



# Utilization of Spent Pulping Liquor Lignin As Soil Conditioner

Harish Chandra<sup>1</sup>, Rakesh Dhaundiyal<sup>1\*</sup>, Sandeep Negi<sup>1</sup>, Deepali Singhal<sup>1</sup> and H V Pant<sup>1</sup>

<sup>1</sup>Associate Professor, Department of Chemistry, S G R R (PG) College, Dehradun 248001, India

Corresponding Author: rakesh21171@gmail.com

## Abstract

The small pulp and paper mill do not have chemical recovery plant because chemical recovery is the most capital intensive single unit operation in a pulp mill. Due to high capital cost, installing a chemical recovery for small mill is not viable. These mills either discharges the cooking liquor into nearby stream or on land which causes water and land pollution. The spent pulping liquor contain lignins as the major organic component responsible for pollution and since lignin is broadly non-biodegradable. The addition of organic matter to the soil usually increases the water holding capacity of the soil. This is because the addition of organic matter increases the number of micro pores and macrospores in the soil either by “gluing” soil particles together or by creating favourable living conditions for soil organism and ultimately soil condition improves. The present study attempt is made to increase the biodegradability by incorporation of nitrogen. The study revealed that the nitrogen enrichment enhanced the biodegradability of lignin. When this modified lignin applied to soil underwent humification and improved the physico chemical properties of soil.

**Key word: Lignin, biodegradation, Soil improvement, Lignin modification**

## I. INTRODUCTION

Lignin is the one of the most abundant biopolymer on earth accounting for 10- 40 % by weight (Kirk et al 1987). Lignin is a generic name of a complex high molecular weight, three dimensional aromatic biopolymer arising from an enzyme initiated dehydrogenative polymerization of trans- p- coniferyl, trans- p- sinapyl and trans – p- coumaryl alcohols in nature (Kirk et al 1987) .Lignin may have huge source of commercially value added aromatic compounds. But more than 98 % of the lignin produced by the pulp and paper industry is used as a fuel while only 2 % is used in the production of commercially value added aromatic compounds (Chan, et al 2020, Rodrigues et al 2018,). The large scale exploration of lignin as a source of value added aromatic compounds may be possible by the some modification in lignin structure. The pulp and paper mills produces large amount of black liquor as a consequences of pulping process. In country like India the mills, which are comparatively of low capacity and not possess the chemical recovery system, are discharging the spent liquor to adjoining recipients which brings forth serious environmental hazards and the same loss of value added aromatic compounds. The black liquors is rich in lignin which is very rich organic carbon contents (Tewari et al., 1988).

The lignin obtained from black liquor can be used to obtain soil conditioners. Soil conditioners were prepared by treating of water soluble lignin derivatives i.e lignosulfonates and nitrolignin with acrylic monomers. Water soluble lignin derivatives can be obtained by treating with nitric acid or nitric acid with KOH , sulfolignin activated lignin by alkali and CuO (Korányi, et al ., 2020), ammoniated nitrolignin etc. These modified lignin

improve the structure and properties of the soil. Modified nitrolignin increases the content of water stable aggregates which improve water and gas exchange in soil. That in result, improves the fertility.

The degradation of lignin into humus is may be free radicals reactions which are catalysed by extracellular enzymes. The transformation of lignin to humic acid at soil is possible at least by two pathways, the abiotic oxidation catalyzed by minerals or metal salts and the enzymatic oxidation by laccase and other oxidative enzymes (Gonzalo et al., 2016, Abdel-Hamid et al .,2013). Kononova (1996) while studying the process of transformation of organic matter in humus found that lignin and humus are very much similar in chemical constitution and lignin is major organic compound that converts into humus in soil and the humus is of enormous significances for improving physical, chemical and biological properties of soil.

The present study is attempt in the direction the lignin is enriched with nitrogen and its rate of humification was studied under controlled temperature and humidity condition. A pot-culture experiment was also conducted to assess the effect of lignin on soil properties.

## II EXPERIMENTAL

**Preparation of spent liquor:** Wheat straw, the raw material for pulping was procured from a nearby market. Storing of Wheat straw was done under atmospheric conditions in open area. The cooking condition employed for pulping of Wheat Straw are chemical charge (alkali) of 15 % on raw material basis was maintained. Bath ratio was 1:5 due to bulky nature of wheat straw “H” factor determines the rate of delignification per degree rise in temperature. At the end of pre-determined time for cooking, the digesters were cooled in water and after cooling the spent liquor was extracted from the pulp by squeezing through a nylon cloth. The resultant spent liquor free from suspended matter was stored at 4 degree C throughout the period of analysis to avoid changes taking place due to the biological activity at higher temperature and air.

