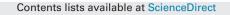
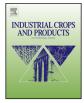
ELSEVIER



## Industrial Crops and Products



CrossMark

journal homepage: www.elsevier.com/locate/indcrop

### Evaluation of industrial lignins for biocomposites production

### Diane Schorr<sup>a</sup>, Papa Niokhor Diouf<sup>a,b</sup>, Tatjana Stevanovic<sup>a,\*</sup>

<sup>a</sup> Wood Research center, Laval University, Department of Wood Science and Forestry, Québec, QC, Canada <sup>b</sup> SEREX (Service de recherche et d'expertise en transformation des produits forestiers), Amqui, QC, Canada

#### ARTICLE INFO

Article history: Received 1 May 2013 Received in revised form 9 October 2013 Accepted 11 October 2013

Keywords: Black liquor Precipitation by CO<sub>2</sub> Industrial lignins Physico-chemical and thermal properties Biocomposites

#### ABSTRACT

Following important market changes to the pulp and paper industry, the interest in valorization of industrial lignins has significantly increased. Recent advancements with the LignoBoost process in Europe have made the availability of Kraft lignins a realistic prospective. The objective of the present study was to identify industrial lignins that have the potential to replace a portion of polyolefins, such as polyethylenes within composites. In order to identify the best lignin candidates for applications in biomaterials, five industrial lignins were compared. Softwood and hardwood Kraft lignins were precipitated by CO2 from black liquor obtained from two Quebec pulp mills. The isolated lignins were characterized along with the commercial Kraft lignin Indulin, Soda (from wheat straw) and pyrolytic lignin obtained from pyrolysis of hardwood biomass. Elementary composition and purity of the studied lignins were determined. Phenolic contents were studied by UV-spectrophotometry, while additional structural characteristics and molecular mass distribution were analyzed by FT-IR, pyrolysis-GC-MS and by GPC. Thermal properties were determined by TGA and TMA. The results obtained confirmed that the major differences between the studied lignins were related to the plant origin and to the industrial process from which they were issued. The properties of Kraft lignins compared to the other lignins samples studied seem to be the best suited for use in biocomposites based on polyolefins. Such application of Kraft lignins could promote new pathways to the value added products based on by-products of pulp and paper industry, while simultaneously contributing to the decrease of greenhouse gases by replacing a part of petroleum origin materials by natural products.

© 2013 Elsevier B.V. All rights reserved.

#### 1. Introduction

Lignins are renewable and natural polymers. Five millions of metric tons of lignins are produced in the world mostly as a noncommercialized waste product per year (Vishtal and Kraslawski, 2011). In pulp and paper industries, lignins are the main components of residual liquors, notably black liquor from the Kraft process. Their principal application is as fuel to produce energy. Only 2% of all industrial lignins and only 100,000 tons of Kraft lignins available are valorized per year (Gosselink et al., 2004b). In Quebec, 130,000t of black liquor containing lignins could be removed by the pulp and paper industries, per year, without disturbing the mill production (MRNF-FPInnovations-Paprican, 2009). Nowadays, 230,000 t of plastics from petroleum origin are produced per year. The production of new polyolefin biocomposites containing industrial lignins could contribute both to creation of new value added products and to a reduction of use of petrol, a nonrenewable resource of polyolefins. Thus, lignin valorization could improve the carbon footprint of the plastics production. Several

studies are already done on the biocomposites based on polyolefins (Doherty et al., 2011); like polypropylene (Maldhure et al., 2011) or polyethylene (Sailaja and Deepthi, 2010). These new products could help improve the economic situation in pulp and paper industry which is in process of integration biorefinery concept and would also bring new knowledge in the eco-materials field, by contributing to the decrease of greenhouse gases by using a natural product in partial replacement of synthetic ones.

