Biochemistry of Soil Organic Matter
in Relation to Crop Production

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Content

Lecture 9.

Slow Releasing Nitrogen Fertilizer from Ligninsulfonates of Cellulose Industry

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1. Importance of "slow releasing nitrogen" fertilizer for plant production.

The fertilization with inorganic nutrients is an absolute preposition of a high and economical plant production. The macronutrients must be available to the crops in sufficient amounts during the whole vegetation.

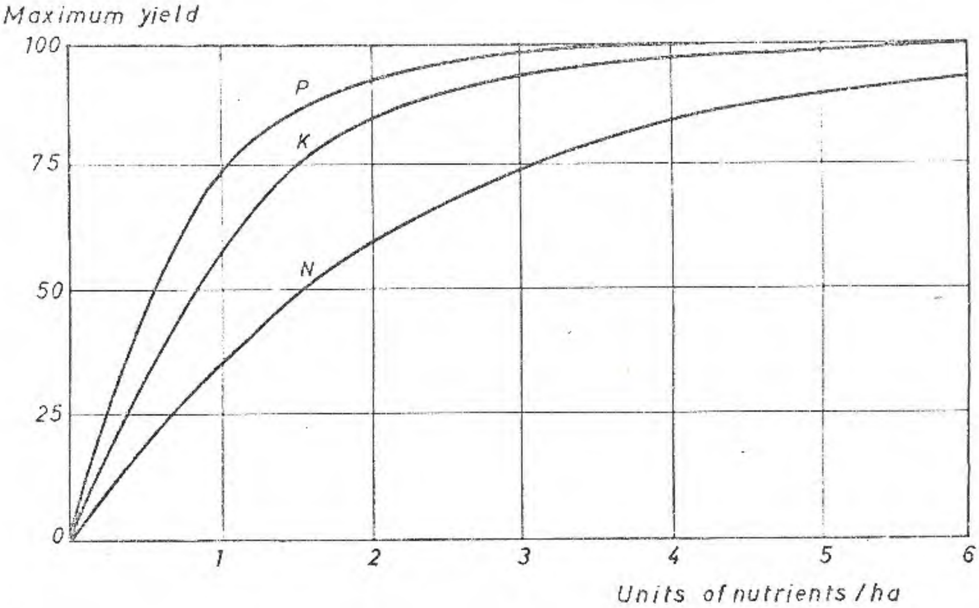


Fig. 1: Increase of yield by plant nutrients (according to Mitscherlich 1948).

From N, P, and K nitrogen has the smallest efficiency factor. To reach high yields - as high as possible - it is necessary to give corresponding high doses of nitrogen fertilizer. A single dosage of nitrogen for the total vegetation period is not possible, because high doses of salts such as ammonium or nitrate salts effect plasmolysis at the young plants. Nitrate ions or ammonium ions transformed in nitrate ions by nitrification can be leached by rainfall.

By these reasons nitrogen fertilizers must be given in two or three doses, which causes additional costs.

Therefore many attempts have been made for the synthesis of the so called "slow releasing" nitrogen fertilizers, which deliver organic bound nitrogen during the vegetation period by the action of microorganisms in form of ions, which can serve for plant nutrition. Several products have been proposed. Many of them would be qualified as "slow releasing" nitrogen fertilizers, but they are mostly too expensive for agriculture and only useful for special purposes. Some of them were cheaper but not appropriate.

2. Sulfonated lignins as initial materials.

In this lecture it will be reported about the synthesis of a more or less "slow releasing" organic nitrogen fertilizer, which is produced by oxidative ammonisation of lignin waste products of cellulose industry, especially of ligninsulfonates.

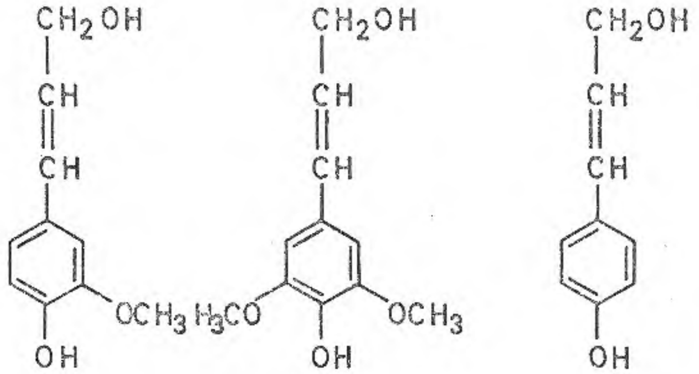
There were mainly two reasons to use ligninsulfonates.
The first was that initial material for the "slow releasing" nitrogen fertilizer is a lignin product, and lignin and its degradation products are important parent material for humic substances in soils. It was not only to expect, it is also the case, that by oxidative ammonisation of ligninsulfonates several physiologically active substances are formed. We know that some are from the same type as those in the soils. The experiments with "N-Lignin" - the designation of this organic nitrogen fertilizer - must be made not only under the aspects of a slow acting fertilizer, but also its content of bioregulating constituents must be born in mind.

The second reason was that nearly the half of the wood in form of the lignin containing residues will be used for a further technical product and is not only burned as till now. The wast liquors can generally no more be discharged into rivers and lakes because of the pollution of the environment. To produce an organic nitrogen fertilizer from lignin residues by oxidative ammonisation is therefore also an important contribution to the hygiene of the environment.

At first the chemical reactions will be described, which occur during the oxidative ammonisation of lignin sulfonates.

2.1 Differences of the chemical structure of spruce and beech lignin.

Mostly spruce and beech wood are used for cellulose production, in some cases also the straw of cereals.

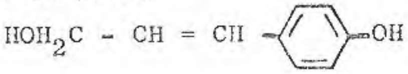
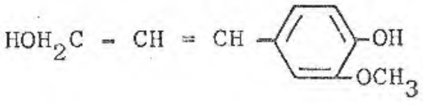
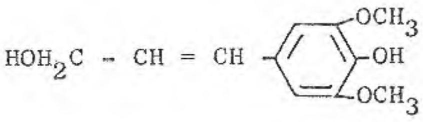


Coniferous trees	+		
Deciduous trees	+	+	
Graminees	+	+	+

Fig. 2: Monomers of lignin.

The three monomers of the different lignins have a different content of methoxyl groups. This fact is important because the fixation of ammonia in ligninsulfonates is accompanied by a decrease of methoxyl content. Coniferous lignin consists mainly of coniferyl alcohol. Beech lignin is formed by a copolymerization of coniferous and sinapyl alcohol, whilst graminaceous lignin contains besides these monomers a larger amount of p-coumarylalcohol. If only the methoxyl content of the lignin would be responsible for the fixation of ammonia, then the nitrogen content of the N-Lignin would be very different. But there are some other reactions such as hydroxylation of p-coumaryl- and coniferylalcohol, which also contribute to the fixation of ammonia.

