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Esterification of organosolv lignin under supercritical conditions

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ABSTRACT

An organosolv lignin, extracted in organic acid media, named Biolignin^{TM}, was acetylated with acetic anhydride in supercritical carbon dioxide ($scCO_2$). The effect of moisture and specific surface of lignin sample, temperature (50, 80, 100, 150 °C), reaction time and the use of a catalyst have been studied using analytical techniques such as FT-IR, quantitative ^{31}P NMR and Differential Scanning Calorimetry (DSC).

The reaction appeared to be more efficient when a dried organosolv lignin was used (97% Dry Matter) and with a specific surface of 0.645 m^2/g. The highest degree of substitution of acetylated samples was obtained after 1 h of reaction at a temperature of 100 °C (180 bar) and in the presence of pyridine as a catalyst.

When compared with conventionally acetylated lignin (using a solvent medium), it appeared that supercritical conditions allowed a higher yield of acetylation and a decrease of the glass transition temperature of the lignin.

1. Introduction

Lignin is composed of three main phenylpropanoid units, namely sinapyl (S), guaiacyl (G), and *p*-hydroxylphenyl (H) unit and clearly is the most abundant substance based on aromatic moieties in nature. The amount of this natural polymer on the earth is estimated at about 300Gt (Singh et al., 2005). It is then a very promising substitute to most of petrochemicals. Chemical modification of lignin, such as esterification, could be used to improve its compatibility for a further transformation. Esterified lignin can be used for example to synthesize durable composites (Olsson, 2011), in unsaturated thermosets (Thielemans and Wool, 2005) or also as a biopolymer precursor for carbon fibers (Zhang and Ogale, 2013). In addition, lignin can be esterified (generally acetylated) in order to determine and quantify its functional groups (El Mansouri and Salvado, 2007; Cateto et al., 2008; Delmas et al., 2011). Lignin is generally esterified with a mixture of anhydride and pyridine (1:1, v/v) and the procedure to recover modified lignin is long and tedious.

In the present work we have developed an efficient and environmental friendly procedure to acetylate lignin using supercritical carbon dioxide as a solvent (termed as sc-conditions) and acetic anhydride as a reagent with or without the presence of pyridine as the catalyst. The aim of the study was to develop a “green” and user-friendly protocol in order to quickly recover the acetylated lignins suppressing most of the time-consuming separation/purification steps. Indeed, the use of sc-conditions instead of conventional conditions has several advantages. As a result, it promotes the induced polymer and biopolymer transformations these were effected to be easier and complete (Yalpani, 1993); the organic solvents and toxic by-products are eliminated and/or significantly reduced; and finally, the separation and purification of the final product is generally faster and easier (Young et al., 2003).

These advantages of the use of supercritical carbon dioxide as a solvent for biopolymer chemical modifications have already been demonstrated in the case of cellulose oxidation (Camy et al., 2009).

Following acetylation under sc-conditions, the modified lignin could then be used for further analysis or for a further chemical transformation.

The procedure was optimized on a type of lignin obtained from an organosolv process. This lignin, named Biolignin^{TM}, is obtained from CIMV refining process (Benjelloun-Mlayah et al., 2009; Benjelloun-Mlayah and Delmas, 2011).

The efficiency of the acetylation was evaluated by conventional analytical methods such as Attenuated Total Reflectance system Fourier Transform Infrared (ATR-FT-IR) as well as quantitative ^{31}P NMR spectroscopy. Comparison between the conventional acetylation of the Biolignin^{TM} showed that the physical parameters were not the same for both procedures. It appeared that the conventional

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media allowed a complete dissolution of the Biolignin^{TM} sample during the reaction; whereas the Biolignin^{TM} sample acetylated in sc-conditions was kept solid state.

The analysis of the acetylated samples by Differential Scanning Calorimetry (DSC) permitted to compare the physical parameters of the samples.

2. Materials and methods

2.1. Materials

The organosolv lignin studied below is named Biolignin^{TM}. Biolignin^{TM} was extracted at pilot scale (CIMV, Pomacle, France) from wheat straw with a mixture of acetic acid/formic acid/water (55:30:15, w/w/w) using the CIMV process (Benjelloun-Mlayah et al., 2009; Benjelloun-Mlayah and Delmas, 2011). The lignin content of the Biolignin^{TM} (i.e. Klason lignin content) was about 89.8% ± 1.5%. The molecular weight in number (M_n) and the molecular weight in weight (M_w) of the Biolignin^{TM} sample were evaluated at 889 and 1719 g/mol, respectively.

All chemicals used were of reagent or HPLC grade and were purchased from Panreac (Castellar del Vallès, España). The CO_2 used for the supercritical esterification was provided by Air Liquide with 99.9% purity.

