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Reference:

Tofani Giorgio, Cornet Iris, Tavernier Serge.- Separation and recovery of lignin and hydrocarbon derivatives from cardboard
Biomass Conversion and Biorefinery - ISSN 2190-6815 - Heidelberg, Springer heidelberg, 2020, p. 1-16
Full text (Publisher's DOI): <https://doi.org/10.1007/S13399-020-00931-7>
To cite this reference: <https://hdl.handle.net/10067/1704560151162165141>

Separation and recovery of lignin and hydrocarbon derivatives from cardboard

Giorgio Tofani,^{,1} Iris Cornet,² and Serge Tavernier,¹*

¹iPRACS – Intelligence in Processes, Advanced Catalysts and Solvents, Faculty of Applied Engineering, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

²BioWaVE – Biochemical Wastewater Valorisation and Engineering, Faculty of Applied Engineering, University of Antwerp, Groenenborgerlaan 171, B-2020 Antwerp, Belgium

Corresponding Author

*Giorgio Tofani e-mail: giorgio.tofani@uantwerpen.be

ORCID:

Giorgio Tofani: 0000-0001-8745-8759

Iris Cornet: 0000-0002-7057-0944

Serge Tavernier: 0000-0002-4739-8883

Abstract

This study investigates the feasibility of acid precipitation for the separation and recovery of lignin and hydrocarbon derivatives from the waste stream of the alkali extraction of recycled cardboard. The recovery of chemicals from this effluent is complex due to their heterogeneity. Apart from the lignin and hydrocarbon derivatives, also, fillers, inks, and polysaccharides are present. A procedure of fractional acid precipitation was designed, reducing the pH from 10.7 to 8.8, 7.2, 5.1, 3.1, and 1.5. Each solid fraction was analyzed by infrared spectroscopy to determine its chemical composition and amount of precipitate. A mixture of lignin and hydrocarbon derivatives was detected in the solids obtained at pH 3.1. A dichloromethane extraction of the hydrocarbon derivatives was performed. Both recovered lignin and hydrocarbon were analyzed by infrared and gel permeation chromatography. The lignin showed similar characteristics (e.g., molecular weight \approx 10.000 Dalton) as commercial lignin from virgin softwood. For the hydrocarbon derivatives, a molecular weight range between 10000 Dalton and 150 Dalton was observed. In conclusion, this paper shows that the recovery of lignin and hydrocarbon derivatives is scientifically and technologically possible from the waste stream of the cardboard recycling processes. Further research is necessary to improve the extraction efficiency that was around 7.9% for the lignin and around 5.5% of the total amount of extractives compared to their amount in cardboard. Despite the low extraction efficiency, the estimated 9.6 million tons of lignin present in cardboard and the lignin price around 300-500 USD/ton make this research of industrial interest.

Keywords

Lignin valorization, hydrocarbon derivatives valorization, pH fractionation, cardboard, solvent extraction.

1 Introduction

The research on the valorization of wastes becomes more and more intensive due to the increasing importance of recovering chemicals and materials and, in this way, reducing the raw material consumption. Zero waste is also one of the main goals of the European Commission for 2050 [1]. Paper & pulp industry offers an interesting opportunity because several side streams contain a wide range of chemicals that can be recovered [2]. A recycling paper mill can be transformed into a biorefinery able to produce paper products and chemicals. The world paper and board production reached 420 million tons in 2017 [3], where the packaging board was around 55 % [4]. Until now, cardboard is only used as a source of fibers to produce new packaging products when it is recycled [5]. However, in addition to fibers (composed by cellulose, hemicellulose, and lignin), it also contains other organic (e.g., waxes and oils) and inorganic materials (e.g., fillers and ink) [6].

Cardboard is a mixture of different types of wood fibers defined as hardwood and softwood that differ by their chemical composition. Softwood fibers are longer than hardwood fibers (2.5-4.5 mm vs. 0.7-1.6 mm) and have a higher lignin content (25-30 % vs. 20-25 %) [7]. Additionally, the chemical structure of the fibers is influenced by the applied pulping process (chemical and mechanical) of the virgin wood to liberate the cellulosic fibers from the wood structure [8]. The chemical pulping consists of partial chemical removal of lignin and hemicellulose. During the main chemical pulping process, called “Kraft”, around 50 % of the lignin is removed when the fibers will be applied in cardboard production. The fibers after chemical pulping are called “unbleached chemical fibers”. If such fibers are bleached, the lignin will be almost totally removed. The mechanical pulping consists of the mechanical breaking down of the wood chips. Nearly the total original amount of lignin and hemicellulose will remain [9]. Cardboard is mainly composed of chemically pulped softwood fibers because they provide better mechanical properties such as tensile strength [5].

When the cardboard is recycled, it is pulped at about 50°C and at a pH around 11 to liberate the fibers from the board structure [5]. Moreover, the pulp can be further treated with alkali (pH around 12-13) to improve the physical properties of the fibers such as flexibility and tensile strength [10, 11]. The recycling process needs a high yield (more than 80%) due to the low cost of the packaging products. For that reason, the pulping of recycled cardboard is done at lower pH and temperature compared to chemical pulping (pH 14 and temperature >160 °C). Moreover, all the effluents generated in the process are generally recirculated to save water [12].

The present paper aims to verify and understand, for the first time, the recovery of lignin and hydrocarbon derivatives by acid fractionation of the extraction liquid from the alkaline treatment of recycled cardboard (pH 12). The extraction liquid contains the several components described above, i.e., lignin, polysaccharides, waxes, oils, inks, and fillers (mainly calcium carbonate and kaolin). This complexity offers a wide range of chemicals that can be recovered but make the recovery process difficult at the same time. The scope is to evaluate if a recycling cardboard mill can be converted into a biorefinery where chemicals (e.g., lignin and hydrocarbon derivatives) are produced together with cardboard products.

