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# "The Conversion of Lignaceous Biomass into Nonleaching Fertilizer by Ammoxidation"


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This report describes the activities carried out in the entitled collaboration project between the three participating universities Guadalajara (UG, Mexico), Oviedo (UO, Spain) and Washington (UW, USA), during the period July to December 1990.

Professor Coca and his group in Spain have been making a great effort introducing changes in the operation of the 400g-pilot reactor in order to carry out ammoxidation reactions of kraft lignin with oxygen-air mixtures. Recirculation of exhausted gases and elimination of fine particles are among the main changes, as well as the monitoring of spent gases by means of gas-chromatograph equipment.

Several samples have been run in the reactor without feeding ammonia to follow more closely the development of the oxidation step, as this has been pointed out as the main factor responsible for the low nitrogen fixation obtained in previous experiments.

Even with those changes, the oxidation level, estimated from the number of miliequivalents per gram of lignin, continued to be poor, only 15 meq/g, well below the 60 meq/g obtained with samples treated at the beginning of the project with nitric acid.

Although the treatment of lignin with nitric acid was considered in the original proposal as an alternative to further increase the nitrogen level, we decided not to continue by this route because of the possible explosive character of the "nitro-lignins". This concern was emphasized to us through a personal communication from Dr. Ingemar Falkehag, a consultant in lignin utilization. Besides this fact, the use of nitric acid imposes additional complexity and cost to the process.

New efforts were then focused on the oxidation step with the use of different oxidants. In Guadalajara, at the UG, Sr. Virgilio Zuniga conducted a series of studies to test the effectiveness of oxidants such as oxygen, hydrogen peroxide and ozone, in contact with kraft lignin suspensions. None of these agents produced good results and the highest nitrogen content attained when the ammoniation was performed on the oxidized products was only 4 %.

Nevertheless, it seemed that the treatment with nitric acid indeed rendered the lignin more suitable for reaction. It was soon realized that the cations associated with the kraft lignin from Atenquique, Mexico, had an ash content of more than 20 %, and that this was playing a decisive role obstructing the mechanism of the oxidation reaction.

Accordingly, experiments were carried out in the 1-inch-glass reactor in Guadalajara after first applying an acidic treatment to kraft lignin in order to free it from the associated metal cations. This was done by adjusting the pH of a lignin suspension down to 4 by means of hydrochloric acid. After this operation, the lignin was washed twice with deionized water, dried and later granulated. After ammoxidation, this lignin had a nitrogen content of about 11 %. Replications of these reactions have shown very good repeatibility.

In addition, Sr. Zuniga has tried to incorporate into the project, other lignocellulosic residues such as pine bark and pine sawdust as possible alternatives that may produce fertilizers with a more appropriate nitrogen content, in view of their greater reactivity.

Samples of these materials were treated under practically the same conditions as the previous samples and the results are rather encouraging. Pine bark was able to fix as much as 12 % nitrogen and showed good handleability. Pine sawdust revealed itself as the most promising material ever treated under this process, yielding a a product with a high 18 % total nitrogen. In particular with this material, the reactor had to be operated as a packed bed rather than a fluidized bed because of the difficulties in suspending of the material at the gas-flow rates of operation.

Some insight has thus been obtained into the conditions required to treat these materials. This will be taken into consideration in the design of the pilot plant in Guadalajara, so that the equipment can be used for any biomass raw materials.

On the basis of these excellent results, new experiments are already been started in Guadalajara oriented to the use of mixtures of oxygen-air mixtures fed to the reactor simultaneously with ammonia. We believe that the fixation of ammonia in the form of organic linkages occurs at a maximum only when oxygen and ammonia are present at the same time, at the right temperature. With this system, we are also interested to observe the nitrogen fixation when oxygen and ammonia are fed at equimolar rate. The same observations will be made on pine bark and sawdust.

With these results in hand, Sr. Zuniga will travel to Spain in February 1991 and spend approximately one month in Spain, to try to get larger quantities of the nitrogen-enriched kraft lignin, prepared in the larger reactor which is in operation in Oviedo. Bark and sawdust samples will also be reacted. At this point, it is reasonable to expect products with more than 15 % of total nitrogen from any of the materials considered. The evaluation of those products as fertilizers will begin immediately after.

Under the guidance of the UW group, the scientists in Guadalajara have already delineated the program under which the fertilizers will be tested. An agronomist, who is a master's candidate at the Instituto de Madera, Cellulosa y Papel at the UG, will carry out such experiments.

The approach selected is based on the findings of the research on bioassay methods and greenhouse tests conducted at the UW. This includes testing of the fertilizers in pots containing growing grass and measuring the vegetation yields cut at frequent short intervals during a certain period of time. The period during which the evaluation will take place may have to be extended beyond the final due date of the project.

At the UW, the main effort has been a search for an appropriate bioassay for testing nitrogenous lignin-type of materials, which reflects more precisely the long term effect of the release of nitrogen on the plant growth and that is simple enough to allow good repetitiveness and facile interpretation of the results.

As was described in previous progress reports, the growth of rice plants had shown certain promise in this respect so that this approach was used to follow the performance of melamine as a surrogate long term fertilizer.The idea was to apply the knowledge learnt here to the subsequent evaluation of the nitrogenous lignin fertilizers.

After two successive rice crops, the results showed no clear evidence about the expected ability of the surrogate melamine to provide nitrogen at a sustained rate.

Some of the difficulties observed in these tests raised questions as to the value of maintaining these crops for a further test period. Among these, were the problems of keeping unaltered the conditions of the soil from cycle to cycle, especially at the time of re-seeding. At this point old roots must be removed before the new seeds are deposited. This causes disruption of the soil conformation plus losses of soil associated with the old roots.

Also, a single seed very often developed more than one tiller, and some never produced grains, making the comparison of single yields somewhat doubtful. Another difficulty encountered in the second rice crop was the fact that almost of all the grain obtained had suffered some kind of damage and looked diminutive, flat and greenish.

The care of the rice plants was made even more difficult by the development of fungi. Normally, fungi are easy to get rid of with carbofuran or copper sulfate applications. In this case the fungi had to be removed manually because of the effect that those chemicals might have had on the plants.

More importantly however, a study of the mechanism of the breakdown of the melamine, and probably of any other long-term fertilizer, requires several cycles of rice growth. This will make all the re-seeding steps and care operations long and tedious.

It seems clear from the experience of growing rice, that what is needed is a crop that is perennial, and not subjected to cycles of re-seedings. This should avoid the introduction of soil changes as well as allowing a simpler evaluation of yield.

After several searches of the pertinent literature and discussions with people involved in this type of research, it was concluded that grass could fulfill most of the requirements acceptably.

This conclusion is validated by a study carried out here at the UW, where turf grass was grown in pots and treated with various melamine based fertilizers. The grass was cut periodically and weighed to determine the yield of vegetation. This experiment was continued for two and a half years. Only during the second year was there a definite improvement in the amount of cumulative dry matter weight with respect to the control sample yield. This trend became more pronounced with increasing time.

This experiment provides some corroboration of the concept, which we have been trying to demonstrate, that in every soil, microorganisms can be found which are capable of degrading complex sources of nitrogen, which in turn can then be available to the plants, and that the breakdown will occur more rapidly once the population of microorganisms able to deal with such materials has increased sufficiently with time to a significant level.

This experiment has produced interesting results that we will apply to the evaluation of the lignin fertilizer. The testing will be carried out here at the UW on a small scale, and in Guadalajara on a larger scale, after Sr. Zuniga and the group in Spain working with the larger reactor in Oviedo, have been able to produce reproducibly samples with a nitrogen content above 12 %.