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FINAL REPORT

"THE CONVERSION OF LIGNACEOUS BIOMASS INTO NONLEACHING NITROGENEOUS FERTILIZER BY AMMOXIDATION"

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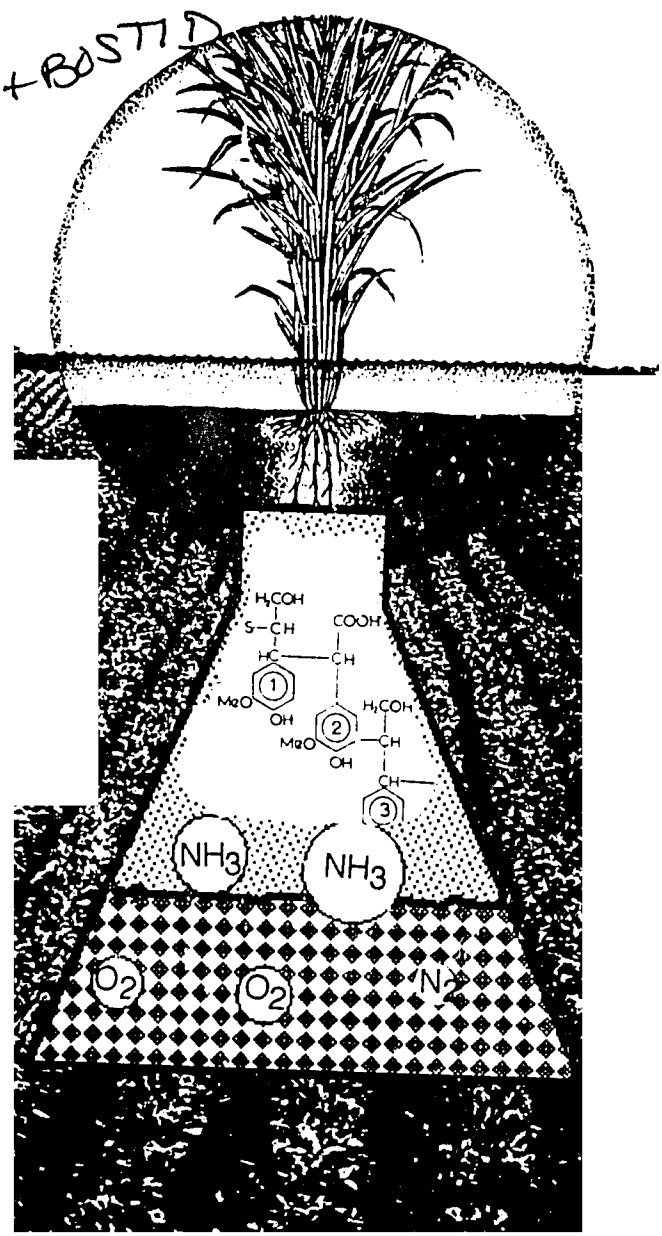

FINAL REPORT

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"THE CONVERSION OF LIGNACEOUS BIOMASS INTO NONLEACHING NITROGENEOUS FERTILIZER BY AMMOXIDATION"

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Executive summary

Project accomplishments

This report deals with the development of the fundamentals and technical procedures to transform lignin and other lignocellulosic materials (sawdust and bark) into long-term fertilizer products.

Kraft lignin, pine sawdust and bark were each subjected to ammoxidation (simultaneous oxidation with air and reaction with ammonia) in a fluidized bed reactor. It was possible to obtain ammoxidized products with maximum nitrogen content over 22% for kraft lignin, 16% for pine sawdust and 14% for pine bark, by operation of the reactor at temperatures between 210-300 °C and 3-8 hours of reaction. Operation at a high temperature is a must in order to limit the duration of the reaction to an economically practical period. However, the highest temperature of operation in practice is fixed by the temperature of carbonization of each raw material. For kraft lignin this temperature is 220 °C.

However, we found that it is possible to fix up to 18 % of nitrogen in kraft lignin after only 6 h of reaction at 210 °C by means of catalysts. One low-cost alternative found to produce interesting results is a mix of iron (III) sulphate and ammonium molybdate when used at 0.2% weight on the substrate to be ammoxidized.

The ammoxidized products contain about 1-2% of nitrogen as ammonium salts. The major content of nitrogen is, however, under the form of amides and possibly lactams. These nitrogen forms are known to hydrolyze in soil at rather slow rates. We believe that the high levels of total nitrogen fixed to lignin obtained in the ammoxidized products, justify the launching of new studies aimed at optimizing the process. More importantly, the results justify the production of larger quantities of ammoxidized products that are necessary for their field testing as fertilizers.

The search for an appropriate bioassay for testing nitrogenous lignin-type materials, which reflects more precisely the long term effect of the release of nitrogen on the plant growth, was also one of the main tasks of this project. Melamine was used as a prototype fertilizer, which contains nitrogen in complex structures similar to the ones that can be found in ammoxidized lignin. The application of melamine to the growing of rice was studied in greenhouse experiments for two consecutive crops. Problems associated with re-seeding and keeping the experiment going through consecutive crops emphasized the inconveniences of rice as an appropriate bioassay for the testing of sustained-release nitrogen fertilizers.

The selection of grass instead of rice as a long-growing crop proved to be a better choice. When we planted grass in soil where melamine and melamine phosphate were applied, we could maintain a greenhouse experiment for several years, cutting the grass periodically and weighing the dry matter to determine the yield. This experiment showed that the soil treated with melamine was indeed able to sustain a larger rate of grass yield over that of the untreated soil. The effect was more dramatic after the second year.

These results provide some corroboration of the concept, which we tried to demonstrate, that in every soil, nitrogen from complex sources can be available to plants, provided there is enough time for the microorganisms responsible for their breakdown to multiply to a significant level. Even though at the moment of the end of the term for this project we were not able to apply this knowledge to the study of ammoxidized lignin products, we remain confident that we have come out with a sound bioassay method that will prove to be effective for the testing of such materials as fertilizers.

Skills or awareness that remain in the participating countries

The state of knowledge about the manufacture of slow-release fertilizers from biomass attained in this project is enormous. However, the technology is not yet complete enough to be used directly by a customer. Nevertheless, even at this stage, the results have attracted the attention of the company, Empresa National de Fertilizantes (ENFERSA) in Spain, which has been in contact with Prof. Coca and the University of Oviedo throughout the project. This company has shown immediate interest in the oxidation of biomass wastes in liquid phase using nitric acid.

We envisage that for Mexico, the use of a fertilizer technology such as the ammoxidation of lignocellulosic materials represents a great potential benefit for the climate and the actual agricultural system, which needs more efficient ways of fertilization that are economically more productive and environmentally protective. The implementation of a nitrogen-enriched-lignocellulosic-based fertilizer technology would contribute effectively to a better agricultural system under Mexico's climatic conditions.

The participation in an international project such like this added a new perspective in the way of thinking and performing of the individuals involved and in the exchange of scientific efforts between participating institutions. From the point of view of individuals, the project produced an interesting frame of work where the investigators benefitted from the free exchange of information and methods of work whose application extends far beyond the grounds of this project.

Also of main importance was the formation of human resources associated to the completion of the different stages of the project. In all three participating universities there were graduate students that received their Master of Science (3) and Ph.D. degrees (3) as a result of their work in the project. This highly qualified labor force is already contributing with their knowledge to achieve goals in both the industry and academic worlds.

The present project has also helped to establish in the University of Oviedo and the University of Guadalajara, and to affirm in the case of the University of Washington, those lines of research on controlled release fertilizers. The experiences obtained in the research and the laboratories and equipment developed for the project form first-hand teaching material that will be used in the chemical engineering studies program of all these institutions.

The heart of the new equipment left by the project was the fluidized bed reactor (pilot-plant) built in the Department of Chemical Engineering of the University of Oviedo and a smaller reactor (bench scale) built in the Instituto de Madera, Cellulosa y Papel of the University of Guadalajara. Both facilities will be used to continue the studies on slow-release fertilizers and other areas of study. In addition to the equipment both institutions now have trained technicians in the operation of these fluidized-bed reactors that will be of invaluable help for future investigations.

In general, the whole group of investigators and technicians that participated in the project have acquired a sound theoretical and practical knowledge of the operation of bed-fluidized reactors that can be used for teaching and training of more graduate and undergraduate students of Chemical Engineering.

It is the feeling of the co-principal investigators of this project that the foundation of a new technology has been laid out and that this can be of great help not only for less developed countries, but also interesting for the developed world. Certainly, more work is necessary to evaluate the performance of the ammoxidized products as fertilizers that can release nitrogen for long time under adverse conditions. We are especially motivated to carry out these studies as we believe that our rationale and techniques, if proven correct, will also revolutionize the concept of testing long-term products in contact with soil.

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1. Research objectives

1.1 Justification

This research was conducted to help the Agency for International Development (AID) bring to many of the less-developed countries the basis of a new technology that would increase the productivity of their agriculture. We believe that a key to this agricultural productivity is the efficient use of fertilizers under often dramatic climatic conditions. By providing the fundamentals and technical procedures to transform agricultural and forest byproducts into fertilizer products capable of releasing their nitrogen to plants for long periods of activity and under adverse weather conditions, this project represents a milestone for the development of that technology.

1.2 Statement of the problem

The bedrock of the development of any society or country is the capability of feeding itself. When this basic need is fulfilled effectively, other resources both material and human can be channelled into the production of different goods and services, initiating the chain of events which will lead to development in non-agricultural areas.

In order to grow crops effectively it is usually necessary to supply a source of nitrogen. In the developed countries this source is commonly either ammonia, urea, or salts containing ammonium and/or nitrate ions. However, these conventional products contain high levels of nitrogen in forms readily available to plants. This availablility characteristic constitutes a problem because leaching by periods of heavy rain and losses due to high temperatures make the delivery of nitrogen to plants far less than effective.

What is needed is a way to provide the plants with the necessary nitrogen for the different stages of plant growth and during the whole period of activity. Most of the products available in the market that attempt to solve this problem are too expensive to be used for ordinary crops and probably out of reach for the econornies of a developing country. Besides, their effectiveness has not yet been conclusively demonstrated.

1.3 Background

Fertilizer science has long recognized the leaching and loss problems of current bulk products and sought to overcome them by conversion into less soluble forms. Sulfur-coated urea and derivatives of urea obtained by condensation with aldehydes have made limited progress, but these high cost approaches are clearly not applicable to the problems of less-developed countries. Unfortunately, there are apparently no practical ways to do this with low-cost ammonia, ammonium nitrate or sulfate.

In contrast, this proposal is directed towards the establishment of the science and technology which allows ammonia, the cheapest form of nitrogen at about $60/ton, to be converted into a water soluble form by a low-cost reaction using indigenous biomass (mainly lignin, but extensible to bark, sawdust, etc.).

The low-cost reaction contemplated was ammoxidation. In ammoxidation a substrate is exposed to a mixture of ammonia and oxygen. The oxygen oxidizes the substrate and causes the formation of carbonyl groups, or their equivalents, which then immediately react with the ammonia to create carbon-nitrogen covalent bonds.

Although an extensive body of knowledge has been developed around this reaction mainly with the objective of converting propylene to acrylonitrile (1,2,3), this information has not seriously been applied to lignin.

The first patented conversion of ammonia nitrogen into organic nitrogen through the ammoxidation of carbonaceous material was credited to N. Caro and A.R. Frank in 1929 (4). These pioneers obtained products containing 10-20% nitrogen by oxidation and ammoniation reactions with various cellulosic starting materials.

Several other patents followed about the same time or shortly thereafter (5,6,7,8). However, the first article in the general literature was published by W. Scholl and R.O.E. Davis in 1933 (9). In this work, the authors obtained products containing 5-22% nitrogen by treatment of peat and sawdust with ammonia under high pressure. After two decades of relative low interest in the ammoxidation of coals or cellulosic materials, new patent activity became apparent (10) and some other articles appeared in the open literature (11,12,13). The researchers from Japan obtained products containing up to 30% nitrogen.

Over the last 20 years there has been a resurgence in research directed toward the conversion of wood biomass to nitrogeneous fertilizers. Among this, the Russians have particularly been quite active in patent work in the late sixties and early eighties (14,15,16,17).

The most informative recent work has originated from the U.S. National Fertilizer Development Center of the Tennessee Valley Authority (18) on the ammoxidation of sawdust. Products with total nitrogen ranging from 20 to 27% by weight were obtained.

Also, Professor Coca, one of the co-principal investigators in this project, applied ammoxidation to some of the low-quality coals of Spain using a fluidized bed-reactor in an attempt to obtain humic fertilizers (19,20). The condensed chemical structure and lack of functionality in the molecular structure of coals limited the nitrogen content of the ammoxidized products to a high of 10%. Because of the shipping and handling costs, this level of nitrogen is not adequate for a commercial fertilizer in a developed country, although the

use of materials such as this might be practical in less-developing countries if the area of use is close to the point of manufacture.

This project deals with the problem of producing long-acting fertilizers from low-cost biomass in a very unique way as is discussed in the following section.

1.4 Innovative aspects of the project

The innovative aspects of the project are three in number: the goal, the approach and the composition of the work team.

The goal of the project is itself truly innovative because it aims at increasing the agricultural productivity (which in turn stimulates the rate of development) of the less-developed countries by cheaply converting indigenous biomass into fertilizers suited for the heavy occasional rainfall and hot weather conditions which exist in many of these places.

The approach is also innovative from the starting material to the process employed. It also combines the knowledge of six separate disciplines: pulp and paper technology, lignin chemistry, petroleum hydrocarbon ammoxidation, controlled release delivery systems, plant fertilization and the chemical engineering of fluidized bed reactors.

Thus, the raw material and process selected represent a step ahead in what is known to date in the area of fertilizers. In reference to the raw material, to overcome the problem of poor functionality, we hypothesize that it is necessary to replace the Spanish coals with a substrate which is not as highly condensed and which has a high chemical functionality. Lignin is such a material. Lignin is a natural polymer present in plants and trees and is available worldwide in less-developed countries from all sorts of indigenous biomass.

Moreover, lignin can be obtained as a byproduct in the chemical manufacture of paper and board and new processes are being developed to extract lignin directly from biomass. Our hypothesis is that lignin would be a suitable substrate for ammoxidation because it contains a variety of carbon-oxygen bonds comprising phenols, ethers, and alcohols as well as carbonyl and carboxyl groups.

With regard to the way of transforming lignin into a suitable long-term fertilizer, we have proposed the ammoxidation process because it offers a direct way to fix nitrogen into a wide range of biomass sources. The use of a fluidized bed reactor to carry out the ammoxidation reaction allows the handling of lignin and other biomass sources in solid form, which facilitates their handling and eventual shipment if necessary. It should be possible then, to find the ammoxidation reaction conditions necessary to introduce more than 20% of total nitrogen to lignin or other raw material.

Of singular importance is that the incorporation of nitrogen into the lignin structure would take place with the creation of different forms, such as ammonium salts, amides and heterocyclic structures. These would hydrolyze in soil at different rates, providing, in the best of the scenarios, a source of nitrogen for long periods of time.

The composition of the research team is likewise innovative since it is composed of three distinctly different goal-oriented scientists from three different universities in the widely different countries who yet have considerable technical overlap and a commonality of interests.