The first target compound is lignin, a three-dimensional phenolic macromolecule composed of oxygenated phenylpropane units that are linked by ether and carbon-carbon bonds. It is the most abundant source of natural aromatics on earth. Lignin can be found and recovered in various plants such as olives [13], rice [14], and oil palm [15]. Several applications of lignin are under study, for example, as a binder [11] or as a source of chemical compounds (e.g., aromatics) [16, 17]. At the industrial level, the primary source of lignin is the one removed from wood during the alkaline “Kraft” pulping process [5]. The remaining alkaline side stream, called “Black liquor”, contains this lignin [18]. Generally, the waste stream is composed of 15 % of solids (10 % organics, 5 % inorganics). Lignin is around 35-45 % of the total organic solid content. The remaining fractions are 40-45% w/w soap and 10-15% w/w other (miscellaneous) organic materials from extractives and polysaccharide degradation [19]. Over the years, numerous studies on lignin isolation from virgin lignocellulosic sources have been published. Different techniques were investigated, i.e., extractions with organic solvents [20, 21], precipitation with inorganic [22], or organic acids [23, 24], enzymatic delignification [25], electrolysis [26] or ion exchange resins [27]. Acid precipitation is the mostly investigated and industrially applied method to recover lignin and tall oil (a mixture of fatty acids and resin acids) from the black liquor of the Kraft process using sulfuric acid, e.g., in the LignoForce system [28] and LignoBoost process [29]. The lignin recovered shows a low amount of contaminants, such as hemicelluloses [30]. The mechanism of the acid fractionation process of lignin was studied on Black Liquors from the pulping of virgin biomass at a laboratory scale [31-33]. In a study of 2009 [31], authors performed an acid fractionation from pH 12.64 to pH 0.72 of a black liquid from the alkaline pulping of *Miscanthus sinensis*. An increase of the solids was observed at pH 10-11 due to the precipitation of the silicate (phytoliths) of the grass and at pH 7-4 attributable to the lignin precipitation. The lignin that precipitated at pH 2.57 and 0.72 exhibited similar characteristics as commercial alkaline lignin. At the higher pHs, the obtained lignin had more impurities due to the presence of hemicelluloses and silicates. The grass, used as raw material, contains a high content of silicate components that are not present in the wood. In contrast, recycled cardboard includes high quantities of insoluble compounds due to the presence of ink, calcium carbonate, and kaolin [5]. Wang et al. [32] researched the acid fractionation of steam-exploded corn stalk for lignin recovery. The acid fractions were extracted at pH 5.3, pH 4.0, and pH 2.0. After the steam-explosion, the corn stalk was washed with water to remove the hemicelluloses. Then, the residual solids (containing lignin and cellulose) were pulped in alkaline conditions to dissolve the lignin. This method cannot be applied for the alkaline effluent from wood or board pulping because hemicellulose would be present. Lourencon et al. [33] compared the different precipitation behavior of two black liquors, i.e., from hardwood pulp and softwood pulp. The solid fractions were collected at pH values of 9, 7, 5, 3, and 1. It was observed that the pKa and molecular weight (Mw) were the two main factors that controlled acid lignin precipitation. Higher Mw lignins were recovered at higher pH values, and the ashes were measured in the fractions at pH 9, 7, 5 and 1 but not at pH 3. It was demonstrated that softwood and hardwood lignins have different characteristics in particular in molecular weight, due to their different natural synthesis. Hydrochloric acid (HCl) was used during the experiments. However, this is a problem for industrial-scale applications in paper & pulp industry because it can cause the formation of chlorinated products with the organic matter [34], for example, through chlorination of the hydroxylic groups in the propane units of the lignin. Furthermore, two different black liquors were

1 studied, each with a specific type of lignin, i.e., derived from hardwood and softwood. Instead, recycled cardboard
2 fibers are a mixture of both.

3 In our study, the recovery of lignin from cardboard was investigated. As far as we know, two studies approached this
4 target. One patent [35] was published concerning the recovery of lignin from side streams of the paper recycling
5 industry. An extraction liquid, composed of glycol and an organic or Lewis acid (e.g., para-toluenesulfonic acid), was
6 used for impregnation of the cardboard at high temperature ($>100\text{ }^{\circ}\text{C}$). This process causes the chemical breakdown
7 of the materials and then their isolation. However, the degradation of cellulose fibers must be avoided if the target is
8 the use of cardboard to produce paper products.

9 The second study is published by Jahan et al. [36], who investigated the lignin recovery from cardboard by cooking it
10 in 90% formic acid at 100°C for 3.5 h. The authors were able to recover 4.3 g of lignin from 100 g of cardboard.
11 However, the lignin was not characterized in detail (only ^1H NMR was done), and the starting lignin amount was not
12 reported. An important parameter for evaluating potential applications is the molecular weight of the recovered lignin,
13 but this was also not reported. The pulp yield after cooking was 73 % on a dry weight basis, and 40 % at the end of
14 the treatment (cooking, alkaline extraction, and bleaching). The reported process is not suitable if the target is to
15 preserve the fibers to reach high pulp yield due to the cellulose degradation that occurs during the cooking.
16 The molecular weight is one of the parameters that influence the applications of lignin, i.e., high-molecular-weight
17 lignin (>1500 Dalton) can be used as a binder because it improves the mechanical properties of the materials by
18 enhancing the strength of the matrix. On the other hand, low-molecular-weight lignin (hundreds Dalton) is a possible
19 feedstock for adhesive manufacturing because it contains a high amount of phenolic hydroxyl groups [37].

20 Besides lignin, the second target compounds in this study are the hydrocarbon derivatives, (e.g., oils and waxes).
21 These olefinic compounds can be present as part of the additives used in paper production (i.e., coating agents and
22 adhesives) [38]. The hydrocarbon derivatives can be removed from paper products using organic solvents. During the
23 lignin recovery from black liquors, tall oil is also recovered [7]. It is a mixture of extractives (fatty and resin acids)
24 from wood (around 2-4 % of the total mass). Tall oil is used as an additive for adhesives, rubbers, and inks, and as an
25 emulsifier. The hydrocarbon derivatives from cardboard could also be studied as additives for different applications.
26 Venditti et al. studied the separation of waxes from cardboard using extraction with supercritical carbon dioxide [39].
27 However, the high costs of this process do not permit its application in recycled paper manufacturing.

28 The research reported in this article investigates the extraction of lignin and hydrocarbon derivatives from recycled
29 cardboard pulp by alkaline treatment. Both lignin and hydrocarbon derivatives are soluble in alkaline conditions [40,
30 41]. The alkaline treatment conditions were pH 12 and 100°C to extract hydrocarbon derivatives [38] and lignin that
31 has a pKa value between 10.5 and 11 [42]. The harsh conditions that are usually applied (temperatures above 150°C
32 and a pH above 13) were avoided as they lead to cellulose degradation, as reported in the literature [9] because
33 cardboard manufacturing requires high yields to be cost-efficient [5]. Afterward, an acid fractionation was performed,
34 inspired by the work of Lourencon et al. [33] on the fractional extraction of lignin from hardwood and softwood, but
35 with both the following differences. Firstly, hydrochloric acid was replaced by sulfuric acid, which is the mostly

applied acid in the pulp & paper industry. Secondly, the acid fractionation was developed to obtain solid fractions at pH 10.7, 8.8, 7.2, 5.1, 3.1, and 1.5.

Finally, the mixture of lignin and hydrocarbon derivatives present in the fraction at pH 3 was separated by organic solvent extraction. Of high interest was to evaluate whether softwood or hardwood lignin (because wood is the primary source to produce cardboard products) was extracted. The cardboard sample taken into account was composed of around 54 % softwood and 46 % hardwood. Therefore, a mixture of lignins could be expected during the fractionation. Another point of interest is the range of molecular weight of the hydrocarbon derivatives.

As far as we know, the present paper elaborates for the first time the valorization of recycled cardboard as a stream of valuable chemicals by using acid fractionation.

2 Experimental section

2.1 Starting materials, reagents and solvents

Recycled cardboard pulp (Ashes: 13.2 %, Consistency (K) 30 %, Fiber composition: unbleached chemical fibers 53 %, bleached chemical fibers 25 %, mechanical fibers 22 %, Wood types: 54 % softwood (STD of 3), 48 % hardwood (STD of 3), Kappa number of 49 STD of 1, Lignin 7.4 % STD of 0.2, Extractives 2.2 % STD of 0.2) is provided from a paper mill located in Belgium. The measurement and calculation of lignin and extractive amounts are reported in the Supporting Information. Commercial Lignin (low sulfonate content, $M_w \approx 10,000$ Dalton, synonym: Lignin, Kraft, CAS: 8068-05-1) was purchased from Sigma Aldrich. Other chemicals were purchased from Acros Organics.

