EFFECT OF LIGNIN ON SOIL PROPERTIES AND PLANT GROWTH

Ву

Ming Yuen Wang

A THESIS

Submitted to the School of Graduate Studies of Michigan

State College of Agriculture and Applied Science

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science

Year 1953



EFFECT OF LIGHIN ON SOIL PROPERTIES AND PLANT GROWTH

By

Ming Yuen Wang

AN ASSTRACT

Submitted to the School of Graduate Studies of Michigan
State College of Agriculture and Applied Science
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Soil Science
Year 1953

Approved L.M. Turk



The Effect of Lignin on Soil Properties and Plant Growth

Lignin prepared by saccharification of corncobs was mixed with surface soil from Miami sandy loam and Brookston clay loam at rates of 0, 2.5, 5.0, and 7.5 tons per acre. After five weeks! incubation, the soils were studied for changes in physical, chemical, and biological properties.

It was found that "lignin" caused an increase in the formation of large stable aggregates, an increase in the percentage of moisture at the moisture equivalent, an increase in the hygroscopic coefficient, and greater values for the upper and lower plastic limits and the sticky point. Percent porosity at tensions, 10, 20, 30, 40, and 60 centimeter water was increased whereas percent capillary porosity was decreased.

Addition of "lignin" to soil tends to increase slightly the base exchange capacity of the soil as determined by the ammonium acetate method. The increase was probably due to changes in the activity or adsorptive power of "lignin" during its transformation, or to the formation of certain complexes. The base exchange capacity of the "lignin" material used was 19 milliequivalents per 100 gram material.

The pH of the soils was slightly increased by the addition of "lignin". The pH of the "lignin" material was only 1.99.



Nitrate content of the soil, determined colorimetrically by phenoldisulfonic acid method, was decreased as rate of "lignin" application increased. This was believed to be due to immobilization of the nitrogen as a result of increased microbial activity.

Exchangeable calcium, magnesium (versenate titration method), sodium and potassium (flame photometer method) were not affected except potassium which showed a slight increase by "lignin" addition.

Buffer capacity of soil treated with "lignin" was increased, although not appreciably. The greatest buffer action of "lignin" lies between pH 6.5-8.0.

Greenhouse experiments on surface soil from Miami sandy loam showed beneficial effect of "lignin" on the yield of tomatoes and spring wheat. Nitrogen, mulching, and liming increased the effectiveness of "lignin" on tomato yield but the latter two did not materially affect the effectiveness of "lignin" on the yield of spring wheat. Results of these experiments indicated that the optinum rate of "lignin" application was five tons per acre.

A comparison of crop yields when ground corncobs, sawdust, and "lignin" were applied at five tons per acre to surface soil from Brookston clay loam was studied under greenhouse conditions. The results showed that "lignin" was preferable to the ground corncobs and sawdust when mixed with soil. When applied as mulch, "lignin" and ground corncobs were preferable to sawdust.



A field experiment on Metea loamy sand was designed to study the effect of various mulching materials on the yield of soybeans. The results showed that when no nitrogen was added, corncobs, wheat straw, and sawdust mulching all tended to decrease yields. The depressive effect disappeared when 60 pounds per acre of nitrogen were applied. An increase in soybean yields was obtained when nitrogen was applied at the rate of 120 and 180 pounds per acre.

It was therefore recommended that when "lignin" could be procured at reasonable cost, it can be used to advantage overcorncobs and sawdust when applied at five tons per acre. Nitrogen application along with "lignin" would be beneficial.



ACKNOWLEDGEMENT

The author expresses his sincere appreciation to Dr. L. M. Turk and Dr. R. L. Cook for their guidance in the research reported in this work and in the preparation of the manuscript. He also wishes to thank Dr. A. E. Erickson, Dr. Kirk Lawton, Dr. E. P. Whiteside, Dr. R. M. Swenson, and fellow students of the Soil Science Department for their helpful suggestions throughout the course of this study.



TABLE OF CONTENTS

Chapter	Pa	ge
I	INTRODUCTION	1
II	REVIEW OF LITERATURE	3
III	LABORATORY STUDIES	.3
	A. Physical	.5
	2. Moisture equivalent	5.8.8.03
***	B. Chemical	25
9	2. pH measurement	58 80 81 81 81 81
	C. Biological	35
IV	GREENHOUSE STUDIES	88
	A. Tomatoes on Miami Sandy Loam	39
	B. Spring Wheat on Miami Sandy Loam	39
	C. Tomatoes on Brookston Clay Loam 4	hΉ
	D. Spring Wheat on Brookston Clay Loam 4	4
V	FIELD STUDIES 4	<u>.</u> 7
VI	SUMMARY	60
VII	conclusions	62
VIII	LITERATURE CITED 5	3



I. INTRODUCTION

The exact chemical and physical structure of lignin and the products formed by its decomposition are not well known. This is due largely to the difficulty involved in isolating lignin in its chemically unchanged form. Therefore, a distinction should be made between two types of lignin: 1. unaltered lignin which occurs in living plants or trees, and 2. altered lignin derived from plants and trees by chemical or biological actions. The lignin material used in this study belongs to the second type.

crude lignin, its derivatives, and lignin-like materials are discharged by paper mills in enormous quantities. The disposal of lignin poses a problem that offers a challenge to paper manufacturers and agriculturists. The paper manufacturer must dispose of the lignin with a minimum pollution to the stream that furnishes water for his plant. This means that some of the organic material may be decomposed without serving any useful purpose.

Farmers too have large amounts of lignin-containing materials such as corncobs and straws which could, by proper management, become very useful in improving soil properties and crop yield.

During recent years, many agriculturists have made



studies on the possible use of lignin for soil improvement and for the betterment of plant growth. Their results have not always agreed. Some workers claimed the products were beneficial while others reported opposite results.

The principal objective of this investigation was to study the effect of lignin on the physical, chemical, and biological properties of the soil as well as its effect on plant growth under greenhouse conditions.



II. REVIEW OF LITERATURE

Literature on the effect of lignin on soil properties and plant growth can be divided into several categories:

1. Its use as a fertilizing material; 2. Its use as a soil conditioner; 3. Its relationship with soil organic matter and soil chemical properties; and 4. Its decomposition in soil.

Lignin as a Fertilizing Material

Aries (4) found that Ca-lignosulfonate from sulfite waste liquor, applied at the rate of ten tons per acre, caused a 60 percent increase in the yield of shelled beans. He also found that the use of lignin from dilute acid hydrolysis increased the starch content of potatoes by 85 percent.

Dunn and Sieberlich (19) found in their greenhouse experiments that potatoes were somewhat improved by an application of five tons of lignin per acre. Onions (one test) were markedly improved but tomato yields were not affected. Almost complete exhaustion of available nitrates was noted in all soils to which lignin was added. Better results, in a limited series of tests, were secured in sand cultures than in water cultures. Lignin in the finely divided state adheres in considerable amount to the fine rootlets of seedlings. They suggested that lignin when



added to the soil might have a role with other humus constituents in forming an intimate film about soil particles and root hairs which aid in the transfer of water and soil nutrients to the root cells.

Waksman and Wissen (71) suggested the possible use of lignin as a nutrient for the cultivated mushroom, Agaricus campestris.

tory, (26) using "lignin" obtained from acid hydrolysis, found that tomato plants grown in soil receiving both lignin (five tons per acre) and fertilizer were more vigorous and bore more fruits than where only fertilizer was applied. The plants in the plot which received lignin and no fertilizer were healthy and bore good fruit, but yields were smaller than from the plots receiving fertilizer alone.

Dunn and Eppelsheimer (26) tested the effect of lignin obtained from wood saccharification on potato production. Thin layers of lignin were applied between layers of soil at a rate equivalent to five tons per acre. The results showed that lignin increased the yield, size and starch content of the tubers.

Harrington (26) reported that chrysanthemums grown in soils to which 10 percent of lignin had been added produced longer stems and bore larger blooms than did the control plants. The stem weight was increased by 30 percent.



Lignin as a Soil Conditioner

Vershinin (61), Sowden and Atkinson (54) reported that lignin, when incorporated in soil, exerted favorable effects on the physical structure of soil.

Miller (38) showed that load-bearing qualities of some soils were improved by mixing lignin or a substantially water insoluble ligneous material with them. Soils which had poor resistance to moisture effects were stabilized in the same manner. Depending on the nature of the soil, 0.2 to 10 percent of ligneous material was required, but three percent or less was preferred.

McCalla (33) found that waxes, fats and lignins in concentrations of one percent or more greatly stabilized soil particles.

Martin and Waksman (36) found that in moist clay loam soil, casein plus lignin brought about considerable aggregation, which was further increased by the addition of lime. The aggregation was not so apparent after the soil dried. They also reported that peat plus lignin did not materially influence the aggregation of the soil.

Nikishkina (42) found that ammoniated lignin increased the structural stability of 3, 2, and 1 millimeter aggregates.

Harris (26) indicated that wood-hydrolysis lignin, when used as a mulch between rows of tomatoes, kept the soil moist and was easily worked into the soil.



Hamilton and Truog (26) tested the use of lignin in both field and greenhouse. They found that additions of lignin resulted in a greater ease of cultivation. Water holding capacity, porosity, rate of water flow through the soil, and soil hardness were also improved. It was found that the beneficial effects continued through several crops.

Nine months after the addition of lignin to a soil, an increase of infiltration rate up to 100-fold was found by Aries (5).

Lignin -- as Related with Soil Organic Matter and Chemical Properties of Soil

Neller and Kelly (41) showed that the organic matter content of soils could be increased by means of waste wood lignin. This organic matter was, by vitrue of its high content of lignin, quite stable even though the temperature, moisture, and aeration conditions were conducive to loss by oxidation throughout most of the year. Under proper soil management in the use of lime, lignin-treated soils were more productive. These writers also reported that neutral and neutralized wood waste lignins retarded the loss by leaching of fertilizer phosphate from sandy soils.

Sowden and Atkinson (55) pointed out that light isolated from soil was different from plant light in many respects. It was very low in methoxyl content, high in total nitrogen, soluble in water, but insoluble in dilute acid. However, the ultra-violet light absorption curve was



similar in many respects to that of lignin and related compounds.

From the results of hydrogenation of "alkali lignin", Gottlieb and Hendricks (25) indicated that lignin in soil undergoes a similar type of change, at a much slower rate, as does lignin treated with alkali. The change consists of a condensation of the lignin molecule with the production of fused ring structures which are more resistant to hydrogenolysis than is the unaltered lignin.