1.5 Support for the project

The funds utilized in this project were provided by the Agency for the International Development and by the University of Washington, the University of Oviedo and the University of Guadalajara (part of faculty salaries).

2 Methods and results

2.1 University of Oviedo

This section addresses the work carried out by Professor José Coca and his team at the University of Oviedo, in Spain. First is described the work done on the production of humic fertilizers by ammoniation of olive pits, almond shells and corncob residues, which are biomass wastes peculiar to Spain. Later in this section an account is presented of the work done on the production of nitrogen fertilizers from kraft lignin and pine sawdust by the ammoxidation reaction using a fluidized bed reactor.

2.1.1 Production of humic fertilizers from olive pits, almond shells and corncob residues.

This work has its origins in the availability of large amounts of agricultural, industrial, and municipal wastes, which makes them an important source of humic material. Those wastes may have to be oxidized, digested, ammoniated, etc., in order to increase their nitrogen content and values as fertilizers (21,22,23,18).

Spain produces annually large amounts of this type of residues, which have been used as raw materials for the production of furfural. Furfural is usually produced by acid-catalyzed dehydration of pentose contained in forestry wastes and agro-wastes as bagasse, corncobs, rice hulls etc. A considerable amount of solid residues is produced in the furfural process. Part of this is used as fuel to generate the steam needed in the process. The remainder may pose a disposal problem. A potential alternative use for this residue is as a source of humic material.

The aim of this work was then to investigate the oxidation of hydrolyzed olive pits, almond shells and corncob residues with nitric acid as the first step and then carry out the ammoniation reaction of the oxidized products to produce a nitrogenous humic-based fertilizer.Carboxyl and hydroxyl groups are formed as a result of the oxidation reaction. By further treatment with ammonia, those groups fix the nitrogen in the form of amides, ammonium salts or cyclic nitrogen compounds.

A summary of the important results is presented below. The details of this work has been published by Riera, Alvarez and Coca elsewhere (25,26,27,28,29).

The main component of olive pits and almond shells as well as corncob residues is lignin, which accounts for almost 30-38% of the total weight. Other components are catechols-tannins and resins and waxes as the chemical composition of Table 1 illustrates.

Table 1. Chemical composition of hydrolyzed olive pits almond shells and corncobs.

Component[a]	Olive pits	Almond shells	Corncobs
C	54.2	55.4	62.95
H	5.9	5.6	4.91
N	1.3	0.3	0.57
S	0.3	0.3	0.22
O (by difference)	38.2	38.4	31.35
catechols-tannins[b]	9.5	21.9	ND
resins-waxes-fats[c]	8.9	10.9	ND
lignin[d]	37.5	30.6	ND
extractives[e]	4.4	12.9	ND

[a]Weight percent dry basis
[b]Ethanol extraction (4 h)
[c]Ethanol-benzene extraction (7 h)
[d]Solids left after digestion with H2SO4 (76%) (2 h)
[e]Boiling water extraction (3 h)

When these residues are treated with nitric acid, carboxyl and hydroxyl groups are generated in the solid and nitrogen may be introduced in the form of nitro and nitroso compounds. Also some soluble acids are generated which go into solution. After the treatment the nitrogen content of the oxidized products is about 3% (Table 2)

Table 2. Optimum oxidation conditions for the treatment of the raw material (olive pits and almond shells) with nitric acid, and product properties.

	Oxidized olive pits	Oxidized almond shells
Conditions:		
T (°C)	20	30
HNO_3 (%wt)	42.3	45
t (min)	240	60
S/L ratio (%wt)	0.163	0.29
Products of the reaction:		
Acidity (mL NaOH/g)	42.0	45.1
Losses in weight (%wt)	34.4	43.6
Total nitrogen (%)	2.6	2.9

The ammoniation (treatment with ammonia in aqueous solution) of oxidized biomass wastes yields two characteristic fractions (Table 3): a solid product separated by filtration which contains 2.6-5% total nitrogen mostly as nitroso and nitro forms and a soluble fraction that contains a maximum of 13% total nitrogen. The ammonia nitrogen in this latter fraction accounts for approximately 45% of the total nitrogen content and is mainly in the form of ammonium polycarboxylates and ammonium nitrohumates.

Table 3. Identification of oxiammoniated biomass wastes added to the soil.

Curves on figures 1&2	Material	Process Conditions					
		N_T[a]	N_{NH_3}[b]	T (°C)	NH_4OH conc. (wt%)	S/L[c]	WSF[d]
1	Soil without product added (control)						
2	Oxidized olive pits	2.6		**			
3	Oxidized almond shells	2.9		**			
4	Oxiammoniated olive pits water-insoluble fraction	2.6		210	2.75	1.65	—
5	Oxiammoniated olive pits water-soluble fraction	12.6	5.0	210	2.75	1.65	48.8
6	Oxiammoniated almond shells water-insoluble fraction	5.3		210	2.40	0.62	—
7	Oxiammoniated almond shells water-soluble fraction	12.6	5.3	210	2.40	0.62	—
8	Ammonium nitrate	35.0	21.0				

[a]Total nitrogen in %
[b]Nitrogen present in ammonium form in %.
[c]Solid/liquid ratio in the ammoniation reaction
[d]Water-soluble fraction percentage.
** Optimum conditions: (2) 20 °C, 42.4 wt% HNO_3, 240 min; (3) 30 °C, 45.0 wt% HNO_3, 60 min.

The nitrification of the oxiammoniated materials (products of the ammoniation of oxidized materials) mixed with standard soil samples, measured as the amount of nitrogen in the form of nitrates being formed at different periods of time, was investigated. Nitrification tests give a good indication of nitrogen to nitrate transformations, when large amounts of fertilizer are not available. It is recognized that this kind of test is only of indicative nature, but it is accepted that nitrogen compounds converted to nitrate are then readily used by plants. In addition, nitrification tests enable comparative studies between the oxiammoniated product and conventional fertilizers, such as ammonium nitrate or urea.

In this study, both the insoluble and soluble fractions of oxiammoniated olive pits and almond shells were mixed with soil and nitrification rates were studied over a 14-week period. It was found (Figure 1) that water-insoluble fractions have no practical influence on the nitrification rate in the soil and behave as inerts, in spite of their nitrogen content (2.6% for olive pits and 5.3% for almond shells). As it can be seen from the tables 2 and 3, this fraction is practically unaffected by the ammoniation process. Its structure is very similar to the oxidized material and the acid content (active centers to fix nitrogen) is very low. It appears that the nitrogen in those samples is not readily available to the soil and microorganisms cannot transform it into nitrates, at least within the test period.

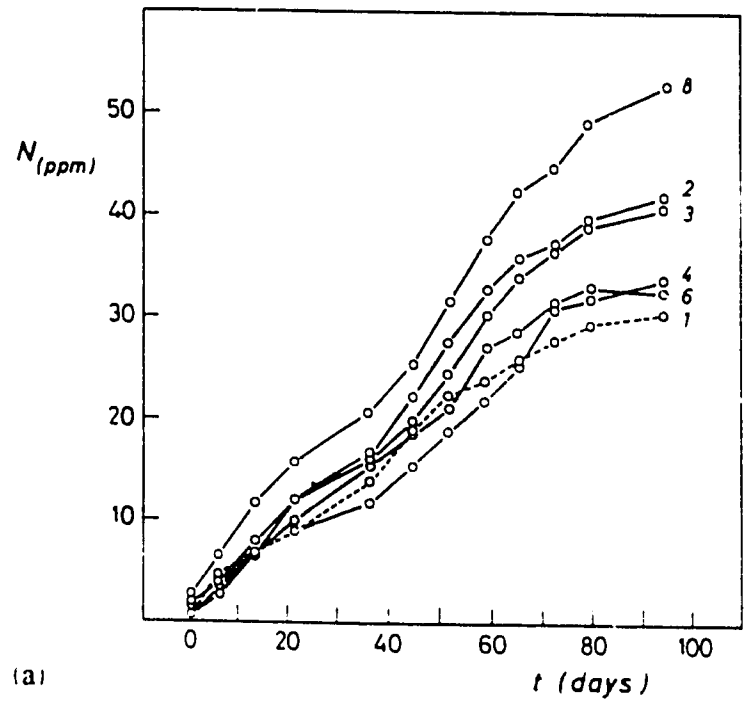
Water soluble fractions proved to be more efficient as fertilizer than ammonium nitrate, which was used as reference material. This is particularly true for olive pits. These results are in good agreement with those reported by other researchers (30), where nitro-humates obtained by treating the pits with aqueous ammonia behaved similarly to commercial ammonium nitrate.

Therefore, it seems that the ammoniation reaction has an influence on the percentage of nitrogen available to the soil and that the total amount of nitrogen fixed in the final product is highly dependent upon the oxidation reactions. Some authors (21,31) suggested that heterocyclic stable nitrogen compounds are formed during oxiammoniation reactions at high temperatures in the gas phase, but it is apparent that different reactions take place during the aqueous phase ammoniation.

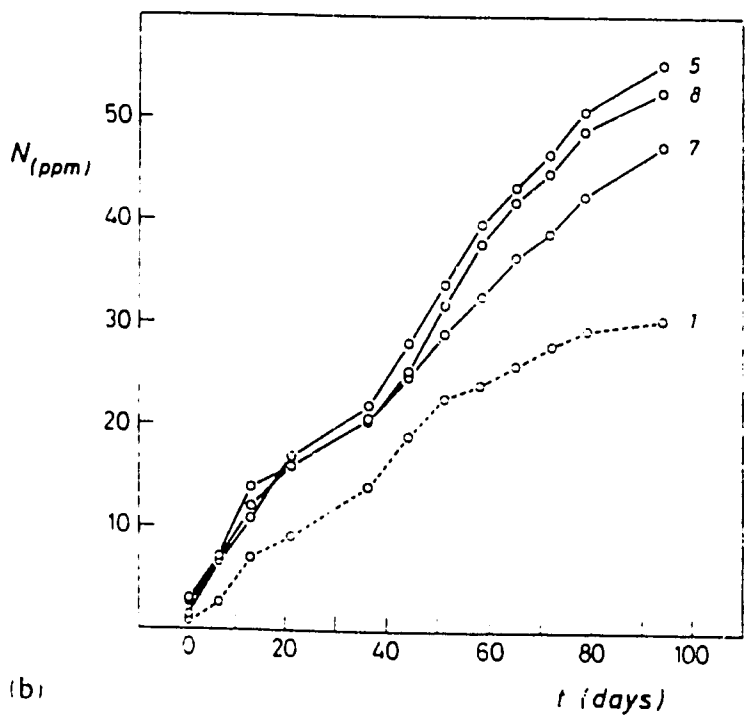
Furthermore, the ammonium nitrogen value in final products represents about 40% of the total nitrogen content. Ammonium nitrogen is considered to be readily assimilable by plants. It can be observed in Figure 2 that at the end of the nitrification test more than 80% of nitrogen in the water soluble fraction of the ammoxidized olive pits was transformed into nitrate (with respect to the control test); about 60% of the same fraction in almond shells was transformed as well.

Interestingly enough, when the oxidized products of both olive pits and almond shells (wastes treated only with nitric acid) were mixed with soil and subjected to nitrification tests, it was found that they had a noticeable influence on nitrification. Thus, after 94 days, 40% of the nitrogen (above that of the control test) was transformed into nitrate, which makes the oxidized products more active than the insoluble fractions of the products studied here, but short of the activity shown by the soluble fraction of the same products. Nitrogen in oxidized products can be either nitro or nitroso forms (30). An important part of the nitrogen is in highly oxidized state and can be easily released as nitrate upon permanganate oxidation. A smaller portion of this nitrogen is in a less oxidized state and can be released as ammonia by alkali boiling.

More investigations are needed to clarify the potential application of these humic products as fertilizers, but undoubtedly they represent an interesting alternative due to the relatively low cost and availability of the starting biomass sources and the simplicity of the process to transform them.



(a)



(b)

Fig. 1. Total nitrogen content analyzed during the incubation test. (1) Control test (no fertilizer added); (2) oxidized olive pits; (3) oxidized almond shells; (4) oxiammoniated olive pits, water-insoluble fraction; (5) oxiammoniated olive pits, water-soluble fraction; (6) oxiammoniated almond shells, water-insoluble fraction; (7) oxiammoniated almond shells, water-soluble fraction; (8) ammonium nitrate.

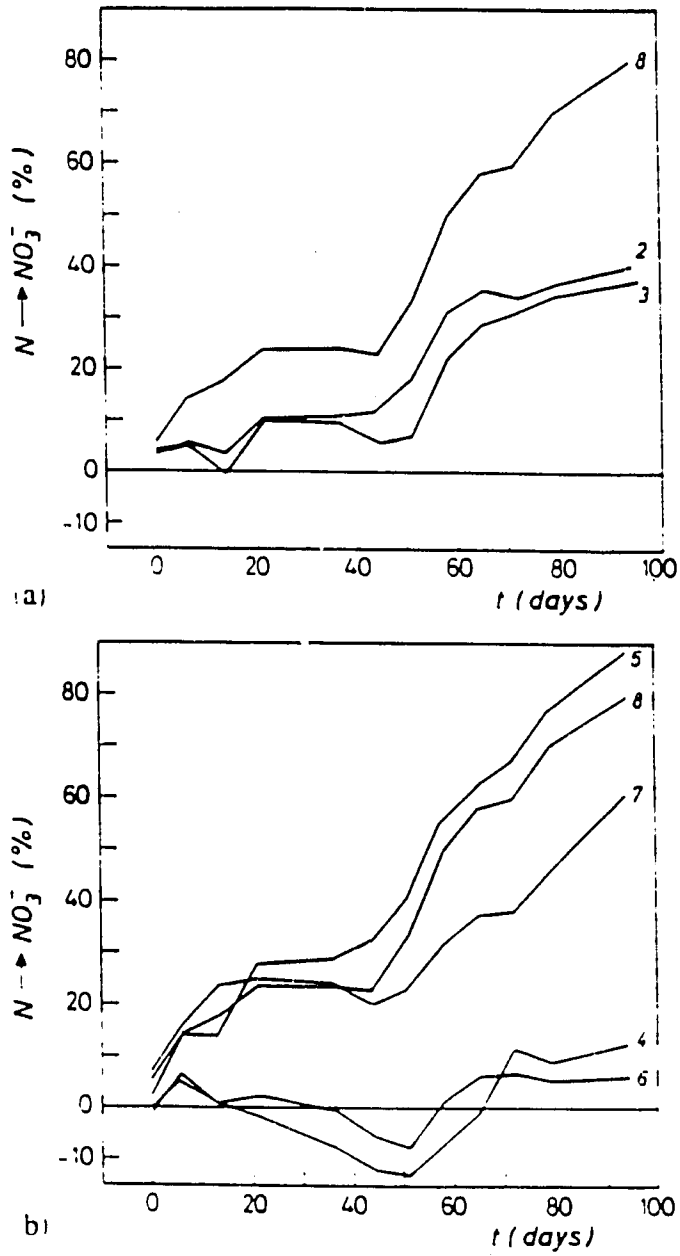


Fig. 2. Nitrification tests in soil for oxidized and ammoniated products. (2) Oxidized olive pits: (3) oxidized almond shells: (4) oxiammoniated olive pits, water-insoluble fraction: (5) oxiammoniated olive pits, water-soluble fraction: (6) oxiammoniated almond shells, water-insoluble fraction: (7) oxiammoniated almond shells, water-soluble fraction: (8) ammonium nitrate.