2.2 Alkali extraction of cardboard

60 g of recycled cardboard pulp (the equivalent of 18 g of dry fibers) was diluted in 500 ml of water. Furthermore, 6 ml of NaOH 2 M and 136 mg of $MgSO_4$ were added to reach pH 11.8. The resulting mixture was heated at 100°C for 1 h in a 1 L closed Parr reactor. At the end of the reaction, the mixture (final pH more than 10.5) was filtered using a sieve in stainless steel with a pore size of 0.16 mm. The waste stream collected (440 g) was centrifuged to separate the liquid phase from the solids (1 h, 20 °C, 4223 Relative Centrifugal Force, RCF). The liquid was used for further experiments.

2.3 Acid Cascade

435 g of liquid phase recovered from the alkaline extractions was placed in a 600 ml beaker, and the pH was measured to be 10.7. An “acid cascade” was then performed. 2 M H_2SO_4 was added to the solution to reach a pH of 8.8. Precipitation was observed. The mixture was centrifuged for 1 h at 20°C at 4223 RCF. The solid was removed, dried, and analyzed by infrared. Then, H_2SO_4 was added until desired pH levels of 7.2, 5.1, 3.1, and 1.5. After each step, the precipitated solid was recovered and analyzed following the same procedure as described above. In the case of the fraction at pH 3.1, the solid was centrifuged, washed with acid water at pH 3, dried in an oven at 50°C and analyzed using infrared. The extra washing step was necessary to remove the residual sulfuric acid from the sample. Furthermore, 40 ml of the residual liquid phase (light yellow) at pH 1.5 was neutralized with sodium hydroxide (0.95

ml) until pH 7, dried, and analyzed by infrared. The neutralization was necessary due to the high quantity of saccharides present in the sample. There was a risk of caramelization at low pH, during the drying process, at 50-60°C.

2.4 Fractionation of the solid fraction at pH 3.1

100 mg of the solid fraction recovered at pH 3.1 was left for 2 h in 6 ml of dichloromethane (DCM) at room temperature. At the end of the treatment, the DCM was removed, and the solid was washed with 3 ml of DCM. Both DCM fractions were combined. The liquid and the solid phases were dried at 30°C for 3 h. The solids (lignin fraction) recovered amounted to 83 mg (yield 83 %). Also, 17 mg of hydrocarbons were collected from the liquid phase.

2.5 Mass Balance

The dry mass of each fraction recovered during the fractionation steps was measured and reported in Section 3.7 **Mass Balance**. 50.58 g of the final liquid phase at pH 1.5 was dried at 30 °C until constant weight. It was used for the mass balance. This further step was necessary because the liquid sample at pH 1.5 previously described was neutralized using sodium hydroxide to prevent the caramelization of the sugars and to maintain the same drying conditions for all the fractions (50-60 °C). All the measurements were made using a scale with a level of accuracy of ± 0.0005 g.

2.6 Analytical methods

2.6.3 Infrared and microscope analysis

Each solid fraction commercial lignin recovered lignin, and hydrocarbons were analyzed by ATR (Attenuated total reflectance) using an ALPHA FTIR (Fourier Transform Infrared Spectroscopy) spectrometer from Bruker. Solid fractions, commercial lignin, and recovered lignin were milled using a mortar to have homogeneous samples. The hydrocarbons, in the liquid phase, were analyzed as such. Each sample was analyzed, doing 64 scans in the range between 4000 and 600 cm^{-1} using a quantity between 2-3 mg.

The microscopic analysis of the solid fraction after centrifugation of the alkaline effluent was observed using a Lumos FTIR-microscope from Bruker with a magnification of 36x.

A list of the main infrared peaks is reported in Table 1 and Table 2.

2.6.4 Water-GPC analysis

Gel permeation chromatography (GPC) of commercial lignin and recovered lignin were performed by an LC-2010A HT Shimadzu, Malvern 270 dual detector. The column was a PolySep-GFC-P 2000 (300 x 7.8 mm) using as eluent phase water: acetonitrile (50:50. v/v) at 0.8 ml/min. 3 mg of solids were completely solubilized in 3 ml of a solution at pH 8. The solution was filtered using a nylon membrane filter (0.2 μm) and analyzed. Commercial lignin (low sulfonate content. $M_w \approx 10,000$ Dalton, synonym: lignin kraft, CAS: 8068-05-1) was used as a reference.

2.6.5 THF-GPC analysis

Hydrocarbon compounds were analyzed by a G1310A IsoPump Agilent, G1329A ALS Agilent autosampler, G1362A RID detector, and a couple of Phenogel™ 5 μm (300 x 7.8 mm) columns. The eluent phase used was tetrahydrofuran (100 % v) at 1 ml/min. 7 mg of solids were solubilized in 2 ml of THF. The solution was filtered using PTFE filters (0.2 μm) and analyzed. Linear hydrocarbons and long-chain ethers (from C-6 to C-44) were used as standards.

2.6.6 NMR-HSQC analysis

A Bruker 400 MHz-NMR analyzed commercial lignin and recovered lignin. The Nuclear Magnetic Resonance Heteronuclear single quantum coherence spectroscopy (NMR-HSQC) analysis was done in the range of 0-9 ppm for ^1H and 0-200 ppm for C^{13} . 20 mg of solids were diluted in 1 ml of D_2O and analyzed.

3 Results and Discussion

3.1 Commercial lignin as a reference sample

Commercial Lignin (synonym: lignin, kraft. CAS: 8068-05-1) was selected as a reference sample for the following reasons. First, Kraft lignin is the most common lignin on the market [9]. The cardboard sample contains 53 % of unbleached chemical fibers. The rest is 25 % of bleached chemical fibers (no lignin) and 22 % of mechanical fibers. So, the lignin from unbleached chemical fibers is the majority. Moreover, the reference lignin is obtained from pulping of softwood fibers (as defined by the Mw of around 10,000 Dalton as reported in **2.1 Starting materials, reagents, and solvents** [33]). The cardboard sample used in this work is composed of around 54 % of softwood fibers. The commercial lignin can be used to evaluate if the lignin extracted from recycled cardboard is softwood, hardwood, or a mixture of both.

3.2 Alkali extraction of cardboard

Cardboard dry fibers (18 g) were subjected to alkali extraction. The overall scheme is presented in Figure 1. The liquid phase was separated from the cellulose fibers by filtration and collected. After centrifugation of the filtrate, a brown solution was obtained. It can be observed that the liquid phase was not completely clear. This is due to the presence of very fine particles of insoluble material. The dry mass of the organic and inorganic components in the supernatant was 1.246 g (6.92 % of the total weight). The solids, separated by centrifugation, were dried. The total dry mass of the pellet was 1.045 g (5.81 % of the total weight). These data are included in a summary of the mass balance in Table 3 (**3.7 Mass Balance**). The solid phase has two layers, a brown bottom layer and a white upper one. Both layers were analyzed by FTIR analysis. The infrared peaks, observed in the range between 4000 and 600 cm^{-1} , in these and later spectra in Figure 2 can be found in Table 1.

