

## USE OF KRAFT BLACK LIQUORS FROM A PULP MILL FOR THE PRODUCTION OF SOIL CONDITIONERS

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The possibility of utilizing kraft black liquors generated in a paper mill, using *Eucaliptus globulus* as raw material, for the production of a nitro-humic soil conditioner was studied. Two processes were considered: (1) oxidation of the kraft black liquors with nitric acid; and (2) precipitation of the lignin contained in kraft black liquors with CO<sub>2</sub> and further oxidation of this lignin by nitric acid. The second process was more efficient regarding product yield and safety of operation. Screening tests at different operating conditions of the latter process indicate that high quality nitro-humic materials can be obtained.

Key Words--Waste kraft black liquors, humic material, soil conditioners, lignin oxidation

### 1. Introduction

Amongst various wood pulping processes, the kraft process is the most commonly used, however, several wastes are produced: gases, kraft black liquors and bleach effluents.

Kraft black liquors with a total solids content of 16 wt% are further processed in order to recover energy and sodium salts. The dilute fraction of kraft black liquors (<7 wt% total solids) is disposed of as a waste effluent causing environmental problems. An alternative approach is the use of lignin contained in the kraft black liquors to make humic fertilizers or soil conditioners.

The use of inorganic fertilizers to improve crop yield has been constantly increasing. However, inorganic fertilizers do not by themselves supply the soil with the necessary organic matter. The humic material obtained from waste kraft liquors could be used as a source of organic matter for the soil, improving its texture, controlling the pH, fostering ion exchange processes and, owing to its nutrient content, enhancing the growth of the microbial population in the soil (Greenland & Hayes 1978). Humic fertilizers are however not a substitute for conventional inorganic fertilizers but are a complementary additive for a balanced agricultural soil.

The first step in making humic materials from either low rank coals or wood agricultural wastes (lignite, peat, sawdust, bagasse straw, hydrolyzed lignin, etc.) is an oxidation process. Air, oxygen and potassium permanganate have been used as oxidizing agents (Mukherjee *et al.* 1961, Mazumdar *et al.* 1967, Prasad *et al.* 1974, Kim *et al.* 1981) the resulting product being humic acids. When nitric acid is used (Mazumdar *et al.* 1967, Jelks 1977, Raskin *et al.* 1981, Coca *et al.* 1985, 1988) nitrohumic acids are produced.

Initially, experiments were performed using a one-step oxidation process of kraft black liquors using nitric acid. Subsequently, an indirect process consisting of two

stages, precipitation of the lignin contained in the kraft black liquors and oxidation of this lignin by nitric acid, was investigated. A study of the literature revealed the possibility of removing the lignin contained in kraft black liquors by acidification, using  $\text{CO}_2$  or  $\text{H}_2\text{SO}_4$  (Alen *et al.* 1979, Sjöström 1981, Kim *et al.* 1987).

The flue gases and the high alkaline gases of a pulp mill contain a substantial amount of  $\text{CO}_2$  at temperatures ranging between 135 and 140°C. As one of the aims of this research is the upgrading of wastes from pulp mills, the use of  $\text{CO}_2$  for partial recovery of kraft lignin from kraft black liquors was considered feasible, particularly as the carbonation process requires minimal heating. The precipitated lignin was then oxidized using  $\text{HNO}_3$  to obtain humic material.

The objective of this work was to study the feasibility of using the lignin contained in kraft black liquors from the pulping process as a source of humic material. An analysis of the operating conditions is made in order to achieve high acidities in the final product, using nitric acid as the oxidation agent.

## 2. Experimental

### 2.1 Materials and equipment

Standard kraft black liquor from a pulp mill Celulosas de Asturias, S.A., Navia (Asturias), Spain, was used as lignin source. The kraft black liquor is generated in the cooking process using eucalyptus (*E. globulus*) as raw material. The kraft black liquor used has a low content of sulphurated compounds and contains neither methanol nor turpentine. Some other parameters of the black liquor were as follows: pH, 12.5–12.9 (caustic liquor); density, 1.1  $\text{g cm}^{-3}$ ; and total solids 7 wt%. The total solids content was determined according to the standards TAPPI T650 su-71, TAPPI T625 ts-64 and CPPA J.15P.