It is well known that lignin structure is dependent on plant origin. Softwood lignins are composed essentially of guaiacyl units (coming from coniferyl alcohol) whereas hardwood lignins are based on varying ratios of guaiacyl (G) and syringyl (S) units (Rohella et al., 1997). Finally grass lignins are composed of G, S and *p*-hydroxyphenyl units (H). Lignin structure changes during the processes of biomass transformation: due to reactions occurring during the pulping (Soda or Kraft for lignins studied here) processes (Chakar and Ragauskas, 2004) or through fast pyrolysis, which is another source of lignin studied in this work. The lignins fragmentations occurring during Kraft or Soda pulping facilitate the solubilisation of the lignins from wood or other lignocellulosic raw materials and they are ultimately found in the residual liquors. These lignins can be recovered by different processes. The most common is the precipitation by strong acid but a new method has

<sup>\*</sup> Corresponding author. Tel.: +1 418 656 7337; fax: +1 418 656 5262. *E-mail address*: Tatjana.Stevanovic@sbf.ulaval.ca (T. Stevanovic).

<sup>0926-6690/\$ -</sup> see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.indcrop.2013.10.014

been proposed recently to replace strong acid by carbon dioxide (Öhman et al., 2006). This process contributes to sequestration of greenhouse gas, the CO<sub>2</sub>, which is generated within Kraft process itself. During biomass pyrolysis, lignins are degraded more drastically than during pulping processes because of high temperatures (500 °C) applied in pyrolytic oil production. Pyrolytic lignin is recovered by pouring the pyrolytic oil in iced water under stirring. This lignin was found to be partly responsible of the instability of the bio oil. Several researches suggested to remove it from bio-oil in order to improve its quality. This pyrolytic lignin may thus become available and it would be necessary to find some applications to justify its isolation (Jiang et al., 2012; Scholze et al., 2001).

Many studies have been done on chemical characterization of different industrial lignins. The isolation and characterization of herbaceous lignins for best application has been recently reported by Monteil-Rivera et al. (2013). Soda lignins were studied by Mousavian and Doherty (2010) for fuel application. Several authors published methods to standardize their experiments (Baumberger et al., 2007) or to compare different methods of characterization of different lignins such as Kraft, lignosulfonate, organosolv lignins (El Mansouri and Salvadò, 2007; Gosselink et al., 2004a). These experiments contributed to better understand the chemical and physical properties of lignins in order to propose new opportunities for their utilisation.

In this investigation, two lignins precipitated from black liquor from two Quebec pulp and paper mills (Domtar Windsor and Kruger Wayagamack) following a procedure inspired by Lignoboost along with one commercial Kraft lignin (Indulin AT), Soda and pyrolytic lignins were studied. The study of thermal and physico-chemical properties of these lignins was performed in order to determine the most appropriate lignin for use in composites based on polyolefins and to propose other applications for the studied lignins. It could promote new pathway to value added products based on by-products of the pulp and paper mill industries.

#### 2. Materials and methods

#### 2.1. Materials

#### 2.1.1. Black liquor

Two Kraft black liquors, used to precipitate Kraft lignin, were furnished by Kruger Wayagamack and Domtar Windsor. Kruger Wayagamack black liquor was determined to have 50.9% of solid content with a pH = 14 and a volumetric mass of  $1.27 \text{ g ml}^{-1}$ . Domtar Windsor black liquor had 24.0% of solid content with a pH = 13 and a volumetric mass of  $1.12 \text{ g ml}^{-1}$ .

#### 2.1.2. Other lignins

Two other commercial lignins were used for comparison with the precipitated lignins from black liquors: Indulin AT lignin from the Westvaco Company, wheat straw Soda lignin (Protobind 2400) from the Green Value enterprises and a pyrolytic lignin supplied by SEREX.

