Waste kraft black liquors as raw material for the production of nitrogeneous humic fertilizers by an oxidation-ammoniation process

C. González, R. Alvarez and J. Coca
Department of Chemical Engineering, University of Oviedo, 33071-Oviedo, Spain

Received 16 April 1992; accepted in revised form 2 November 1992

Key words: Kraft liquors, kraft black liquors, kraft lignin, humic fertilizers, nitrogenous humic fertilizers

Abstract

The total acidity of humic materials obtained by oxidation of kraft black liquors was previously found to have a very important effect on the results of their ammoniation process (which yields nitrogenous humic fertilizers). This paper deals with a further study of the ammoniation process of two humic materials (with 20 and 60 ml NaOH 0.1 N/g of sample of total acidity) by using liquid NH₄OH. The influence of four independent variables (NH₄OH concentration, reaction temperature, NH₄OH/humic material ratio and reaction time) on the reaction yield, total and ammoniacal nitrogen content of the fertilizers was studied. A $2^4$ factorial design was followed to carry out the experiments. Four models equations, which establish a quantitative relation between the independent and the dependent variables, for each kind of humic material, were found as a result of this work.

Introduction

The organic load of waste kraft black liquors requires a treatment process before discharge. One option is the biological or secondary treatment which yields an activated sludge which can be disposed off in a flash dryer/incinerator or dried and used as a fertilizer [5]. A second approach is to remove the lignin present in the liquor in order to avoid the costly drying process. Lignin can be separated from black liquors by precipitation with CO₂, readily available in paper mills. Lignin is composed of aromatic compounds of high molecular weight and has applications as adhesive, emulsifier, cement additive, surfactant in the sulfonated form for tertiary oil recovery, etc. [7]. As lignin is degraded in the pulping process and has lost much of its reactivity, this is one reason for its low demand compared to the amount that may become available. One possible route to upgrade and recycle lignin is to use it as a source of nitrogenous humic fertilizers.

Earlier investigations have attempted to develop a humic fertilizer from lignin through a sequence of oxidation and ammoniation reactions [9]. It was concluded that the acidity of the resulting product from the oxidation reaction had an important influence on the nitrogen content of the ammoniated product.

This study is an extension of a former work, in which a more detailed investigation of the variables in the oxidation-ammoniation process has been undertaken, including additional variables such as the (NH₄OH/humic material) ratio and the reaction time.

Experimental

Waste kraft black liquors supplied by a pulp mill Celulosas de Asturias, S.A., Navia (Spain) were
used as raw material. Their properties have been reported in a previous paper [8]. Two humic materials with 20 and 60 ml NaOH/(g of sample) of total acidity (hereinafter low acidity and high acidity humic materials, respectively) were prepared by oxidation of lignin from kraft black liquors. HNO₃ was used as oxidation agent. Details of the process and the characteristics of the lignin and the humic materials have been previously reported [8]. The ammoniation process was carried out in a 400 ml stainless steel batch reactor (Autoclave Engineers, USA). Following a standard experimental technique, two fractions of fertilizer were obtained. The first fraction, insoluble in the NH₄OH solution, was removed by filtration through a porous glass filter. The second fraction, soluble in the NH₄OH solution, was removed by evaporating the remaining NH₄OH solution. Both fractions of fertilizer were analyzed for determining their total and ammoniacal nitrogen content. The total nitrogen analyses were carried out combining the methods reported previously [2,9,10] with the Kjeldahl distillation method [11]. The determination of ammoniacal nitrogen has been also reported [11,13].

Experiments were carried out following a 2⁴ factorial design; the ranges and levels of the four independent variables are listed in Table I. They were replicated to provide a suitable estimation of the experimental error. Results were statistically analyzed following methods in the literature [1,12,14].

The dependent variables were: total weight loss (TWL), the percentage of soluble fraction (PPS), total nitrogen content of the soluble fraction (TNS), ammoniacal nitrogen content of the soluble fraction (ANS), (ANS/TNS) ratio and total nitrogen of the insoluble fraction (TNI).

Total weight loss (TWL) is:

\[
TWL = \frac{\text{Weight of humic material fed to the reactor}}{\text{Weight of fertilizer recovered}} \times 100
\]

Thus, negative values of TWL indicate reaction yields higher than 100%.

**Results and discussion**

**Ammoniation of low acidity humic material**

The ammoniation conditions and results for humic material with an acidity of 20 ml NaOH/(g of sample) are summarized in Table II. The ammoniation product is a soluble product in the reaction mixture in most cases. Only in a few runs an insoluble fraction was obtained, hence the statistical analysis of the variables PPS and TNI was not carried out. For the remaining variables an analysis of variance and an analysis of residuals of the model was performed. A ‘critical’ significance level \( \alpha = 0.5\% \) and, therefore, an F-statistic \( F(1,16)_{0.5} = 10.57 \) were considered in all cases. Model equations for the dependent variables and plots showing the fitness between experimental and predicted values are illustrated in Figs. 1, 2, 3 and 4 and equations (1), (2), (3) and (4).

\[
\begin{align*}
\text{TWL (\%)} & = -3.36 + 1.43 C - 3.21 T + \\
& + 5.35 (\text{AM/MH}) + 4.06 T(\text{AM/MH}) \\
& + 0.84 CT(\text{AM/MH}) + 0.96 T^t \\
& + 2.19 (\text{AM/MH})^t + 1.69 C(\text{AM/MN})^t \\
& + 1.98 T(\text{AM/MH})^t \quad (1)
\end{align*}
\]

\[
\begin{align*}
\text{TNS (\%)} & = 2.32 + 0.11 C + 0.33 T + \\
& + 0.08 (\text{AM/MH}) - 0.09 T^t \\
& - 0.14 T(\text{AM/MH})^t \quad (2)
\end{align*}
\]

<table>
<thead>
<tr>
<th>Coded variable</th>
<th>Actual variable</th>
<th>Lower level</th>
<th>Upper level</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄OH Concentration (wt%)</td>
<td>2</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Reaction temperature (°C)</td>
<td>100</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td>(NH₄OH/humic material) ratio (wt/wt)</td>
<td>25 : 1</td>
<td>100 : 1</td>
<td></td>
</tr>
<tr>
<td>Reaction time (min)</td>
<td>60</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>