Tab. 1: Lignin and methoxyl content as well as the content of monomers in the lignin of spruce and beech (weight %)

		Spruce	Beech
Content of Lignin (Klason)		27 %	21 %
Methoxyl content of lignin		13 %	22 %
Composition in % of Monomers			
p-Coumarylalcohol		14 %	5 %
Coniferylalcohol		80 %	52 %
Sinapylalcohol		6%	43 %

The lignin content of the plants is different. Spruce contains 27% lignin and beech 21% lignin. The methoxyl content of beech lignin is nearly the double of this of spruce lignin. To built up a structure scheme of the lignins of spruce and beech different amounts of units are necessary as it can be seen from tab. 1.

Some two further results of lignin research must be mentioned in connection with a combined celluslose and organic nitrogen fertilizer production, because in this case lignin residues are no more a waste product.

Tab. 2: Methoxyl and nitrogen content of different lignin in percent (BONDY and MEYER, 1948).

	% OCH_3	% N
Hartholz	20,0	0
Weichholz	15,0	0,2-0,3
Gramineen	10,0	1,2-1,6
Leguminosen	5,0	2,9-3,4

The methoxyl content of the lignins of grasses and leguminoses is lower than this of the trees, but the nitrogen content is higher. This means that the initial material contains already nitrogen. If lignin sulfonates are used, which have been produced by cooking the wood with ammonium bisulphite, the initial material contains up to 6% nitrogen. The efforts to increase the nitrogen content are then not so high.

The cooking process with ammonium bisulphite has some further advantages. The quality of cellulose is high and the free and fixed ammonia contained in the digesting liquor can be reused as fertilizer nitrogen. The same is also the case for neutral sodium sulphite as pulping agent for production of corrugated board.

When under special circumstances the production of organic fertilizer is the main reaction and not that of cellulose, plants with a high lignin content may become important.

Tab. 3: Lignin content of different plants in different climatic zones (MIGITA and KAWAMURA 1944)

Lignin content of different plants in different climatic zones
(MIGITA and KAWAMURA 1944)

Coniferus trees		
Picea abies (L.) Karst.	Pinaceae	27,5
Pinus densiflora Sieb. et Zucc.	Pinaceae	27,5
Cryptomeria japonica D. Don	Pinaceae	34,1
Chamaecyparis obtusa Sieb. et Zucc.	Pinaceae	31,0
Larix gmelinii Leder	Pinaceae	29,9
Deciduous trees		
Cold temperate zone		
Popolus davidiana Dode	Salicaceae	20,1
Fagus crenata Blume	Fagaceae	21,0
Temperate zone		
Alnus firma Sieb. et Zucc. var. Sieboldiana Winkl.	Betulaceae	23,2
Quercus serrata Thunb.	Fagaceae	19,3
Euptelea polyandra Sieb. et Zucc.	Euptelaceae	25,7
Platanis orientalis L.	Platanacea	22,8
Cornus controversa Hemsl.	Cornaceae	24,0
Tropical zone		
Dalbergia cochonchinensis Pierre	Leguminosae	33,4
Pterocarpus santalinuns L.	Leguminosae	37,6
P. macrocarpus Kurz.; P. indicus Willd.	Leguminosae	40,9
Cassia siamea Lam.	Leguminosae	34,3
Diospyros Ebenum Koenig	Ebenacae	45,8
Macaranga hypoleuca Müll.Arg.	Euphorbiaceae	28,0
Phyllostachys reticulata C. Koch	Gramineae	25,4

Many plants in more tropical zones have a high content of lignin. This could be used for the production of organic N-fertilizers, when not the cellulose as such, but the carbohydrates formed by hydrolysis of cellulose with mineral acids, are important products for animal nutrition. According to a rough estimation both would be needed approximately to the same amount as by-products either for fertilizers or for feedstuffs. The laboratory experiments demonstrate that in semiarid and tropical zones organic nitrogen fertilizers may be more effective for plant production than in humid climate. The plants with a higher lignin content grow in the mentioned zones and could be used as raw materials.

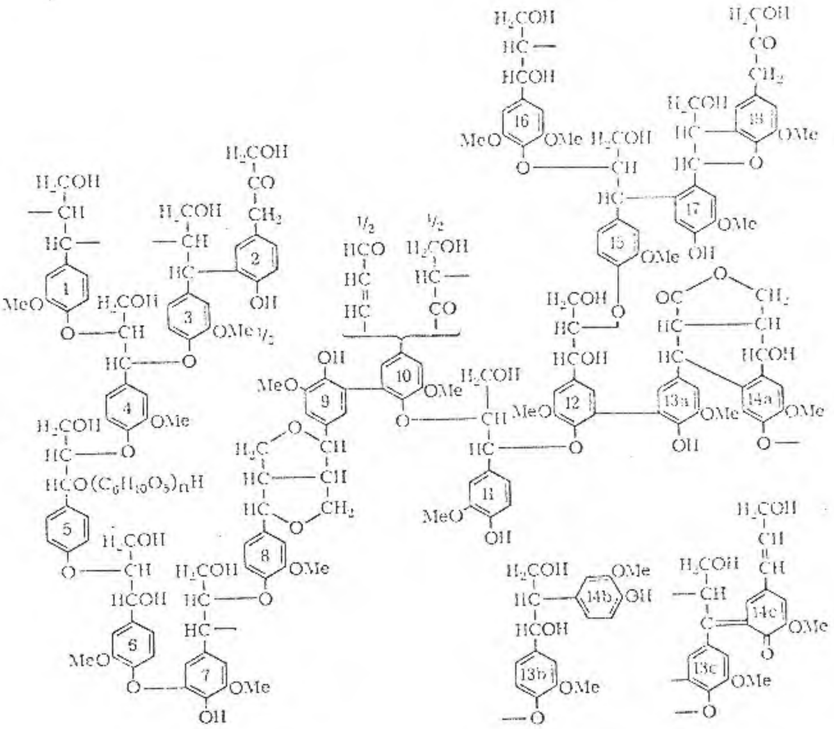


Fig. 3: Structure scheme of coniferous lignin (FREUDENBERG et al. 1968)