**Isolation of lignin:** Black liquor lignin originated from wheat straw is used in the present study. The mechanism of lignin precipitation performed in three stages. In first stage, 8 hours after acidification using 4N H<sub>2</sub>SO<sub>4</sub> and agitation, dark colour precipitate was obtained as floating layer at the surface of solution. In the second stage, the liquor was resettled for 8 hours. In this stage the lignin precipitate was concentrated and filtrate came up at the surface replacing the lignin layer, which then can be siphoned to separate. In the third stage, another 8 hours precipitated was performed. The clear filtrate at the surface was again separated from the system. The colour of the precipitated lignin was dark brown while that of the filtrate was clear and yellowish.

**Modification of lignin:** The precipitated lignin was washed till free of acid and dried at 35-40 °C. It was enriched with nitrogen by treating in following ways (i) with urea at 120 °C (ii) Liquor ammonia (12 %) (iii) nitric acid in presence of oxygen and (iv) nitric acid in presence of KOH. The modified lignin was maintained at 25 °C temperature, 25 % moisture and 80 % humidity for 24 months for studying the rate of decomposition.

**Pot- Culture Study:** The plastic pots were filled with 5kg of soil mixed with untreated lignin and the modified lignin. The soil had 98 percent sand, 0.24 percent organic carbon.0.03 percent total nitrogen, 0.28 percent CaO, 0.26 percent MgO and traces of P<sub>2</sub>O<sub>5</sub> and 7.3 pH. The modified lignins were applied in four different does viz., 0.5 %, 1.0 %, 1.5 % and 2.5 % of soil. The pots were arranged in randomized block design with 6 replication.

**Analysis of Soil and Lignin:** Soil was analysed for mechanical composition, pH, calcium, magnesium, phosphorous and nitrogen by the method described by Jackson (1967). The water holding capacity and permeability were determined by adopting the methods given by Black (1965).

In order to find out the rate of decomposition of lignin and its transformation into humus, the lignin treated soil was analysed for carbon, nitrogen and functional groups. The organic carbon in the amended soil was determined by Walkey and Black titration and the nitrogen by Kjeldahl method. The phenolic and carboxylic functional groups were analysed by the potentiometric titration (Jackson 1967) .The methoxyl group were determined by converting the methoxyl groups to methyl iodide by heating with hydroiodic acid and the stream carrying methyl iodide was absorbed in alcoholic solution of silver nitrate to obtain silver iodide which was washed, dried and weighed (Kononova et al., 1961)

Table: 1 Change in Carbon and Nitrogen Content of Modified Lignin

Time	Urea Treated lignin			Ammonified lignin			Nitric Acid treated lignin			Nitric Acid/ KOH treated lignin		
	C	N	C:N	C	N	C:N	C	N	C:N	C	N	C:N
Initial Time	52.28	3.48	15.02	51.26	3.70	13.82	52.25	3.98	13.13	51.87	4.12	12.58
After 3 month	51.32	3.68	13.94	51.09	4.02	12.70	51.02	4.72	10.82	50.89	4.32	11.78
After 6 month	51.15	4.09	12.52	51.63	4.76	10.84	50.32	5.06	09.94	49.52	5.63	08.79
After 9 month	49.78	4.95	10.65	50.36	4.96	10.15	49.25	5.97	08.24	48.39	6.06	07.98
After 12 month	48.62	5.58	08.71	48.96	5.52	08.86	48.02	6.23	07.70	47.36	6.97	06.79
After 15 month	47.36	6.52	07.26	48.02	6.10	07.87	47.79	7.23	06.61	46.92	7.92	05.93
After 18 month	46.54	6.87	06.77	47.56	6.32	07.52	46.02	7.89	05.83	45.63	8.23	05.55
After 21 month	45.23	7.02	06.44	46.23	6.90	06.90	45.01	8.12	05.54	44.52	8.96	04.97
After 24 month	46.02	7.32	06.28	46.78	6.96	06.72	44.96	8.23	05.46	44.03	8.99	04.90

- Carbon and nitrogen in untreated lignin were 55.03 and 0.089 percent respectively and there were little change in C:N ratio was observed.