[1]Total nitrogen in %.
[2]Nitrogen present in ammoniacal forms in %.
Water-soluble fraction percentage.
**Optimum conditions: (2) 20°C, 42·4 wt% (HNO_3), 240 min.
(3) 30°C, 45·0 wt% (HNO_3), 60 min.

The importance of this study for the goals of the project relies upon two main facts: first, the similarity of the chemical nature of agro-wastes with kraft lignin itself and sawdust which poses the same challenges for their transformation into nitrogen fertilizers and second the importance of these biomass resources to the countries that will benefit from this technology. On this basis, the work summarized here provided most of the needed grounds for the study of the transformation of kraft lignin and pine sawdust by means of the ammoxidation reaction performed in a fluidized bed reactor.

2.1.2 Ammoxidation of kraft lignin and pine sawdust in a fluidized bed reactor.

2.1.2.1 Raw materials

The feasibility of preparing a nitrogen humic fertilizer from lignin and pine sawdust was studied. Kraft lignin (Lignaten) samples were obtained from The Compañía Industrial de Atenquique, Mexico. Pine sawdust samples were a gift from a sawmill in Spain.

The pine sawdust samples were dried at room temperature for three days and then screened. After preliminary fluidization runs, the particle size fraction between 0.5 and 0.8 mm was found to be the easiest to fluidize and that was used for carrying out the ammoxidation experiments.

Lignaten is a kraft lignin prepared commercially by The Compañía Industrial de Atenquique. It is isolated from kraft black liquor from a mix of softwoods by precipitation at pH 3 with sulfuric acid at 60 °C. The fraction of this lignin with a particle size between 0.2 and 0.8 mm was used for the ammoxidation studies.

The elemental composition of both pine sawdust and kraft lignin are reported in Table 4.

Table 4. Elemental composition of kraft lignin and pine sawdust.

Material	Ash content (%)	C (%)	H (%)	N (%)	O (%)
Lignin	12	55.6	4.9	0.1	39.4
Pine sawdust	0.3	55.6	5.9	0.4	33.8

2.1.2.2 Equipment

The experimental equipment is illustrated in Figure 3. The fluidized bed reactor consists of a stainless steel pipe (6.5 cm i.d. and 48 cm height) with a coarse sintered glass partition plate near the bottom. The upper end is connected to a wider tube (expansion zone, 22 cm i.d. and 35 cm height) designed to decrease the surface speed of the reaction gas and thus decrease the amount of fine particles removed from the reactor. Heating is provided by an electrical resistance Thermocoax coiled externally to a tube attached underneath the partition plate and filled in with steel balls of 6.32 mm of diameter. Temperature was controlled by means of a PID (proportional-integral-derivative) controller that operates on the heating resistance.

Air was fed to the reactor from a compressor and ammonia was fed from a 50 L-tank. The flow rates were controlled independently by two rotameters and the two streams combined in a Y-tube before introduction to the preheater tube.

2.1.2.3 Experimental procedures

Ammoxidation of sawdust was carried out by first preheating the fluidized bed reactor with hot air to the temperature value designed for the experiment and introducing after that 100 g of sawdust through the top of the reactor, meanwhile the air valve was kept closed. More hot air was introduced then, until the temperature reached the specified value. At this point the ammonia-air mix was fed into the reactor according to the established ratio.

When lignin was used, the reactor was preheated with hot air up to 120 °C and lignin (150 g, dried at 60 °C for 24 h) was introduced into the reactor with the air flow shut off. The air flow was restablished until the desired value of temperature was achieved. After the system reached this temperature, the air temperature was increased progressively up to 220 °C. The ammonia-air mix was then fed into the reactor according to the established ratio.

2.1.2.4 Ammoxidation of sawdust

2.1.2.4.1 Fluidization studies

Several runs were carried out aimed at establishing the optimal conditions for operation of the fluidized bed reactor. Of importance here was to determine the minimum rate of fluidization as well as the size of the fractions that allow a uniform fluidization. The optimal rate of fluidization obtained was 2020 L/h, which corresponds to 2.5-3.7 times the minimum rate of fluidization.

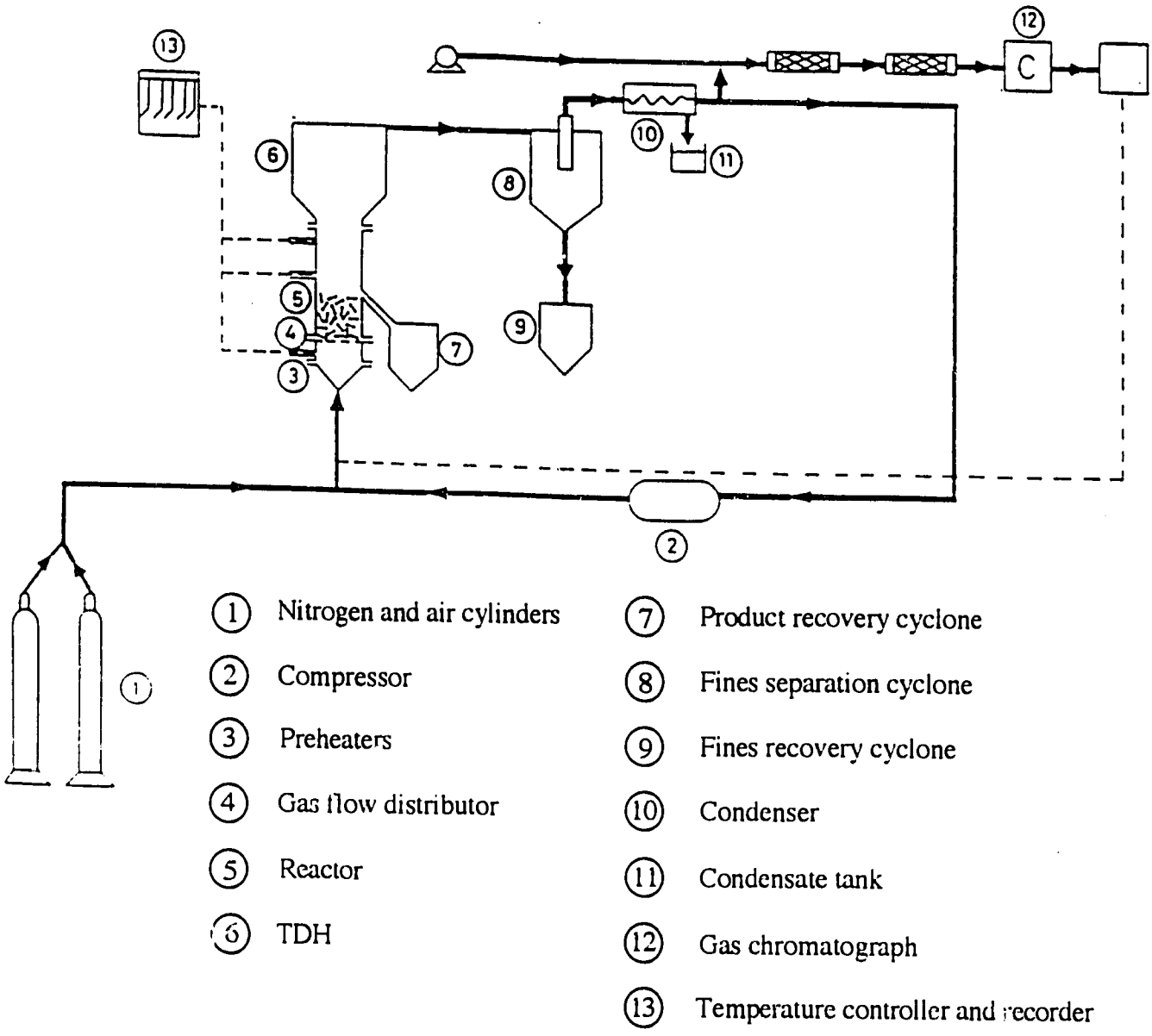


Figure 3. Schematic diagram of the pilot plant fluidized bed reactor.

2.1.2.4.2 Selection of variables for the ammoxidation reaction

Three independent variables were selected for this study: reaction time, temperature of reaction and percentage of ammonia in the fluidization gases. The following variables were kept constant : gas flow rate (2020 L/h) and the particle size (0.5-0.8 mm). The ranges and levels of the four variables studied are listed in Table 5.

Table 5. Limit values for the independent variables.

Variable	Inferior limit	Superior limit
Temperature (°C)	150	280
Time of reaction (min)	60	420
Ammonia (%)	12.5	33.3

The upper limit of temperature was set up by the point of combustion of sawdust, which is 280 °C. The lower limit of temperature is determined by economic considerations. Lower temperatures are possible but the rate of reaction is lowered and the time of reaction has to be extended. The range of reaction times was determined on a similar basis.

The range of the ammonia content of the fluidization gases was selected by taking into account the need not to exceed the explosion limits of ammonia in air at the maxima temperature of operation.

The main dependent variables selected for this study were: total nitrogen fixed (N_t), ammonium nitrogen (N_{NH3}), weight loss and humic content of product.

2.1.2.4.3 Results and discussion

In Table 6, the weight loss and elemental analysis of the products of ammoxidation are shown. The maximum nitrogen content of 16.6% was obtained when the temperature was 280 °C and the reaction time was 3.5 h, with an ammonia content of 33.3% in the fluidization gases. The fixation of nitrogen increased according to corresponding increments of the reaction temperature. This latter variable and time of reaction were found to exert the major influence on the fixation of nitrogen. The ammonia content of the fluidization gases seemed not to have any significant influence in the fixation of nitrogen, supporting the view that the oxidation was the controlling step.

Table 6. Weight loss and elemental analysis of the products of ammoxidation

Run	Temperature (°C)	Time (min)	Ammonia (%)	Weight loss (%)	N (%)	C (%)	H (%)	O[1] (%)
1	150	60	12.5	15.2	0.7	57.3	6.1	35.9
2	150	60	12.5	14.7	0.6	57.1	6.2	35.5
3	150	60	33.3	14.2	0.8	57.1	5.8	35.3
4	150	60	33.3	14.6	0.8	56.5	6.0	36.7
5	150	420	12.5	15.3	1.1	57.1	5.9	35.9
6	150	420	12.5	15.7	1.1	57.3	6.4	35.2
7	150	420	33.3	14.9	1.2	56.6	6.1	36.1
8	150	420	33.3	14.5	1.3	57.9	6.3	34.5
9	150	210	12.5	15.8	0.9	48.5	6.4	44.2
10	200	60	12.5	13.7	1.7	49.8	6.2	42.3
11	200	50	12.5	11.7	1.9	48.8	6.4	42.9
12	200	210	12.5	16.6	2.7	50.1	6.1	41.1
13	200	420	12.5	20.5	4.2	50.1	5.9	39.8
14	200	60	33.3	13.5	1.6	49.5	6.3	42.6
15	200	210	33.3	15.3	3.0	49.9	6.2	40.9
16	200	420	33.3	19.3	4.4	50.3	6.1	39.2
17	240	60	12.5	31.8	4.1	62.5	4.9	28.5
18	240	60	12.5	30.6	4.1	61.7	5.4	28.8
19	240	210	12.5	50.3	8.2	63.0	4.7	24.1
20	240	420	12.5	73.6	10.6	62.3	4.5	22.6
21	240	420	12.5	69.8	10.7	60.8	4.4	24.1
22	240	60	33.3	26.3	4.2	59.8	5.0	31.0
23	240	60	33.3	27.5	4.2	61.4	5.0	29.4
24	240	210	33.3	41.1	9.4	52.2	5.3	33.1
25	240	420	33.3	60.2	10.7	63.3	4.4	21.6
26	240	420	33.3	62.2	10.7	63.3	4.4	21.6
27	280	60	12.5	52.3	11.0	55.4	4.8	28.8
28	280	60	33.3	34.4	10.4	54.1	5.1	30.4
29	280	120	12.5	62.3	13.6	55.9	4.4	26.1
30	280	210	12.5	76.3	16.3	56.8	4.4	22.5
31	280	210	33.3	69.5	16.6	57.3	4.5	21.6

[1]Calculated by difference.

The loss of material also increased continuously with temperature and time of reaction. Its minimum value was 14.5 % at 150 °C and corresponded to approximately the moisture content of the raw material. In this case the loss by carryover of particles was insignificant. The maximum loss occurred at 280 °C, 3.5 hours and ammonia level of 12.5 %. There seemed to be a clear trend to get losses of material when the concentration of oxygen in the fluidization gases increased.

Table 7 shows the ammoniacal nitrogen and humic material content (fraction soluble in 0.1 N NaOH and humic acids) of the ammoxidation products. The ammoniacal nitrogen content was low in almost every case, similarly to what happens in general for a pure ammoniation reaction in the gas phase. The yield of ammonium nitrogen increased with temperature up to 240 °C, after which it stabilized. Contrary to the effect observed on total nitrogen, the content of ammonia in the fluidization gases had a positive effect on the fixation of nitrogen in the ammonium form.

Table 7. Ammonium nitrogen and humic substance in the ammoxidation products of pine sawdust.

Run	Temperature (°C)	Time (min)	Ammonia (%)	Ammonium N (%)	Fraction soluble in NaOH (%)	Humic acids (%)
1	150	60	12.5	0.2	9.0	0.3
2	150	60	12.5	0.1	8.5	0.3
3	150	60	33.3	0.4	6.8	0.2
4	150	60	33.3	0.5	8.8	0.4
5	150	420	12.5	0.5	6.9	0.3
6	150	420	12.5	0.2	10.4	0.5
7	150	420	33.3	0.3	8.4	0.4
8	150	420	33.3	0.6	12.1	0.5
9	150	210	12.5	0.3	6.7	0.3
10	200	60	12.5	0.4	6.3	0.5
11	200	50	12.5	0.2	5.1	0.4
12	200	210	12.5	0.3	16.5	1.8
13	200	420	12.5	0.4	19.6	4.0
14	200	60	33.3	0.5	10.2	0.5
15	200	210	33.3	0.6	13.2	1.8
16	200	420	33.3	0.5	16.2	3.6
17	240	60	12.5	0.4	20.8	4.5
18	240	60	12.5	0.6	22.1	4.9
19	240	210	12.5	0.4	48.1	21.8
20	240	420	12.5	1.6	46.8	26.7
21	240	420	12.5	1.5	54.1	28.7
22	240	60	33.3	0.8	19.3	4.9
23	240	60	33.3	0.4	17.6	3.8
24	240	210	33.3	1.3	37.5	13.2
25	240	420	33.3	1.7	44.4	23.7
26	240	420	33.3	1.9	40.1	23.2
27	280	60	12.5	0.5	17.8	4.4
28	280	60	33.3	0.7	18.0	3.4
29	280	120	12.5	0.6	15.4	3.5
30	280	210	12.5	1.0	10.6	1.5
31	280	210	33.3	1.2	13.5	0.7

The amount of humic acids reached a maximum of 28 % at 240 °C. At higher temperatures the fraction of humic acids decreased probably due to degradation of the raw material. At higher ammonia levels in the fluidization gases, the amount of humic acids decreased as well, in direct response to the decreasing oxygen ratio.