The carbonation and oxidation processes were carried out in a stainless steel high-pressure batch reactor (Sotelem, Paris, France). This reactor can work up to a maximum temperature of 200°C and a pressure of 5 MPa. It has a volume of 5 litres, and is provided with magnetic stirring to prevent any leaks that would cause a pressure change during the reaction if a mechanical stirrer was used.

### 2.2 Direct oxidation process

Experimental conditions based on preliminary trials were as follows: reaction time, 45 min; pressure, 2.5 MPa; stirring rate, 1050 r.p.m. The range of independent variables considered was nitric acid concentration (10–35 wt%), reaction temperature (20–70°C) and the nitric acid/total solids ratio in kraft black liquors (4:1–10:1).

### 2.3 Indirect oxidation process

#### 2.3.1. Step 1: Precipitation and removal of kraft lignin

Previous work (Alen *et al.* 1979) on the precipitation process of kraft lignin from pine kraft black liquors using  $\text{CO}_2$  recommends the following experimental conditions:

- Total solids content in the kraft black liquor: 27 wt%.
- Pressure of carbonation process: 1.5 MPa.
- Carbonation time: 20 min.

Based on the aforementioned conditions the kraft black liquor used in this work was concentrated from 7 wt% to a total solids content of about 27 wt% using a rotary evaporator. The concentrated liquor then underwent the carbonation process in the batch reactor previously described. Three litres of concentrated liquor were fed into the batch reactor and it was hermetically sealed. Then, the reactor was heated up to 80°C. Carbon dioxide was introduced into the reactor and the pressure was increased up to 1.5 MPa and maintained by adjusting a valve. The mixture was constantly stirred and the carbonation time was 60 min. Finally, the reactor was opened and its contents immediately filtered through a cloth filter under vacuum. The filter cake containing the precipitated kraft lignin was then dried in an oven at 40–45°C for 48 h. The dried lignin was ground in a blade mill.

### 2.3.2. Step 2: Oxidation of kraft lignin

The kraft lignin particles from the previous step were then oxidized with HNO<sub>3</sub> in order to obtain the humic material as follows: 150 g of kraft lignin and 200 ml of water were poured into the high pressure reactor and mixed to get a homogeneous mixture. The reactor was then closed and nitric acid of a known concentration was fed into the reactor (both nitric acid concentration and the amount of nitric acid were varied in the different experimental runs). The volumetric flow rate of nitric acid was 1.3 l min<sup>-1</sup>. Stirring rate, reaction time and reaction pressure were kept constant at 1050 r.p.m., 30 minutes and 2.5 MPa, respectively. Nitrogen was used as the pressurizing agent. The temperature of each run was varied depending on the experimental requirements.

When the desired reaction time was reached, the pressure was released and the reactor cooled down. Then, the contents of the reactor were filtered through a No. 3 borosilicate sintered glass plate funnel (pore diameter ≤ 40 μm) in order to remove the humic material. The nitric acid imbibed in the humic material was washed off twice using 1.5 l and 1 l of water, respectively. The precipitate was washed with water until the filtrate had a constant pH. The humic material was dried at 40–45°C in an oven for 48 h and then milled. A block diagram of this process is shown in Fig. 1.

The humic material was then weighed to determine the reaction yield, which is related to the weight loss during the reaction:

Weight loss (%) =

$$\frac{(\text{weight of lignin fed to the reactor}) - (\text{weight of humic material recovered})}{(\text{weight of lignin fed to the reactor})} \times 100$$

The acidity of the humic material was determined following a previously described method (Toynbee & Fleming 1963) with slight modifications. In our work, a time of 20 min for sample digestion was considered optimum to achieve complete digestion of the sample. The acidity was expressed in ml 0.1 N NaOH per gram of sample. The acidity of the humic material is a quantitative measure of the number of acidic groups in the lignin structure resulting from the oxidation reaction. As the acidity of humic material increases so does the quality of the product.