Harris (26) pointed out that lignin is slowly changed to humic substances when mixed with soil. Even before it is converted to humus, it has many properties of humus, such as the ability to react with minerals in the soil, to control the size of aggregates in clay, and to aid in controlling the alkalinity of soil.

Evidence of the presence of lignin in soil organic matter, according to Bertramson and White (13), rests on results from decomposition studies, on resistance of 30 to 50 percent or more of organic matter to cold strong acids, and on the presence of methoxyl groups. They also found that greater alkali solubility and exchange capacity, partial demethylation, possible introduction of carboxyl groups and depolymerization resulted from changes which lignin had undergone in soil.

Millar, Smith and Brown (37) agreed with McGeorge (34), Bartlett and Norman (9) that during the decomposition of organic matter, there is a highly significant correlation



between percent increase in base exchange capacity and the amount of lignin in soils. But since the increase in the base holding power was so much greater than the increase in the lignin content, it has been suggested that a change in the adsorptive capacity or activity of the lignin had taken place.

McGeorge (35) reported that the exchange capacity of soil lignin is not a constant quantity but varies in different soils. Leaching the lignin and ligno-humate with water increased the exchange capacity which he believed was due to hydrolysis.

Anderson (3) claimed that the exchange capacity of the sulfite waste liquor depends on the sulfonic acid groups in the lignin molecule. Under the experimental conditions, the maximum capacity of the exchangers did not exceed a value of 0.6 milliequivalent per milliliter or 1.20 milliequivalent per gram.

Waksman and Tyer (68) found that lignin alone had a low base exchange capacity. The base exchange capacity of protein was low but somewhat higher than for lignin. When the two were chemically combined in the form of a complex, the base exchange capacity was greatly increased. As the proportion of protein to lignin was increased, the base exchange capacity increased within certain limits. The various proteins gave different values, but the general relationships were similar. Drying the complexes reduced their base exchange capacities to some extent. The nature



of the base used in preparing the complexes also influenced their base exchange capacities considerably. The highest base exchange capacities were obtained with Ca-complexes and the lowest with aluminum-complexes.

Bartlett and Norman (9) found that the magnitude of the increased base exchange capacity observed on decomposition of lignin was entirely disproportionate with the limited demethylation that occurred.

Aries (4) found that application of sulfite lignin to soil in pots increased the organic content, pH, soluble phosphorus, and calcium content of the soil. He also mentioned that sulfite lignin could be used as a substitute for liming materials and that the prevention of leaching was an added advantage.

Nikishkina (42), Waksman and Hutchings (65), and Honcamp and Wiessmann (28) all agreed that lignin has the tendency to preserve the absorbed ammonium nitrogen of the soil and the ammonia in liquid manure.

Lignin -- Its Decomposition in Soil

Waksman and Iyer (67) and Osugi and Endo (45) observed the depressive effect of lignin on the decomposition of protein. The effect, they claimed, was not due to any toxic action of lignin but was a result of interaction between lignin and protein. Waksman and Cordon (64) and Fuller and Norman (23) found similar depressive effects in cellulose decomposition. They attributed this to the physical

binding together of lignin and cellulose. Olson, Peterson and Sherrard (44) and Levine and others (32), on the other hand, claimed the binding to be of a chemical rather than a physical nature.

Bennett (12) studying the decomposition of oat hay, corn stilage, timothy hay and corn stalks with and without the addition of 13 percent lignin found that under certain conditions the presence of lignin was not inhibitory.

Waksman and Tenney (70) pointed out that lignins are more resistant to the actions of fungi and bacteria than are any of the other major ingredients of the natural organic materials. The accumulation of lignin in soil is believed by them to account for a large part of soil humus.

Waksman and Hutchings (66) summarized the accumulated evidence concerning the action of microorganisms upon lignin, in the process of decomposition of plant and animal residues in nature as follows:

- 1. Lignin is, among chemical complexes, most resistant to attack by fungi, bacteria and invertebrate animals living in soils, peat bogs and composts.
- 2. Lignin does not accumulate quantitatively in the same state in which it exists in plant materials but undergoes a slow process of transformation.
- 3. Certain specific groups of microorganisms, found largely among the higher fungi, are capable of bringing about active destruction of lignin, frequently even to a greater extent than that of



cellulose and hemicellulose.

- 4. Lignin is subject to decomposition by these organisms so long as it is present in fresh or in partly decomposed plant tissues; once it is prepared in a purified state, it becomes completely resistant to attack even by these organisms.
- 5. The effect of lignin upon microbial activities, such as cellulose decomposition, glucose fermentation and nitrate formation, is not injurious and may even be favorable.
- 6. The gradual transformation of the lignin consists in:
 - a. a loss of methoxyl groups
 - b. darkening in color, accompanied by absorption of oxygen
 - c. combination with protein
 - d. increase in alkali solubility

Although lignin is resistant to attack by microorganisms, it does not possess antiseptic properties (53). It will decompose gradually with the rate of decomposition depending upon environmental conditions (9, 47).

Norman (43) found that under aerobic conditions and in situ lignin is quite stable, but undergoes a slight decomposition during fermentation extending over months or years. Fungi of the Basidiomycetes type slowly attack lignin as well as cellulose and the hemicellulose. Under anaerobic conditions, lignin is slowly attacked by both mesophilic and thermophilic organisms, but to a lesser



extent than are other plant constituents. Isolated lignin is not attacked by aerobic and anaerobic microorganisms and apparently has a definite bacteriostatic action.

Fuller and Norman (23) found that the extent of decomposition accomplished by the vigorous organisms, Pseudomonas ephemerocyanea, and Sporocytophaga myxococcoides, increased as the lignin content was reduced. Less vigorous organisms such as Bacillus apporhoeus were little affected by the lignin content of the substrate.

Fischer and Schrader (22) showed the relative biological inertness of lignin, and concluded that lignin was therefore the "mother substance" of residual soil organic matter.

Gottlieb and Geller (24) found that lignin could be decomposed by using commercial mushroom spawn as an enzyme which is an intimate mixture of mycelium of Agaricus campestris and well decomposed horse manure. The enzyme was activated by citrate and phosphate ions and buffered to pH 6.0.

Denkho (18) claimed that lignin decomposes faster in an acid medium than in a neutral or alkaline medium. As lignin is decomposed microorganisms immobilize nitrogen.

Bartlett, Smith and Brown (10) believed that there was some sort of direct chemical process which broke down the original "natural lignin" into a more readily available form before active microbiological decomposition set in.



III. LABORATORY STUDIES

Material used and procedure:

The lignin used in this investigation was received from Agricultural Residues Division, North Regional Research Laboratory, U. S. D. A., Peoria 5, Illinois. The lignin which had been prepared by saccharification of corncobs was not as free from carbohydrates as was anticipated.

If the work on the saccharification process is continued, they believe that the carbohydrate material can be reduced, but it will not be entirely eliminated. Table 1 shows the proximate analysis of the lignin used.

The soils used in this study were surface samples of Miami sandy loam and Brookston clay loam soils. The pH of the two soils was found to be 6.52 by Beckman pH meter. For convenience these soil samples are referred to by the soil type names throughout this thesis.

Three levels of "lignin" were applied to the two soils as follows:

L	0	0	tons	per	acre
L	2.5	2.5	tons	per	acre
L	5.0	5.0	tons	per	acre
L	7.5	7.5.	tons	per	acre

Each treatment was replicated four times, making a total of 32 pots.



TABLE 1

PROXIMATE ANALYSIS OF "LIGNIN" PRODUCED BY SACCHARIFICATION OF CORNCOBS IN SYNTHETIC LIQUID FUELS SEMI-WORKS PLANT, PEORIA, ILLINOIS. JUNE, 1950

	Percent
Lignin	42.53
Cellulose Monoethanolamine method (pentosan free) Alpha-cellulose (pentosan free)	42.10 14.20
Alcohol-benzene extractions	13.74
Pentosans	3.57
Titratable acidity (as SO3)	0.86
Alkali solubility (1% NaOH)	66.27
Methoxyl	6.37
Moisture	6.70
N (Kjeldahl)	0,23
Ash	0.87



One thousand grams of soil and "lignin" of the various rates were well mixed and put into half-gallon pots. The moisture content of each pot was maintained at approximately moisture equivalent with distilled water. After five weeks, the soils were air dried. Fifty grams of the air dry soil was sampled from each pot for aggregate analysis, while the remaining soil was passed through a two millimeter sieve for laboratory studies.

Unless otherwise stated, all the figures reported in the tables herein are averages of four replications.

Experimental:

A. Physical

(1) Aggregate analysis

Fifty grams of air dry soil was used for aggregate analysis according to Yoder's wet sieving method (74). The percentage of aggregates as affected by "lignin" treatment at various rates are shown in Tables 2 and 3.

The effect of "lignin" on the percentage of aggregates greater than 0.25 mm is shown by the curves presented in Figures I and II.

It can be seen from Tables 2 and 3 that the addition of "lignin" to the soil increased aggregation considerably. Since it was suggested by Tiulin (57) that only those aggregates larger than 0.25 mm are responsible for stable structure, special attention was given to those aggregates.



