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# Lignin recovery from brewer's spent grain black liquor

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## Abstract

The present study describes the precipitation of lignin by acidification of a black liquor (pH 12.56 and 12.44 g/l soluble lignin) produced by soda pulping of brewer's spent grain. Sulfuric acid was added to the liquor to decrease the pH, forming a lignin-rich precipitate. Ten pH values (varying from 12.56 to 2.15) were studied. The lignin mass precipitated for each pH condition was determined, and the obtained liquors were evaluated regarding the color and concentration of soluble lignin. Some phenolic acids (vanillic, syringic, *p*-hydroxybenzoic, ferulic and *p*-coumaric) were quantified in the liquors to verify their removal profiles as a function of the pH alteration. Significant lignin precipitation was only observed at pH < 7.7. At pH 2.15 the concentration of soluble lignin was reduced to 2.31 g/l (removal of 81.43%) and the color of the liquor was strongly modified from dark brown to pale yellow. The phenolic compounds concentration was reduced in different proportions (from 74.4% to 32.1%), suggesting that each lignin derived compound is differently affected by the pH alteration.

*Keywords:* Acidification; Brewer's spent grain; Black liquor; Lignin; Precipitation; Soda pulping

## 1. Introduction

Lignocellulosics are the main raw material for pulp and paper industries. Among these, the woods are the most important, corresponding to 95% of all raw materials used by these industries (Jiménez, Ramos, Rodríguez, de la Torre, & Ferrer, 2005). Nevertheless, some agricultural or agro-industrial residues such as brewer's spent grain, maize stems, and some cereal straws can also be used for this purpose (Mussatto, Dragone, Rocha, & Roberto, 2006; Navaee-Ardeh, Mohammadi-Rovshandeh, & Pourjoozi, 2004; Xiao, Sun, & Sun, 2001). Developing countries, particularly those in Asia, which do not have adequate wood supplies use straws and other non-wood materials as lignocellulosic fiber sources for pulp and paper production (Lawther & Sun, 1996). China, for example, has a long tradition for using non-wood raw materials for pulp and paper due to its limited forest resources and rich supply of agricultural residues, such as cereal straws of wheat, rice, and barley (Hammett, Youngs, Sun, & Chandra, 2001).

The major constituents of lignocellulosics are cellulose, hemicellulose, and lignin, polymers that are associated with each other constituting the cellular complex of the vegetal biomass. Lignin is a three-dimensional polyphenolic macromolecule of very complex structure whose function is to provide rigidity and cohesion to the material cell wall, to confer water impermeability to xylem vessels, and to form a physic–chemical barrier against microbial attack (Fengel & Wegener, 1989). An example of structure proposed for the lignin is given in Fig. 1 (Adler, 1977).

For the lignocellulosic materials be susceptible to the pulp and paper production, the separation of their cellulosic fibers is necessary. Several processes have been used with this finality, and the soda pulping is one of the most relevant and most used for delignification of agricultural residues (Iglesias, Bao, Lamas, & Vega, 1996). During the pulping process, the lignin is dissolved from the raw material, being separated in the form of a liquor rich in phenolic compounds that represents the process effluent (Fengel & Wegener, 1989). This effluent is dark brown or black in