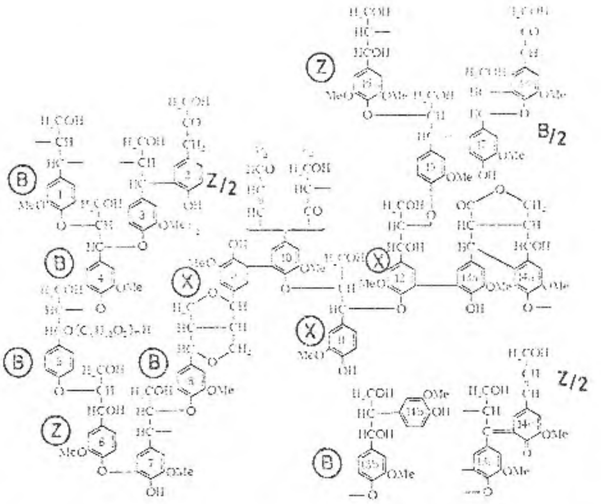
Some reactions during sulfonation and oxidative ammonisation of ligninsulfonates will be explained with the structure scheme of FREUDENBERG et al. (1968). The constitution model consists of 18 units, 14.5 (80%) of coniferyl-, 2.5 (14%) of p-coumaryl- and 1 (6%) of sinapylalcohol molecules. During polymerization a loss of 1,96 atoms of hydrogen and an addition of 0,4 molecules of water per unit of 9 carbon atoms occurs. According to a proposal of HOLMBERG (1942) the basic formulae of the different lignins are calculated for 9 carbon atoms, because all lignins are composed by phenylpropane = C_6-C_3- units. The differences between the lignins of different plants and alterations in the high molecular weight structure can be better overlooked in this way. One does not give only the elemental analysis as it is generally done in the case of other organic compounds.

It shall be mentioned that the connection between units 2 and 3 as well as units 13 and 14 can partly also occur by an o-quinonoid structure (FREUDENBERG and HARKIN, 1964). Such types of compounds add relatively easily ammonia.

Furthermore methoxyl groups in semiquinonoid structures have in alkaline solution more a character of ester than of ether groups and can be hydrolyzed in alkaline solution. The o-diphenols formed in this way are very reactive compounds for transformation of ammonia in organic bound nitrogen or for further condensation reactions even for heterocyclic nitrogen compounds.

2.2 Reactions of lignin with salts of bisulphite.

Not all units of the molecule react with the acid bisulphite salts, such as calcium, magnesium or ammonium. The sulfonation depends upon the substitution of the carbon atom 1 - the next to the phenyl-ring - of the side chain. One differentiates between the units X, Z and B. Without going further into details it was found that sulfonisation occurs exclusively at the secondary alcohol group of the carbon atom 1 of the side chain. Thereby not only the unsubstituted secondary alcohol groups in the units Z- were sulfonated. After the cleavage of the dialkylether linkage in the units X and the cleavage of the alkylarylethers in the units B by the acidic sulphite solution the additionally formed secondary alcohol groups are also sulfonated.



	Sulfonated	Not sulfonated
Units	1,4,5,6,8,9, 11,12,13b,16, 10/2,14c/2, 17/2	2,3,7,15,18, 10/2,14c/2, 17/2
total	ca. 11,5 units or 64 %	total ca. 7,5 units or 36 %

Distribution of sulfogroups in the units of lignin on the single groups (FREUDENBERG and NEISH, 1968):

	Found or estimated	Deducted from model
Group X	0,15	0,17
Group Z	0,15	0,20
Group B	0,30	0,28
Sum	0,60	0,65

Fig. 4: Sulfonated units in the model of the constitution of spruce lignin.

In the graph the numbers of the units are mentioned, which are sulfonated and which are not. 11.5 units or 64% are sulfonated and 7.5 units or 36% remain unsulfonated.

By sulfonation the molecule of lignin is degraded to smaller parts. For the following oxidative ammonisation some reactions during sulfonation are very important.

First of all the lignin becomes water soluble and the oxidative ammonisation can be carried out in a homogenous system. This has many advantages for the technical process.

Furthermore, the content of phenolic hydroxyl groups may be increased by the cleavage of alkyl-arylether groups during sulfonation. Thereby the possibilities of reactions with ammonia become increased.

During the process of oxidative ammonisation of the sulfonates the methoxyl content decreases and concurrently the content of organic bound nitrogen increases. The phenols which are formed by the methylether cleavage react with ammonia to different compounds, which contain nitrogen in different organic linkage.

The fixation of nitrogen in organic linkages occurs only when oxygen and ammonia are present contemporarily. For the case of at first oxidation and then ammonisation or vice versa nearly no nitrogen fixation can be observed.

Lignin treated with mineral acids such as hydrochloric or sulphuric acid is changed partly by condensation and partly by cleavage reactions. Primary results of oxidative ammonisation of such pretreated lignins show however that the production of organic nitrogen fertilizers is also possible. Only for large scale production the special conditions must be worked out.

In countries in which humus problems in connection with physical properties of the soil - for instance erosion and others - exist, in the type of organic nitrogen fertilizer on lignin basis - also an important material for humus formation - not only the nitrogen component but also the organic part is of great interest. In was found, that an increase of soil carbon content of about 10% and of nitrogen content of about 60% occured in pot experiments with pseudogley chernozem after ten years under our humid climatic conditions.

2.3 Degradation of ligninsulfonates in alkaline solution.

Only by the use of labelled compounds a part of the mechanism of degradation of ligninsulfonates could be elucidated.

2.31 in absence of oxygen

In the presence of oxygen with labelled ligninsulfonates it could be shown that their degradation is faster than that of lignin itself . When the sulfonic acid rest is split off mainly vanillin and acetaldehyde is formed to a higher amount. Acetaldehyde is able to condense with phenolic compounds. This reaction may lead to alterations of the final products such as organic nitrogen fertilizer (KRATZL et al. 1964, 1966).

2.32 in presence of oxygen

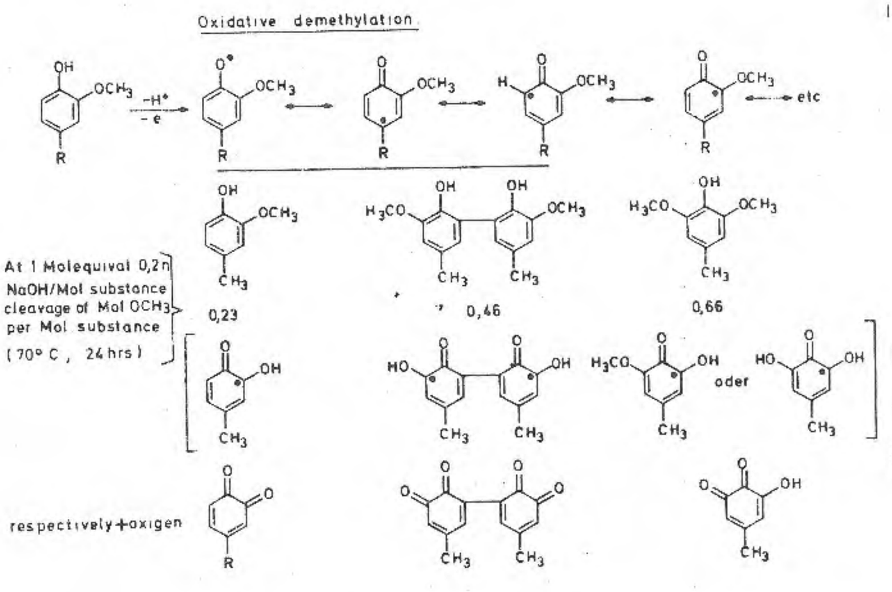


Fig. 5: Oxidative demethylation

In 0.2 N NaOH solution methoxylated phenols split off different amounts of methylalcohol. The amount increases with the tendency of these compounds to form semiquinonoid intermediates.