The independent variables considered in this investigation were: nitric acid concentration (5–35 wt%), reaction temperature (20–160°C) and nitric acid-lignin ratio (4:1–8:1, by wt). The values of the remaining variables were kept constant in all the trials. All these operating conditions and their levels and values were chosen on the basis of previous experiments described in the literature using the direct oxidation process.

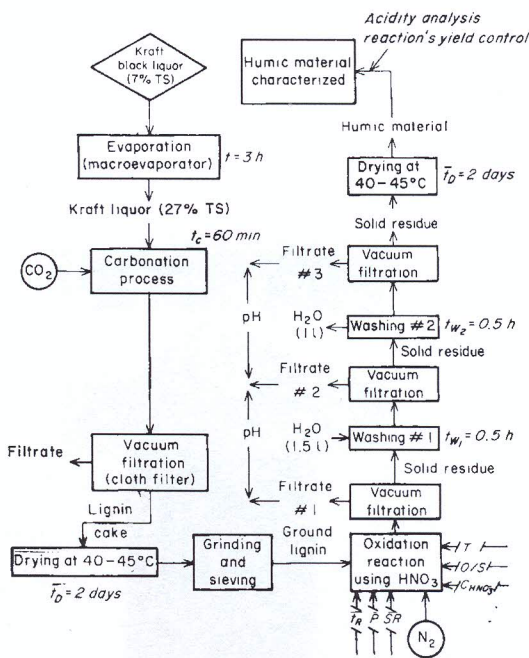


Fig. 1. Block diagram of the process for production of humic material from kraft black liquors.

### 3. Results and discussion

#### 3.1 Direct oxidation process

Several trials at different experimental conditions were carried out and replicated. The experimentation was conducted using the "one factor at a time" method. Table 1 illustrates the range of conditions examined.

From the experimental runs the following information was gathered:

- In all experiments when nitric acid was pumped at fast rates there was a sudden temperature and pressure rise in the reactor. The reactor had to be refrigerated and the relief valve opened for safety reasons. This caused a release of foam containing NO<sub>2</sub> and solids from the reactor.
- To avoid the aforementioned problems the nitric acid was pumped slowly into the reactor over a period of 10 min. However, if the experiment was performed at temperatures higher than 20°C, sudden, uncontrollable temperature and pressure rises occurred as soon as heating of the reactor started. It was again necessary to refrigerate the reactor and to open the relief valve. The same behaviour was observed at nitric acid concentrations above 10 wt% even when the operating temperature was 20°C. Consequently, good control of the operating conditions and conducting systematic studies were impossible.
- Experimental runs could be carried out at very gentle operating conditions (10 wt% HNO<sub>3</sub>, 20°C and an oxidant/solids ratio of 4:1). However, the acidities of the oxidation products obtained were much lower (c. 4 ml NaOH per gram of sample) than what would be required for suitable humic materials.

TABLE 1  
Experimental conditions for the oxidation of kraft black liquors (KBL) with nitric acid using the direct oxidation process

Experimental run	HNO <sub>3</sub> (%, by wt)	HNO <sub>3</sub> /solids in KBL ratio (by wt)	T(°C)
1	10	4:1	20
2	22.5	4:1	70
3	35	4:1	70
4	22.5	10:1	20
5	35	10:1	20

Stirring rate: 1050 r.p.m. Reaction time: 30 min. Reaction pressure: 2.5 MPa.

These observations led us to conclude that direct oxidation processing of kraft black liquors with nitric acid to obtain suitable humic materials was not technically feasible.

### 3.2 Indirect oxidation process

#### 3.2.1. Precipitation process of kraft lignin

The yield of precipitated lignin varied between 67 and 74%. Particle size analysis of the lignin (Fig. 2) shows that about 90% of all particles were in the range 0.03 to 0.30 mm.