TABLE 2

AGGREGATE ANALYSIS OF MIAMI SANDY LOAM SOIL TREATED WITH DIFFERENT RATES OF "LIGNIN"

Particle size mm	Treatments percentage of total weight					
	LO	L 2.5	L 5.0	L 7.5		
> 4	5.22*	6.84	8.74	9.46		
2-4 1-2	3•32 4•60	3.48 4.64	3.58 5.76	4.18 5.22		
0.5-1	7.98	8.30	8.98	_ 8.22		
0.25 -0.5	23.76	24.24	22.10	22.76		
0.105-0.25	24.56	20.04	23,82	22.48		
< 0.105	30.56	32.46	27.02	27.68		

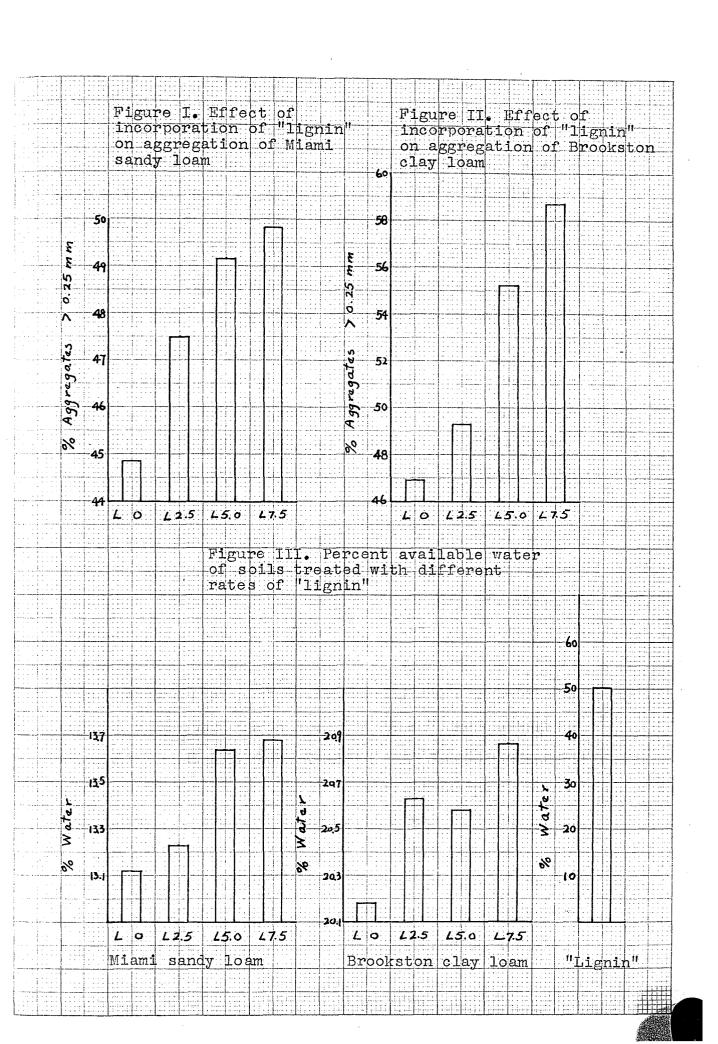
^{*}Average of three replications

TABLE 3

AGGREGATE ANALYSIS OF BROOKSTON CLAY LOAM SOIL TREATED WITH DIFFERENT RATES OF "LIGNIN"

Particle sîze mm	pe:	Treat: rcentage o	ments f total we:	ight
	LO	L 2.5	L 5.0	L 7.5
> 4	3.14	3.24	4.36	10.44
2-4	3.96	5.24	6.26	5.80
1-2	5.28	6.92	7.66	7.66
0.5 -1	10.42	10.94	12.78	12.14
0.25 -0.5	24.18	22.34	24.14	22.72
0.105-0.25	24.86	22.68	25.74	16.94
<0.105	28.16	28.6lf	19.06	24.30





As shown in Figures I and II, the percent aggregates greater than 0.25 mm increased with the rate of "lignin" application. This agrees with the results reported by Nikishkina (42).

It has been universally agreed that the soil colloidal material is responsible for the cementation of primary particles into stable aggregates. The soil colloids may be divided into at least three distinct groups so far as their cementation effects are concerned. They are clay particles themselves, irreversible or slowly reversible inorganic colloids, and organic colloids. As isolated lignin is generally considered to be of colloidal nature and since it possesses adsorptive properties (5, 19), it is believed that lignin itself may in one way or another bind the soil particles together to bring about increased aggregate formation. The nature of binding is, however, unknown. It could be a physical or chemical linkage or a combination of the two. Since experiments have shown that isolated lignin shows great affinity for positivelycharged basic dye, it is apparent that lignin possesses a negative charge. This suggests that the linkage between soil and lignin is more of a chemical than physical nature since clay particles are also negatively charged.

It is known that microbial products tend to cement soil particles. Since lignin promotes microbial activity (see Table 12), there is a possibility that the improved aggregation may be indirectly due to organism activity.



(2) Moisture equivalent

Thirty-gram samples of air dry soil were used for moisture equivalent determinations. Only 10-gram samples of the original material ("lignin") were used due to the bulkiness of this material. Briggs and McLane's method (16) which defines the term "moisture equivalent" as the amount of water held by soil against a force 1000 times gravity (equivalent to the centrifugal force at 2440 rpm for 30 minutes) was used. The percent moisture at moisture equivalent is shown in Table 4.

It is known that addition of organic matter to soil increases the percent moisture at moisture equivalent since organic matter has a high water holding capacity. Likewise it may result in a higher wilting point. The addition of lignin to soil gives results similar to those obtained from addition of organic matter. As indicated in Tables 4 and 5, there was a definite trend toward increased moisture percentages, at both moisture equivalent and hygroscopic coefficient, with increased applications of "lignin". It is not surprising that the increases are small when it is remembered that a five ton application is equal only to 0.5 percent of the soil.

(3) Hygroscopic coefficient

Ten-gram samples of air dry woil were weighed, oven-dried, and reweighed. The percent moisture (on the oven-dry soil basis) was calculated and is shown in Table 5.



TABLE 4

PERCENT MOISTURE OF SOILS TREATED WITH DIFFERENT RATES
OF "LIGNIN" AT MOISTURE EQUIVALENT

	L O	L 2,5	L 5.0	L 7.5	
Miami sandy loam	13.58	13.76	14.16	14.21	
Brookston clay loam	21.51	22.04	22.18	22.59	
"Lignin"					54.45

TABLE 5

PERCENT MOISTURE OF SOILS TREATED WITH DIFFERENT RATES OF "LIGNIN" AT HYGROSCOPIC COEFFICIENT

	ΓO	L 2.5	L 5.0	L 7.5	
Miami sandy loam	0.46	0.53	0.52	0.53	
Brookston clay loam	1.33	1.405	1.60	1.72	
"Lignin"					4.29



In studying soil moisture, one is often concerned with the amount of water available to plants which may or may not be increased by the addition of organic matter, as clearly shown by Feustel and Byers (20). For practical purposes, the term "available water" could be interpreted as the amount of water held at field capacity minus the amount of water held at hygroscopic coefficient, or for loams, the amount of water held at moisture equivalent minus the amount of water held at hygroscopic coefficient since it has been found (2, 52) that the field capacity for loams was about the same as moisture equivalent. The available water of the differently treated soils is thus compared in Figure III. Note the slight increase in available water for treated soils over that of check soil, and the tremendous amount of available water held by "lignin".

(4) Rheological properties

All the plasticity studies in this investigation were determined by Atterberg's procedure (6). Shown in Table 6 are percent moisture at upper and lower plastic limits, sticky point and plasticity number.

As indicated in Table 6, the addition of "lignin" increases the percent moisture at upper and lower plastic limits and sticky point despite the fact that "lignin" itself does not display any plasticity.

It has been demonstrated that in order for a soil to become plastic, sufficient water must be added to provide



TABLE 6

PERCENT MOISTURE OF SOILS TREATED WITH DIFFERENT RATES OF "LIGNIN" AT UPPER AND LOWER PLASTIC LIMITS,

STICKY POINT AND PLASTICITY NUMBER

	L 0	L 2.5	L 5.0	L 7.5
Upper plastic limit Miami sandy loam	24.32	25.27	25.18	26.08
Brookston clay loam	38.72	40.67	42.75	40.71
Lower plastic limit Miami sandy loam	17.28	17.52	18.38	18. կկ
Brookston clay loam	24.02	214.94	25•35	24.71
Sticky point Miami sandy loam Brookston clay loam	17•37 24•06	17.36 24.90	18.00 25.90	18.49 25.45
Plasticity number Miami sandy loam	7•05	7•75	6.80	7.64
Brookston clay loam	14.70	16.73	17.40	16.00



a film around each particle. The orientation of particles and their subsequent sliding over one another then takes place. Such orientation increases the amount of contact between the colloidal surfaces. This greater contact, together with an increase in the proportion of water-film surface to the particle mass, may be considered as producing the plastic effect.

Isolated lignin-like organic matter has a high absorptive capacity for water. It takes up the first water added which would have been available for crientation of soil particles. Hydration of lignin must be fairly complete before sufficient water becomes available for film formation around mineral particles. Consequently, the plasticity limits and sticky points occur at relatively high moisture content. This means that the lignin-treated soil would be less easily puddled. It means also that soil working tools would be less likely to "scour" in soil where lignin was added.

Russel (50) has reported that the plasticity number is a linear function of the clay content (5 u particles). The plasticity number as shown in Table 6 changes with "lignin" addition although the clay content remains relatively constant. Baver (11) pointed out that the plasticity number was proportional to the ratio $(\frac{F_1 - F_2}{F_1F_2})$ where F_1 and F_2 are the film tensions at upper and F_1 lower plastic limits. He claimed that the nature of colloidal material might change the proportionality constant. Since



lignin is different in nature from colloidal clay, it is possible for it to affect this constant.

(5) Porosity

The method of Learner and Shaw (31) was used for the determination of porosity with the modification that the soil passing through a two millimeter sieve was used instead of an undisturbed sample. The modification was necessary because of a limited amount of soil. Approximately equal amounts of soil were placed in the brass cylinders and determinations were made for total porosity, capillary porosity and porosity at 10, 20, 30, 40, and 60 cm water tensions. The data are tabulated in Tables 7 and 8.

In order to have a better evaluation of the data presented in Tables 7 and 8, percent porosity at various soil moisture tensions as affected by "lignin" treatments is shown graphically in Figure IV.