Dimerisation of the monomers and formation of o-diphenols has been established. By further oxidation corresponding quinones are formed (KRATZL et al. 1967).

In connection with the use of ligninsulfonates from beech for the production of organic nitrogen fertilizers it is interesting that the syringyl components are remarkably faster deme-thylated than these of guaiacyl type. This may be the reason, that lignin of beech wood is faster transformed by oxidative ammonisation than this of coniferous trees.

3. Oxidative ammonisation of ligninsulfonates.

3.1 Nitrogen fixation in dependence of oxygen consumption.

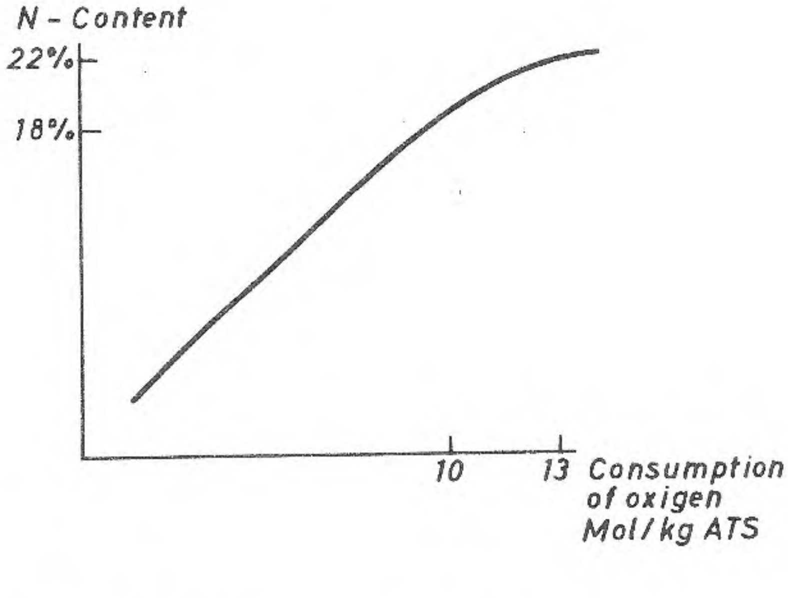


Fig. 6: Scheme of the formation of "N-Lignin"

With increasing consumption of oxygen the nitrogen content of the final product increases. After a turnover of 10 to 13 Mol oxygen per kg dry matter of lignin containing waste liquor the N-Lignin contains 18 to 22% of total nitrogen. By a good mixture of gaseous and liquid phase the reaction is carried out at 10 to 30 atmospheres and 110-130°C. The distribution of nitrogen in the organic nitrogen fertilizer N-Lignin is:

Total N 18-20% N
from this (total N content = 100 %)
30-40% NH_4 - N
Ca 10% "Amide - N"
50% bound in other organic form.

"Amide - N" is nitrogen, which can be hydrolized with 30% sodium hydroxide solution after the destillation of the ammonium ions with magnesium oxide. With urease about 11% of the total nitrogen of N-Lignin can be determined as urea nitrogen. The total amount of urea in the product is about 5%. N-Lignin is soluble respectively dispersable in water. 50% of the product consists of high molecular weight substances, which do not dialize. In the high molecular weight fraction are about 40-45 % of the organic bound nitrogen. This is important in connection with its properties as nitrogen fertilizer because this part of N-Lignin is not leached by heavy rainfall.

Reductive cleavage with sodium amalgam according to Burges et al. (1964) in N-Lignin from spruce the main product is vanillic acid. This and other physiologically active substances cause special properties of this organic nitrogen fertilizer.

3.2 Principle of method of operation.

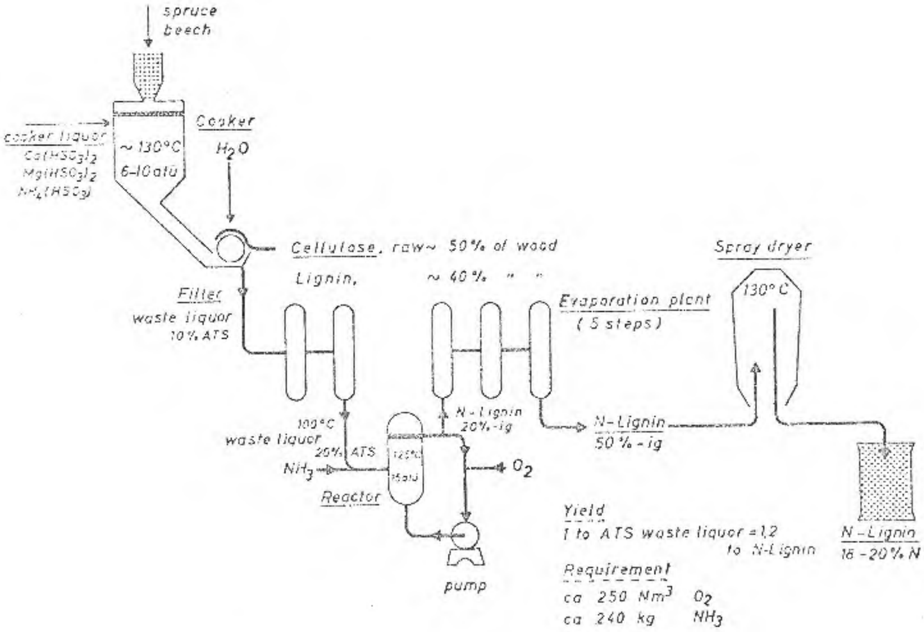


Fig. 7: Flow scheme for production of N-Lignin (organic nitrogen fertilizer) from waste liquors of cellulose industry.

After cooking the wood with sulphite solution the waste liquor is filtrated from cellulose and preconcentrated to a dry matter content of 20 %.

In the reactor the waste liquor is oxidized and ammonised at a temperature of 125°C and a pressure of 15 atmospheres by circulating with a pump. After one or two hours the reaction mixture is concentrated by an evaporation system to a dry matter content of about 50% and then dried in a spray dryer to a powder. The powder is granulated and bagged for shipment.