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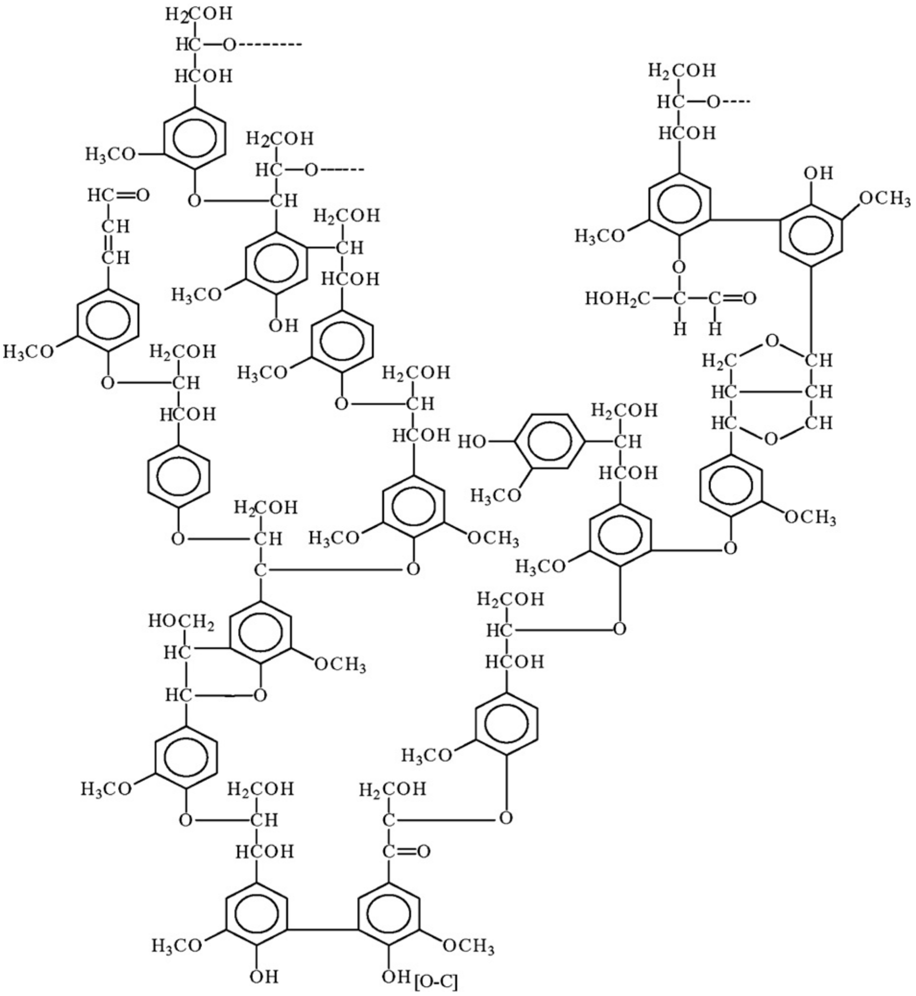

Fig. 1. Structure proposed for the lignin of conifer according to Adler (1977).

color and hence is called black liquor. The black liquor contains a wide variety of compounds (chemicals and derived from lignin), most of them are toxic and need to be removed before the effluent discharge to the environment (Karam & Nicell, 1997). Aiming to decrease the environmental impact, the pulp and paper industries normally burn the lignin dissolved in the black liquor for energy generation. However, the lignin can be isolated and used as the starting material for a series of useful products, such as vanillin, phenols, benzene, dispersant, emulsificant and chelant agents, antioxidants, pesticides, fertilizers, vegetal charcoal, polymers, adhesives, concrete additives, component for resins, among others (Gargulak & Lebo, 2000). Conventionally, the Kraft lignin has been recovered from black liquor, in laboratory or industrial plants, by precipitation with mineral acids like sulfuric or hydrochloric acid, followed by filtration and washing, the last one being the critical stage for obtainment of a lignin with high purity (Santos & Curvelo, 2001).

In the present work, a black liquor was obtained by soda pulping of brewer's spent grain (BSG), the main brewery by-product. BSG is a raw material recently evaluated for cellulose pulp production (Mussatto et al., 2006), and until now, there is not yet any work about the lignin recovery from the black liquor produced during its pulping. This report is thus the first paper concerning the studies in this area and has as objective the evaluation of the pH influence on lignin precipitation.

## 2. Materials and methods

### 2.1. Raw material

The BSG used in the experiments was kindly supplied by the Microbrewery of the Engineering College of Lorena, and presented the following chemical composition (% dry weight, w/w): 16.8% cellulose, 28.4% hemicellulose, 27.8% lignin, 4.6% ashes, 15.2% proteins, 5.8% extractives, and 1.4% acetyl groups. As soon as obtained, the material was washed with water (for removal of the residues proceeding from wort) and dried at 50 ± 5 °C until approximately 10% moisture content.

Table 1
Volume of concentrated sulfuric acid added in each sample of the brewer's spent grain black liquor, characterization of the obtained liquor (pH and soluble lignin), and quantification of the precipitated lignin mass

| Sample | $H_2SO_4$ (ml) | pH | Soluble lignin (g/l) | Lignin removal (%) | Precipitated lignin mass (g) | Yield[a] (g/100 ml) |
|---|---|---|---|---|---|---|
| 1 original | – | 12.56 | 12.44 | – | 0.0301 | 0.1505 |
| 2 | 0.14 | 10.61 | 12.42 | 0.16 | 0.0361 | 0.1805 |
| 3 | 0.16 | 9.90 | 12.40 | 0.32 | 0.0373 | 0.1865 |
| 4 | 0.18 | 7.71 | 12.40 | 0.32 | 0.0383 | 0.1915 |
| 5 | 0.20 | 5.98 | 10.49 | 15.67 | 0.0909 | 0.4545 |
| 6 | 0.22 | 4.30 | 3.92 | 68.49 | 0.2939 | 1.4695 |
| 7 | 0.24 | 3.23 | 2.63 | 78.86 | 0.3100 | 1.5500 |
| 8 | 0.26 | 2.62 | 2.45 | 80.30 | 0.3202 | 1.6010 |
| 9 | 0.28 | 2.48 | 2.33 | 81.27 | 0.3209 | 1.6045 |
| 10 | 0.30 | 2.15 | 2.31 | 81.43 | 0.3208 | 1.6040 |

[a] Lignin recovery yield from 100 ml of liquor.