It can be noted from Figure IV that "lignin" alone showed very low porosity but when it was added to soil and allowed to stand for five weeks during which water was added periodically as described under procedure for laboratory studies, it increased percent porosity at varicus tensions and decreased the capillary porosity (Tables 7 and 8). This relation can be explained by the fact that "lignin" alone, due to its low force of cohesion, does not form stable aggregates and it holds water against various



TABLE 7

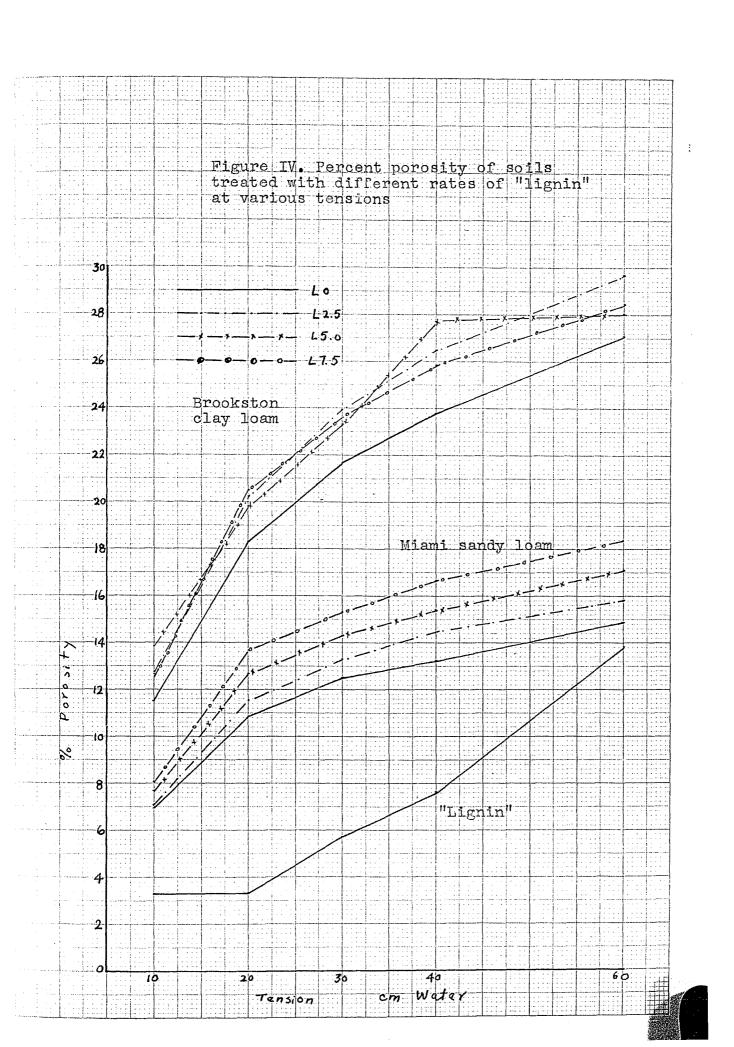
PERCENT POROSITY OF MIAMI SANDY LOAM SOIL TREATED WITH DIFFERENT RATES OF "LIGNIN" AT VARIOUS TENSIONS

	L O	L 2.5	L 5.0	L 7•5
Total porosity Porosity at	54.74	54.95	54.85	55.67
10 cm H ₂ 0	6.98	7.07	7.71	8.03
20	10.92	11.58	12.72	13,65
30	12.51	13.28	14.27	15.35
40	13.25	14.41	15.43	16.65
60	14.85	15.84	17.13	18.39
Capillary porosity	41.48	40.54	39.42	39.02

TABLE 8

PERCENT POROSITY OF BROOKSTON CLAY LOAM SOIL TREATED WITH DIFFERENT RATES OF "LIGNIN" AT VARIOUS TENSIONS

	L O	Г 2•2	L 5.0	L 7.5	"Lignin"
Total porosity	63.83	66.47	66.65	65.42	65.20
Porosity at 10 cm H ₂ 0	11.54	12.79	13.93	12.76	3•33
20	18.32	20,20	19.92	20.54	3.33
30°	21.65	23.99	23.27	23.60	5.71
40	23.82	26.50	27.72	25.83	7.63
60	27.15	29.70	28.05	28.45	13.81
Capillary porcsity	40.01	39•97	38.93	39.61	57.57



tensions with greater force because of its high water holding capacity which reduces percent porosity considerably. When it was added to soil on the other hand, it resulted in increased aggregation because of its strong adhesive force as illustrated in Tables 2 and 3. The relationship between size of aggregates and percent porosity has been demonstrated by Doiarenko (30). He found that as the size of aggregate increased, the total porosity and non-capillary porosity increased while the capillary porosity decreased.

It should be pointed out that total porosity is not as important for characterizing the structural properties of soils as is the relative distribution of the pore sizes. That is the relative proportion of capillary to non-capillary pores is a better measure of soil structure than is total space (11). The narrower the proportion of capillary to non-capillary pore spaces, the better the structure of the soil. A value of unity is considered to be ideal, since at this value, the large and small pores are about equally divided. The addition of "lignin" to soil tends to narrow this proportion and therefore improves the structure of the soil (Tables 7 and 8).

B. Chemical

(1) Exchange capacity determinations were made according to the methods prescribed by Peech, Dean, and Reed (46).

Twenty-five grams of air dry soil was shaken with 250 ml neutral N ammonium acetate solution, allowed to stand



for 20 minutes, and filtered.

Excess ammonium acetate was washed out from the ammonium-saturated soil with 250 ml 95 percent ethyl alcohol, using small portions at a time and draining well each time. Then the soil was leached with 200 ml 10 percent NaCl solution to extract adsorbed ammonium from the soil.

The NaCl extract was transferred to a Kjeldahl flask, to which NaOH was added to make an approximately N solution, and distilled into 50 ml of 4 percent boric acid. The distillate was titrated with standard 0.1 N HCl, using bromcresol green as indicator. The exchange capacities of the soils thus determined are shown in Table 9.

The results of the analyses of the base exchange capacities, given in Table 9, tend to demonstrate that "lignin" when added to soil slightly increases the exchange capacity. Different views have been expressed by various authors as to the cause of this increase. Bartlett and Norman (9) believed that the increase in base exchange capacity was due to an increase in activity of the lignin. Millar and his co-workers (37) agreed with them in that they found a change in the adsorptive capacity of lignin occurred on decomposition. Waksman and Iyer (68), on the other hand, attributed the increase in exchange capacity to the formation of a ligno-protein complex which has an exchange capacity considerably higher than that of lignin or protein alone. It is not possible to tell from the



TABLE 9

EXCHANGE CAPACITIES OF SOILS TREATED WITH DIFFERENT RATES OF "LIGNIN"

	Milliequivalents per 100 grams						
	Miami sandy loam	Brookston clay loam	"Lignin"				
r o	7.17	18.18	19.00				
L 2.5	7•43	18.37					
L 5.0	7•42	18.39					
L 7.5	7.59	18.61	,				



data reported in this study which hypothesis should be used to explain this increase.

The groupings active in retention of cations are likely to be phenolic hydroxyl groups and possibly carboxyl groups, though it is doubtful whether the latter are present in normal lignin (9).

It is believed that if a larger amount of "lignin" were used, the degree of increase in exchange capacity would also be increased. In this experiment, the highest level of "lignin" application was 0.75 percent (on a soil basis) of which only 42.53 percent was reported to be actual lignin (see Table 1).

The exchange capacity of the "lignin" used in this study was found to be 19 milliequivalents per 100 grams of the material. This is in close agreement with the value of 17.9 reported by Waksman and Iyer (68).

(2) pH measurement

To 25 grams of air dry soil was added 100 ml of distilled water. After stirring for one minute the pH of the sample was determined with a Beckman pH meter. The results are reported in Table 10.

Despite the low pH of the "lignin" material used, its addition to soil tended to increase the pH value of the soil slightly (see Table 10). Aries (4) also found this same type of increase. The increase in pH of the soil due to the addition of "lignin" can possibly be attributed to either one or both of the following two factors: First,



TABLE 10

ph of soils treated with different rates of "Lignin"

	Miami sandy loam	Brookston clay loam	"Lignin"
r o	6.52	6.52	1.99
L 2.5	6.81	6.89	
L 5.0	6.88	6.56	
L 7.5	6.90	6,58	



the increased adsorptive capacity of the treated soil which may retain more bases than the untreated soil, and second, the possible changes which lignin undergoes on decomposition. Bertramson and White (13) pointed out that there are at least two changes known to occur during decomposition of lignin which expose OH groups of the lignin molecule. These changes are partial demethylation and depolymerization both of which will cause an increase in pH value.

(3) Nitrate determinations were made according to the method suggested by Prince (49).

Fifty grams air dry soil were placed in a 500 ml flask, to which was added 1.5 grams of pulverized quick-lime (CaO) and 200 ml distilled water. Shaken for 3-5 minutes, allowed to stand for 20 minutes and filtered.

Fifty ml of the filtrate was placed in a 100 ml beaker and evaporated just to dryness on warm plate. When cool, the residues were moistened quickly and thoroughly with two ml phenoldisulfonic acid. The sides of dish were rubbed with a flat stirring rod and allowed to stand for 10 minutes.

After diluted with 20 ml water, excess ammonium hydroxide was added until yellow color was fully developed. The solution was made up to 50 ml with water and the nitrate content was determined colorimetrically, using a blue filter.



(4) Phosphate determinations were made according to methods suggested by Bray and Kurtz (15).

"Acid soluble and adsorbed" phosphate:

Seven ml of 0.1 N HCl-0.03 N NH₄F solution and one gram of air dry soil was placed into a flask, shaken for one minute and filtered.

To six ml of the filtrate were added five drops of NH_{ll}Mo-HCl solution and five drops F-S reagent. The transmission was read on Lumetron colorimeter in 5-6 minutes, using red filter (650 mu).

"Adsorbed" phosphate:

Same as above except the extracting reagent was 0.025 N HCl-0.03 N NH $_{\rm h}$ F.

(5) Ca, Mg determinations were made according to methods suggested by Cheng and Bray (17).

Ca:

Five grams air dry soil were shaken with 10 ml 23 percent NaNO3 for one minute and filtered. Five ml of the filtrate were diluted to 50 ml with water, to which were added two ml 10 percent KOH solution and 0.3 gram of indicator powder. The solution was stirred and titrated with 0.4 percent versenate solution to end point. The color was compared with standards. The solutions were saved for Mg determinations.

Mø.

Five ml $\mathrm{NH}_{\begin{subarray}{c} \mathrm{L}}\mathrm{Cl-NH}_{\begin{subarray}{c} \mathrm{NH}}$ OH buffer, one ml 2 percent KCN



solution and six drops F-241 indicator were added. The solution was stirred and titrated with 0.4 percent versenate solution to end point.

Note -- one ml of 0.4 percent versenate solution is equivalent to 0.435 mgm Ca or 0.198 mgm Mg.

(6) Determination of exchangeable Na and K in soil

To five grams of soil was added 0.5 gram ammonium
oxalate crystal and 50 ml of extracting solution (2 N NH₄Ac and 0.04 N ammonium oxalate). The solution was shaken,
allowed to stand overnight and filtered. The flask was
rinsed three times with the extracting solution. Made up
to 100 ml and the concentrations of Na and K were determined with flame photometer.

The results of chemical analyses are shown in Table 11.