In Figure 2, both spectra present a mixture of cellulose fibers, calcium carbonate, and kaolin [43-45]. The “Brown” fraction differs from the “White” layer by the intensity of the infrared cellulose fibers peak ($\approx 1000 \text{ cm}^{-1}$). Another main difference is the presence of a broad peak at 3300 cm^{-1} of the fiber’s hydroxyl groups in the “Brown” fraction.

This hydroxyl peak, mainly caused by the fibers, has a higher intensity in the “Brown” extracted fraction than the “White” one. The reason is that the “White” fraction contains more fillers than the “Brown” fraction. As consequence, the fibers are less present in the ‘white fraction’. The identification of filler peaks (calcium carbonate and kaolin) confirms the hypothesis about the presence of fine particles in the supernatant. Furthermore, the solid after centrifugation and drying was observed using a microscope (Figure 3).

Figure 3 permits to observe the presence of fine particles (fillers), brown fibers, and colored pigments (ink). These results give the information that the alkali-insoluble materials present in the alkaline effluent after filtration is a mixture of cellulose fibers and inorganic materials.

3.3 Acid Cascade

The supernatant after centrifugation was fractionated by acid precipitation at different pH values (8.8, 7.2, 5.1, 3.1, and 1.5). The process permits to obtain different solid fractions.

FTIR analyzed the solids recovered at the different pH values. The list of the main peaks identified in the FTIR spectra is reported in Table 1. The infrared spectrum in Figure 4 shows a mixture of inorganic and organic compounds for the first solid fraction at pH 8.8. Calcium carbonate [44], kaolin [45], polysaccharides of cellulose fibers [42,46], and other organic compounds [43] were identified (see Table 1). The presence of organic compounds can be explained by the fact that the fine particles of insoluble components (calcium carbonate and kaolin) adsorbed to organic material [47,48] and precipitated together. This phenomenon is caused by intermolecular bonds between the hydroxyl groups of organic compounds and inorganic materials such as the interactions with the cationic ions (Ca^{2+} of calcium carbonate) and the formation of hydrogen bonds with the hydroxyl groups of kaolin. The heterogeneity of the components present in the mixture does not permit a further explanation of the type of interactions present between organic and inorganic matters.

The FTIR spectrum of the fraction at pH 7.2 (Figure 5) shows that the inorganic fillers described above are still present but, in particular, calcium carbonate, at a lower concentration. Consequently, the presence of organic compounds, such as lignin and polysaccharides, becomes more relevant. Polysaccharides, in particular, hemicelluloses, are soluble in alkaline solutions, and they can be precipitated by protonation of the hydroxyl groups [49]. Moreover, their molecular weight and branching influence the precipitation, but the heterogeneity of the sample prevents to obtain more detailed information. The precipitation of organic matter at pH 7 is expected when compared to other studies [31, 33], where it was reported that the lignin fraction at a pH above 3 was contaminated by hemicellulose. An increase in the amount of precipitate starting from pH 7 was observed. However, the amount of solid recovered from recycled cardboard at pH 7.2 (25 mg) was smaller than in the case of solid at pH 8.8 (36 mg). The higher amount of solids obtained at pH 8.8 compared to the mass at pH 7.2 is not in accordance with the results reported in the literature [31,33]. The minor amount of hemicellulose and lignin and higher amount of ashes in recycled cardboard with respect to virgin lignocellulose materials can be due to the chemical pulping of 78 % of the fibers and addition of fillers to made paper products. During pulping of the original wood, hemicelluloses and lignin will have been totally or partially removed.

The infrared spectrum obtained at pH 5.1, as presented in Figure 6, shows the presence of polysaccharides (such as hemicellulose) and other organic compounds such as lignin, see Table 1. The analysis of this fraction presents the first observation of lignin, but the sample is still contaminated. The co-precipitation of lignin in the presence of other materials at pH around 5 is similar to the case of lignin recovered from black liquor [31]. The lignin is precipitated because the hydrogen ions (from sulfuric acid) interact with the phenolic groups destabilizing the polymer and permitting the precipitation [41]. The lignin is protonated because the pH is below the pKa of the phenolic groups (pKa 9.4–10.8) [50]. The infrared analysis shows that the fraction is still “contaminated” by other organic compounds (i.e., polysaccharides). It can be assumed that inorganic compounds are not present anymore. In fact, the shape of the peaks around 1000 cm^{-1} has changed. The acid pH of this fraction (pH 5.1) guarantees the removal of calcium carbonate by reacting with the sulfuric acid that was added during the process, forming calcium sulfate and carbon dioxide [51]. However, the presence of said calcium sulfate is not detected. Probably, it is due to a too low concentration to be detected by the infrared.

In the infrared spectrum, after precipitation at pH 3.1 (see Figure 7), lignin and hydrocarbon derivatives such as fatty acids and waxes can be identified (see Table 1). This spectrum will be discussed more in detail further on (see section **3.4 Organic solvent extraction of the solid fraction pH 3.1**). 127 mg of solid material was collected. The precipitation of lignin at this pH is due to its lower molecular weight, which increases its solubility [41]. The carbonyl groups are protonated because the pH is below their pKa (≈ 4.4) [41]. The presence of hydrocarbon derivatives is explained by their conversion from salts ($-\text{COO}^-\text{Na}^+$) to acid ($-\text{COOH}$) at low pH, which makes them less soluble. For example, oleic acid becomes insoluble at a pH lower than in 4 [52]. This fraction is extremely interesting because it is a mixture of lignin and hydrocarbon derivatives and differs from the literature. In fact, the lignin recovered at pH of around 3 from black liquors is almost pure, with a low amount of impurities (hemicelluloses and inorganics) [31,33].

On the infrared spectrum of the precipitate at pH 1.5 (Figure 8), the predominance of sulfate ion (SO_4^{2-}) [44] was observed (see Table 1), which is caused by the constant addition of sulfuric acid. The fraction seems to be a mixture of insoluble inorganic salts such as calcium sulfate dihydrate [51]. The final liquid obtained at pH 1.5 is a clear yellow solution (Figure 1).

Figure 9 shows the infrared spectrum of the solids after evaporation of the liquid phase at pH 1.5. As in the previous fraction, it is a mixture of inorganic materials, e.g., sulfates, and organic compounds mainly sugars formed during the alkaline extraction and acid hydrolysis that caused the degradation of the polysaccharides [9]. The peak at 1570 cm^{-1} can be related to the presence of amine N-H bending. The latter can be justified by the presence of azo dyes [54]. The amine is formed by hydrolysis of the nitrogen-nitrogen double bonds. Such kind of dyes is usually applied on cardboard to give a homogeneous coloration. It is another difference between acid fractionation of recycled cardboard and wood pulps.

The yield of the process is described in paragraph **3.7 Mass Balance**.

3.4 Organic solvent extraction of the solid fraction pH 3.1

The solid fraction at pH 3.1 was identified as a mixture of lignin and hydrocarbons. The precipitation at this pH value is caused by the protonation of ionized reactive groups phenols and carboxylic acids because the pH is below the pKa of the functional groups. (respectively pKa 9.4–10.8 and ≈ 4.4) [41]. The acid precipitation with fractionation allowed to remove the polysaccharides and inorganic materials that could otherwise contaminate lignin and hydrocarbons. Afterward, the two latter components were separated with dichloromethane extraction. They can be observed in Figure 1.