### 2.2. Pre-treatment conditions

BSG was pre-treated with dilute sulfuric acid under the conditions previously optimized by Mussatto and Roberto (2005): 100 mg $H_2SO_4$/g dry matter, a solid:liquid ratio of 1:8 g:g, at 120 °C for 17 min. At the end of the reaction, the solid residue was separated by centrifugation, washed with water until neutral pH and dried at $50 \pm 5$ °C until approximately 50% moisture content.

### 2.3. Soda pulping

The soda pulping of the pre-treated BSG was performed using 2% w/v NaOH solution, in a solid:liquid ratio of 1:20 g:g, at 120 °C for 90 min, as optimized by Mussatto et al. (2006). Afterwards, the reaction medium was cooled in ice bath and filtered in a 100% polyester cloth to separate the black liquor, which had a pH of 12.56.

### 2.4. Lignin recovery from black liquor

A 20 ml volume of the black liquor was treated with different volumes of concentrated sulfuric acid (98% w/w) to obtain a range of different pH values (Table 1). After the acid addition, the liquor was centrifuged at 4000 rpm for 10 min. The precipitated lignin was separated, thoroughly washed with water until the supernatant was neutral, and then dried at 60 °C until constant mass. The obtained liquors were maintained at 4 °C during 24 h and centrifuged again at 4000 rpm for 10 min. The lignin thus precipitated was washed with water and dried at 60 °C until constant mass. The total precipitated lignin mass was considered as the sum of the mass recovered after the acid addition and the mass recovered after cooling. The obtained liquors were characterized regarding the pH, total concentration of soluble lignin, and concentration of the phenolic acids: vanillic, *p*-hydroxybenzoic, syringic, *p*-coumaric, and ferulic.

### 2.5. Analytical methods

The total concentration of soluble lignin in the liquors was determined according to the methodology described by Mussatto and Roberto (2006). The phenolic acids concentration was obtained by high performance liquid chromatography using a UV (276 nm) detector and a Waters resolve $C_{18}$ 5 μm (3.9 × 300 mm) column. The samples were filtered in 0.45 μm Millipore membrane and injected in the chromatograph under the following conditions: column at room temperature; acetonitrile/water (1/8, with 10 g/l acetic acid and pH adjusted to 2.5 by $H_3PO_4$ addition) as eluent; a flow rate of 0.9 ml/min and injection volume of 20 μl.

The lignin removal (LR, %) was calculated by the Eq. (1), where $SL_i$ is the initial concentration of soluble lignin in the original liquor, and $SL_f$ is the total soluble lignin concentration in the liquor after the sulfuric acid addition.

$$LR = \frac{SL_i - SL_f}{SL_i} \times 100 \qquad (1)$$

Origin version 7.0 was the software used for graphical analysis of the results.

## 3. Results and discussion

The process used for cellulose pulp obtainment from BSG was previously established (Mussatto et al., 2006). By using this process, 95.3% w/w of the BSG lignin was removed, and the produced black liquor presented a soluble lignin concentration of 12.44 g/l. The reduction in the pH of this liquor, proportioned by the sulfuric acid addition, caused the precipitation of the solubilized lignin, so that the lower the pH the higher the recovered lignin mass (Table 1). According to Fengel and Wegener (1989) the lignin is highly soluble in alkaline medium but its solubility in the black liquor really decreases when the pH is reduced. Nevertheless, since the lignin nature varies according to the nature of plant species (Hon, 1996) the precipitation profile of this fraction can also vary according to the raw material employed.