2.1.2.5 Ammoxidation of lignin.

2.1.2.5.1 Preliminary experimentation

The fraction of lignin used for the reaction was the one with a particle size between 0.2 and 0.8 mm, according to the fluidization studies carried out at room temperature. The minimum rate of fluidization was found at 7.7 cm/s and the optimal rate established for the operating temperature was 11.3 cm/s.

The maximum temperature that could be reached under these conditions was 220 °C. At higher temperatures the lignin samples started to burn.

2.1.2.5.2 Results and discussion.

Table 8 shows the elemental analysis of ammoxidized lignin prepared by reaction at 220 °C for 7 hours under 4:1 and 2:1 air/ammonia ratios.

Table 8. Elemental analysis of ammoxidized lignin.

Run	Air/ammonia ratio	C (%)	H (%)	N (%)	O (%)	Ash content (%)
1	4:1	54.3	4.6	7.6	35.5	13
2	2:1	54.6	4.4	7.5	35.5	12

It is seen that the amount of nitrogen fixed is about 7.5 % for the conditions employed here, which represent the maximum temperature possible and a long time of reaction. The concentration of ammonia in the fluidization gases seemed to play only a minor role on the fixation of nitrogen.

It was speculated that the reason for the low content of nitrogen in the ammoxidized products could be related to some inefficiencies on the oxidation step. In order to prove this point a series of oxidation experiments were carried out using exclusively air as oxidant and carrier. The results secured are shown in Table 9.

Table 9. Oxidation of lignin with air in a fluidized bed reactor.

Run	Temperature (°C)	Time (min)	Weight loss (%)	Acidity (mL NaOH 0.1 N/g)
3	220	120	31.3	5
4	220	240	41.3	14
5	220	420	45.3	18

By determining the number of mmol of sodium hydroxide needed to neutralize the acidity of the oxidized products, it was demonstrated that the total amount of acidity centers was low in all ammoxidized products. Earlier studies had shown that the lower limit number of acidity in products that yielded reasonable good levels of nitrogen was about 4 mmol per gram of product. Other experiments carried out by varying temperature, time of reaction and air/ammonia ratios continued yielding low acidity products as it is shown in Table 10.

Table 10. Oxidation of lignin with oxygen in a fluidized bed reactor.

Run	Temperature (°C)	Time (min)	Air/oxygen ratio	Weight loss (%)	Acidity (mL NaOH 0.1 N/g)
13	220	240	4:1	33.3	16
14	220	240	4:2	33.0	12
15	220	240	4:3	25.0	15

According to the results in Table 10, the acidity values did not increase significantly by using oxygen as the fluidization gas either. Our next step was then to carry out the oxidation of lignin in the liquid phase using nitric acid. The equipment used in this case was a 5 L glass round-bottom flask stirred mechanically. The average value of acidity determined on the new oxidized products was 5.6 mmol per gram of product, which was even higher than that obtained in earlier studies with other lignocellulosic materials. It was surprising

to observe that the lignin oxidized in this way contained already about 4 % of nitrogen. When this oxidized lignin was ammoniated in the fluidized bed reactor, the fixation of nitrogen ranged between 9 and 13 %, far better than the fixation of nitrogen carrying out the oxidation and ammoniation simultaneously in the gas phase. These results are presented in Table 11.

Table 11. Ammoniation of lignin oxidized with nitric acid.

Run	Temperature (°C)	Time (min)	Fluidization rate (cm/s)	C (%)	H (%)	N (%)	O (%)
16	120	120	33.4	50.7	5.0	9.4	34.8
17	120	240	33.4	50.5	5.2	9.1	35.2
18	170	120	29.6	60.1	4.6	11.2	24.1
19	170	240	29.6	58.2	4.8	11.7	25.3
20	220	120	22.3	57.9	4.7	10.2	27.2
21	220	240	22.3	60.4	4.4	12.9	22.3
22	220	420	22.3	60.9	4.3	13.4	21.4

2.1.2.6 Conclusions.

2.1.2.6.1 Ammoxidation of pine sawdust.

Pine sawdust was difficult to fluidize. In order to carry out the ammoxidation in a fluidized bed, it was necessary to use only the fraction with particle size between 0.5 and 0.8 mm, which corresponded to 27 % of the entire sample.

The maximum level of nitrogen fixation in pine sawdust was 16.6 %, of which only 1.2 % was ammonium nitrogen. The conditions to obtain this product were: 280 °C, 3.5 h and 33.3 % of ammonia in the fluidization gases. The amount of ammonium nitrogen could be increased only slightly by working at higher temperatures. Under these conditions the fixation of nitrogen in other forms increased more rapidly.

The total amount of humic substances in the ammoxidized pine sawdust increased with temperature up to a maximum of 30 % at the boundary of 265 °C and 7 h. Beyond this temperature the humic substance content decreased sharply.

The percentage of ammonia in the fluidization gases exerts a minor influence on the total fixation of nitrogen. However, it decreases the total yield by having a negative effect in the total yield of humic material.

2.1.2.6.2 Ammoxidation of kraft lignin.

The kraft lignin precipitated with sulfuric acid from kraft black liquors had a wide range of particle sizes and its fluidization was particularly difficult because of the presence of a large amount of very fine particles.

The ammoxidation of lignin in the gas phase yielded products with low levels of nitrogen when an air/ammonia mix was used as the fluidization gas. It can be argued here that the low level of nitrogen fixation has its origin in the small amount of acidic centers generated during the oxidation stage of the reaction, since an increase in the amount of ammonia fed to the reactor did not produce a corresponding increase of nitrogen content in the product.

When the oxidation of lignin was carried out with nitric acid in a separate stage and then the oxidized product was ammoniated in the fluidized bed reactor at 220 °C for 4 h using ammonia gas, the total amount of nitrogen fixated in the product went up to 13.4 %. It was still possible to obtain a yield of 13 % total nitrogen by running the reaction at the same temperature and times of reaction slightly less than 4 h.

2.2 University of Guadalajara

This section contains the studies carried out by Professor Virgilio Zúñiga and his team at the University of Guadalajara (Mexico) on the ammoxidation of kraft lignin and pine bark using a fluidized bed reactor.

2.2.1 Ammoxidation of kraft lignin and pine bark in a fluidized bed reactor.

2.2.1.1 Raw materials

The raw materials used for the ammoxidation studies were a gift from the Compañía Industrial de Atenquique, Mexico. The main product of this company is kraft paper for packaging. The company processes a mix of the following pine species: *Pinus michoacana, Pinus douglasiana and Pinus oocarpa.* Pine bark was collected from the woodyard and lignin was precipitated from samples of black liquor from the second stage of evaporators of the chemical recovery system.

Bark samples were dried at room temperature and reduced to smaller particles in a Wiley mill. The dried bark samples were screened and the particle size fraction retained in the 0.4 mm-wire mesh was kept for the ammoxidation studies.

Kraft lignin was isolated from the black liquor through two stages of neutralization. The first one was accomplished by bubbling carbon dioxide through the liquor at 60 °C until the pH went down to 8.5. The second stage consisted in the precipitation of lignin at 60 °C by further reduction of the pH to 2.5 using sulfuric acid. The precipitated lignin was separated from the rest of the black liquor by centrifugation and the solid residue washed thoroughly with hot water. The lignin samples were then dried at room temperature and ground in a mortar. The ground lignin samples were screened and the fraction collected on a 0.4 mm-wire mesh was kept for the ammoxidation studies.

2.2.1.2 Equipment

Most of the studies of ammoxidation were carried out in a fluidized bed reactor built specifically for this project. The reactor was built in glass (lab-bench scale) to handle samples of about 12 g. Some other experiments were performed on the semi-pilot reactor built at the University of Oviedo (Spain), which allowed the preparation of about 450 g of ammoxidized product. The details of this reactor and its operation have already been described in section 2.1.2.2.

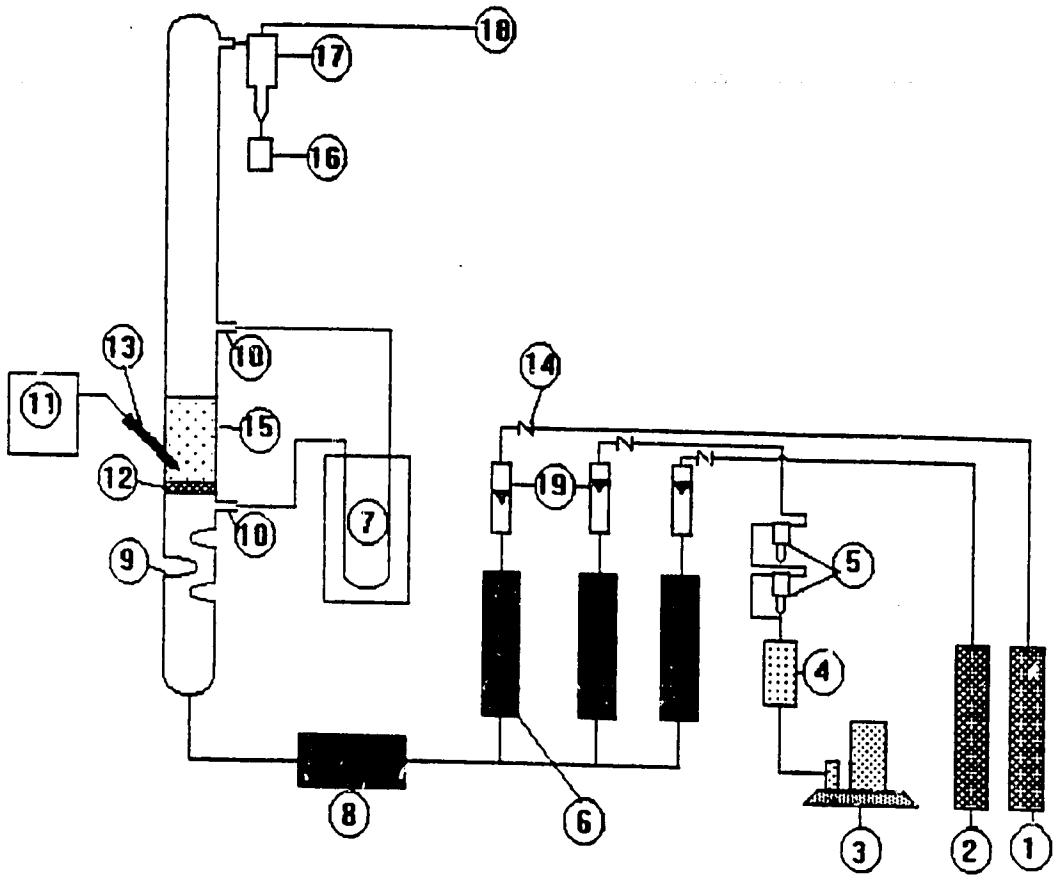
Figure 4 shows a scheme of the fluidized bed reactor built in glass. The main body of the reactor consists of a Pyrex-glass tube of 20 mm i.d. with a sintered-glass plate located at the bottom for distribution of the fluidization gases. Air is heated directly by means of electrical resistances meanwhile ammonia is heated indirectly as it is shown in the figure. The hot gases are combined at a "Y" joint and are fed at the bottom of the reactor. Gas flows are controlled by means of needle valves and temperature was controlled using a PID device. The total gas flow rate was established for each raw material based on 2.5 times the minimum rate of fluidization. In accordance to this, the flow rate was adjusted in the range of 25 to 30 L/min.

A typical ammoxidation run proceeded according to the following description. Air was pre-heated up to 120 °C and time was allowed for the system to stabilize at this temperature. With the air flow closed for a moment, a lignin sample was then introduced at the top of the reactor. The air flow was then re-established and the temperature increased to 170 °C. At this point ammonia was introduced to the reactor and the flow rate was adjusted to the desired value during an interval of 15 to 20 min. At these conditions the reaction was continued for the time specified, then the ammonia flow was stopped and the reactor emptied quickly.

2.2.1.3 Analytical techniques

The ammoxidized products were analyzed according to the following techniques:

Total Nitrogen. Micro-Kjeldhal (32).
Infrared Spectroscopy. A Nicolet 510 FT-IR spectrometer was used.



1 Ammonia cylinder
2 Nitrogen cylinder
3 Air compressor
4 Air cylinder
5 Air filter
6 Heat exchangers
7 Manometer
8 Mix chamber
9 Deflectors
10 Outlets for manometers
11 Temperature controller
12 Gas distributor
13 Thermocouple
14 Needle valves
15 Reaction chamber
16 Fines recovery tank
17 Fines separator
18 Gas outlet

Figure 4. Schematic diagram of the bench scale fluidized bed reactor.

2.2.1.4 Results and discussion

2.2.1.4.1 Preliminary study

The study of the ammoxidation of lignin described here started on the basis of the results obtained by Professor Coca and his group at the University of Oviedo. As can be recalled from the discussion of the results obtained at the University of Oviedo (section 2.1.2.5.2), the ammoxidation of lignin in gas phase using the fluidized bed reactor, showed that the fixation of nitrogen attained very low values (about 7.5%). By careful examination of these results, it was realized that the ash content of the lignin samples was extremely high and that the cations associated with the kraft lignin could have been playing a decisive role obstructing the mechanism of the oxidation reaction.

It is known that the pH of precipitation of lignin determines its ash content. Accordingly, a series of experiments were performed in which lignin was isolated from kraft liquors with sulfuric acid at different pH values and its ash content determined. After this operation, the lignin was washed twice with deionized water, dried and later granulated. These lignin samples were then ammoxidized in the lab-bench scale fluidized bed reactor.

Figure 5 shows the influence of the pH of precipitation and the ash content of lignin on the amount of nitrogen fixed in the ammoxidized product. It is clear that as the pH of the precipitation decreased, the amount of nitrogen fixed was higher. There was a particularly sharp increase in the nitrogen fixation when lignin was precipitated at pH below 6.

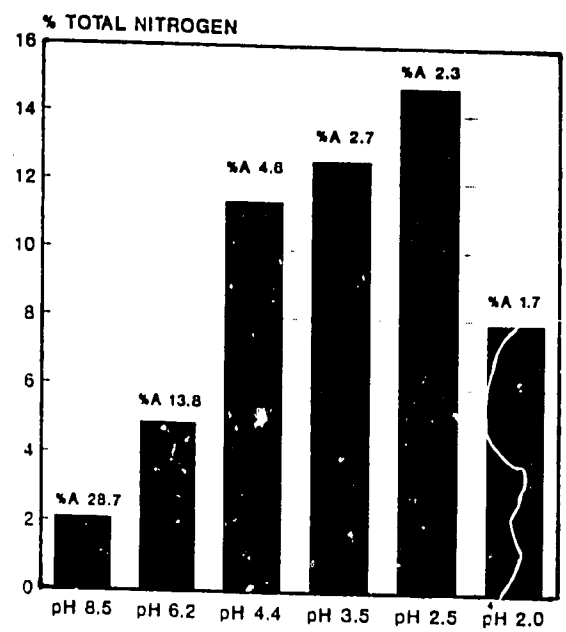


Figure 5. Influence of pH of precipitation and ash content on fixation of nitrogen on ammoxidized lignin (temperature: 200 °C; air/ammonia ratio: 2.5; time: 5h; % A: ash content).

It is known that at alkaline pH values some normally active groups in lignin are in the form of sodium carboxylates. It seems that in that form those groups do not react under the ammoxidation conditions. However, if these groups are free from the metal ions associated with them, they can readily react with ammonia. This was found to be correct as the nitrogen content of lignin samples precipitated at pH 2.5 showed.