At the moment a pilot plant is running with 500 tons per year. This will be enlarged in next time.

For 1 ton N-Lignin 0,85 ton of dry matter from sulphite waste liquor is required. This corresponds to 8,5 ton sulphite waste liquor taken at an average 100 % dry matter content of 10 %. The requirement of ammonia is about 0,25 ton and the requirement of oxygen about 280 Nm^3. The yield of N-Lignin is about 110 % of the theory.

4. Oxidatively ammonised ligninsulfonates as organic nitrogen fertilizer (N-Lignin).

With the next illustrations the effect of N-Lignin as a "slow releasing" nitrogen fertilizer, as well as the bioregulating influence of some of its constituents on plant growth will be explained.

4.1 Effect of "slow releasing" nitrogen.

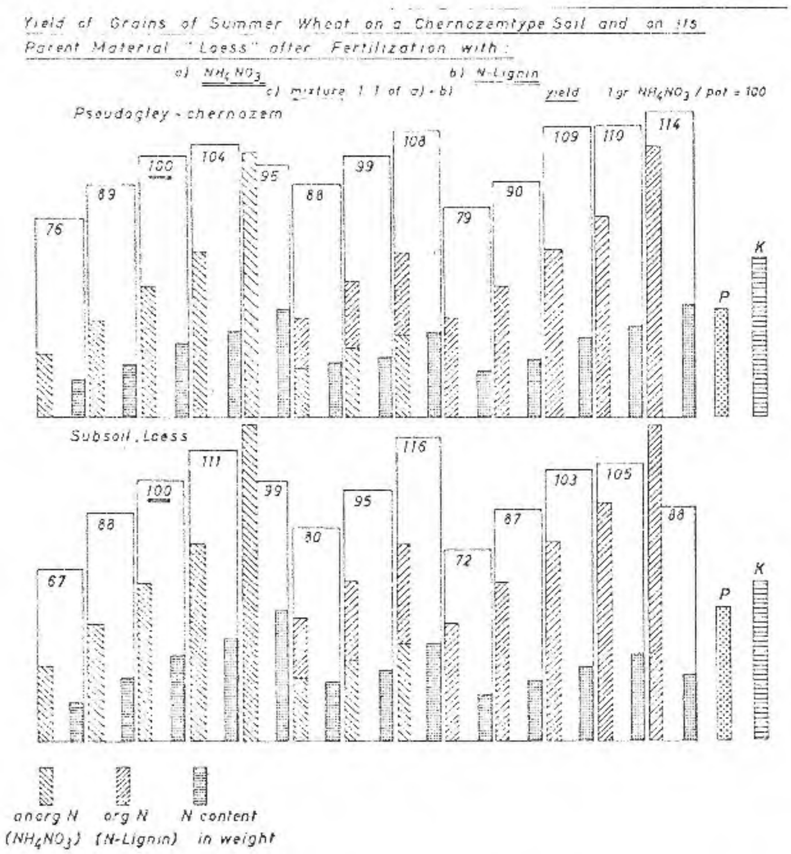


Fig. 8: Yield of grains of summer wheat on a chernozem type soil and on its parent material "loess" after fertilization with: a) ammonium nitrate (left), b) N-Lignin (right), c) mixture 1:1 of (a) and (b) (middle).

The effect of N-Lignin will be demonstrated with the results of a pot experiment. It is only possible to mention some of our investigations. We have an experience of more than 10 years and work since about 4 years with several other institutions in Germany, Europe and Overseas. This cooperation is concerned with pot and field experiments.

The pot experiment depicted in fig. 8 was made with two different substrates. One was a pseudogley-chernozem with a high biological activity and a high amount of organic matter, whilst the other substrate was the parent material of the chernozem, it was loess. This substrate had only clay minerals as sorption components and was largely sterile (FLAIG and SÖCHTIG 1967, FLAIG 1970).

The larger columns are relative yields, whereby the yield with 1 g ammonium nitrate per pot on both substrates has the number 100.

The differently hatched columns are the different amounts of ammonium nitrate dosages (right) or these of N-Lignin dosages (left). In the middle the pots have been fertilized with mixtures 1:1 of inorganic and organic fertilizer. The fertilization with potassium and with phosphorus was the same in the two cases. Punctated columns are the withdrawal of nitrogen.

In the case of the highest dosage of ammonium nitrate a depression of the yield of grains occurs, whilst in the case of N-Lignin the highest yield may not yet be reached. The increase of 10% is statistically significant.

At comparable amounts of fertilization the variant with mineral nitrogen alone is somewhat lower than the mixture of the organic fertilizer alone.

The depression of the yield at high dosage of organic nitrogen fertilizer in the experiment with loess may be explained by its low microbial activity. But it is important that the mixture of organic and inorganic fertilizers caused an increased yield of grains. The difference between inorganic and organic fertilization is not so distinct in all cases of straw yield. It seems to be, that mainly the generative phase of the growth is influenced. In this connection there are some interesting problems, which must be solved by further research.

By such and similar experiments we could demonstrate that the use of mixtures of inorganic and organic nitrogen fertilizers - also in complex fertilizers - gave the best results.

The following graphs will show the main properties of the organic nitrogen fertilizer, N-Lignin in comparison with inorganic nitrogen fertilizer, which contain ammonium and/or nitrate ions. Most of the graphs are schematised. Furthermore it must be born in mind that the different facts, which are described in the graphs occur in nature as a resultant of severals. Here it is only possible to show the principles.

Furthermore it must be mentioned, that not all effects observed by the use of N-Lignin can be explained only by its property as a "slow releasing" nitrogen fertilizer, for instance when it is compared with other "slow releasing" fertilizers. To a larger extent also the content of physiologically active substances plays an important role for the explanation of the effects of N-Lignin.

Some further observations will be reported, which are connected with physical and chemical properties of N-Lignin.