#### 2.2. Precipitation and purification of lignins from black liquor

#### 2.2.1. Precipitation and purification

The lignins were precipitated following the procedure inspired by LignoBoost process (Öhman et al., 2006; Öhman and Thelandier, 2007). Black liquor (25% in solid content), was heated to 75 °C under stirring and pH-meter control. Carbon dioxide was diffused in the black liquor when the temperature has reached 60 °C. The heating was stopped when the pH of the solution dropped from 13–14 to 8–9. The gas flow was controlled (23.6–25.4 ml s<sup>-1</sup> of CO<sub>2</sub>) in order to estimate the total carbon dioxide used during the experiment (3.5 h). The non-purified lignin was recovered by filtration and dried during two days at 60 °C to reduce the quantity of solvent required for purification. The purification step consisted of washing lignins with sulfuric acid (1 M) at 70 °C with stirring during 1 h. Lignins were filtrated and finally washed with distilled water. The precipitate was dried at 60 °C in oven during two days to decrease the moisture content. These precipitation and purification protocols were designed to contribute to greenhouse gas  $(CO_2)$  sequestration and sustainable chemistry principles application (use of sulfuric acid at low concentration without any solvents). In this experiment, we calculated the quantity of  $CO_2$  required during this process (Eq. (1)). To precipitate and purify 1 kg of lignins at 75 °C under the pressure of 1 bar, 861 g of  $CO_2$  were used.

$$m \operatorname{CO}_2 = \sum_{1}^{a} \left( \frac{t \times d}{P \times 1/RT} \times \frac{1}{M} \right) \tag{1}$$

where a = number of experiments; t = reaction time with CO<sub>2</sub> (min); M = molecular mass of CO<sub>2</sub> (g mol<sup>-1</sup>); P = Pressure (Pa); R = 8374 J K<sup>-1</sup> mol<sup>-1</sup>; d = gas flow (min<sup>-1</sup>); T = temperature (K).

#### 2.3. Characterization of lignins

#### 2.3.1. Acetylation

The acetylation of the studied lignins was required for the determination of the phenolic/aliphatic ratios by FT-IR and for the distribution of molecular mass by GPC. Amounts of 300 mg each lignin were mixed with 3 ml of acetic anhydride and 3 ml of pyridine catalyst. The reaction was carried out at 25 °C for 18 h under nitrogen atmosphere. To isolate the acetylated lignin, 150 ml of a mixture of dichloromethane/methanol (9:1 v:v) was added to the mixture and mixed during 30 min. Organic phase was washing with 150 ml of HCl solution (2 M), then, with 150 ml of NaHCO<sub>3</sub> aqueous solution. The last washing was performed with 150 ml of distilled water to eliminate traces of NaHCO<sub>3</sub>. The organic phase was then dried by adding MgSO<sub>4</sub>. The organic phase was removed by rotary evaporation at reduced pressure. The success of acetylation was confirmed by ATR FT-IR.

#### 2.3.2. Chemical composition and functional groups

The ash content was determined following the ASTM D 1102-84 (ASTM D, 2001a). To determine purity of the lignins, the acid-soluble, Klason lignin and the polysaccharide content were determined according to ASTM D 1106-96 (ASTM D, 2001b), Tappi UM250 (TAPPI, 1991) and ASTM D 5896-96 (ASTM D, 2007), respectively.

Elemental analysis was performed with elemental analyser Perklin Elmer 2400. The oxygen was deduced by difference from the total sum (including the ashes). The methoxyl group content was determined according to the ASTM D 1166-84 (ASTM D, 1995). The C9 formulae were calculated from these data using the equation proposed by Freudenberg (1968).

The phenolic hydroxyl groups content was determined by differential UV-spectrophotometric methods as described in the literature (Gärtner and Gellerstedt, 1999; Liitia and Tamminen, 2007) using a UV visible spectrophotometer (Varian, Cary 50). By comparing the absorbance of neutral lignin solution to an alkaline lignin solution at 292–300 and 350–370 nm, the phenolic hydroxyl content was calculated using Eq. (2).

Phenolic OH (mmol/g) = 
$$\frac{0.25 \times A_{300nm} + 0.107 \times A_{350nm}}{0.03} \times \frac{m}{10}$$
 (2)

with  $A_{300nm}$  and  $A_{350nm}$  = absorbance at the wavelength of 292–300 nm and 350–370 nm, 0.03 is the concentration in gl<sup>-1</sup> of lignin in the diluted solution and m is the mass of sample.

Download English Version:

# https://daneshyari.com/en/article/4513468

Download Persian Version:

# https://daneshyari.com/article/4513468

Daneshyari.com