The sudden decrease in nitrogen content of the lignin precipitated at pH lower than 2.5 seems to indicate that some other reactions, possibly condensation of lignin moieties, took place at extreme acidic conditions, which resulted in lower carbonyl and carboxyl centers for reaction with ammonia.

Besides the more favorable response of cation-free lignin to ammoniation, it was observed that this form of lignin minimized attrition under fluidization.

2.2.1.4.2 Study of the ammoxidation process variables

Three independent variables were selected for study: time of reaction (**t**), temperature (**T**) and the air/ammonia ratio (**C_{gases}**). The total flow of gases was kept constant throughout all the study. The dependent variable was the total nitrogen content (**%N**) of ammoxidized products.

The variables were studied using a second order rotational central composite experimental design (33).

The assignment of the variable ranges were done according to results obtained in preliminary runs. It was observed for example that kraft lignin burns at temperatures higher than 220 °C and that pine bark starts to char at temperatures higher than 300 °C. Tables 12 and 13 show the range and level of the variables.

Table 12. Range and level of independent variables for the ammoxidation of bark.

Coded variable	Real Variable	Levels				
		-2	-1	0	1	2
X_1	**t** (time, h)	1	2	3	4	5
X_2	T (temperature, °C)	200	225	250	275	300
X_3	C_{gases} (air/ammonia)	1.50	2.25	3.00	3.75	4.00

Table 13. Range and level of independent variables for the ammoxidation of kraft lignin.

Coded variable	Real Variable	Levels				
		-2	-1	0	1	2
X_1	**t** (time, h)	12.5	10	7.5	5	2.5
X_2	T (temperature, °C)	220	210	200	190	180
X_3	**C gases** (air/ammonia)	1.50	1.75	2.50	3.75	4.00

The coded values (X_1 to X_3) were related to the actual variables and their levels by the following expressions:

for bark $X_1 = \mathbf{t} - 3$ $X_2 = (\mathbf{T} - 250)/25$ $X_3 = (\mathbf{C_{gases}} - 3)/0.75$

for lignin $X_1 = (\mathbf{t} - 7.5)/2.5$ $X_2 = (\mathbf{T} - 200)/10$ $X_3 = (\mathbf{C_{gases}} - 2.5)/0.75$

where,(**t**),(**T**) and (**Cgases**) are the independent real variables and X_1, X_2 and X_3 are the coded independent variables.

The experimental design model is the complete quadratic surface between the measured property (response), and the independent variables or factors. The model can be presented in its codified form as following:

$$\%\mathbf{N} = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \qquad \text{Equation (1)}$$

where **% N** is the dependent variable.

The term b_0 is the mean of the six replicates at the center of the experimental design; b_1 through b_3 are the respective effects of each variable for one coded unit of increase; b_{11} through b_{33} indicate curvature for the respective variable; and the coefficients b_{12}, b_{13}, b_{23} indicate the interaction of two independent variables or how the level of one variable affects the response caused by a second variable.

Table 14 summarizes the coefficient values of the mathematical models which were determined by least squares for the measured response (% **N**) for both pine bark and kraft lignin.

Table 14. Coefficients of the second degree model for total nitrogen of oxidized pine bark and kraft lignin.

Coefficients	Values for Pine bark	Values for Kraft Lignin
b_0	8.777956	14.4568
b_1	1.230625	2.7500
b_2	2.285625	3.4375
b_3	-0.818748	-0.4250
b_{11}	-0.772732	-0.2966
b_{22}	-0.610234	0.1043
b_{33}	-0.172733	-0.2090
b_{12}	6.374 E -2	0.4000
b_{13}	0.362501	-0.6999
b_{23}	7.875 E -2	-0.6250
Coefficient of correlation	0.990	0.9958
Pure error	1.254	0.0683
Standard deviation	0.209	0.1138

The correlation coefficient (R) indicates the fraction of total variability for the total nitrogen content about its mean that is explained by the model. The "pure error" is the standard deviation of the experimental values between and within replicates. The standard deviation reported here is based on how well the calculated values of % **N**, using the equation (1) with the appropriate coefficients of the Table 14, agree with all experimental values. If equation (1) were to predict exactly the mean of the replicates for each test condition, then the standard deviation would equal the pure error, except for the degrees of freedom involved for each. In this case, the fact that the difference between the pure error and the standard deviation are small and that are of the same order of magnitude, at least for the ammoxidation of lignin, indicates that the models describe the results with about the same precision that could be duplicated by the experimental technique.

Figure 6 shows a comparison between the profile of nitrogen fixation on kraft lignin obtained experimentally and the response obtained using the mathematical model (equation 1). The agreement between experimental and calculated results shown in the graph is quite acceptable.

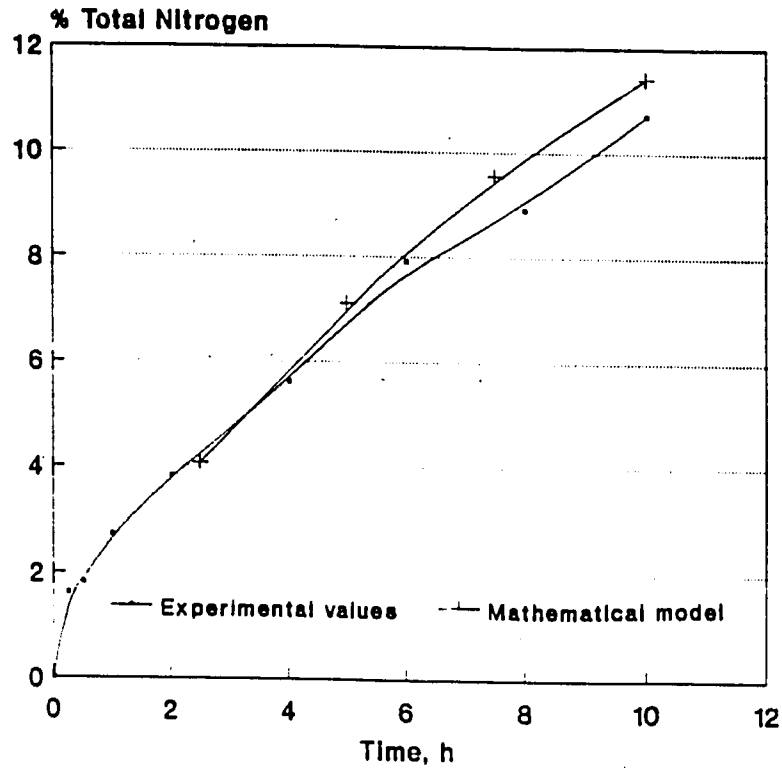


Figure 6. Comparison between experimental and calculated nitrogen fixation on ammoxidized lignin.

Tables 15 and 16 show the experimental results obtained by ammoxidation of kraft lignin and pine bark respectively, applying the composite experimental design.

Table 15. Results of the experimental design for the ammoxidation of kraft lignin.

Run	Time X_1	Temperature X_2	O_2 gases X_3	% N_{total}
1	-1	-1	-1	7.4
2	1	-1	-1	12.0
3	-1	1	-1	15.0
4	1	1	-1	21.9
5	-1	- 1	1	9.1
6	1	- 1	1	12.0
7	-1	1	1	14.3
8	1	1	1	18.7
9	-2	0	0	7.3
10	2	0	0	19.6
11	0	-2	0	8.5
12	0	2	0	21.6
13	0	0	-2	14.8
14	0	0	2	12.8
15	0	0	0	14.7
16	0	0	0	14.4
17	0	0	0	14.5
18	0	0	0	14.5
19	0	0	0	14.4
20	0	0	0	14.6

Table 16. Results of the experimental design for the ammoxidation of pine bark.

Run	Time X_1	Temperature X_2	C gases X_3	% N total
1	-1	-1	-1	[illegible]66
2	1	-1	-1	[illegible].50
3	-1	1	-1	9.50
4	1	1	-1	12.33
5	-1	- 1	1	3.78
6	1	- 1	1	7.30
7	-1	1	1	8.67
8	1	1	1	11.71
9	-2	0	0	5.47
10	2	0	0	9.70
11	0	-2	0	3.40
12	0	2	0	12.70
13	0	0	-2	8.87
14	0	0	2	7.58
15	0	0	0	9.77
16	0	0	0	8.53
17	0	0	0	8.57
18	0	0	0	8.53
19	0	0	0	8.60
20	0	0	0	8.50

Effect of temperature and time of reaction on the ammoxidation reaction.

Figure 7 shows the effect of temperature and time of reaction on the fixation of nitrogen in pine bark keeping the air/ammonia ratio in the fluidization gases constant at 3. High temperature and long time of reaction increased the total amount of nitrogen. Within the limits of the variables used in this study, it can be said that the gain in the fixation of nitrogen is greater by choosing to work at higher temperatures keeping the time of reaction constant at any value (8-9 %) than that working at longer times keeping the temperature constant constant at any value (4-5 %).

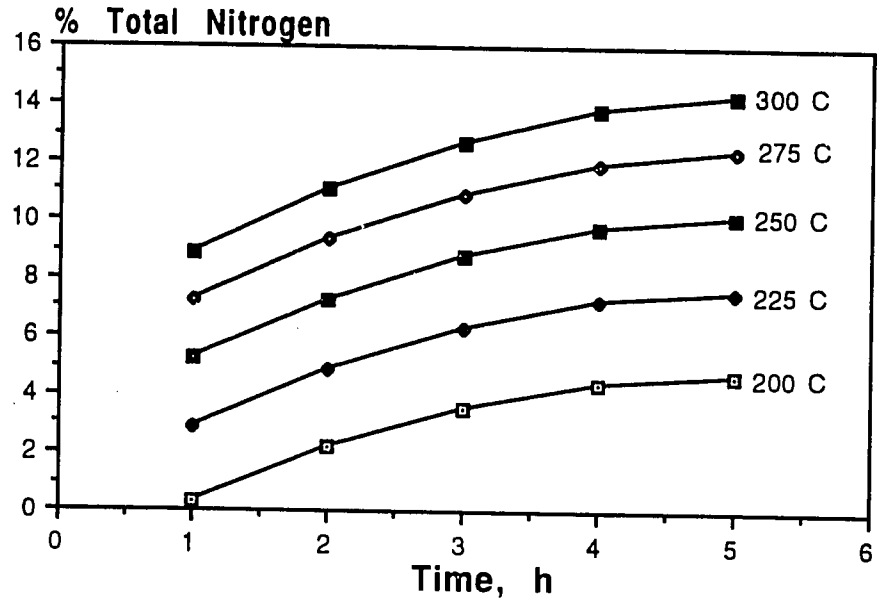


Figure 7. Effect of temperature and time of reaction on the ammoxidation of pine bark (air/ammonia ratio; 3).

For kraft lignin the influence of temperature and time of reaction was very similar, as it can be seen in Figure 8. By comparing the profiles of both the kraft lignin and pine bark at 200 °C, it is clear that lignin offers a better reactivity expressed as higher total nitrogen content at any comparable time of reaction. However, in the case of pine bark the temperature can be increased safely up to 300 °C without degrading the sample. Kraft lignin cannot be heated above 220 °C.

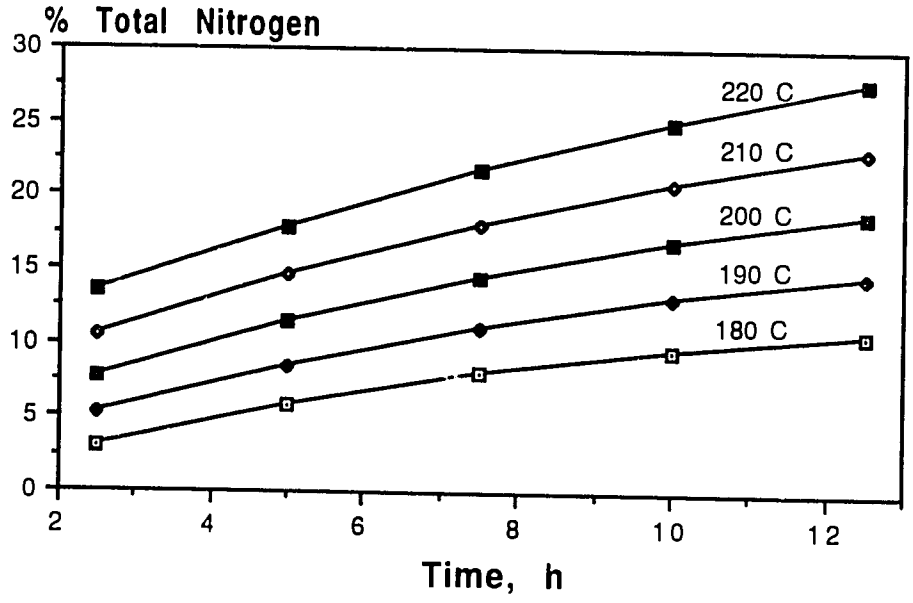


Figure 8. Effect of temperature and time of reaction on the ammoxidation of kraft lignin (air/ammonia ratio; 2.5).

An important conclusion that can be derived here is that total nitrogen contents close to 15 % can be obtained with lignin at 210 °C and about 5 h of reaction.

The ammoxidation reaction in pine bark proceeded much more slowly due probably to diffusional restrictions which inhibit penetration of the gases to the interior of the particles. From the results obtained at 300 °C after 1 hour of reaction, it can be seen that the total nitrogen fixated to bark was about 63 % of the total attainable after 5 h of treatment. This could mean possibly that the reaction of the functional groups present on the surface of the sample occurred more or less readily, but after this point the reaction was slowed by restricted diffusion of the gases to the functional groups inside the particle.

Effect of air/ammonia ratio on the ammoxidation reaction.

The effect of the air/ammonia ratio on the fixation of nitrogen in pine bark is presented in Figure 9. This graph indicates that at short times of reaction the fixation of nitrogen was greater when the gas phase was rich in ammonia. At longer times of reaction the composition of the gas phase was less important. This was indicated by the convergence of the different profiles around 10 % total nitrogen after 5 h of reaction..

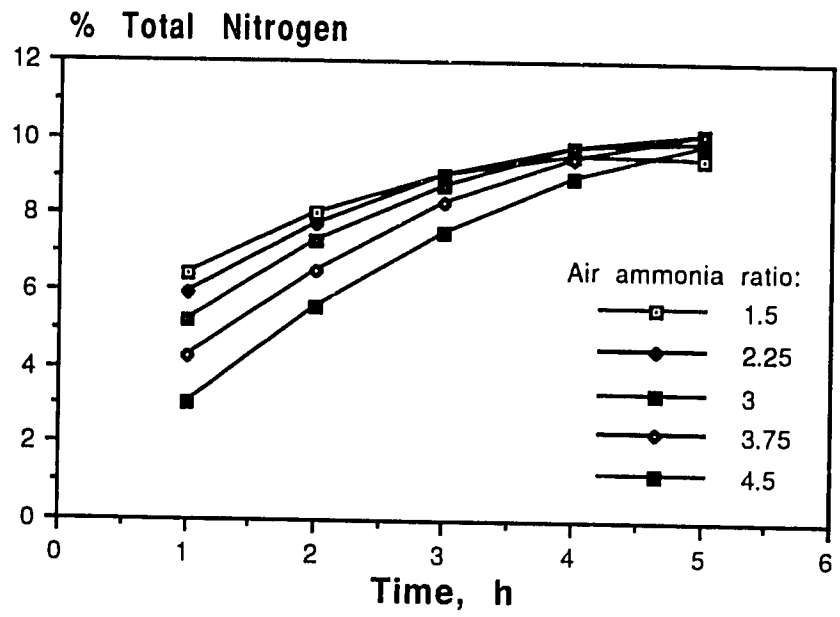


Figure 9. Effect of time on the fixation of nitrogen in pine bark at different air/ammonia ratios (temperature; 250 °C).