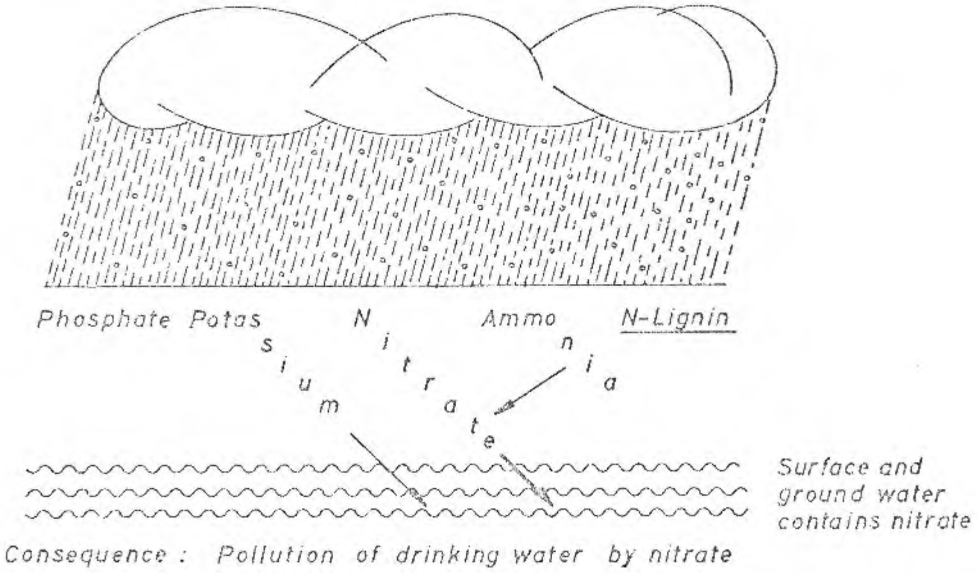


Fig. 9: Less leaching of N-Lignin in comparison to mineral fertilizers.

In the case of heavy rainfalls potassium and nitrate ions are leached in different soils. Whilst ammonia is retended by sorption complexes of the soil, some losses occur by the transformation of ammonia in nitrate by nitrification.

By the leaching of nitrate into the surface and ground water finally the drinking water may be polluted. This type of water pollution increases in future more and more in some regions and becomes a serious problem.

N-Lignin consists of about half of high molecular weight substances, which are sorbed by other soil colloids, and is therefore not leached to the same extent as nitrate fertilizers. This property will perhaps become important for irrigated fields. In some cases we also observed that the plots fertilized with N-Lignin were a longer time wet than the controls with inorganic fertilizers.

The chemical structure of N-Lignin effects that this is a high molecular weight cation exchanger with an exchange capacity of about 100 meq. per 100 g.

The influence of N-Lignin on physical properties of soils is not well known.

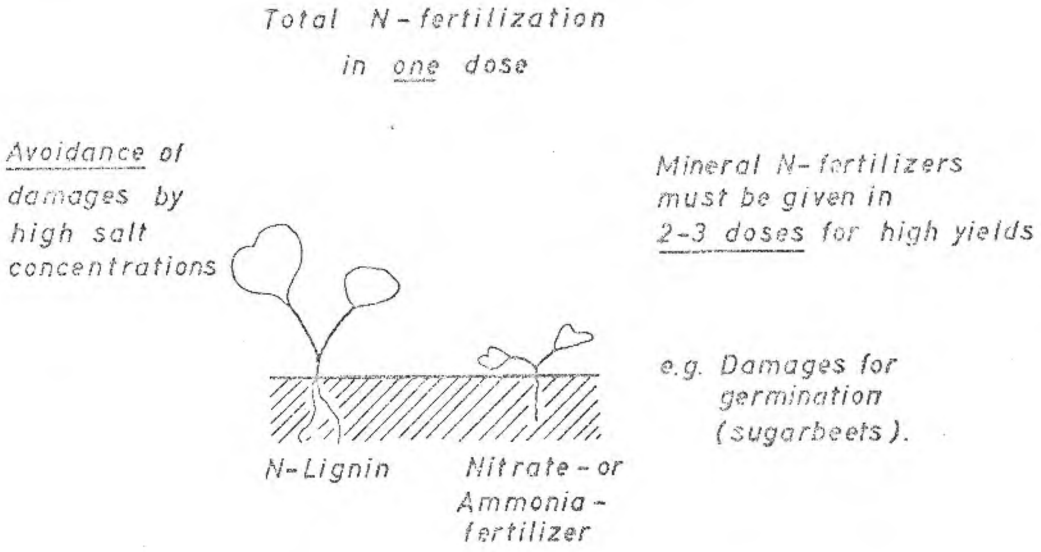


Fig. 10: The larger compatibility of N-Lignin.

From many investigations it is known that it is not possible to give all the needed inorganic nitrogen fertilizer in only one dosage because damages occur for germination and growth of seedlings. The inorganic nitrogen must be given in several doses to reach high yields.

The nitrogen in N-Lignin is only up to 40 % in form of ammonium ions. By this reason nearly the double amount of N-Lignin can be added to soil without damages for plant growth.

If one compares the availability of the nitrogen from ammonium nitrate with this of N-Lignin and one gives the availability of nitrogen from ammonium nitrate the number 100 then the availability of the nitrogen of N-Lignin is in the first vegetation period up to about 80 %. A part of the organic bound nitrogen becomes available in the years. An increase of soil nitrogen occurs with the years, when N-Lignin is used as nitrogen fertilizer. The increase of soil nitrogen by fertilization with N-Lignin depends upon the climatic conditions as it could be shown by laboratory experiments.

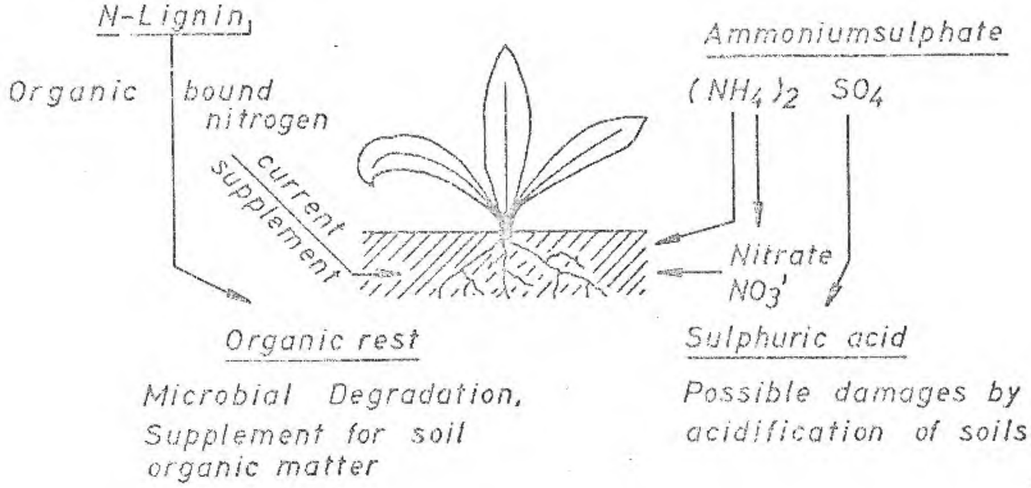


Fig. 11: Advantage of the organic rest in N-Lignin.

In the case of ammonium sulphate ion remains in the soil after the use of ammonium ion for plant nutrition. The soils can be acidified by this process.