Interestingly, Table 1 shows that the pH reduction to 7.71 practically did not influence the lignin precipitation, whose removal from black liquor was only 0.32%, proportioned by the cooling and not by the acid addition. Nevertheless, the pH decrease to a value near to six started to influence the precipitation of this fraction, proportioning

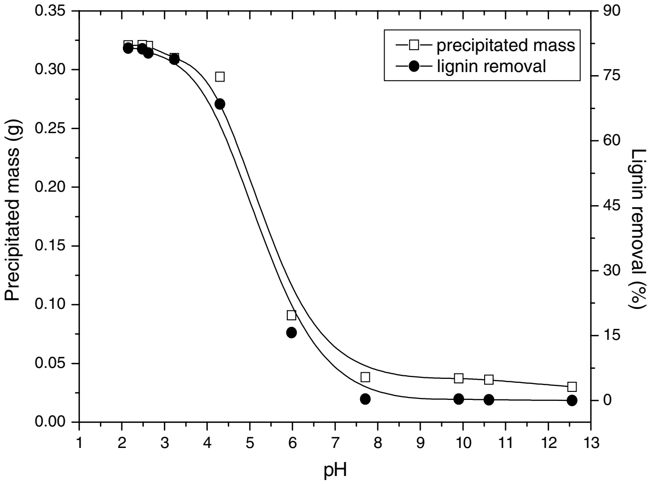

Fig. 2. Precipitated mass and lignin removal as a function of the drop in the pH of the brewer's spent grain black liquor.

a removal rate of 15.67%. This value was increased 4.4-fold when the pH was reduced from 5.98 to 4.3. Fig. 2 clearly shows that the highest increase in the lignin precipitated mass occurred in the pH range between 7.71 and 4.3, reaching a removal rate of 68.49%. For pH values lower than 4.3 the lignin removal was still increased in around 13%, but this removal increment was five fold lower than the increment observed in the pH range between 7.71 and 4.3.

At the lowest pH value (2.15) 81.43% of the lignin solubilized in the liquor was recovered. A similar lignin recovery yield (87.8%) was obtained by Santos and Curvelo (2001) when the pH of the black liquor of *Eucalyptus urograndis* wood was decreased from 13.6 to 3.0. However, if compared with the lignin recovery at pH 3.23, the present work result was lower (78.86%). Such difference probably is not only due to the raw material used. According to Rohella, Sahoo, Paul, Choudhury, and Chakravortty (1996) the lignin composition varies from biomass to biomass, and also with the chemical pulping process used for the biomass. The black liquor used in the present work was obtained by soda pulping, while the black liquor used by Santos and Curvelo (2001) was obtained by Kraft pulping.

The acid precipitation is the most common method used to recover Kraft lignin from black liquors, being able to cause a complete lignin precipitation when the pH is reduced to a range of 2–3 (Villar, Caperos, & García-Ochoa, 2001). In the present work, the lignin solubilized by soda pulping was not completely recovered when the pH was acidified to 2.15, suggesting that the chemical pulping process really influences the lignin recovery from the black liquor.

Although the incomplete lignin recovery, decreasing pH from 12.56 to 2.15 strongly influenced the soluble lignin concentration in the BSG black liquor. Similar results were obtained by Sun, Tomkinson, and Bolton (1999) when reduced from 13.8 to 2.0, the pH of the black liquor obtained from oil palm empty fruit bunch fibers. These authors recovered 1 g lignin to each 100 ml of liquor acidified with 9.68N $H_3PO_4$. However, the precipitated also contained polysaccharides degradation products because the raw material had not been pre-treated. In the present work, the lignin recovery yield at pH 2.15 was 1.6 g/100 ml liquor (Table 1), and this mass was basically derived from lignin because the hemicellulose was removed during the pre-treatment stage, and the cellulose was practically not affected during the pulping process (Mussatto et al., 2006). Considering this fact, the lignin recovery yield was practically twice higher than that obtained by Sun et al. (1999), what is justifiable because BSG contains 27.8% w/w lignin while the oil palm empty fruit bunch fibers contain 14.2% w/w. These results suggest thus that the efficiency of the concentrated $H_2SO_4$ is very similar to that of 9.68 N $H_3PO_4$ for lignin precipitation from black liquors.

As a consequence of the lignin removal, the color of the BSG black liquor was altered. It can be observed in Fig. 3 that in the original form (sample 1), the liquor was dark brown, but it was clarified with the pH reduction. At the lowest pH value (2.15), the liquor color passed to be pale yellow. According to Fengel and Wegener (1989), the dark color of the liquor is derived from the chromophoric functional groups, including quinones, carbonyl groups, carboxylic acids, hydroperoxy radicals, phenolic hydroxyl groups, among others, generated during the lignin degradation, which are soluble in alkaline medium.