Although Aries (4) reported an increase in soluble

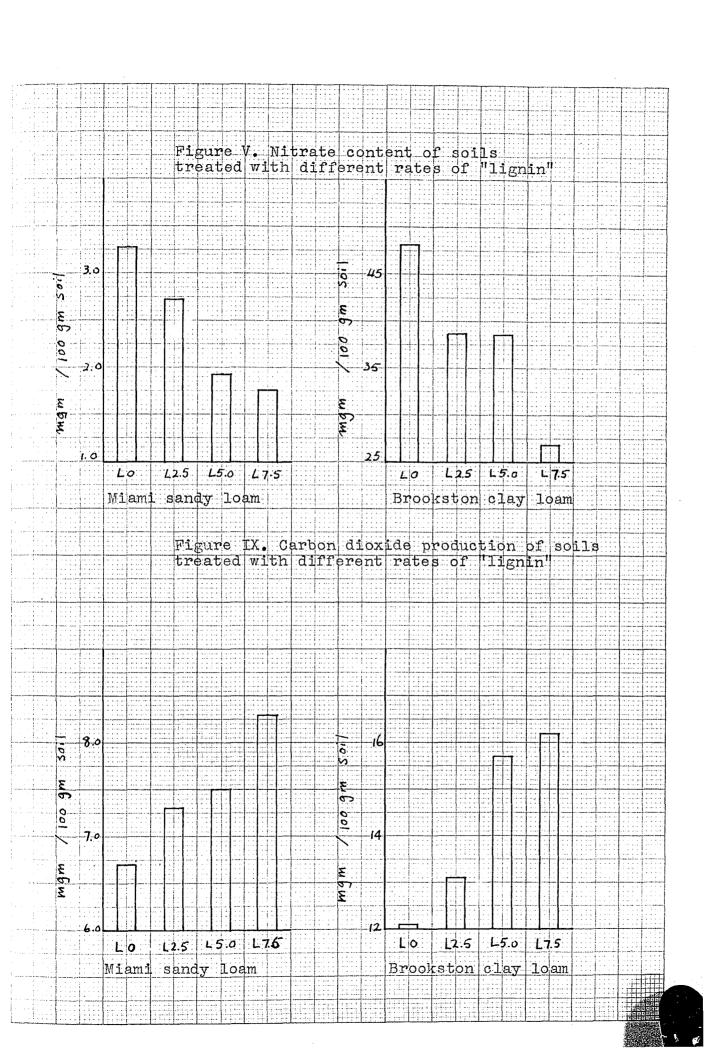
P and Ca of sulfite lignin-treated soil, it was not observed in this experiment. As can be seen from Table 11, the results of P, Ca, Mg, and Na determinations were rather inconsistent. "Lignin" did, however, cause an increase in the exchangeable potassium content of soil. It is interesting to note that "lignin"-treated soil contained a higher total content of exchangeable Ca, Mg, Na and K than did the untreated soil. It should also be noted that as the rate of "lignin" application increased there was a corresponding decrease in the nitrate content of the soil (Figure V). This change can be attributed to the increased



TABLE 11

TOTAL AND ADSORBED P (PPM), EXCHANGEABLE Ca, Mg, Na, K, AND NO (MGMS PER 100 GRAMS OF SOIL) OF SOILS TREATED WITH DIFFERENT RATES OF "LIGNIN"

		Miami sa	ndy loam		E	rookston	clay loam	1	"Lignin"
	r o	L 2.5	L 5.0	L 7.5	r o	L 2.5	L 5.0	L 7.5	
Total P	7.08	7.05	5.52	5.46	31.53	30.90	30.42	30.66	1.2
Ad. P	3.60	2.88	3.00	3.12	4.14	4.26	4.50	4.08	1.2
Ca	39.60	39.20	36.60	37.60	91.20	87.80	89.00	87.80	25.80
Mg	3.02	4.72	1.89	3.20	9.44	17.76	11.52	12.84	0
Na	4.80	4.92	4.72	7.20	3.42	3.38	3.94	4.42	7.00
K	3.04	2.92	3.72	3.32	12.90	14.54	14.56	16.66	0.50
NO ₃	3.28	2.72	1.92	1.76	48.08	38.64	38.56	26.80	4.56



microbial activity (see Table 12) which immobilized the soil available nitrate.

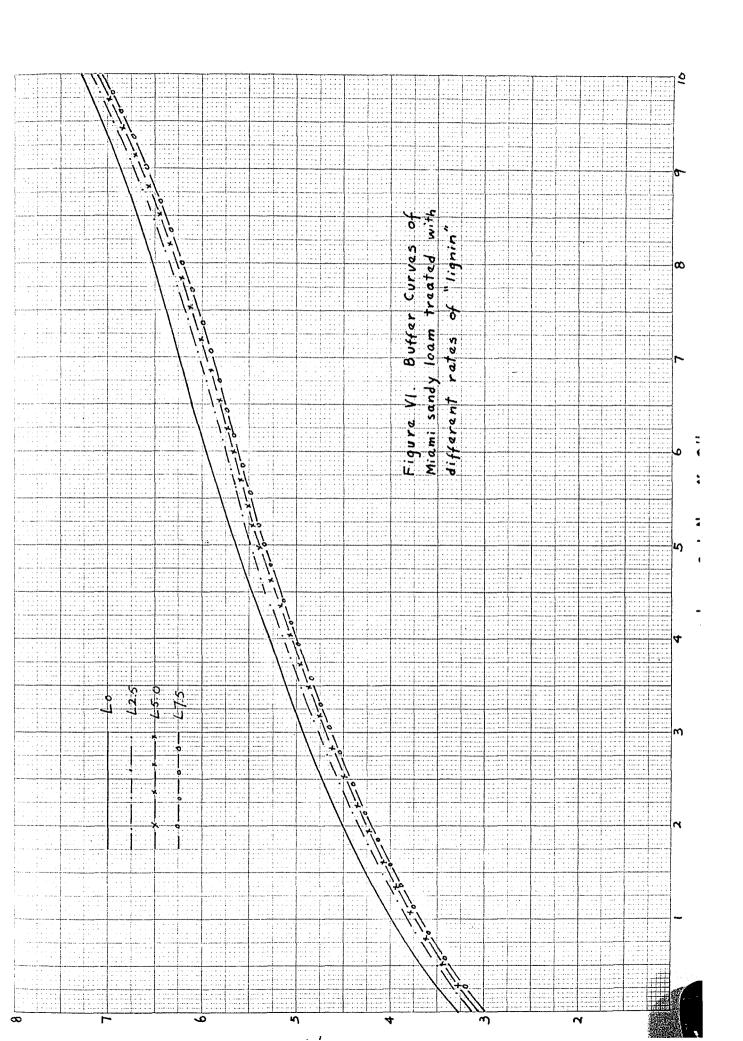
(7) Buffer curve

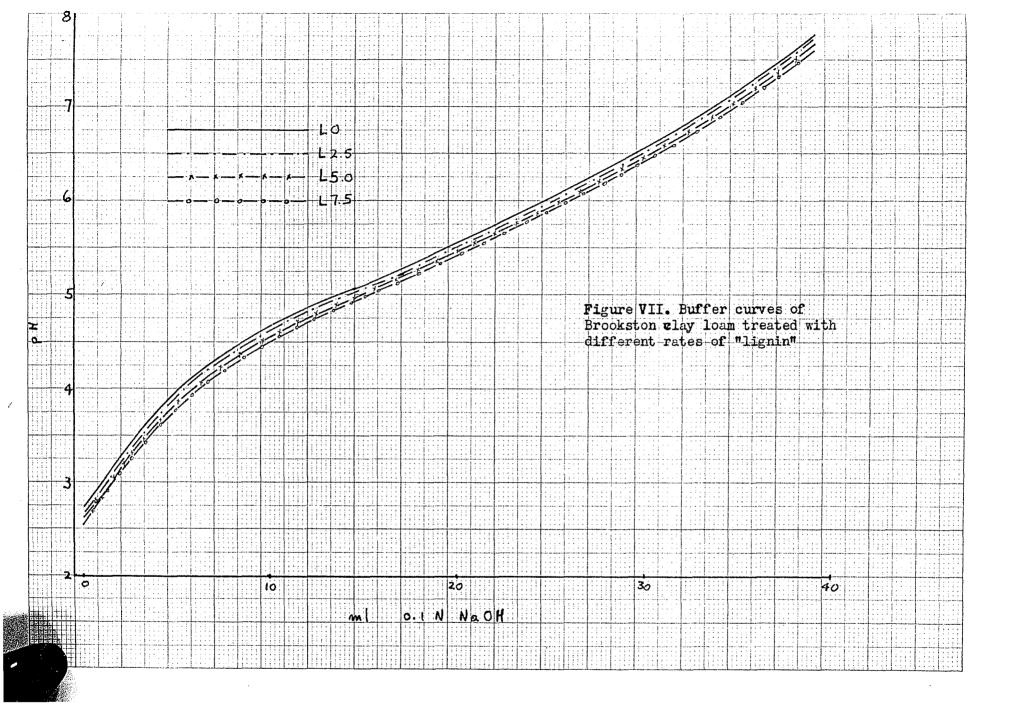
Twenty-five grams of air dry soil and 100 ml 0.1 N HCl were placed into a 250 ml Erlenmeyer flask, shaken, allowed to stand overnight and filtered. It was leached with additional 200 ml 0.1 N HCl and washed with 250 ml 95 percent alcohol and then with 300 ml of distilled water, adding a small portion at a time. The soil was transferred to 250 ml beaker and allowed to air dry. Twenty-five ml of water were added and the soil was titrated with 0.1 N NaOH potentiometrically. The "lignin" was washed only with water. After air drying, 25 ml water and BaCl₂ in excess were added and then titrated with 0.106 N NaOH potentiometrically. The results are shown in Figures VI, VII, and VIII.