The effect of the composition of the gas phase on the fixation of nitrogen in lignin was practically the inverse of what was observed for pine sawdust, as it is illustrated in Figure 10. It seems that nitrogen was fixed onto lignin more readily in a phase rich in oxygen at short times. At longer times, *i.e.* after 5 h, a higher concentration of ammonia favored the incorporation of nitrogen into the lignin matrix. These results suggest that variation of the composition of the gas phase during the reaction might be necessary for optimum fixation of nitrogen on lignin, *i.e.* starting with a gas phase rich in oxygen and finishing with a gas phase rich in ammonia.

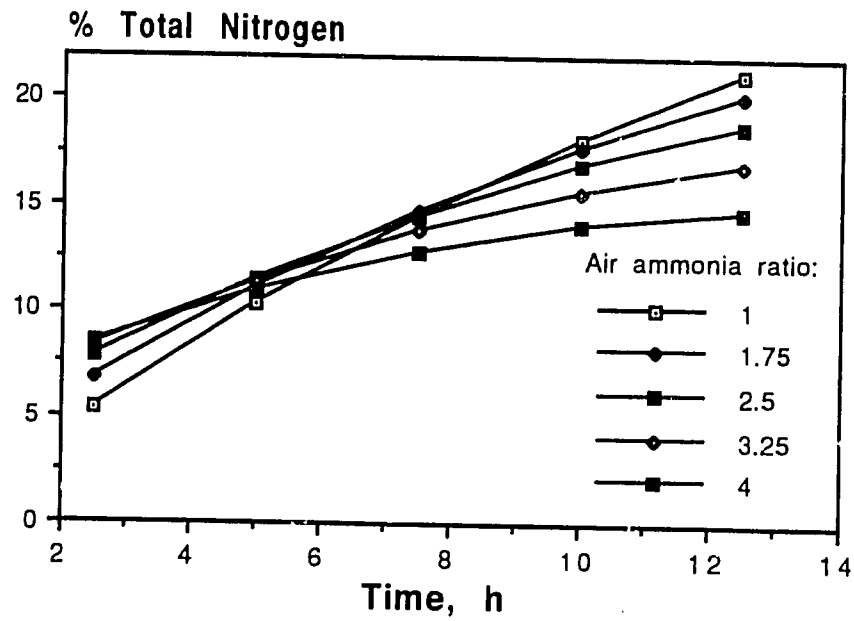


Figure 10. Effect of time on the fixation of nitrogen in kraft lignin at different air/ammonia ratios (temperature; 200 °C).

2.2.1.4.3 Transformation of lignin in the ammoxidation reaction

In order to gain some information regarding the basic transformations that take place in the lignin composition as the ammoxidation reaction proceeds, an experiment was carried out where a sample of lignin was subjected to the ammoxidation reaction and samples were taken out at different times and examined by infrared spectroscopy and chemical analysis (total hydroxyl, carbonyl and carboxyl groups content).

First of all, the elemental analysis of the samples is shown in Table 17. Table 18 shows the variation of hydroxyl, carbonyl and carboxyl group content in the kraft lignin at different times of reaction.

Table 17. Variation of the elemental composition of lignin subjected to ammoxidation.

Time (min)	C (%)	H (%)	N (%)	O (%)
0	61.72	5.90	0.63	31.71
15	63.33	5.59	1.95	29.13
30	63.15	5.38	3.47	28.00
60	62.62	5.43	3.93	28.02
120	61.72	5.07	5.27	27.94
360	57.66	4.50	10.99	26.85
600	55.92	4.22	14.02	25.84

Table 18. Variation of the functional groups of kraft lignin subjected to ammoxidation.

Time (min)	OH_{total} (%)	Carboxyl (%)	Carbonyl (%)	Nitrogen (%)
0	8.2	ND		--
15	8.2	2.2	0.9	2.4
30	7.4	ND	0.5	2.9
60	7.4	2.8	0.6	4.0
120	7.3	2.8	0.7	5.6
240	9.1	1.3	0.7	7.8
360	7.1	2.8	0.6	9.9
480	7.9	2.8	0.5	11.4
600	7.4	3.0	0.7	12.9

From the point of view of elemental analysis only, it is quite difficult to draw definitive conclusions about what happens in lignin as the ammoxidation reaction proceeds. There is indeed some evidence that a small fraction of hydroxyl groups and carbonyl groups is exhausted within the very first hour of reaction and that is in turn reflected in the increasing fixation of nitrogen. After this stage there is no sign of further transformations taking place and it is difficult to explain what groups are involved in the continuing fixation of nitrogen.

The use of infrared spectroscopy in the examination of the samples at the different stages of the ammoxidation of lignin produced two noticeable clues about the changes taking place in the structure of this polymer (Figure 11). Firstly, there is a sign of destruction of aromatic groups in the lignin as the reaction occurs, as evidenced by the decrease in the absorption bands of guaiacyl groups at 1510 and 1270 cm^{-1}. Second, the increase of the absorption band at 1715 cm^{-1} that can be assigned to the formation of carbonyl-amide type of bonds.

A further effort aimed at learning about the chemical nature of nitrogen present in the ammoxidized products was conducted using pyrolysis chromatography coupled to a mass spectrometer. At the moment of writing this report, nothing can be said with confidence about those structures. The analysis was complicated by the large number of low molecular fractions of lignin present in the cracked products and the difficulty in assigning the responses of those fragments to those of known compounds contained in the master library of the equipment used.

2.2.1.4.4 Catalysis of the ammoxidation reaction

It has been shown so far that reasonable amounts of nitrogen (about 15-18%) can be fixed to the different raw materials that have been investigated in this project, by means of ammoxidation performed in a fluidized bed. This is remarkable taking into account that this is a heterogeneous phase reaction and that obvious factors limit its efficiency. We have demonstrated experimentally that substantial amounts of nitrogen can be introduced chemically to any of these raw materials at expense of long times of reaction. It was then advisable to look for ways to speed the reaction in order to save some time and increase productivity. With this purpose in mind a series of experiments were implemented to examine the effect of catalysis on the ammoxidation reaction.

The catalysts selected for the experimentation were taken from among a group of materials that could be reasonably available in a developing country. Accordingly, iron salts were selected mainly in the basis of their low cost and their lack of phytotoxicity. The salts employed were iron (III) sulphate, iron ammonium sulphate and a mix of iron (III) sulphate and ammonium molybdate, added at a 0.2% weight level based on the substrate to be ammoxidized.

The experimental profiles of nitrogen fixation for kraft lignin is shown in Figure 12 (temperature: 210 °C; air/ammonia ratio; 1.75). Both the iron ammonium sulphate and iron (III) sulphate yielded products with similar nitrogen content along the entire range studied. The best catalyzing effect was obtained with the mix of iron (III) sulphate and ammonium molybdate.

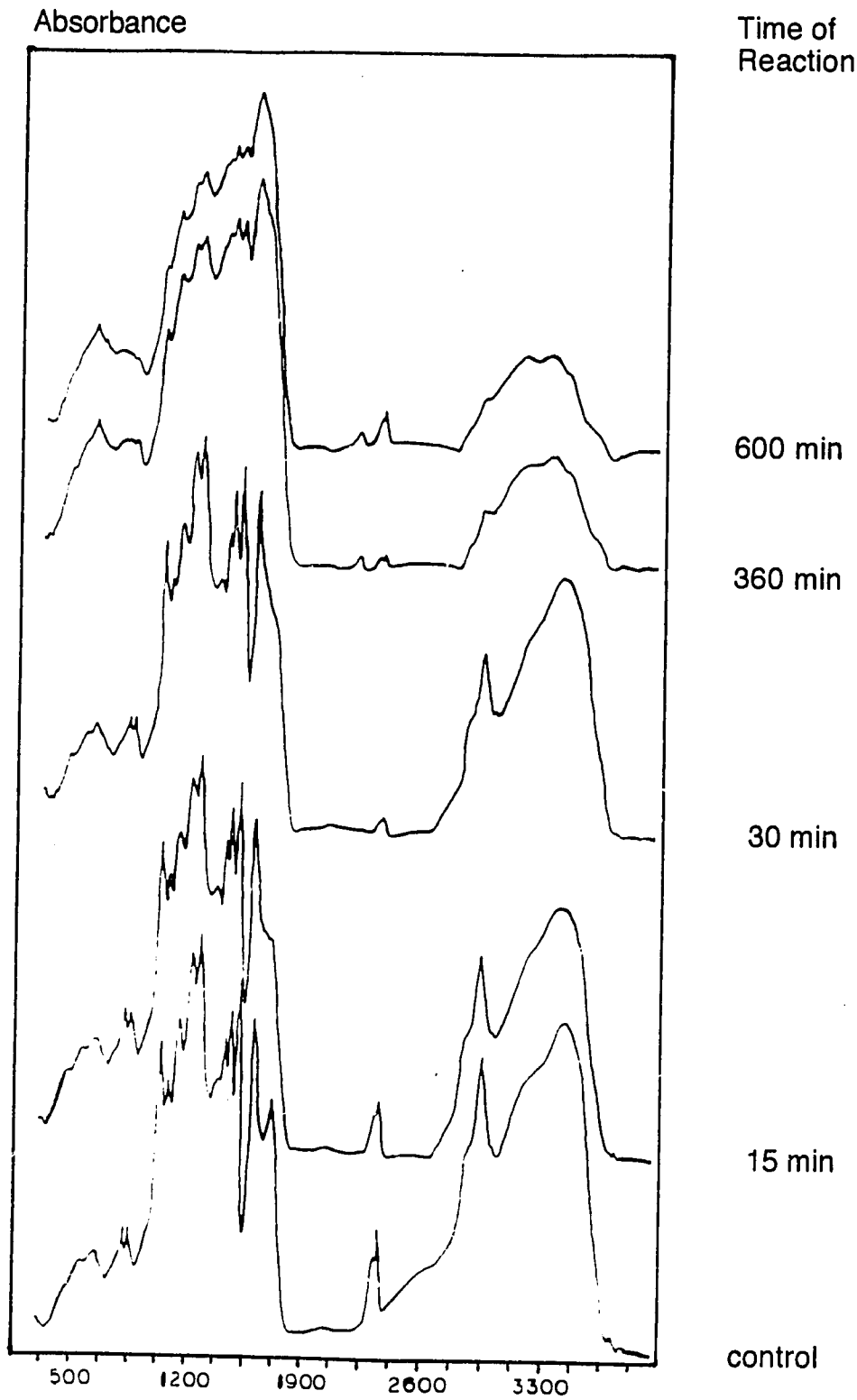


Figure 11. Infrared spectra of ammoxidized kraft lignin (temperature: 250°C; air/ammonia ratio: 1.75).

It is important to notice that the greatest difference in nitrogen fixation between the catalyzed reactions and the control one occurred within the first 2 h of the reaction. After 6 h, the increment in nitrogen content of the products reached almost 50 % over that of the control sample.

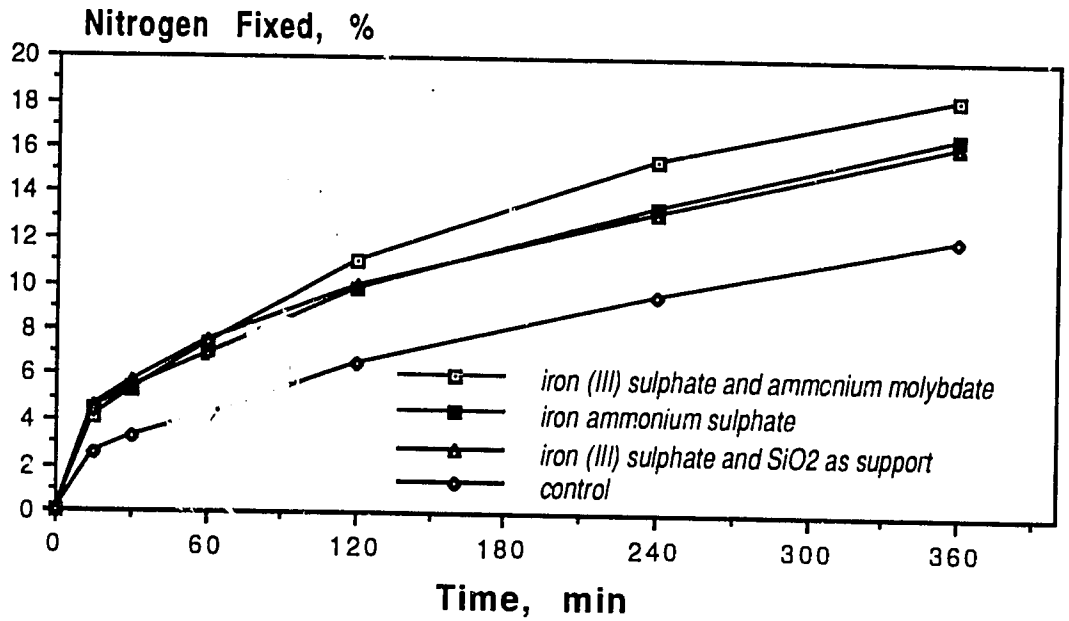


Figure 12. Effect of catalysts on the ammoxidation reaction of kraft lignin (temperature: 210 °C; air/ammonia ratio; 1.75).

2.2.1.5 Conclusions

It is possible to obtain ammoxidized products with nitrogen contents over 10 % for pine bark and over 20 % for kraft lignin.

Temperature and time of reaction are the most important variables in the process of ammoxidation of these raw materials. The operation at high temperature is a must in order to limit the time of the reaction under economically reasonable grounds. However, the highest temperature of operation in practice is fixed by the temperature of carbonization of each raw material.

It is possible to fix up to 18 % of nitrogen in kraft lignin after only 6 h of reaction by the use of catalysts. Conversely, the use of catalysts can reduce substantially the time needed to get a desired nitrogen level in the ammoxidized products. One low-cost alternative found to produce interesting results is a mix of iron (III) sulphate and ammonium molybdate.

We believe that the high levels of total nitrogen fixed to lignin obtained in this project, justify the launching of new studies aimed at optimizing the process. More importantly, the results justify the building of a pilot plant that would allow the production of larger quantities of ammoxidized products that are necessary for their field testing as fertilizers.

2.3 University of Washington

This section deals with the work carried out by Prof. G. G. Allan and his team at the University of Washington. The work of this team focused on the evaluation of the ammoxidized products and other complex materials as fertilizers.