The infrared spectra of the hydrocarbon fraction (H) in Figure 10 present mainly oils and waxes. It is a mixture of several components, such as polyolefins and waxes [5]. The main peaks identified are reported in Table 2.

According to the literature [47], the peaks in the spectra of lignin (L) in Figure 10 were identified. Its interpretation is reported in Table 2. The presence of the peak at 1080 cm^{-1} (C-O deformation in secondary alcohol and aliphatic ether) indicates that this lignin is from softwood when compared to the literature [33]. The main differences between the commercial lignin and the recovered lignin from cardboard are visible at wavenumbers 2926 cm^{-1} and 1651 cm^{-1} . These two peaks are indicative of the presence of residual hydrocarbon derivatives. A 2D-NMR analysis was performed to confirm this hypothesis (Figure 11). The commercial lignin and recovered lignin were compared in the area of hydrocarbon derivatives to observe the contamination in the lignin.

The 2D-NMR analysis showed a difference between the two lignins in the aliphatic area (0-50 ppm for C^{13} , 0-2 ppm H^1). The signals of the cardboard recovered lignin are more intense and more present than commercial lignin signals. It can be correlated to the presence of hydrocarbon derivatives [43] because the carbon atoms of the aliphatic chains are present between 10 and 50 ppm of C^{13} . The protons of the alkyl groups are detected in the area from 0.9 to 2 ppm H^1 . The protons of the alcohol groups are observed between 1 and 4 ppm H^1 . This information supports the hypothesis that hydrocarbon derivatives still contaminate the recovered lignin.

Finally, the GPC analysis is necessary to determine the molecular weight of the lignin that is a crucial parameter to differentiate the two types of wood. Further discussion can be found in Section 3.5 Lignin analysis.

3.5 Lignin analysis

The lignin fraction obtained after extraction was analyzed by GPC (Figure 12), which was performed to allow the comparison between the recovered lignin from cardboard and the commercial lignin “Mw $\approx 10,000$ Dalton”. The two compounds have a similar molecular weight as an overlap of the main peak at 4.8 ml of retention volume was found for both. It means that the recovered lignin is similar to the commercial lignin.

This analysis permits to presume that the recovered lignin is originating from softwood because it has a high molecular weight similar to the commercial lignin (softwood) and to the literature [33] (the authors found that lignin fraction at pH 3 has an Mw of 10.301 for softwood and 3890 for hardwood). However, further analysis is necessary to evaluate the structure of the recovered lignin because it is hard to differentiate between softwood and hardwood due to the heterogeneous composition of the recycled cardboard used as starting material.

3.6 Hydrocarbon analysis

The hydrocarbon fraction was also analyzed by gel permeation chromatography. Figure 13 shows a wide range of molecular weights. The elution time spread from 11.7 min to 16.4 min., corresponding to an Mw-range from 10000 Dalton to 150 Dalton. This wide range of molecular weights is caused by the heterogeneous source of the hydrocarbons present in cardboard. This fraction needs further investigation to increase the recovered quantity and to find applications for its use as a commodity chemical. e.g., for binders. Maybe, this hydrocarbon mixture can even be further fractionated to become a source of chemical compounds.

3.7 Mass Balance

The mass balance after alkali treatment, acid cascade, and extraction steps are reported in Table 2. The alkali treatment permitted to recover around 1 g of solids from the filtrate by centrifugation. This value is dependent on the pore size of the filter. Losses could be decreased by reducing the pore size.

During the acid fractionation, 366 mg of sulfuric acid was needed to reach pH 3.1, which permitted the precipitation of lignin and hydrocarbons (in total 127 mg). Instead, 1.324 g of sulfuric acid was used to achieve a pH of 1.5. For further optimization studies of the acid cascade, several options are proposed. Firstly, the number of pH steps in the acid cascade can be reduced to decrease the costs. It is not necessary to go to pH 1.5 because the target products are already recovered at pH 3.1. In this way, high amounts of acid could be saved. However, a future study of the recirculation and reuse of the acid in the acid cascade is still necessary for cost savings. Furthermore, a study on the recovery of the lignins present in the fractions at pH 7.2 and 5.1 is suggested.

After the DCM extraction of the pH 3.1 precipitated solid, 83 % (105 mg) of the mass is the lignin fraction (with a residual amount of hydrocarbon derivatives). The other 17 % (22 mg) is the hydrocarbon part. Hydrocarbon derivatives are present in low amounts because they originate from additives in cardboard production. Typical substances are waxes (e.g. paraffin and polyethylene resins), coating agents (e.g. polyethylene and polypropylene), and other additives (e.g. fatty acids). This part of the process can be optimized, searching for a greener solvent that could replace the dichloromethane. In comparison to the starting 18 g of cardboard fibers, the masses obtained for the lignin and the hydrocarbon fractions are respectively around 0.58 % and 0.12 %. The amount of the lignin present in the 18 g of cardboard (starting material) is 1.332 g (7.4 % of the mass, as reported in the **Experimental section**). Therefore, the lignin recovered by the acid fractionation and solvent extraction (105 mg) is less than 7.9 % of the total lignin present. Moreover, the 105 mg of lignin from 18 g of cardboard (around 0.56 g of lignin in 100 g of cardboard) is a low amount in comparison to the lignin recovery reported in the literature from Jahan et al. [36] where 4.3 g of lignin were recovered from 100 g of cardboard. Jahan et al. measured a starting Kappa number of 41.4. It is possible to estimate a lignin amount of 6.2 % in the starting material using the formula reported in the **Supporting Information**. It means that around 69 % of lignin was extracted. However, the cooking process reported in the literature also caused cellulose degradation.

Instead, the starting quantity of extractives present in the pulp is 0.398 g (2.2 % of the mass, as reported in the **Experimental section**). It means that the hydrocarbons recovered are around 5.5 % of the total extractives. The values

are not high because of the alkali extraction, was deliberately done in a “soft” way in order to preserve the quality of the fibers. Their mass after the alkali treatment was around 16.3 g (91 %). The mass loss of only 9 % shows that this process can be used to preserve the fibers and valorize the liquid “waste stream”. If the primary target would be the recovery of the lignin, then the alkali extraction could be performed in “harder” conditions to favor the delignification of the fibers, as reported in the literature [9].

3.8 Future research

Further studies will enable to increase the purity and quantity of lignin and hydrocarbon derivatives by a selection of greener solvents and improvement of the precipitation conditions. If the quantity of hydrocarbon derivatives recovered continues to be low, they have to be considered as a contaminant. The study on the recovery of the lignin present in the fractions at pH 7.2 and 5.1 will permit to obtain lignin fractions having different properties for diverse applications because their water solubility at different pH and molecular weight will be different. Further research can be done to improve the process. Some possible approaches are the reduction of the acid amount and its recirculation, the removal of insoluble inorganic suspensions by flocculation using a coagulating agent (e.g., aluminum sulfate) and the study of green solvents to improve the separation of hydrocarbon derivatives from lignin. Moreover, lignin and hydrocarbon derivatives recovered by this process can be studied to evaluate their possible applications, for example, binder, absorber, or a source of chemical compounds.