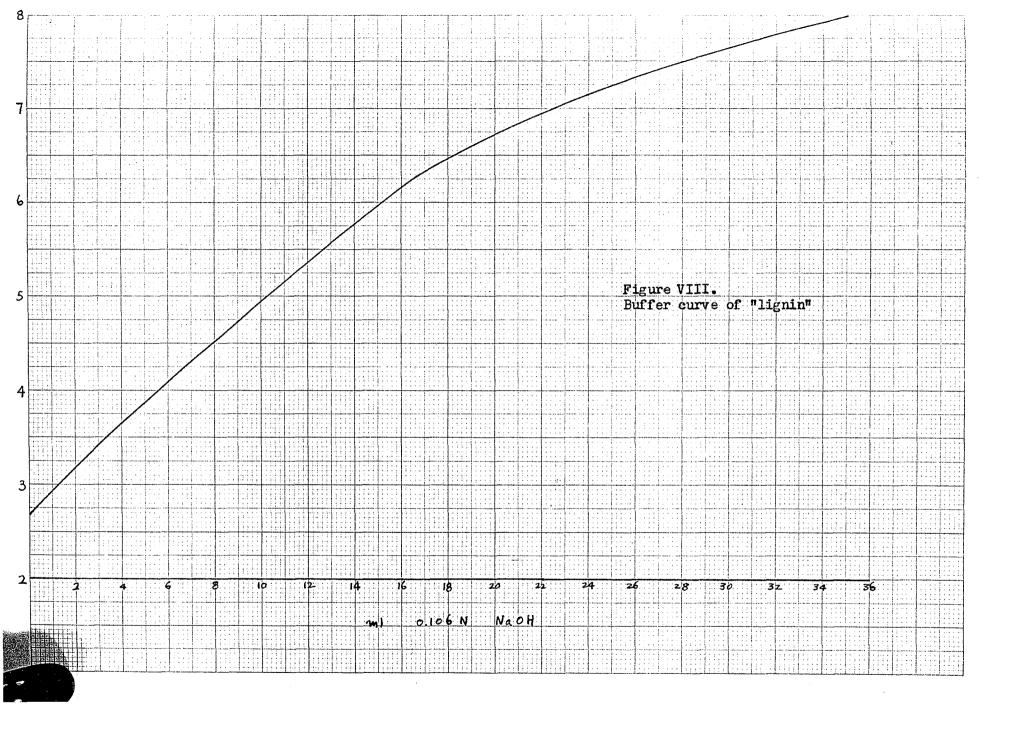
It appears that the buffer capacity of both soils was slightly increased as a result of "lignin" addition. The greatest buffer action of "lignin" lies between pH 6.5 and 8.0 (see Figure VIII).

A comparison between the pH of the H-saturated "lignin" and that of original "lignin" reveals that there was an increase of 0.71 in the pH value of the former. This difference leads one to suspect that some change had taken place during the hydrogen saturation process. The nature of the change is unknown.









C. Biological

One method for measuring changes in the metabolic activities of soil microorganisms is to measure carbon dioxide production in the soil. The carbon dioxide production in this experiment was determined according to Waksman's method (62). One hundred grams of air dry soil was placed in a 125 ml Erlenmeyer flask. Sufficient water was added to bring the soil to moisture equivalent according to the data recorded in Table 4. The apparatus used in this experiment is diagrammed in Figure X. Air was passed successively through a strong NaOH solution, over the soil, and through a standard KOH solution. Air flow was regulated to approximately 20 bubbles per minute and allowed to flow for a period of five minutes. This process was repeated after a period of two days and again before titration two days later. The KOH solution was titrated with standard HCl and the weight of carbon dioxide evolved from the soil calculated. The data obtained in this experiment are shown in Table 12.

The results of this experiment indicate that the addition of "lignin" to the soil stimulated the microbial activity. The increase in carbon dioxide, as illustrated in Figure IX, indicated that decomposition of the "lignin" material was taking place. As shown by the data reported in Table 1, the "lignin" material used in this study contains 56.3 percent cellulose and 42.53 percent lignin. This



TABLE 12

CARBON DIOXIDE PRODUCTION OF SOILS TREATED WITH DIFFERENT RATES OF "LIGNIN"

	Milli	grams per 100 grams s	oil
	Miami sand y loam	Brookston clay loam	"Lignin"
r o	6.7068	12.075	18.400
L 2.5	7.2818	13.110	
L 5.0	7.4570	15.699	
L 7.5	8.2800	16.160	



complicates the problem of determining whether the lignin or the cellulose was being attacked by the soil microrganisms. Many workers have shown that isolated lignin was quite resistant to microbial attack. Others (63) indicated that lignin was not absolutely resistant to decomposition but could be gradually oxidized by certain fungi. The latter, however, takes a relatively long time whereas the "lignin" and soil in this experiment were incubated only five weeks. It is believed that the period of incubation in this experiment was not long enough to bring about any considerable transformation of the "lignin" material. It is, therefore, concluded that most of the increased carbon dioxide production which resulted from the applied "lignin" was due to the decomposition of the cellulose contained in the "lignin" material.



IV. GREENHOUSE STUDIES

Procedure:

Two split plot experiments were designed to study the effect of "lignin" used as a mulch and mixed with soil on the yield of tomatoes (Stokesdale) and spring wheat (Henry), with and without fertilizer and lime on Miami sandy loam soil. The plants were grown in two-gallon jars and each experiment was replicated four times. The treatments used in these experiments are outlined below:

1. "Lignin

Rate of application

0 tons per acre L 0

2.5 tons per acre L 2.5

5.0 tons per acre L 5.0

7.5 tons per acre L 7.5

2. Fertilizer

4-16-8 for tomatoes; 3-12-12 for spring wheat

Rate of application 0 lbs/acre F 0
1000 lbs/acre F 1

3. Lime

Rate of application 0 lbs/acre 1000 lbs/acre

"Lignin", fertilizer and lime were mixed with the soil just before transplanting of the tomato plants or seeding of spring wheat. "Lignin" was applied as a mulch when the plants had recovered from transplanting or after thinning in case of wheat. Watering was done with distilled water.



A. Experiment with Tomatoes on Miami Sandy Loam

The effect of "lignin" on tomato yields is shown in Table 13.

It can be noted from the data that the average yields of tomatoes in "lignin"-treated soils exceeded significantly those from untreated soils. The increase was in proportion to the "lignin" treatment up to the five ton rate. The relationship did not hold for the 7.5 ton "lignin" application. This coincides with the results reported by Aries (4) and U. S. Forest Product Laboratory (26).

A breakdown of Table 13 gives interesting results which are tabulated in Table 14.

It is apparent that mulching, fertilizer application and liming increased the effectiveness of "lignin". Note the depressive effect of mixing at high level of "lignin" application where no fertilizer and lime were used. This suggests that the drop in yield beyond five tons per acre was due probably to the lack of nitrogen supply.

B. Experiment with Wheat on Miami Sandy Loam

Twenty wheat seeds were sown in each pot. After the seedlings reached 1-1.5 inches high, they were thinned down to six plants per pot. After the plants were mature, the heads were harvested, threshed and the weight of grains recorded. The yield of spring wheat grains as affected by different rates of "lignin" application is shown in Table 15.



TABLE 13

EFFECT OF "LIGNIN" ON THE YIELD OF TOMATO PLANTS
GROWN ON A MIAMI SANDY LOAM SOIL

		Grams per pot				Average
		Fert	ilized	Not fe	rtilized	
		Lime	No lime	Lime	No lime	
r o		162.2	123.6	141.4	103.1	132.6*
L 2.5	mulched mixed	180.0 165.5	148.7 179.5	174.7 176.5	201.2 164.7	173.8
L 5.0	mulched mixed	214.5 193.5	218.7 163.7	221.5 155.2	195.2 176.0	192.3
L 7.5	mulched mixed	228.8 161.7	199.7 170.0	218.5 84.5	204 . 5 76 . 0	167.9

TABLE 14

EFFECT OF MULCHING, FERTILIZER AND LIMING ON THE USE
OF "LIGNIN" -- MIAMI SANDY LOAM SOIL

		Yiel	d of tomato	in grams per	pot	
	Mulched	Mixed	Fertilized	Not fertilized	Lime	No lime
r o	13	2.6	142.90	122.30	151.85	113.40
L 2.5	176.15	171.55	168.40	179.30	174.20	173.50
L 5.0	212.48	172.10	197.60	187.20	196.05	188.40
L 7.5	212.98	133.05	190.05	145.90	173.40	162.55
Ave.	200.53	152.32	174.74	158.70	173.88	159.46
L.S.D. 5% 1%	4.34 5.75	·	4.40 5.83		4.31 5.75	



TABLE 15

EFFECT OF "LIGNIN" ON THE YIELD OF SPRING WHEAT GROWN ON MIAMI SANDY LOAM SOIL

			Grams per	six plar	nts	Average
		Feri	ertilized Not fertilized			
		Lime	No lime	Lime	No lime	
r o		2.13	2.38	1.70	1.51	1.93*
L 2.5	mulched	3.45	2.75	1.96	1.51	2,55
	mixed	3.20	2.91	2.28	2.38	
L 5.0	mulched	3.16	3.29	2.77	2.33	2.89
	mixed	2.69	3.34	2.47	2.66	•
L 7.5	mulched	2.47	3.39	1.85	2.36	2.33
	mixed	2.08	3.27	1.73	1.51	
L.S.D.	5% - 0.10	05; 1% -	0.135		•	



Again, the average yield of wheat grown on "lignin"treated soil was significantly higher than on the control
soil. The increases show a similar trend to that obtained
with tomatoes (Table 13). Mulching and liming, however,
did not have any favorable influence on the increases
which resulted from "lignin" application. This is shown
in Table 16.

From these two experiments, it seems that the optimum rate of "lignin" application was five tons per acre.

Comparison of the Effect of "Lignin" with Ground Corncobs and Sawdust Used as Mulches and as Mixture with Brookston Clay Loam on the Yield of Tomatoes and Spring Wheat

Another two experiments were designed to compare the effect of "lignin" with ground corncobs and sawdust which are often used as mulching material and mixed with soil. These two experiments were carried out with Brookston clay loam soil under greenhouse conditions. The treatments involved were as follows:

Rate of application

1. Material

Check				
"Lignin"		tons		
Ground corncobs		tons		
Sawdust	5	tons	per	acre

2. Fertilizers

0-12-12		1000	lbs.	per	acre	$N_{\rm C}$
6-12-12		1000	lbs.	per	acre	Νη
12-12-12		1000				
18-12-12		1.000				B



TABLE 16

EFFECT OF MULCHING, FERTILIZER, AND LIMING ON THE USE OF "LIGNIN" -- MIAMI SANDY LOAM SOIL

	Yie	eld of sp	oring wheat -	grams per s	ix plant	s
	Mulched	Mixed	Fertilized	Not fertilized	Lime	No lime
r o	1.94		2.28	1.60	1.94	1.94
L 2,5	2.41	2.79	3.18	2.02	2.83	2.38
L 5.0	2.89	2.79	3.12	2.56	2.77	2.91
L 7.5	2.50	2.15	2.81	1.86	2.09	2.65
Ave	2.45	2.41	2.85	2.01	2.41	2.47
L.S.D. 5% 1%	0.079 0.105		0.081		0.079	



C. Experiment with Tomatoes on Brookston Clay Loam

Effect of the different organic materials, with and without nitrogen on the yield of tomatoes is shown in Table 17.