2.3.1 The concept of slow-release fertilizers from lignaceous biomass

The whole merit of the research proposed in this project rests on the ability of the ammoxidized materials to release nitrogen in forms assimilable by the plants for longer periods of activity and under adverse weather conditions. The release of nitrogen from the ammoxidized products may occur through the combined action of two mechanisms: the breaking down of the polymeric matrix of lignin by the action of the microorganisms present in soil and by chemical degradation of the material, *ie.* hydrolysis. In fact, lignin and other lignocellulosic materials are known for their susceptibility to be degraded to humic materials by the action of microorganisms when in contact to soil (34,35). This assures that the polymer we chose as carrier for nitrogen (lignin and carbohydrates) would be certainly broken down to small units in a rather slow process. Of relevance for our project is the hypothesis that the incorporation of nitrogen into the lignin structure would take place mainly with the creation of ammonium salts, amides and heterocyclic structures. In the best of the cases, these forms would hydrolyze in soil at different rates releasing nitrogen for long periods of time (36,19). Putting all the pieces together, we have then a system with high potential to act as a slow-release nitrogen source. The next step is to prove it under real circumstances.

We have noticed that previous efforts reported in the literature on the performance of long-lasting fertilizers (18,19), have not given enough attention to the role of microorganisms in the effectiveness of fertilizers and the effects induced by the different materials employed as fertilizers on the microflora of the soils (37,38). We believe that the breakdown of complex nitrogen-containing substances such as the structures that may be created by the ammoxidation treatment of lignin, will occur more rapidly once the population of microorganism able to deal with such complex structures has increased with the time (39).

At the University of Washington, efforts were concentrated at finding out ways to assess the performance of such complex materials as fertilizers.

2.3.2 Greenhouse tests of complex nitrogen-containing substances as slow-release fertilizers.

2.3.2.1 Experimental

2.3.2.1.1 The effect of melamine on rice

Four fertilizer formulations were studied: 100% urea, 95% urea-5% melamine, 90% urea-10% melamine and 80% urea-20% melamine. Each of the four fertilizer formulations was evenly mixed into the top one inch layer of soil (3.5 Kg dry soil/pot, passing 1/4 inch sieve opening, Garden Grove CA) at an amount equivalent to 300 lb of nitrogen per acre, eight replicates per formulation. The perforated pots (eight inch diameter) were flooded with distilled water, the level kept constant throughout the experiment (1 to 1 1/2 inch above the surface of the soil), and air bubbled through the supernatant water. Rice seeds (M-201) were germinated for 48 h before the 1/8 inch long sprouted seeds were transplanted into the pots (25 sprouts per pot). The total duration of the experiment was 110 days, after which the plants were harvested. The organic matter of the plant from the base to tip of the flag leaf and the rice grains produced were harvested separately. The harvested material from seven representative plants in each pot was then immediately placed into tared bags, oven-dried at 60 °C, and weighed. The nitrogen content of the dry matter was determined by Kjerdhal analysis. After this first crop, the roots of the harvested plants were removed trying not to disturb the structure of the soil and new sprouted rice seeds were planted. The second crop was kept for 212 days, after which seven representative plants were harvested. This time, only the rice grains produced were harvested, placed into tared bags, oven-dried at 60 °C and weighed.

2.3.2.1.2 The effect of melamine and melamine phosphate on grass

Turf grass seed (400 mg/pot Scotts Shady Area) was evenly distributed on the surface of nine perforated plastic planting pots (6.5 x 6.5 x 6.5 cm) containing sterilized soil (Coles starter mix). Commercial melamine (100 mg powder/pot) was spread on the surface of three of the pots. Another three pots were treated with melamine phosphate (100 mg powder/pot) and the remaining three pots were left untreated. The pots were placed in a controlled environment (approximately 21 °C, 50% RH) with a continuous overhead fluorescent light source. The pots were regularly watered from above and periodically the grass was cut, dried and weighed. The experiment ran for a duration of 1100 days.

2.3.2.2 Results and discussion

The initial attention was focused on the possibility of using the growth of rice in greenhouse as a bioassay for new fertilizers. This test was developed in collaboration with Dr. Steve Roberts, a professor of Agronomy at Washington State University, who was a visiting scholar for six months in Professor Allan's laboratories at the University of Washington. The basis for the new test was the idea that breakdown of complex nitrogeneous substances would occur more rapidly under the warm, water-saturated conditions of rice cultivation rather than, for example, in the milder and drier conditions appropriate for most crops.

To attempt to establish the validity of this concept, melamine (2,4,6-triamino-1,3,5-triazine) was used as an exemplar of a complex nitrogeneous heterocycle, keeping in mind that the ammoxidation of biomass may create analogous nitrogeneous heterocyclic structures. Freepons and coworkers (40) had previously shown that melamine can function as a fertilizer for rice in California under large scale field conditions . The idea was then to test the effect of melamine as surrogate long term fertilizer in the growing of rice and apply the knowledge obtained here to the subsequent evaluation of the nitrogen lignin fertilizer.

For the purpose of this experiment, four fertilizer formulations were studied: 100% urea, 95% urea-5% melamine, 90% urea-10% melamine and 80% urea-20% melamine. Sprouted rice seeds were incorporated into the mix soil-fertilizer under flooded conditions. After 110 days, the plants were harvested and the yield of rice, plant matter and the nitrogen content of plant matter were recorded. Although the quantities of fertilizer added to the soil were in each case calculated taking into account all nitrogen forms and adjusted to render 300 lb of nitrogen per acre of soil, it is convenient to analyze the results obtained for the actual availability of nitrogen to the plants, by separating the nitrogen present in urea (defined here as "effective nitrogen") from that present in melamine. Accordingly, experimental results have therefore been graphed as functions of only the "effective nitrogen". In this way any effect related to the nitrogen released from melamine may be more easily identified.

Yields of rice grains obtained in the first harvest are shown in Figure 13, where the limits within the eight replicates of any one set of fertilizer formulation varied are defined by the vertical lines through the data points.

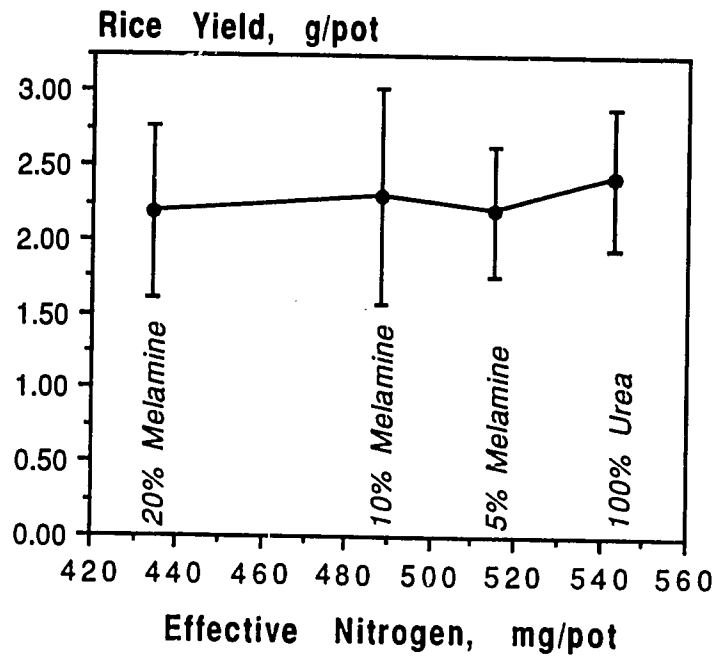


Figure 13. Effect of effective nitrogen in fertilizer on rice yield.

This first crop of the rice plants does not allow to observe any major differences due to the presence of enough "easily available" nitrogen from urea in all the formulations. The 5% melamine-urea formulation seems to have a slight edge in yield, even over the 100% urea addition, but this difference is arguably not statistically significant.

One can argue that plant cornposition should be taken into account in order to draw more complete conclusions about how well the plant use the nitrogen available. Of certain interest is then the yields of dried plant matter harvested and the nitrogen recovered in this form by the plant showed in Figures 14 and 15. The total nitrogen uptake values used in Figure 15 resulted from multiplying the dry matter yield by its nitrogen content as determined by Kjehldal analysis and can be used as some estimation of part of the nitrogen recovered by the plant.

As it can be seen in Figure 14, the dry matter yield follows a similar pattern as the rice grain yields, with a slight preponderance of the 5% melamine-urea over even the 100% urea addition, but again this is not statistically significant. But when the total nitrogen uptake by the plant matter is analyzed, it is interesting to observe that the 20% melamine-urea formulation seems to have some extra beneficial effect with a somewhat wide range of response from the replications.

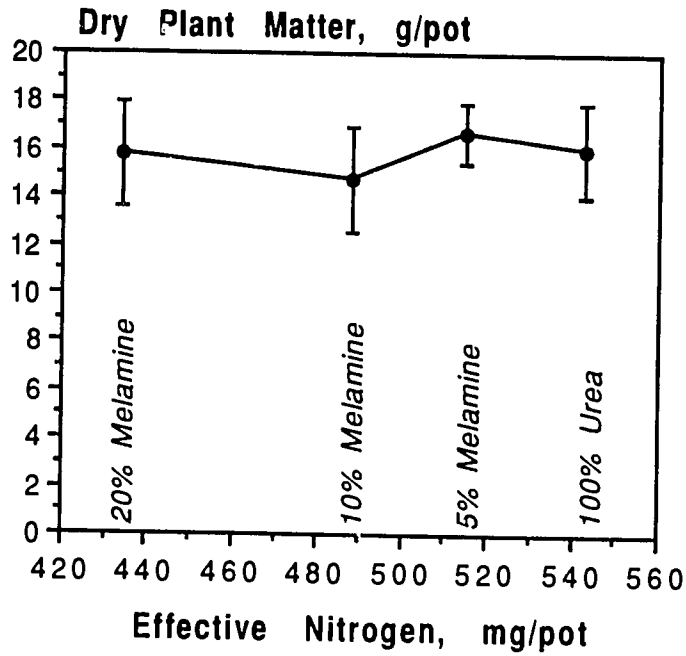


Figure 14. Effect of effective nitrogen in fertilizer on rice dry matter

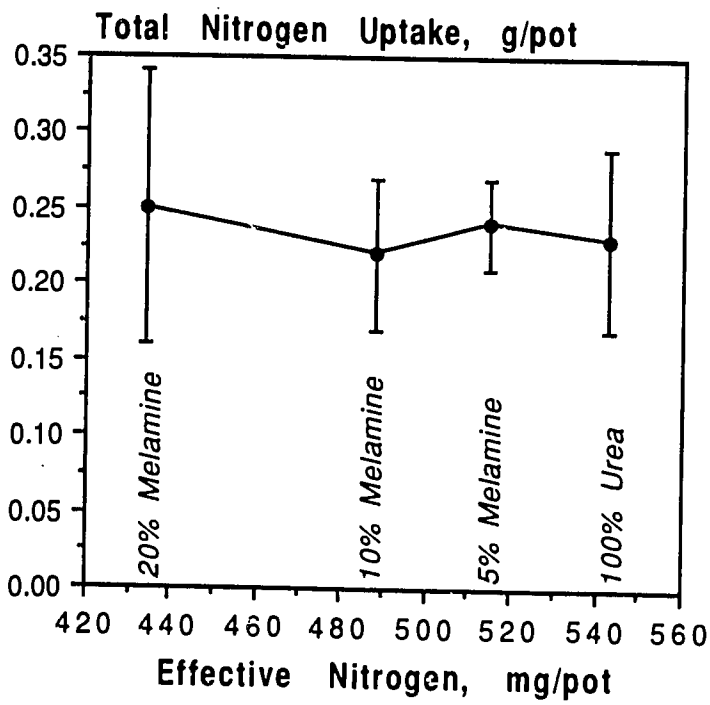


Figure 15. Effect of effective nitrogen in fertilizer on total nitrogen uptake by dry matter in rice plants.

After the initial dubious and a little discouraging results observed in the first crop, a second planting of rice seeds was carried out and the analysis of results presented some definitive doubts about the effectiveness of the bioassay system selected, in showing the effects of melamine as a slow release fertilizer.

The yield of rice in this second crop is presented in Figure 16 as a function of the effective nitrogen added in the fertilizer formulations. As it is clear from this plot, all the formulations containing melamine produced nearly the same yield of grain, which is below the level reached by the 100% urea addition. It is also noticeable that the overall yield of rice from the second crop is far smaller that the one obtained from the first crop.

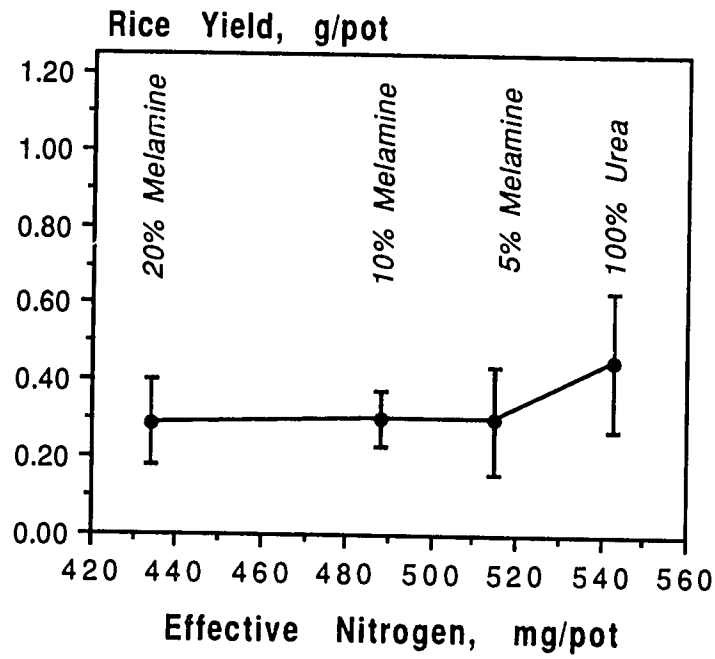


Figure 16. Effect of effective nitrogen in fertilizer on rice yield for the second cycle of planting.

The results from this crop could not substantiate any conclusive evidence of the expected overall increase in yield for the melamine treated products or about the expected ability of the surrogate melamine to provide nitrogen at a sustained rate.

Some other difficulties observed in this experiment convinced us not to pursue 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 seed 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 from the crop

had suffered some kind of damage and looked diminutive, flat and greenish, signs of unhealthy products. The care of the rice plants was even made 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 the addition of 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 it 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 for an extended period of two and a half years. The grass was cut periodically and weighed to determine the yield of vegetation. The plot of the grass yield as a function of the time of the experiment for the two melamine systems and an untreated control is shown in Figure 17.