In the case of N-Lignin however the nitrogen is liberated slowly during vegetation by the activity of microorganisms. Thereby the organic rest of the N-Lignin is degraded. A part of it contributes also to supplement the humus content in soil, as we found in some cases. At the moment we study the dynamics of humic systems after repeated addition of N-Lignin. The values give us some evidence about transformation of N-Lignin in dependence of climate.

4.2 Effect of physiologically active substances.

Future agriculture has not only to increase the yield per hectare but also to produce foodstuff of high biological value.

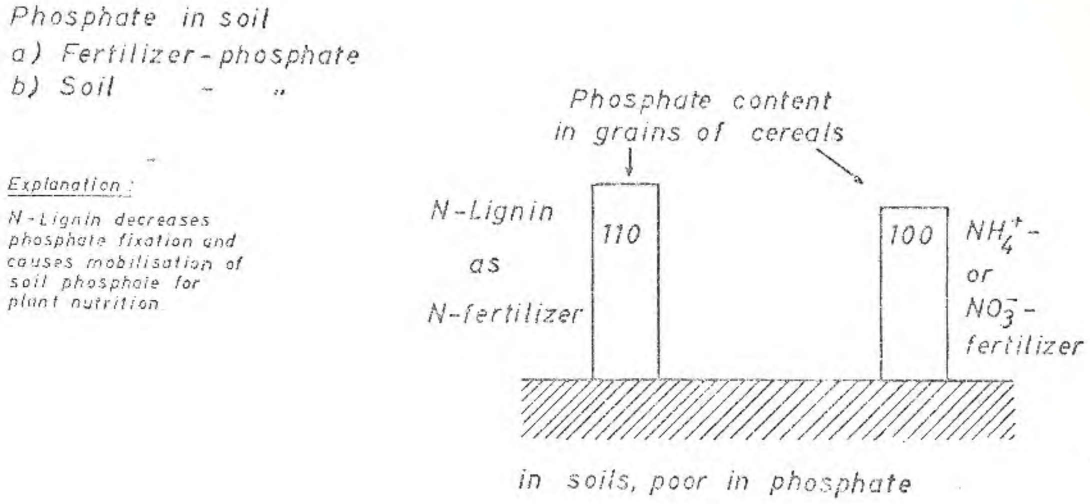


Fig. 12: Increase of phosphate content of crops by N-Lignin

The phosphate content is one of the measure for the quality of food and feedstuff because this element is of great importance in metabolism.

The phosphate occurs in soils as fertilizer phosphate or as soil phosphate. The increase of quality through a higher phosphate content in plants is caused by the addition of N-Lignin in this way that fixation of phosphate in soil is diminished and a part of soil phosphate becomes available to plant nutrition. This effect is mainly observed in soils of less phosphate content. The phosphate content in grains of cereals was found increased up to 10 % in the case of ryegrass sometimes up to about 2o %.

Furthermore we have some preliminary results about the influence of physiologically active substances of N-Lignin on some metabolic pathways.

The glycolysis is altered in the direction of a higher content of soluble sugars. Furthermore we observed in some cases a higher lysine content in the fraction of free amino acids. Also the ratio of some proteins in the grains of cereals is altered but not their composition; this is also not possible from genetical point of view.

In sugarbeets the content of sugar is increased and the content of the so called "noxious nitrogen" decreased. Even when the yields of beet per hectare is lower the two mentioned effects can increase the yield of sugar production per hectare.

We have some results that some other favourable effects such as an increase of wilting and frost resistance of plants may be caused by physiologically active compounds of N-Lignin. In a dry summer the yield of barley fertilized with N-Lignin was remarkably increased in comparison with mineral fertilizer.

4.2 Inhibition of nitrification

One has tried in different ways to inhibit nitrification, so for instance with special chemicals as "nitrogen serve". For diet of babies and sick persons the content of nitrate in some vegetables should be as low as possible.

Investigations about the nitrification of N-Lignin have demonstrated that it contains substances which inhibit the nitrification (SÖCHTIG 1967, 197o). With increasing soil temperature the rate of mineralization of the nitrogen of N-Lignin increases. To the same extent the inhibition of nitrification decreases. But the nitrification of N-Lignin is always less than this of ammonium sulphate. The inhibition of nitrification in brown earth is larger than in chernozem.

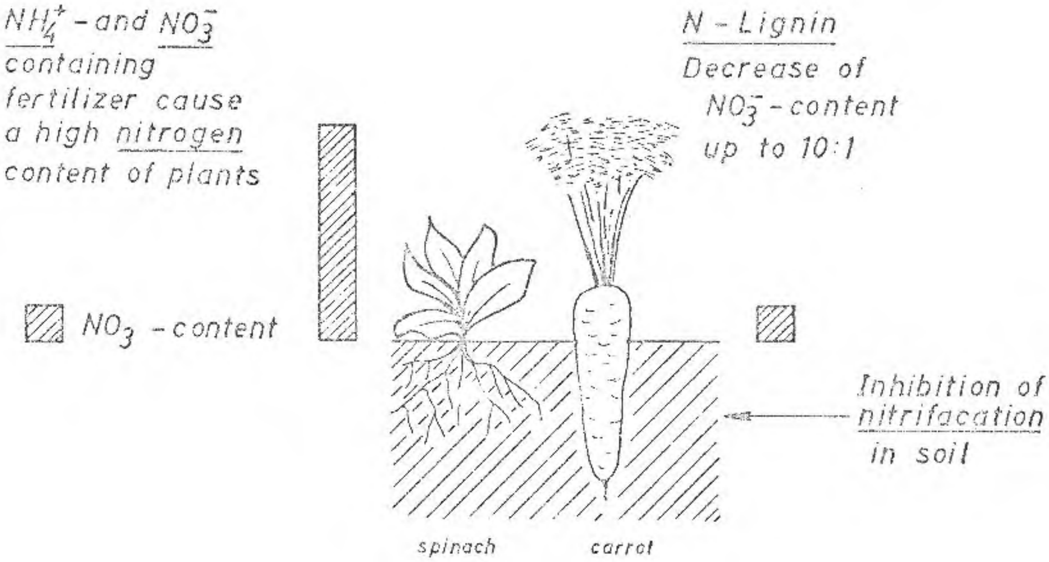


Fig. 13: Diminution of nitrate content in food.

It could be demonstrated that N-Lignin can decrease the nitrate content of spinach in springtime up to a tenth of the controls with ammonium sulphate and "FLORANID" BASF (Crotonylidendiurea). In this case the yield is not so high, but the product has a higher economical value. In summertime the differences of yield are no more so large, but the decrease of nitrate content is about 25 %. The uptake of nitrate from N-Lignin depends also upon the time between addition of N-Lignin to the soil and the time of sowing of the seed. According to the conditions of climate and soil the rate of mineralization of nitrogen and its nitrification is different. The inhibition of nitrification was also observed in the case of mixtures of N-Lignin with ammonium fertilizers.