4 Conclusion

This study was the first work that wanted to verify the feasibility of the recovery of lignin and hydrocarbon derivatives from alkaline effluents of recycled cardboard using an acid fractionation process. It was demonstrated that this process is similar to the fractionation of black liquor generated during the chemical pulping of wood [33]. However, the following differences were observed:

1. Alkaline effluents from recycled cardboard contain insoluble materials, e.g., inks and calcium carbonate that are not present in alkaline effluents from wood (Black liquor).
2. The precipitation of inorganic materials at a pH above 7 is observed both during the acid fractionation of recycled cardboard effluent and during the precipitation of silicates from *Miscanthus sinensis* described in the literature [31]. The reason is that recycled cardboard contains a high amount of ashes (13.2%) composed of filler compounds such as kaolin and that *Miscanthus sinensis*, and in general grasses, contains a significant amount of silicates. Instead, the precipitation of inorganics is not that evident during the fractionation of black liquors from wood pulping because this raw material contains low amounts of ashes (around 2-4 %) [5,6].
3. The acid water at pH 1.5 of recycled cardboard contains dyes that are not present in Black liquors of wood and other virgin biomasses.

4. The hemicellulose that precipitated at pH 7.2 is present in smaller quantities in recycled cardboard than in wood pulp because the recycled cardboard is composed of 78% of chemical fibers of which the hemicelluloses were almost totally removed during the Kraft pulping.
5. The fraction at pH 3.1 from recycled cardboard is different from the same fraction obtained from Black liquor, generated during the chemical pulping of wood. The lignin from black liquors is the major component of the fraction, with only a low amount of contaminants. Instead, the lignin recovered from recycled cardboard is mixed with hydrocarbon derivatives. It means that the lignin requires a further purification step.
6. The infrared and GPC analysis of the recovered lignin in comparison with the commercial lignin and literature study [33] permits us to assume that the recovered lignin is a softwood type. This result is reasonable because recycled cardboard considered in this study is composed of around 54 % of softwood fibers. However, the reason why hardwood lignin is not detected has to be investigated because the provenience of the different fibers that compose the recycled fibers and how many times they were recycled is not known.

Further research in the laboratory is needed to enable an economic analysis to verify a possible industrial scale-up. However, the continuation of this work can be extremely beneficial due to the considerable amount of recycled cardboard, around 130 million tons worldwide, used in packaging manufacturing. As an estimation, recycled cardboard contains around 9.6 million tons of lignin (considering a lignin percentage of 7.4). It means that the method proposed in this research can extract around 0.8 million tons of lignin. When the method is further improved, this will be a significant contribution to the recycling of valuable compounds.

To evaluate the impact of lignin recovery from cardboard, the actual lignin market must be considered. Around 100 million tons/y of lignin are produced worldwide (\approx 50 million tons/y of kraft lignin that are in the majority directly burned in the mill for energy purposes) valued at USD 732.7 million in 2015 [55]. If a total of 9.6 million tons of lignin estimated in the cardboard are recovered, their potential value is narrow to 10 % of the total lignin market. Lignin is a cheap compound that can be used directly as a binder or as raw material to obtain high-value compounds such as phenolic compounds (1,000–2,000 USD/ton), carbon fibers (7,000–11,000 USD/ton) and vanillin (15,000–40,000 USD/ton) [55,56].

Moreover, the valorization of the waste streams from cardboard recycling is not only important from an economic point of view but also for environmental reasons. This valorization is in line with the directions of the Green Deal of the European Commission [1] because a sludge can be transformed into a source of chemicals and materials.

Supporting Information

Measurement and calculation of lignin and extractive amounts.

Acknowledgment

The authors would like to thank Prof. dr. Christophe Vande Velde of the iPRACS research group of the University of Antwerp for the help in the spectra interpretation and Prof. dr. ir. Wim Thielemans of the University of Leuven for the help in the interpretation of GPC chromatograms.

Funding

This study was supported by research funding from Flanders Innovation & Entrepreneurship (VLAIO) (Pr. Nr. IWT.155050) and the University of Antwerp.

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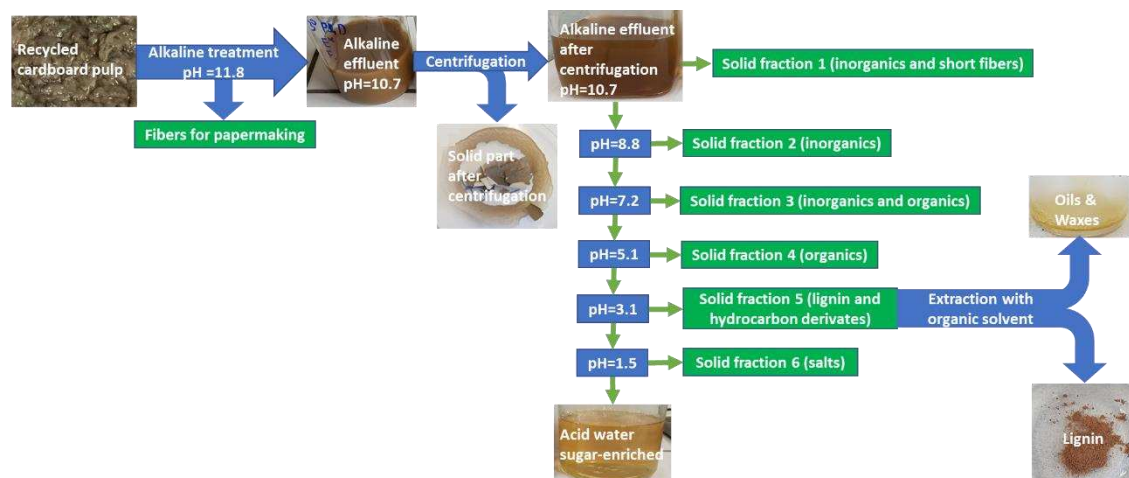


Figure 1 Scheme of the process for the extraction of lignin and hydrocarbon derivatives from the alkaline effluent generated during alkaline treatment of recycled cardboard

Table 1 The list of the main infrared peaks observed in the spectra in Figure 2 and from Figure 4 to 9

Peaks (cm ⁻¹)	Type of vibration	Compounds correlated	Identified in Figure nr.	Reference
1400-1417 and 873-875	asymmetric vibration of carbonate CO ₃ ²⁻	Calcium carbonate	2,4,5	[44]
3694	stretching of hydroxyl -OH	Kaolin	2,4,5	[45]
1000	stretching of Si-OH	Kaolin	2,4,5	[45]
3300	stretching of O-H	Polysaccharides, lignin	2B,3-9	[43]
1000-1006	stretching of ether C-O-C	Cellulose, hemicellulose	2,4,5,6	[43]
1330	bending of C-H	hemicellulose, lignin	5,6,7	[43]
1148	stretching C-O	Polysaccharides, lignin	5,6,7	[43]
1500 and 1400	stretching double bonds C=C in aromatic rings	Aromatics in lignin	5,6,7	[43]
2924 and 2853	asymmetric vibration -CH ₂ and -C-H stretching	Organic compounds (polysaccharides lignin and hydrocarbon derivatives)	4,5,6,7	[43]
1646-1543	carbonyl stretching C=O	Organic compounds (lignin and hydrocarbon derivatives)	4,5,6,7	[46]
1653 and 1147-1037	stretching of sulfate ion (SO ₄ ²⁻)	Sulfates	8,9	[44]
1077	stretching of ether C-O-C	Sugars	9	[43]
1570	bending of amine N-H	Azo dye	9	[43]