The results of this experiment (Table 17) indicate that the application of sawdust to soil significantly decreases the tomato yield. Allison (1) attributed the depressive effect of sawdust to the formation of toxic constituents, such as tannins, resins, and turpentine, to an increase in soil acidity, and to the depletion of available nitrogen.

The average yields of tomatoes on soils treated with corncobs and "lignin" were not significantly larger than they were on the control soils. It should be noted, however, when nitrogen was supplied at a rate of 180 pounds per acre, the tomato yields of "lignin"-treated soil were significantly increased over those obtained where "lignin" was not applied but where nitrogen was applied.

D. Experiment with Spring Wheat on Brookston Clay Loam

A similar experiment was carried out using spring wheat and three levels of nitrogen fertilizer. The results of three replications are shown in Table 18.

The results of the experiment indicate (Table 18) that application of "lignin", ground corncobs, and sawdust significantly increased the yield of spring wheat. A



TABLE 17

COMPARISON OF THE EFFECT OF "LIGNIN", SAWDUST, AND GROUND CORNCOBS ON THE YIELD OF TOMATO PLANTS GROWN ON BROOKSTON CLAY LOAM SOIL

			Grams	per pot	
		Check	Corncobs	Sawdust	"Lignin"
NO	mulched	126	141	113	114
Ů	mixed		90	80	113
N_{1}	mulched	170	240	191	161
	mixed		149	140	184
N_2	mulched	261	267	241	222
	mixed		228	187	234
N 3	mulched	278	281	179	329
	mixed		293	268	316
	Average	206.1	207.3	170.1	209.1
	L.S.D. 5% - 15.83;	1% - 20	96		

TABLE 18

COMPARISON OF THE EFFECT OF "LIGNIN", SAWDUST, AND GROUND CORNCOBS ON THE YIELD OF SPRING WHEAT GROWN ON BROOKSTON CLAY LOAM SOIL

	Check	Corncobs	Sawdust	"Lignin"
N _O mulched	3.24	4.23	3.37	4.18
mixed		2.93	3.16	2.98
N ₁ mulched	3.32	5.19	4.63	4.69
mixed		3.74	3.76	4.64
No mulched	3.74	3.81	3.99	4.52
mixed		4.02	3.47	4.47
Average	3.43	3.99	3.73	4.25

comparison of the results from these three materials show that average yield of wheat was highest on "lignin"-treated soil, intermediate on corncob-treated soil and least on the sawdust-treated soil.

Mulching in this experiment resulted in yields definitely higher than were obtained where the materials were mixed with soil at a low nitrogen level. At the highest nitrogen level, however, the difference in favor of mulching was less marked.



V. FIELD STUDIES

An experiment designed to compare various mulching materials was carried out in the field. The experiment was located on Metea loamy sand soil on the Michigan State College Farm at East Lansing, Michigan. Soybeans were planted on June 9, 1952, in 28 inch rows 14 feet long. There were four rows in each plot. On June 25, 0-20-20 at the rate of 1000 pounds per acre was sidedressed and enough ammonium nitrate to make four levels of nitrogen was applied by broadcasting. The nitrogen applied was enough to raise the 0-20-20 grade to grades containing 0, 6, 12, 18 percent nitrogen, respectively. Ground corncobs, wheat straw and sawdust were applied as mulches at a rate of five tons per acre. The field was cultivated three times, twice before and once after the mulching. The beans of the central two rows were harvested on October The average yields of shelled beans are shown in Table 19.

The results of this experiment indicate that the use of mulch without nitrogen application had a depressing effect on the yield of soybeans. When nitrogen was applied at a rate of 60 pounds per acre, the depressive effect was minimized. A slight increase in yield by mulching with the exception of wheat straw was obtained when 120



TABLE 19

EFFECT OF VARIOUS MULCHING MATERIALS ON THE YIELD OF SOYBEANS GROWN ON METEA LOAMY SAND SOIL

		Grams per	two rows		
	Check	Corncobs	Wheat straw	Sawdust	Average
м ^О	1007	794	816	817	858
Nı	1085	1085	1072	1079	1080
N_2	1167	1280	1245	1188	1220
^N 3	1313	1329	1294	1345	1320
Ave.	1143	1122	1107	1107	



and 180 pounds of nitrogen per acre was applied.

Others (48, 60) have observed similar depressing results in yield when no nitrogen was added. The factors causing the decrease in yield by mulching at low soil nitrogen levels can be summarized as follows:

- 1. reduction of nitrate production (58, 39)
- 2. retarded accumulation of nitrate in soil (14, 27, 29, 40)
- 3. decrease in total exchangeable bases (59)
- 4. increased biological activity immobilizes the available nitrogen in soil (21, 40)
- 5. presence of toxic substances in mulching material (1, 56)
- 6. increase in soil acidity (1)

Favorable effects of mulching have also been reported such as increase in replaceable potassium under straw mulch (7, 8, 73, 74) and improvement in physical properties of soil.

The results of this field experiment tend to show that when no nitrogen was added the detrimental effects of mulching masked the beneficial effects. When sufficient nitrogen was applied, the depressive effects, as pointed out above, were reduced and a slight increase in yield was obtained if 180 pounds of nitrogen per acre was added.



VI. SUMMARY

- 1. Surface soil from Miami sandy loam and Brookston clay loam, well mixed with "lignin" at 0, 2.5, 5.0, and 7.5 tons per acre and with moisture maintained approximately at moisture equivalent for five weeks were brought to the laboratory for studies of their physical, chemical, and biological properties.
- 2. The addition of "lignin" to soil increased the aggregates greater than 0.25 millimeter, percent moisture at moisture equivalent, hygroscopic coefficient, plastic limits, sticky point and amount of available water. It also increased percent porosities at various tensions and decreased percent capillary porosity.
- 3. Mixing "lignin" with soil increased slightly the base exchange capacity, buffer action, pH and exchangeable potassium whereas total and adsorbed phosphate, exchange-calcium, magnesium and sodium were not affected.
- 4. In greenhouse experiment, Miami sandy loam surface soil produced higher yields of tomatoes and spring wheat on "lignin"-treated soils. The average yield was highest on soil which received five tons per acre of "lignin".

 Application of fertilizer and lime and mulching increased the effectiveness of "lignin" on the yield increase of tomatoes but the latter two did not materially affect that of spring wheat.

- 5. A comparison between the effect of ground corncobs, sawdust and "lignin" (at five tons per acre) used as mulch and mixed with soil on the yield of tomato and spring wheat was studied on Brookston clay loam surface soil in the greenhouse. The results showed that "lignin" was preferable to corncobs and sawdust when mixed with soil. When used as mulches, "lignin" and corncobs were preferable to sawdust.
- 6. Mixing these materials with soils resulted in decreased yields. The least depression occurred with "lignin".

 The depressive effect gradually disappeared as the rate of nitrogen application increased.
- 7. The effect of sawdust, wheat straw and ground corncob mulches on the yield of soybeans was studied on the Metea loamy sand soil at the Michigan State College Farm, East Lansing, Michigan. The results indicated that when no nitrogen was applied they all decreased the yield of soybeans. The detrimental effect was in the following order: wheat straw = sawdust > ground corncobs. The depressive effect was minimized when nitrogen was applied at a rate of 60 pounds per acre. Where 120, and 180 pounds of nitrogen per acre were added, an increase in soybean yield was obtained.



VII. CONCLUSIONS

- 1. "Lignin" produced from saccharification of corncobs improved both the physical and chemical properties of the surface soils from Miami sandy loam and Brookston clay loam.
- 2. The incorporation of "lignin" depletes available soil nitrogen but to a lesser extent than was the case with ground corncobs and sawdust.
- 3. On the average, "lignin" applied at a rate of five tons per acre gave the highest yield of both the tomato and spring wheat under greenhouse conditions.
- 4. Where "lignin" is available and can be procured at reasonable cost, it can be used to advantage over ground corncobs and sawdust when applied at five tons per acre.



VIII. LITERATURE CITED

- Allison, F. E. and M. S. Anderson. Use of sawdust for mulches and soil improvement. U. S. Ag. Circ. 891: 1-19, 1951.
- 2. Alway, F. J. and G. R. McDole. Relation of water-retaining capacity of a soil to its hygroscopic coefficient. Jour. Agr. Res. 9: 27-71, 1917.
- 3. Anderson, C. C. Cation exchangers from sulfite liquor. Kgl. Norske Videnskab. Selskabs, Forh. 22(18): 70-75, 1949. Published in 1950 in English.
- 4. Aries, R. S. Lignin as a fertilizer material. Paper Trade Jour. 123: 47-51 N21, 1946.
- 5. Aries, R. S. Research on lignin as a soil builder. Northeast Wood Utilization Council Bull. No. 7: 56-62, 1945.
- 6. Atterberg, A. Die Plastizal der Tone. Intern. Milt. Bodenk. 1: 10-43, 1911.
- 7. Baker, C. E. Effectiveness of some organic mulches in correcting K deficiency in peach trees on a sandy soil. Proc. Amer. Soc. Hort. Sci. 51: 205-208, 1948.
- 8. Baker, C. E. Further results on the effect of different mulching and fertilizer treatments upon the K content of apple leaves. Proc. Amer. Soc. Hort. Sci. 42: 7-10, 1943.
- 9. Bartlett, J. B. and A. G. Norman. Changes in the lignin of some plant materials as a result of decomposition. Proc. Soil Sci. Soc. of Amer. 3: 210-216, 1938.
- 10. Bartlett, J. B., F. B. Smith and P. E. Brown. Lignin decomposition in soils. Proc. Iowa Acad. Sci. 44: 97-101, 1937.
- 11. Baver, L. D. Soil Physics. John Wiley and Sons, Inc., New York, 1948.
- 12. Bennett, E. Decomposition of certain plant tissues with and without added lignin. Proc. Amer. Soc. Hort. Sci. 47: 252-254, 1946.
- 13. Bertramson, B. R. and J. L. White. Soil chemistry notes. Student Book Corp., Washington State College, Pullman, 1948.
- 14. Bischoff, A. Straw as a fertilizer under various conditions. Jour. Landw. 62: 1-95, cited in U.S.D.A. Exp. Sta. Rec. 31: 226, 1914.