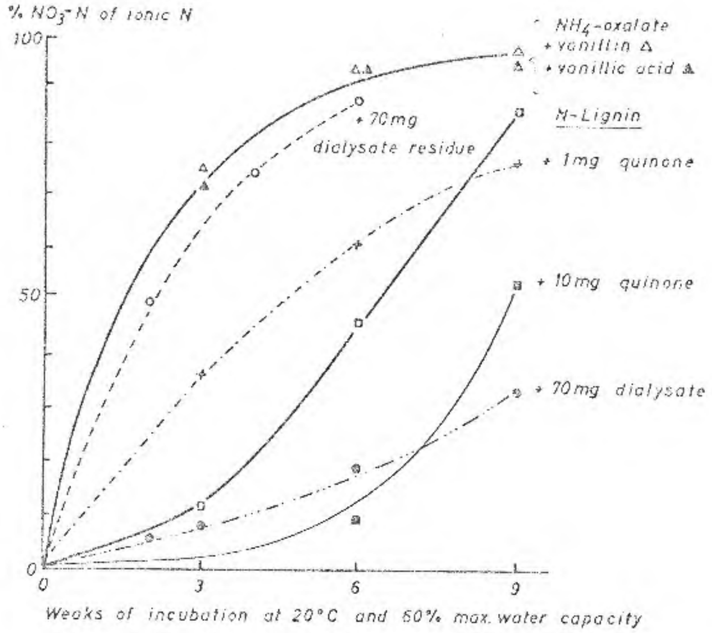


Fig. 14: Influence of different substances from N-Lignin on nitrification.

Some further investigations have been made to determine the constituents of N-Lignin, which cause the inhibition of nitrification. For this purpose N- Lignin was dialysed. The graph shows that the residue of dialysis has nearly no effect on nitrification in a chernozem soil at 20°C and 60 % of maximal water capacity, whilst the dialysate inhibits the nitrification strongly during several weeks.

In the dialysate of N-Lignin are only low molecular compounds. Therefore some compounds from which is known that:

1. they could be present in the sulphite waste liquor and get into N-Lignin such as cellulose or glucose, (for comparison also milled straw) were added in amounts of 1o to 1ooo mg to 1oo g soil.
2. they are formed by oxidative degradation of lignin such as p-hydroxybenzaldehyde or its acid, vanillin or vanillic

acid, syringaldehyde or its acid were also added up to 1o mg per 1oo g of soil.

3. they can be used as model substances of oxidized lignin degradation products or microbial synthesized phenolic compounds, such as phenols and quinones, for instance thymohydroquinone, were investigated in nitrification experiments.

In the case (1) also different nitrogen sources such as ammonium oxalate, acetate chloride and sulphate or organic nitrogen sources such as glutamin or "Floranid" BASF were additionally added. The nitrification was not inhibited. But as it was to expect a decrease of the plant available nitrogen occured by fixation of the nitrogen from the different nitrogen sources with increasing addition of carbon sources such as glucose, cellulose and milled straw.

The graph shows that the ammonium salt of oxalic acid and the different phenol carboxylic acids such as vanillin, vanillic acid etc. had no influence on the nitrification.

But the addition of a quinone as a model substance of oxidised lignin degradation products such as thymohydroquinone diminished the rate of nitrification, The addition of 1 mg quinone per 1oo g soil reduced nitrification, 1o mg quinone stopped nitrification during 6 weeks nearly completely. After 9 weeks the inhibiting effect of the quinone decreased rapidly.

According to some further investigations the effects of the quinone seems to be not only limited on nitrification but also on mineralization (FLAIG and SÖCHTIG, 1967). In this connection it may be interesting to mention that phenols or quinones which are possibly formed during humification of plant residues and from which is known that they have an influence on plant growth (summarised: FLAIG 1968) may effect that ammonium ions are available for the plants during a longer time also under natural conditions. This large complex of problems which is important for stabilization of plant production is nearly not elucidated and needs much more attention.

In the last graph the present knowledge about the properties of N-Lignin shall be summarised.

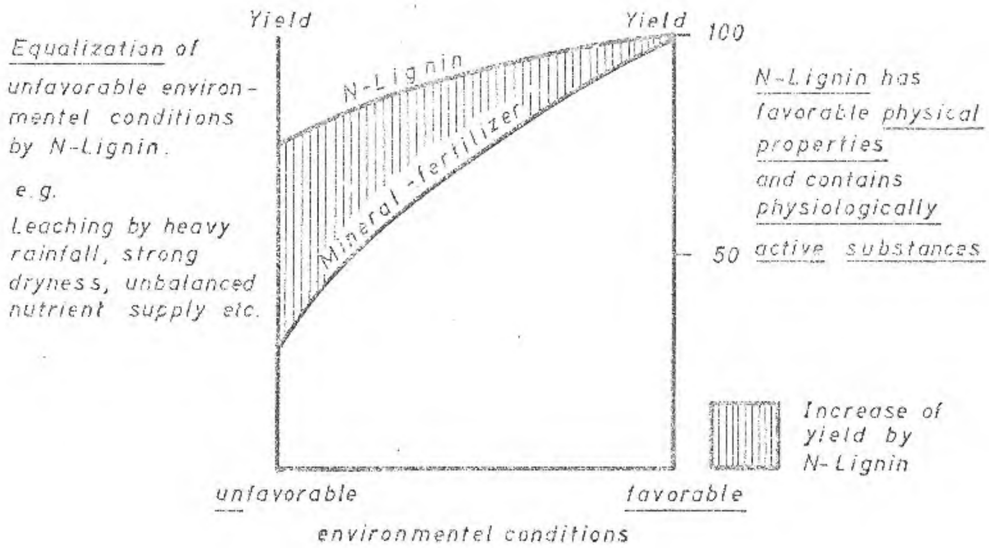


Fig. 15: Diminishion of risk of yield formation by N-Lignin.

The effect of N-Lignin on plant production is not only this of a nitrogen fertilizer with special properties such as slow nitrogen release - fixed in organic compounds comparable with soil organic matter -, with favourable physical properties, but also its content of physiologically active constituents plays an important role. These special properties may be the reason that N-Lignin has the largest effect under unfavourable environmental conditions. They may be equalized to a certain extent by N-Lignin, because it is not leached by heavy rainfalls. Strong dryness is moderated by increased wilting resistance of plants. Also the influence of unbalanced nutrient supply on plant nutrition is moderated.

Oxidative ammonisation of ligninsulfonates is one of the new and necessary trends for the development of nitrogen fertilizers.

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