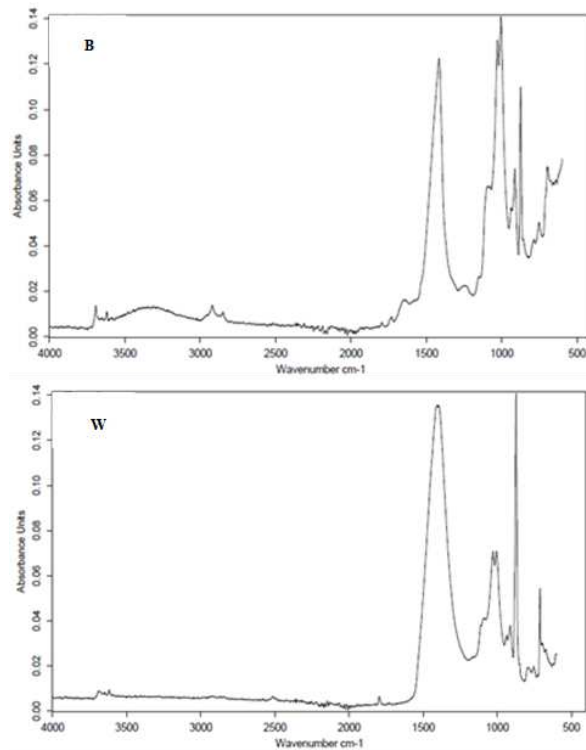


Figure 2 Infrared spectra of the “brown layer” (B); Infrared spectra of the “white layer” (W)

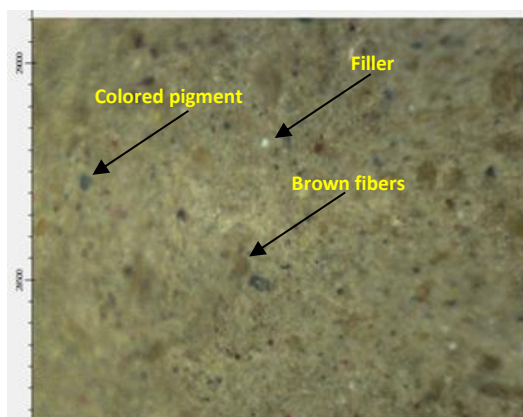


Figure 3 Microscope image of solid after centrifugation and drying

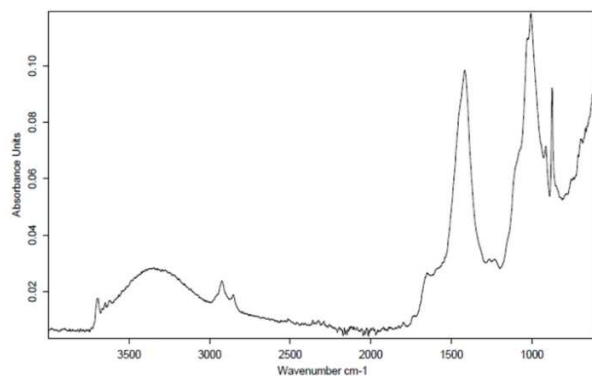


Figure 4 Infrared analysis of the dry solid obtained by the acid precipitation from pH 10.7 to 8.8

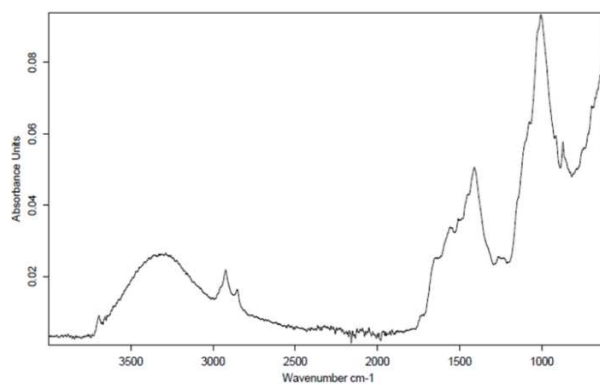


Figure 5 Infrared analysis of the dried solid obtained by acid precipitation from pH 8.8 to 7.2

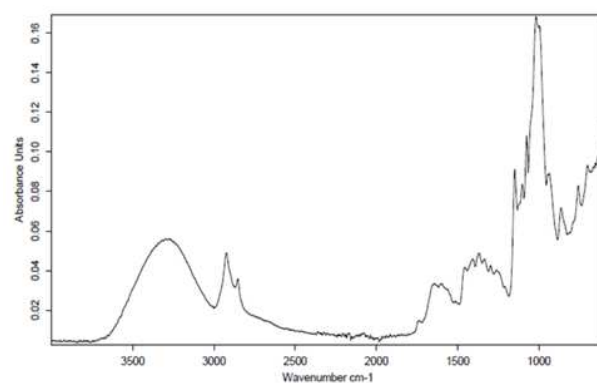


Figure 6 Infrared analysis of the dried solid obtained by acid precipitation from pH 7.2 to 5.1

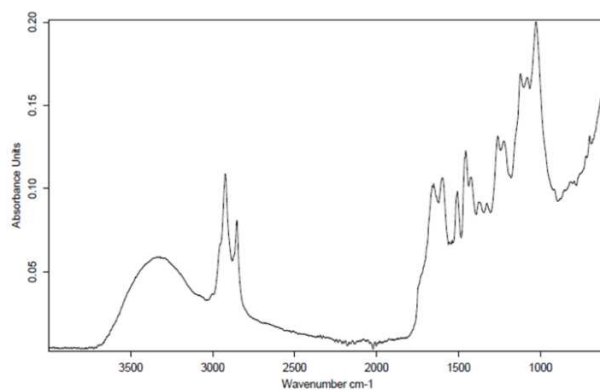


Figure 7 FTIR analysis of the dried solid from the fraction at pH 3.1 after the acid cascade of the cardboard waste stream.

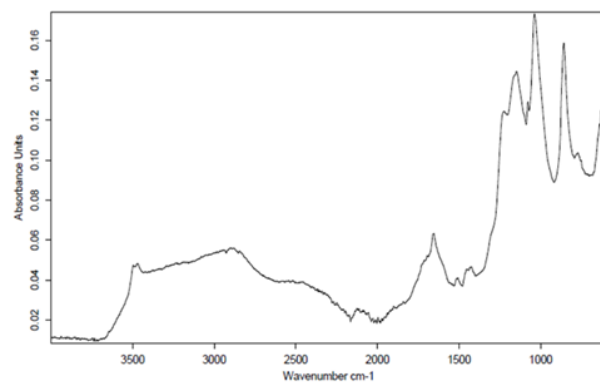


Figure 8 Infrared analysis of dried solid obtained by acid precipitation from pH 3.1 to 1.5.