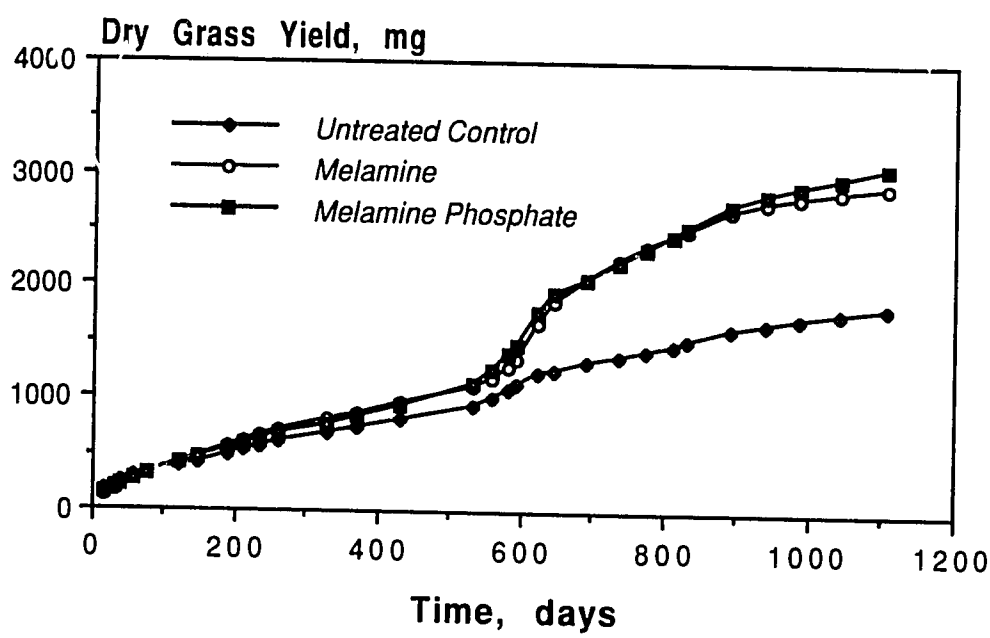


Figure 17. Effect of melamine and melamine phosphate on cumulative yield of grass.

As it is shown in the first part of the curve of Figure 17, the rate of growth of grass is almost the same for any of the fertilizer systems studied, including the untreated control. It was only after approximately the first 700 days when a definite improvement in the amount of cumulative dry matter weight with respect to the control sample yield could be seen. This trend became more pronounced with increasing time and close to the time in which the experiment was finished a difference in favor of melamine phosphate was also evident.

2.3.2.3 Conclusions

At the University of Washington, the main effort focused on the search for an appropriate bioassay for testing nitrogenous lignin-type 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.

Melamine was used as a prototype fertilizer which contains nitrogen in complex structures similar to the ones that can be found in ammoxidized lignin. The application of melamine to the growing of rice was studied in greenhouse experiments. After two consecutive crops, it was not possible to draw any conclusive effect of the availability of nitrogen from the melamine on the yield of rice nor on the organic matter of the plants. Only a slight increment of the total amount of nitrogen recovered by the plants treated with 20% melamine-urea over the rest of the fertilizer formulation, including the 100% urea addition was detected. Problems associated with re-seeding and keeping of the experimental pots through consecutive crops pointed out inconveniences of rice as an appropriate bioassay for the testing of sustained-release nitrogen fertilizers.

The selection of grass instead of rice as a growing crop proved to be a better choice. By application of melamine and melamine phosphate to soil where grass was planted, we could keep a greenhouse experiment for several years, cutting the grass periodically and weighing the dry matter to determine the yield. This experiment showed that the soil treated with melamine was indeed able to sustain a larger rate of grass yield over that of the untreated soil. The effect was more dramatic after the second year of the experiment and we were able to observe even a better effect of the use of melamine phosphate over plain melamine.

This experiment provides some corroboration of the concept, which we have been trying to demonstrate, that in every soil, nitrogen from complex sources can be available to plants, provided there is enough time for the microorganisms responsible for their breakdown to grow to a significant level.

Even though at the moment of the end of the term for this project we were not able to apply this knowledge to the study of ammoxidized lignin products, we remain confident that we have come out with a sound bioassay method that will prove to be effective for the testing of such materials as fertilizers.

3. Impact, relevance and technology transfer

3.1 Use of project findings in the developing country

The findings of the project will be useful in the developing country in two ways mainly. First, the conditions for the conversion of indigenous biomass into a high-nitrogen-enriched product of potential use as fertilizer have been established for the first time. The use of lignin, bark or sawdust as raw materials, will help to integrate with the growing use of paper in these places by adding a benefit to materials normally considered byproducts of the pulping industry.

Specifically, in Spain the results have been partially useful to the Empresa National de Fertilizantes (ENFERSA) which has been in contact with Prof. Coca and the University of Oviedo throughout the project. This company has shown immediate interest in the oxidation of biomass wastes in liquid phase using nitric acid. The company considers the ammoxidation process using a fluidized bed reactor to be a technology of interest but more difficult to use in the short run.

For Mexico, the use of a fertilizer technology such as the ammoxidation of lignocellulosic materials represents a great potential benefit for the actual agricultural system which needs of more efficient ways of fertilization both economically productive and environmentally protective. Most of the land devoted to agriculture receives brief periods of strong and abundant rainfall throughout sometimes long rain seasons, which limits the use of water-soluble inorganic fertilizers such as urea and ammonium sulfate. Moreover, when these fertilizers are used, it is necessary to make successive applications to get acceptable yields. Even in this case, a considerable portion of the applied soluble fertilizers is leached out from the soil and concentrates in underground streams creating a potential pollution problem. To this problem, it adds the erosion of the soil due mainly to excessive use of the land and the lack of new incorporated organic matter. For this reason, the implementation of an organic-based fertilizer technology will contribute effectively to a better agricultural system.

3.2 Impact of project

The participation in an international project such like this added a new perspective in the way of thinking and performing of the individuals involved and in the exchange of scientific efforts between participating institutions.

From the point of view of individuals, the project produced an interesting frame of work where the investigators benefitted from the free exchange of information and methods of work whose application extends far beyond the grounds of this project. Also, the setting up of a receptive and open atmosphere for comunication provided the participants with numerous opportunities to receive

useful criticism to their own ideas and criticize the ones of the peers. As it was expressed by one of the co-principal investigators of the project, Prof. Zúñiga from the University of Guadalajara, the process of working with scientists of other countries helped him to experience a qualitative change in his development as researcher, mainly by building confidence in his ability to generate and communicate his own ideas.

Also of main importance was the formation of human resources associated to the completion of the different stages of the project. In all three participating universities there were graduate students that received their Master of Science (3) and Ph. D. degrees (3) as a result of their work in the project. This highly qualified labor force is already contributing with their knowledge to achieve goals in both the industry and academic worlds.

The present project has also helped to establish in the University of Oviedo and the University of Guadalajara and to reinforce in the case of the University of Washington, the lines of research on fertilizers. The experiences obtained in the research on this field and the laboratories and equipment developed for the project form a first-hand teaching material that will be used in the chemical engineering studies program of the mentioned institutions.

3.3 Utilization of technology

The state of knowledge about the manufacture of sustained-release nitrogen fertilizers from biomass is now enormous as a result of the work done in this project. However, this information is far from being complete enough to be used directly by a customer. For this reason the results from this stage are mainly important and useful for the University of Washington, the University of Guadalajara and the University of Oviedo, which can start from this platform to gather new and extensive information on the use of ammoxidized products with actual crops in real fields. It is after this stage that the results from this idea will start to get the attention of possible clients willing to try this new technology.

3.4 Potential of large scale trials

As it is discussed in section 3.1 of this report, the outcome of the project has set up the basis for a sound technical process that will help to increase productivity in crop fields by the transformation of cheap biomass into a product with potential to be used as a long-term fertilizer. The potential of ammoxidized products as fertilizers has yet to be assessed under both greenhouse and field tests. Therefore, the results obtained in this work are very encouraging and justify the launching of studies to gather data on the behavior of ammoxidized products in the growing of crops.

3.5 Benefits associated with the project

The heart of the new equipment left by the project was the fluidized bed reactor (pilot -plant) built in the Department of Chemical Engineering of the University of Oviedo and a smaller reactor (bench scale) built in the Instituto de Madera, Cellulosa y Papel of the University of Guadalajara. Both facilities will be used to continue the studies on slow-release fertilizers and other areas of study. Additionally to the equipment both institutions have now trained technicians in the operation of these fluidized-bed reactors that will be of invaluable help for future investigations.

In general, the whole group of investigators and technicians that participated in the project have acquired a sound theoretical and practical knowledge of the operation of bed-fluidized reactors that can be used for teaching and training of more graduate and undergraduate students of Chemical Engineering.

3.6 Improvement of collaborators scientific capabilities

A truly benefit derived from the project is the establishing of scientific relationships among the College of Forest Resources of the University of Washington, the Department of Chemical Engineering of the University of Oviedo and the Instituto de Madera,Cellulosa y Papel of the University of Guadalajara. The foundation for the collaboration of the mentioned institutions in new research projects in the area of fertilizers and other areas of interest has been laid out. This foundation is based on the realization of research fields of interest and a knowledge of the facilities and expertise that every institution can contribute with for achieving common goals.

For the University of Oviedo and the University of Guadalajara part of this project allowed them to participate actively in the Second Science and Technology Latin American Congress commemorating the 500th Anniversary of the Discovery of America by Columbus (CYTED-V), which embodied representatives from all Latin American countries as well as Portugal and Spain.

4. Project activities and outputs

4.1 Meetings

There were four meetings held by the co-principal investigators throughout the project:

The first meeting took place in Oviedo, Spain between Professor Coca and Professor Zúñiga of the University of Guadalajara during the summer of 1989. Prof. Zúñiga spent two months at the Chemical Engineering Department of the University of Oviedo, time in which he helped to upgrade the lab-scale fluidized bed reactor to a pilot plant reactor capable of handling 450 g of raw material. He also brought with him samples of the Mexican lignin kraft (Lignaten) and started a preliminary study to define the main conditions needed to treat this material in the fluidized reactor.

The second meeting was held in Mexico in September 1990 with the visit of Prof. Coca to the University of Guadalajara. During this meeting, important details concerning the treatment of lignin with acid to get rid of metal cations and the building of a small fluidized bed reactor at the University of Guadalajara to carry out experiments using catalysts were discussed. This meeting took place during the program of the Second Science and Technology Latin American Congress commemorating the 500th Anniversary of the Discovery of America by Columbus (CYTED-V). Professor Coca and Professor Zúñiga are members of this committee and research on the use of lignin is one of the subjects of interest for the participants of the congress, which embodies representatives from all Latin American countries as well as Portugal and Spain.

The third meeting took place in Seattle in June of 1991. Professor Zúñiga spent one month at the University of Washington helping to prepare the third annual report and did some literature work on the testing of sustained controlled-release fertilizers.

The last meeting took place in Seattle in June and August of 1992 with the visits of Prof. Zúñiga and Prof. Coca respectively to the University of Washington. The subject in both cases was the discussion of the final results and elaboration of the final progress reports on the activities carried out by each of the universities to conclude the project.

Due to a travel funding freeze by AID, no travel by the University of Washington personnel to either Oviedo or Guadalajara was undertaken.

4.2 Publications

The following publications and presentations in congress have been produced as a result of this project.

PUBLICATIONS

Riera, F. A., R. Alvarez and J. Coca
"Humic Fertilizers by Oxidative Ammoniation of Hydrolyzed Corncob Residues", Ind. Eng. Chem. Res., 30, (4), 636 (1991).

Riera, F. A., R. Alvarez and J. Coca
"Oxidation of Hydrolyzed Olive Pits and Almond Shells with Nitric Acid in the Production of Humic-Based Fertilizer",
Ind. Eng. Chem. Res., 30, (1), 267 (1991).

Riera, F. A., R. Alvarez and J. Coca
"Humic Fertilizer Effects on the Rate of Nitrification in Soil Tests",
Bioresource Technology 39: 49-54, 1992.

Riera, F. A., R. Alvarez and J. Coca
"Reuse of Nitric Acid in the Oxidative Pretreatment Step for the Production of Biomass-Based Fertilizer", Bioresource Technology 36: 185-187, 1991.

Riera, F. A., R. Alvarez and J. Coca
"Humic Fertilizers by Oxiammoniation of Hydrolyzed Olive Pits Residues", Fertilizer Research 28:341-348, 1991.

CONGRESS PRESENTATIONS

Zúñiga, V., A. Martínez, E. Delgado, G. G. Allan, V. González and A. Camacho, "Ammoxidation of Lignocellulosic Materials in a Fluidized Bed Reactor" Proceedings of the Second European Workshop on Lignocellulosics and Pulp (EWLP) "Oxidation of Lignocellulosic Materials", p. 235-236, September 2-4, 1992, Grenoble, France.

Zúñiga, V., A. Martínez, E. Delgado, G. G. Allan, J. Coca and A. Camacho, "Ammoxidation of Lignaceous Materials in a Fluidized Bed Reactor", Second Brazilian Symposium on the Chemistry of Lignins and Other Wood Components", 2-4 September 1991, Sao Paulo, Brazil.

Martínez, A., V. Zúñiga, E. Delgado, A. Camacho, V. González and G. G. Allan, "Producción de Fertilizantes Nitrogenados mediante Oxi-amoniación de Corteza de Pino en Lecho Fluidizado", XII Encuentro Nacional de la Asociación Mexicana de Investigación y Docencia en Ingeniería Química (AMIDIQ), 24-26 de Abril de 1991, Xalapa, Veracruz, México.

5. Goals still to be accomplished

There were some goals that the project did not accomplish. The main aspect that was not covered in this work was the testing of the ammoxidized products as fertilizers. There was not possible to count with enough amounts of ammoxidized lignins with a high content of nitrogen that could be used in greenhouse tests and larger field trials at earlier stages of the project and thus nothing could be investigated on the fate of these products in contact with soil.

Contrary to what was planned, the running of preliminary experiments to establish the best conditions for treatment of lignin and other lignocellulosic materials in the fluidized bed reactor did not work smoothly. First of all the relocation of the pilot plant fluidized bed reactor that was available in the Chemical Engineering Department at the University of Oviedo to new facilities posed more challenges than expected. Second, lignin, bark and sawdust are materials that burn easily under fluidized conditions and the search for the best working conditions took a long time. One modification to the normal operation of the system that proved to be worthwhile was the attachment of a gas chromatograph to the spent gases coming out from the reaction, but also it took a few months of work to figure out the best way of operation. In addition to this, the presence of metal cations in kraft lignin prevented the attachment of reasonable levels of nitrogen fixation in the ammoxidation reaction in early stages.

The fact that high levels of nitrogen in the ammoxidized products were secured only towards the expiration of the initial period of the project illustrate the difficulties experienced.

The uncertainty about the optimal conditions to get high levels of nitrogen in the ammoxidized products and administrative difficulties in the delivery of the payments from the University of Washington to the University of Guadalajara also delayed considerably the starting of the construction of a bigger pilot plant reactor at this latter university. Because of this, it was more sound to get the amounts needed from continuous runs of the small reactor built at the University of Guadalajara to provide samples for the diverse analyses and tests of the products, rather than to attempt the construction of a bigger reactor.

For the same reason, the analyses of key ammoxidized samples that should have been made at the University of Washington could not be done as planned. Some attempts were made at the University of Guadalajara, which are mentioned in section 2.2.1.4.3 of this report, but at this time very little can be said conclusively about the chemical nature of nitrogen associated with the ammoxidized products.

6. Future work

It is the feeling of the co-principal investigators of this project that the foundation of a new technology has been laid out and that this can be of great help not only for less developed countries, but also interesting for the developed world . Certainly, more work is necessary to evaluate the performance of the ammoxidized products as fertilizers that can release nitrogen for long time under adverse conditions. Also, it is needed to know more about the chemical nature of the products in order to understand their mode of operation and to be able to optimize the conditions of their manufacture. We are especially motivated to carry out these studies as we believe that our rationale and techniques, if proven correct, will also revolutionize the concept of testing long-term products in contact with soil.

The details of a what is necessary to do in the future on this subject will be put together in a proposal to be submitted soon to the Agency for international Development.

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