The supercritical experiments were performed in a stainless steel high pressure vessel with an internal working volume of 90 mL (Top Industrie, France) equipped with an ISCO pump (Teledyne Isco, model 260D) to fill the reactor from the CO_2 tank.

2.2. Biolignin^{TM} acetylation using supercritical carbon dioxide (sc-conditons)

About 1 g of a Biolignin^{TM} sample with a known moisture content was put in an empty tea bag and placed in the 90 mL-scCO_2 reactor. Before pressurization with CO_2, a large excess of acetic anhydride was added in the reactor (about 5 g, i.e. > 10 eq/free OH of the Biolignin^{TM} sample) (Fig. 1). For the experiments which required a catalyst, 100 μL of pyridine were added to acetic anhydride.

The scCO_2 reactor was heated until reaching the desired temperature and then the CO_2 was introduced into the reactor thanks to the pump with a low flow rate (4–6 mL/min) to avoid any Biolignin^{TM} powder dispersion until the desired pressure was reached. In this work, the CO_2 is used as a solvent in order to allow the contact between acetic anhydride and solid lignin.

At the end of the defined reaction time, the pressure was slowly released using the release valve (Fig. 1). When the pressure in the reactor reached the atmospheric pressure, it was unsealed and the modified Biolignin^{TM}, contained in the tea bag, was recovered and placed in an oven dryer at 50 °C during 48 h.

The temperatures studied in this work were 50, 80, 100 and 150 °C and the pressure range was 100–180 bar. In this work, the different pressures used were selectively chosen from the experimental liquid-fluid diagram of the CO_2–acetic anhydride binary system previously described by Calvo and de Loos (2006) and Muljana et al. (2011) in order to ensure a single-phase system which is necessary for optimal reaction conditions.

2.3. Biolignin^{TM} acetylation using conventional procedures

Acetylation was conducted using acetyl anhydride and pyridine. Conventional acetylations were performed for comparison of experimental results with acetylated Biolignins^{TM} under sc-conditions. Three reference experiments were conducted (Table 1):

- Control 1: The conditions selected in this experiment were these usually selected for the acetylation of lignin used for a further analytical analysis. Hence, 2 mL of pyridine and 2 mL of acetic anhydride were added to 200 mg of Biolignin^{TM} with known moisture content. The sample was stirred at room temperature during 72 h.
- Control 2: 4 mL of pyridine and 4 mL of acetic anhydride were placed in a 100 mL-flask equipped with a condenser. 400 mg of Biolignin^{TM} were then added. The sample was stirred at 100 °C during 1 h.
- Control 3: 4 mL of 1,4-dioxane, 4 mL of acetic anhydride and 100 μL of pyridine were placed in a 100 mL-flask equipped with a condenser. 400 mg of Biolignin^{TM} were then added. The sample was stirred at 100 °C during 1 h.

The reaction was quenched by adding a mixture of methylene chloride and methanol (8:1, v/v, 18 mL for 200 mg of unmodified Biolignin^{TM}). Stirring was maintained at room temperature during 30 min. The mixture was then transferred to a funnel and washed

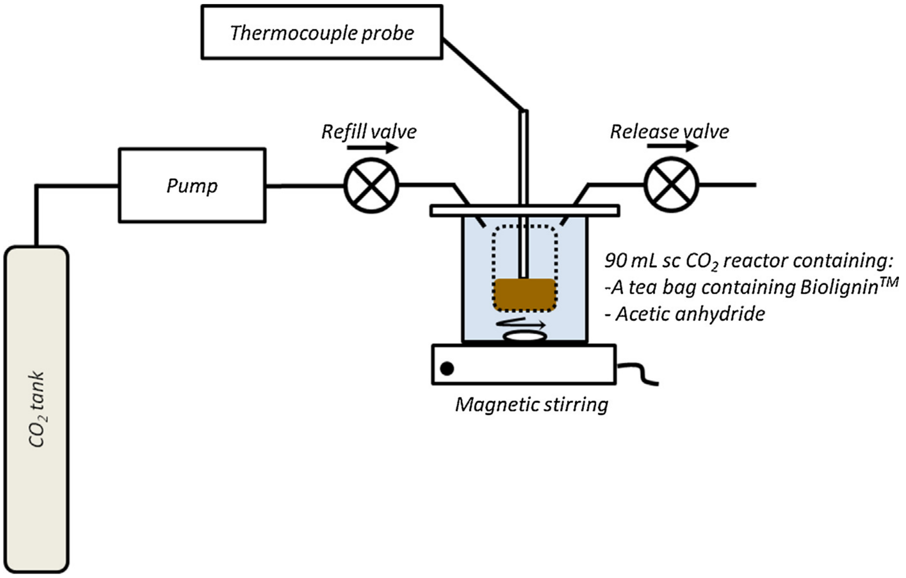

Fig. 1. Scheme of the Biolignin^{TM} acetylation under sc-conditions.