#### 3.2.2 Oxidation of kraft lignin

After preliminary experimentation in order to establish a systematic procedure for the oxidation process, shown in Fig. 1, several trials were carried out. The purpose was two-fold: first, to determine whether this process would yield humic materials with reasonably high acidities, and second, whether it would be justified to undertake more systematic experimentation. The experimental results obtained are summarized in Table 2. All experimental trials were replicated.

Results obtained at 160°C were not very reliable because the products obtained were partially carbonized. This may be partially due to the characteristics of the kraft lignin used in this work, which probably had a softening temperature lower than most typical lignins, owing to the nature of the pulping process. During the oxidation process the resulting lignin is carbonized when the softening temperature is exceeded (Bristow & Kolseth 1986, Goring 1971).

At milder operating conditions (trials 1 to 6) the humic materials obtained did not show high acidities, usually lower than 20 ml NaOH per gram of sample. At more drastic reaction conditions (trials 7 and 10) higher values for acidity were obtained. When the experimental conditions were very drastic (trials 8, 9, 11, 12), solubilization of lignin took place yielding soluble aliphatic and aromatic materials. However, in spite of the high weight losses after reaction, it can be pointed out that the products from lignin solubilization could be useful as protective agents against alkaline degradation of polysaccharides.

## 4. Conclusions

It was found that direct oxidation processing of waste kraft black liquors could be accomplished only under very gentle conditions (HNO<sub>3</sub> concentration 10 wt%, 20°C and

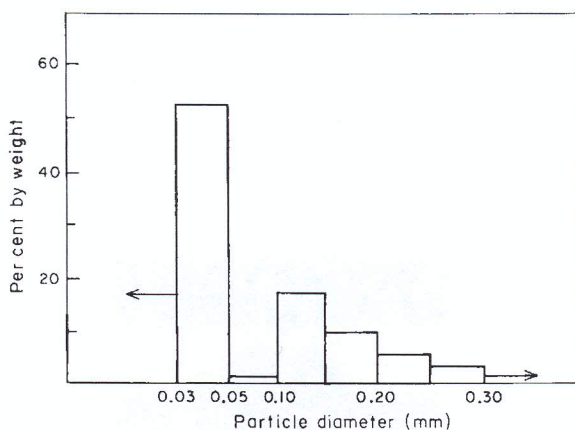


Fig. 2. Particle size distribution of the lignin particles obtained after carbonation of the kraft black liquor.

TABLE 2

Experimental trials carried out using the indirect oxidation process for the oxidation of lignin from kraft black liquor with nitric acid

Experimental run	HNO <sub>3</sub> (%, by wt)	T(°C)	HNO <sub>3</sub> /lignin ratio (by wt)	Acidity (ml NaOH/g sample)	Weight losses (%)
1	5	20	4:1	7.2	46
2	10	40	4:1	12.5	66.2
3	10	90	4:1	14.1	70.4
4	10	160	4:1	16.8	76.2
5	10	160	8:1	21.6	83
6	20	40	4:1	20.1	67.2
7	35	20	6:1	55.2	95.6
8	35	55	6:1	—	100
9	35	90	6:1	—	100
10	35	20	8:1	65	86.2
11	35	55	8:1	—	100
12	35	90	8:1	—	100

Stirring rate: 1050 r.p.m. Reaction time: 30 min. Reaction pressure: 2.5 MPa.

a HNO<sub>3</sub>/solids ratio of 4:1). However, the acidities of the oxidation products were much lower (c. 4 ml NaOH per gram of sample) than the values required for suitable humic materials. At higher nitric acid concentrations the direct process was unsafe and not technically feasible.

In the indirect oxidation process humic materials with acidities up to 65 ml NaOH per gram of sample were obtained. The screening trials carried out suggest the possibility of obtaining nitro-humic materials of a high quality from waste kraft black liquors. High weight losses after reaction have been obtained in these trials. However, the soluble products recovered from the process are also useful as protective agents against alkaline degradation of polysaccharides.

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