It can also be noted in Fig. 3 that, although in the sample 5 (pH 5.98) the lignin had been removed in 15.67%, the

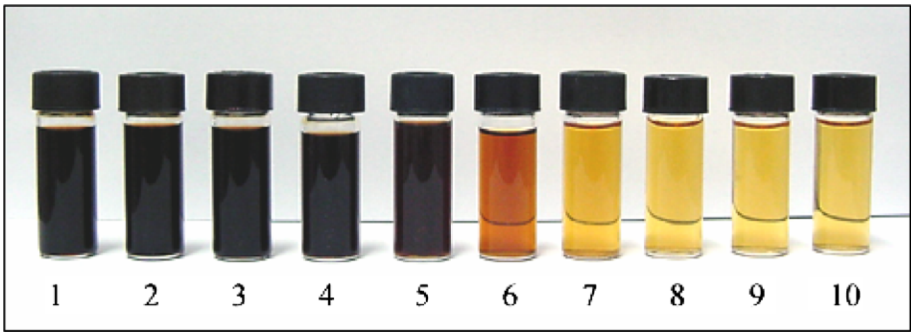

Fig. 3. Color of the brewer's spent grain black liquor as a function of the drop in the pH value from 12.56 (sample 1) to 2.15 (sample 10).

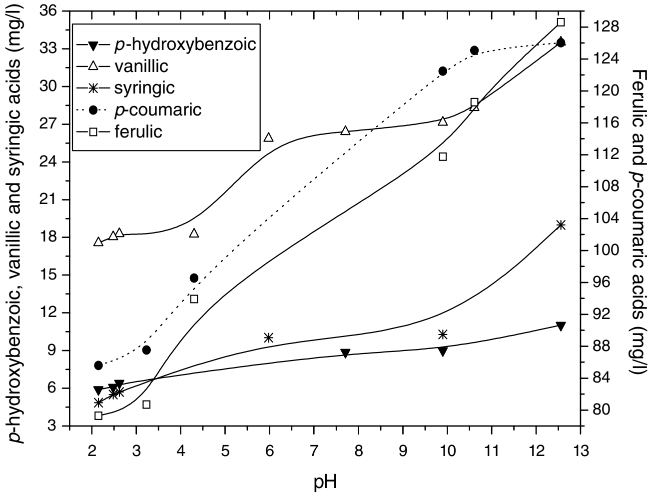

Fig. 4. Phenolic acids removal with the drop in the pH of the brewer's spent grain black liquor.

color of the liquor was not altered, being as dark as in the original form (sample 1). Probably the compounds that confer color to the liquor were not removed in this pH range (between 12.56 and 5.98). In the sample 6 (pH 4.30), 68.49% of the lignin was removed and a strong alteration in the liquor color was observed. The pH decrease from 4.30 to 3.23 (sample 7) also caused a strong influence on the liquor color, which passed to be yellow and almost did not modify with the pH reduction to 2.15 (sample 10). It is evident, thus, that the liquor color was strongly affected in acid pH, suggesting that the chromophores compounds are removed in this pH range, mainly between 5.98 and 3.23.

Five phenolic acids were quantified in the liquors obtained after pH adjustment. The choice for these compounds was based on the fact that they are the acids most quantitatively present in BSG (Athanasios, Georgios, & Michael, 2007). Thus, their removal profiles can give an idea about the pH decrease influence on the concentration of the lignin derived compounds in the liquor. Fig. 4 shows that these compounds were not similarly removed from the liquor when the pH was decreased. The vanillic acid, for example, presented a removal profile very different of those observed for the other acids, since its concentration was practically not altered in the pH range between 9.9 and 5.98, while the removal of the other acids was more significant at these pH values. In addition, the removal percentage varied with each acid evaluated. The highest removal was observed for syringic acid (74.4%) and the lowest for *p*-coumaric acid (32.1%), whose values varied 42.3% among themselves. The other analyzed acids, vanillic, *p*-hydroxybenzoic, and ferulic, were removed in 47.6%, 46.5%, and 38.3%, respectively. Sun et al. (1999) also observed the removal of these same phenolic acids as a function of the decrease in the pH of the black liquor produced from oil palm empty fruit bunch fibers, obtaining different removal values for each compound.

## 4. Conclusions

The pH is a variable of large influence on the precipitation of the lignin from the black liquor produced by BSG soda pulping. Decreasing the pH from 12.56 to 2.15 resulted in an increase of precipitated lignin mass, being recovered 81.43% of the lignin solubilized in the liquor. The lignin recovery is not only interesting from an environmental, but also from an economical point of view, because it can be reused for obtainment of several chemical products of commercial interest. Further works on the application of lignin from BSG black liquor will be investigated in our laboratory.

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