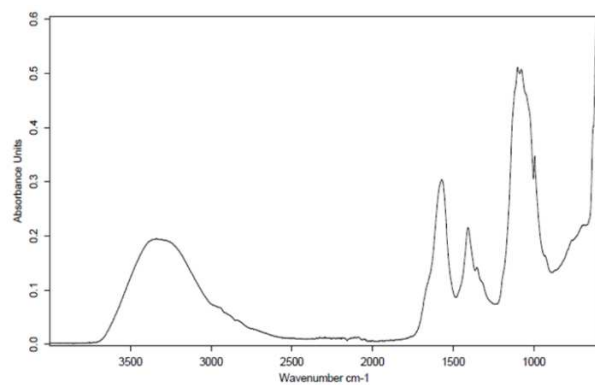


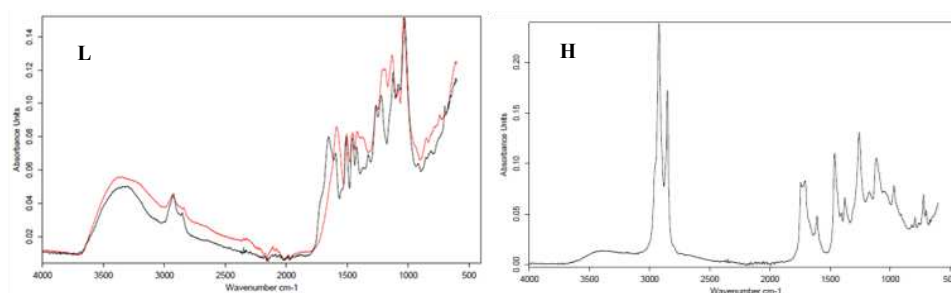
Figure 9 Infrared analysis of dried solid obtained by liquid acid phase at pH 1.5.

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Table 2 The list of the main infrared peaks observed in the spectra of Figure 10

Peaks (cm ⁻¹)	Type of vibration	Compounds correlated	Reference
2922 and 2853	C-H stretching	Hydrocarbon derivatives	[44]
1743	C=O stretching		
1608	C=C stretching		
1462	CH ₂ bending		
1377	CH ₃ bending		
1173	C-O stretching		
722	CH ₂ bending		
3311	O-H stretching	Lignin	[47]
2926	-CH ₂ asymmetric vibration (guaiacyl-syringyl)		
2853	C-H stretching in methyl and methylene groups		
1651 and 1594	conjugated C-O vibration		
1509	C=C aromatic ring vibration (guaiacyl-syringyl)		
1454	C-H asymmetric deformation		
1422	aromatic skeletal combined with C-H in-plane deforming and stretching		
1368	aliphatic C-H stretching in methyl and phenol O-H		
1326	syringyl ring breathing with C-O stretching		
1264	guaiacyl ring breathing, C-O stretching in lignin and C-O linkage in guaiacyl aromatic methoxyl groups		
1222	C-O and glucopyranosic ring syringylic symmetric vibration		
1124	aromatic skeletal and C-O stretching		
1080	C-O deformation in secondary alcohol and aliphatic ether		
1028	C-H plane deformation in guaiacyl and C-O deformation in primary alcohol		
919	=CH out of plane deformation in aromatic ring (guaiacylic-syringylic)		
850	aromatic C-H out of plane deformation		

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4**Figure 10** FTIR spectra with (L) (—) Commercial lignin, (---) recovered lignin at pH 3.1 after solvent extraction; (H) Hydrocarbon fraction.

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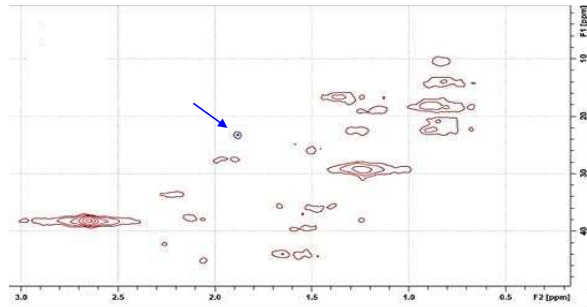


Figure 11 NMR-HSQC analysis of (Blue) Commercial lignin and (Red) recovered lignin

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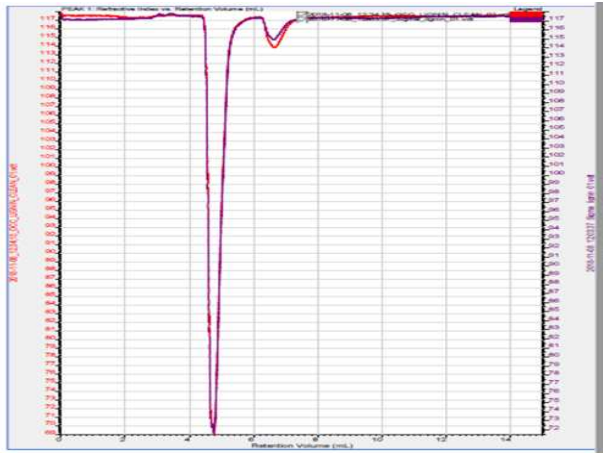


Figure 12 GPC analysis of (-) recovered lignin and (-) commercial lignin (Mw 10,000 Dalton) for molecular weight determination

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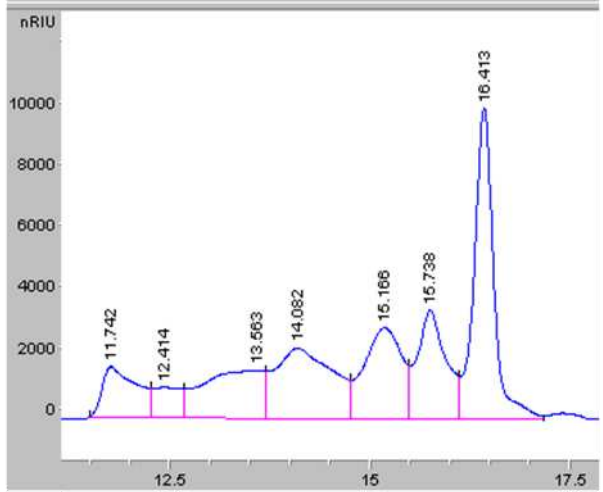


Figure 13 GPC analysis of hydrocarbon fraction for the molecular weight determination

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Table 3 Mass balance of the alkali treatment and acid cascade.

Sample	Mass (%)	Mass (g)	NaOH 2 M (g)	MgSO ₄ (g)	H ₂ SO ₄ (g) ^A
Alkali treatment					
Starting material	100 ^B	18.000	0.480	0.136	
Residue	87.7	16.325 ^C			
Solid-phase Filtrate	5.6	1.045			
Liquid phase Filtrate	6.7	1.246 ^D			
Acid Cascade					
pH 8.8	0.2	0.036			0.052
pH 7.2	0.1	0.025			0.087
pH 5.1	0.5	0.085			0.200
pH 3.1	0.7	0.127			0.366
pH 1.5	0.1	0.027			1.324
Liquid 1.5	5.1	0.946 ^E			
DCM solvent extraction					
pH 3.1 Hydrocarbon	0.1	0.022			
pH 3.1 Lignin	0.6	0.105			

A: Amount of acid reported was obtained by adding up the previous steps; B: The 100 % consists in the sum of all starting materials, 18 g of cardboard, 0.48g of NaOH and 0.136g of MgSO₄; C: calculated by (Starting material minus Solid-phase and Liquid phase); D: the mass was obtained by the sum of acid cascade fractions minus the 1.324g of sulfuric acid; E: it is the total amount of solids (after correction for the sulfate content).

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