- 15. Bray, R. H. and L. T. Kurtz. Determination of total, organic and available form of P in soils. Soil Sci. 59: 39-45, 1945
- 16. Briggs, L. J. and J. W. McLane. The moisture equivalent of soils. U.S.D.A. Bur. Soils Bull. 45, 1907.
- 17. Cheng, K. L. and R. H. Bray. Determination of Ca and Mg in soils and plant material. Soil Sci. 72: 449-458, 1951.
- 18. Denkho, Khan. Influence of the reaction of the medium on the decomposition of organic matter in soils at various C:N ratios. Trans. Dokuchaov Soil Inst. (U.S.S.R.) 23: 139-144, 1940. In English, 1945.
- 19. Dunn, S. and J. Seiberlich. Uses of lignin in agriculture. Mech. Eng. 69: 197-198, 212, 1947.
- 20. Feustel, I. C. and H. G. Byers. The comparative moisture-absorbing and moisture-retaining capacities of peat and soil mixtures. U.S.D.A. Tech. Bull. 532, 1936.
- 21. Fight, I. A. Corncob mulch. Horticulture 27: 403, 1949.
- 22. Fischer, F. and H. Schrader. On the origin and chemical structure of coal. Brennstoff Chem. 14: 147, 1937.
- 23. Fuller, W. H. and A. G. Norman. Effect of lignin on cellulose decomposition by aerobic mesophilic bacteria from soil. Jour. Bact. 46: 291-297, 1943.
- 24. Gottlieb, S. and J. H. Geller. Enzymatic decomposition of lignin. Science 110: 189-190, 1949.
- 25. Gottlieb, S. and S. B. Hendricks. Soil organic matter as related to newer concepts of lignin chemistry. Proc. Soil Sci. Soc. of Amer. 10: 117-125, 1945.
- 26. Harris, E. E. Lignin for better crops. U.S.D.A. Yearbook, p. 883-885, 1950-1951.
- 27. Harris, G. H. Sawdust as a mulch for strawberries. Scientific Agriculture 31: 52-60, 1951.
- 28. Honcamp, F. and H. Wiessmann. Experiments on the fixation of the N of liquid manure by "humus coal" and lignin. Z. Pflanzenernahr. Dungung u. Bodenk. 17A: 194-199, 1930.
- 29. Johnson, W. A. Effect of sawdust on the production of tomatoes and fall potatoes and on certain soil factors affecting plant growth.

 Proc. Amer. Soc. Hort. Sci. 44: 407-412, 1944.
- 30. Krause, Martin. Russian investigations in the field of soil structure (German). Landw. Jahrb. 73: 603-690, 1931.



- 31. Learner, R. W. and B. Shaw. A simple apparatus for measuring non-capillary porosity on an extensive scale. Jour. Amer. Soc. Agron. 33: 1003-1008, 1941.
- 32. Levine, M., G. H. Nelson, D. Q. Anderson, and P. B. Jacobs. Utilization of agricultural wastes; lignin and microbial decomposition. Ind. and Eng. Chem. 27: 195-200, 1935.
- 33. McCalla, T. M. Influence of microorganisms and some organic substances on soil structure. Soil Sci. 59: 287-297, 1945.
- 34. McGeorge, W. T. The base exchange property of organic matter in soils. Ariz. Agr. Exp. Sta. Tech. Bull. 30, 1930.
- 35. McGeorge, W. T. Organic compounds associated with base-exchange reactions in soils. Ariz. Agr. Exp. Sta. Tech. Pull. 31: 215-251, 1931.
- 36. Martin, J. P. and S. A. Waksman. Influence of microorganisms on soil aggregation and erosion. Soil Sci. 52: 381-294, 1941.
- 37. Millar, H. C., F. B. Smith, and P. E. Brown. The base exchange capacity of decomposing organic matter. Jour. Amer. Soc. Agron. 24: 753-766, 1936.
- 38. Miller, A. B. Stabilization of road soils. U. S. 2, 375, 019, May, 1945.
- 39. Mooers, C. A., J. B. Washko, and J. B. Young. Effects of wheat straw, lespedeza sericea hay, and farmyard manure, as soil mulches, on the conservation of moisture and production of nitrate. Soil Science 66: 307-315, 1948.
- 40. Murry, T. J. The effect of straw on the biological soil process. Soil Science 12: 233-259, 1921.
- 41. Neller, J. R. and W. H. Kelley. Wood waste ligning to produce soil organic matter of a stable nature. Proc. Soil Sci. Soc. Amer. 14: 212-215, 1949.
- 42. Nikishkina, P. I. Structure-forming materials. Pedology (U.S.S.R.): 667-674, 1946.
- 43. Norman, A. G. Biological decomposition of lignin. Science Progress 30: 442-456, 1936.
- 叫。Olson, F. R., W. H. Peterson, and E. C. Sherrard. Effect of lignin on fermentation of cellulosic materials. Ind. and Eng. Chem. 29: 1026-1029, 1937.



- 45. Osugi, S. and T. Endo. The effect of lignin upon the decomposition of protein. Jour. Sci. Soil Manure (Japan) 9(1): 15-24, 1935.
- 1.6. Peech, M. L., A. Dean, and J. F. Reed. Methods of soil analysis for soil-fertility investigations. U.S.D.A. Circ. 757, 1947.
- 1.7. Phillips, M., H. D. Weihe and N. R. Smith. Decomposition of lignified materials by soil microorganisms. Soil Sci. 30: 383-390, 1930.
- 48. Pinck, L. A., F. E. Allison and V. L. Gaddy. The effect of straw and nitrogen on the yield and quantity of nitrogen fixed by soybeans. Jour. Amer. Soc. Agron. 38: 421-431, 1946.
- 49. Prince, A. L. Determinations of total nitrogen, ammonia, nitrate and nitrite in soils. Soil Sci. 59: 47-52, 1945.
- 50. Russel, J. C. Variations in the B-horizon. Amer. Soil Survey Assoc. Bull. 9: 100-112, 1928.
- 51. Seay, W. A., J. O. Attoe and G. Truog. Elimination of Ca interference in photometric determination of Na in soils and plants. Soil Sci. 71: 83-90, 1951.
- 52. Shaw, C. F. The normal moisture capacity of soils. Soil Sci. 23: 303-317, 1927.
- 53. Smith, F. B. and P. E. Brown. Decomposition of lignin and other organic constituents by certain soil fungi. Jour. Amer. Soc. Amer. 27: 109-119, 1935.
- 54. Sowden, F. J. and H. J. Atkinson. Waste sulphite liquor solids as a soil treatment. Sci. Agr. 38: 175-182, 1948.
- 55. Sowden, F. J. and H. J. Atkinson. Composition of certain organic matter fractions. Soil Sci. 68: 433-440, 1949.
- 56. Standen, J. H. Toxic substances occurring in certain maize cobs. Boyce Thompson Inst. Contrib. 14: 277-281, 1946.
- 57. Tiulin, A. F. Questions on soil structure. II. Aggregate analysis as a method for determining soil structure. Perm. Agr. Exp. Sta. Div. Agr. Chem. Rpt. 2: 77-122, 1928.
- 58. Turk, L. M. Effect of sawdust on plant growth. Mich. Agr. Expt. Sta. Quar. Bull. 26: 10-22, 1943.
- 59. Turk, L. M. and N. L. Partridge. Effect of various mulching materials on orchard soils. Soil Sci. 64: 111-125, 1947.
- 60. VanDoren, C. A. and R. S. Stauffer. Effect of crop and surface mulches on runoff, soil losses, and soil aggregation. Proc. Soil Sci. Soc. Amer. 8: 97-101, 1944.

- 61. Vershinin, P. V. Theoretical problems of soil structure. Sovel Agron. No. 1: 22-26, 1948.
- 62. Waksman, S. A. Principles of soil microbiology. Ed. 2. The Williams and Wilkins Co., Baltimore, Md., 1932.
- 63. Waksman, S. A. Soil microbiology. John Wiley and Sons, Inc., New York, 1952.
- 64. Waksman, S. A. and T. C. Cordon. Method for studying decomposition of isolated lignin, and the influence of lignin on cellulose decomposition. Soil Sci. 45: 199-206, 1938.
- 65. Waksman, S. A. and I. J. Hutchings. The function of cellulose and lignin in the preservation of nitrogen in soils and composts. Soil Sci. 40: 487-497, 1935.
- 66. Waksman, S. A. and I. J. Hutchings. Decomposition of lignin by microorganisms. Soil Sci. 42: 119-130, 1936.
- 67. Waksman, S. A. and K. R. N. Iyer. Contribution to our knowledge of the chemical nature and origin of humus. I. The synthesis of the "humus nucleus". Soil Sci. 34: 43-69, 1932.
- 68. Waksman, S. A. and K. R. N. Tyer. Contribution to our knowledge of the chemical nature and origin of humus. III. The base exchange capacity of "synthesized humus" (ligno-protein) and of "natural humus" complexes. Soil Sci. 36: 57-67, 1933.
- 69. Waksman, S. A. and K. R. N. Iyer. Contribution to our knowledge of the chemical nature and origin of humus. IV. Fixation of proteins by lignin and formation of complexes resistant to microbial decomposition. Soil Sci. 36: 69-82, 1933.
- 70. Waksman, S. A. and F. G. Tenney. On the origin and nature of the soil organic matter or soil "humus". III. The substance contributing to the formation of humus. Soil Science 22: 323-333, 1926.
- 71. Waksman, S. A. and W. Wissen. Lignin as a nutrient for the cultivated mushroom, Agarious campestris. Sci. 72: 401, 1930.
- 72. Wander, I. W. and J. H. Gouley. K content of soil beneath a straw mulch. Science 86: 546-547, 1937.
- 73. Wander, I. W. and J. H. Gouley. Available K in orchard soils as affected by a heavy straw mulch. Jour. Amer. Soc. Agron. 30: 438-446. 1938.
- 74. Yoder, R. E. A direct method of aggregate analysis. Jour. Amer. Soc. Agron. 28: 337, 1936.