyl units (G) and *p*-hydroxyphenyl units (H). Lignin presents a complex structure with irregular and specific ether or carbon-carbon bonds including mostly β -O-4, β -1, β - β , 4-O-5, 5-5, β -5. Units and bonds proportions vary according to plant species, plant origins or agronomic parameters such as harvesting time. In lignocellulosic structure, lignin is moreover linked to sugar polymers (cellulose and hemicelluloses) with ether and ester bonds creating a “lignin-carbohydrates complex” (Manara et al., 2014; Vanderghem et al., 2012; Zikeli et al., 2016).

Different processes are able to partially break lignin bonds in lignocellulosic structures. Chemical pretreatments are particularly effective for lignin extraction/recovery. Commonly, mineral or organic acid and bases and/or organic solvents (organosolv process) are used alone or in combination. In the specific case of organosolv pretreatments, methanol, phenol, 1,4-dioxane, ethanol, acetic acid, acetic acid/formic acid are the most convenient organic solvents for industrial pretreatments process. Organic acids give good separa-

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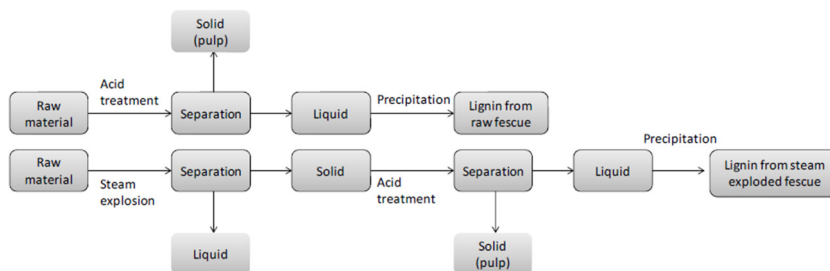


Fig. 1. Pretreatment diagram of tall fescue.

tion yields between carbohydrates and lignin with different effects on lignocellulosic structure, the hydrogen ions, formed during dissolution, increase the delignification, the hemicelluloses hydrolysis and lignin solubilization (Delmas, 2011; Vanderghem et al., 2012).

In another way, literature shows that steam explosion technology impacts lignin structure (Balat 2011; Kataria et al., 2016). Steam explosion is a thermophysico-chemical process which provides mechanical destructuration of lignocellulosic material by a combination of two steps: vapocacking and explosive decompression. Chemical reactions are initiated by thermo-hydrolyzed of biomass (Duque et al., 2016; Jacquet et al., 2015; Kataria et al., 2016; Sun and Cheng, 2002).

This technology does not require any chemical products for the pretreatment. The overall process carbon footprint depends on the heat source used to produce steam and recycling of vapor generated. Steam explosion biomass pretreatment for the second-generation biorefinery is currently in industrial prospect. Future technical challenges aim to obtain a continuous or semi-continuous process in high scale with a minimum of investment and an optimum energetic efficiency.

The purpose of the study is to combine the steam explosion low environmental impact technology with organosolv process (acetic acid/formic acid pretreatment) to increase significantly lignin extraction yield and obtain specific product. Results obtained show effects of this pretreatment combination on lignin extraction yields and lignin structural properties and take place in a context of global biorefining of lignocellulosic material.

2. Materials and methods

2.1. Raw material

Tall fescue (*Festuca arundinacea*) was cultivated in Belgium by Walloon Agricultural Research Center in Gembloux. Material was previously dried (three days at 60 °C) and milled to reach a particle size of 0.75 mm.

2.2. Steam explosion process

Steam explosion pretreatment was carried out in prototype pilot scale equipment with a 50 L reactor volume (Jacquet et al., 2011, 2012). This prototype consists in a steam generator (29.4 kW, operating pressure: 6.0 MPa), a 50 L vessel designed to reach a maximum operating pressure of 5.1 MPa and an explosion tank, in which the product is recovered. A quick-opening ball valve, placed between the vessel and the explosion tank, is used to decrease quickly the pressure and gives the explosion effect. Steam explosion pretreatments were carried out on 1 kg of tall fescue (91.4% of dry matter). After placing the material in the reactor, combination of steam pressure and retention time was adjusted to obtain a severity factor ranging from 1.4 to 4.2 (Fig. 2). This range was selected to preserve cellulose from thermal degradations as observed by Jacquet et al., (2011). As described further in Fig. 1, pretreated material was cen-

trifuged in a Rousset RC40VxR (18 L bowl volume) at 3000 rpm to separate solid from liquid. Severity factor are calculated with the relation developed by Jacquet et al. which obeys to Arrhenius law (kinetics of first order):

$$S = \log_{10} \sum \frac{14,75(t_{n+1} - t_n)}{(T_{n+1} - T_n)} \left[\exp\left(\frac{T_{n+1} - 100}{14,75}\right) - \exp\left(\frac{T_n - 100}{14,75}\right) \right]$$

Where: S = severity factor, t = process time (s) and T = process temperature (°C). Time needed to reach the desired temperature is also taken into account (Jacquet et al., 2011).

2.3. Organosolv process and lignin purification

Raw tall fescue and steam exploded tall fescue were pretreated according to the protocol described in Vanderghem et al. (2012) with some adaptations (Fig. 1). Pretreatments were performed in 500 mL double-necked boiling flasks at 107 °C in a formic acid/acetic acid/water mixture of 50/30/20 (% volume ratio) for 3 h at a liquid/dry matter ratio of 25/1. During cooking, stirring was continuously applied at 400 rpm. After the reaction, media were vacuum filtered on a fritted disk (40–100 μm pore size; Robu Glasfilter-Geräte GmbH) to recover solid and liquid fractions (“pulp” and “black liquor”). Pulps were then washed twice with the same cooking mixture (added to black liquor) and distilled water (2 L). Pulp yield after pretreatment was determined gravimetrically after drying at 50 °C to constant weight. Black liquor (containing mostly the lignin) was diluted 1/10 in water and pH was adjusted to 2.0 in order to precipitate lignin, which were recovered by centrifugation (Beckman Coulter Avanti J-E, 8000g, 10 min) and freeze-dried.

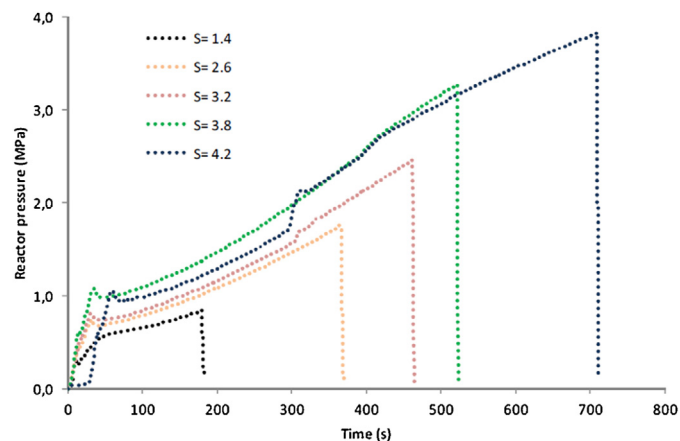


Fig. 2. Reactor pressure during steam explosion pretreatment under different severity factors (S).

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