Table: 2 Functional Group Analysis of Lignin After 24 Months

Functional group	Untreated lignin	Urea treated lignin	Ammonified lignin	Nitric Acid treated lignin	Nitric Acid/ KOH treated lignin
Methoxyl	12.47	03.48	3.02	2.96	2.87
Total Hydroxyl	06.02	05.02	5.78	6.32	6.78
Phenolic Hydroxyl	01.89	02.96	3.46	4.26	4.78
Aliphatic Hydroxyl	05.2	3.24	3.12	2.96	2.71
Carboxyl	01.89	5.96	6.02	6.89	6.98

Table : 3 Effect of Modified Lignin on Some Soil Properties

Treatment	Lignin dose, %	Initial stage			After 6 month			After 12 month			After 18 month		
		pH	WHC	Perm	pH	WHC	Perm	pH	WHC	Perm	pH	WHC	Perm
Untreated lignin		7.25	12.89	0.022	7.20	12.78	0.027	7.19	12.70	0.026	7.16	13.025	0.022
Urea treated lignin	0.5	7.99	12.96	0.036	7.92	13.25	0.032	7.83	13.55	0.030	7.56	13.96	0.027
	1.0	8.02	13.02	0.032	7.98	13.89	0.030	7.80	13.99	0.028	7.23	14.20	0.020
	1.5	8.29	13.32	0.026	7.88	13.97	0.024	7.76	14.35	0.021	7.19	14.80	0.018
	2.0	8.52	13.52	0.023	7.80	14.20	0.020	7.67	14.68	0.019	7.15	14.90	0.017
Ammonified lignin	0.5	7.62	12.46	0.034	7.52	12.98	0.028	7.32	13.08	0.026	7.31	13.15	0.025
	1.0	7.50	12.92	0.026	7.42	13.09	0.026	7.22	13.22	0.024	7.20	13.32	0.023
	1.5	7.20	13.12	0.020	7.18	13.98	0.023	7.06	14.26	0.022	7.05	14.36	0.020
	2.0	7.18	13.22	0.018	7.08	14.18	0.016	7.04	14.39	0.015	7.03	14.40	0.018
Nitric Acid treated lignin	0.5	7.69	12.99	0.033	7.51	13.13	0.030	7.49	13.18	0.029	7.48	13.20	0.029
	1.0	7.96	13.18	0.030	7.49	13.38	0.028	7.44	13.53	0.027	7.43	13.54	0.026
	1.5	8.19	13.42	0.028	7.48	13.92	0.025	7.42	13.98	0.024	7.40	13.99	0.023
	2.0	8.36	13.82	0.024	7.36	13.96	0.023	7.34	13.98	0.022	7.32	13.99	0.022
Nitric Acid/ KOH treated lignin	0.5	7.70	12.99	0.034	7.56	13.00	0.032	7.46	13.06	0.030	7.44	13.18	0.029
	1.0	8.06	13.29	0.029	7.56	13.39	0.028	7.36	13.42	0.027	7.34	13.40	0.026
	1.5	8.34	13.62	0.024	7.44	13.56	0.027	7.34	13.86	0.024	7.33	13.87	0.024
	2.0	8.56	13.96	0.022	7.36	13.96	0.024	7.33	13.99	0.023	7.33	13.98	0.023

WHC – Water holding Capacity (%) Perm- Soil permeability

### III. RESULTS AND DISCUSSION

A sandy soil, poor in organic matter content and nutrient was used in the study. The soil with such attributes has low water holding capacity, poor nutrient status and, as such can be treated as representative of degraded soil.

**Decomposition and Humification of lignin:** The carbon content in the modified and unmodified lignin was almost same and very small change at the time of commencement of study. It reduced gradually with the time in case of modified lignin but remained almost same in the untreated lignin (table 1). The nitrogen was in traces before treating the lignin, but it increased between 3.48 to 8.99 percent due to modification with different reagents. The nitrogen content maintained an increasing trend throughout the course of study and it was more than 7 percent at the time of final observation. The C: N ratio narrowed down from 15.02 to 6.28 in case of urea

treated lignin and similar trend was observed in ammonified, nitric acid treated lignin and nitric acid in presence of KOH treated lignin.

The narrowing of C: N ratio is an indication of either loss of carbon or gain of nitrogen or both. In any case this is expression of decomposition of lignin which results in loss of carbon as carbon dioxide due to microbial activity. This lead to infer that the lignin in its original form is almost inert and undergoes little biodegradation but, when enriched with nitrogen, it turns into a dynamic substance whose biodegradation is rapid.

The methoxyl group reduced remarkably in all the 4 types of modified lignin in comparison to untreated lignin in 24 months (table 2). The group was 12.47 in case of untreated lignin and ranged between 2.87 and 3.48 in modified lignins. The reduction was maximum in nitric acid/ KOH treated lignin (76.99 %) followed closely by nitric acid treated lignin (76.27 %), ammonified lignin ( 75.79 %) and urea treated lignin (72.10 %). The phenolic hydroxyl group increased from 1.89 in untreated lignin to 4.78 nitric acid in presence of KOH treated lignin. In the same fashion the carboxyl group also increased from 1.89 to 5.96, 6.02, 6.89 and 6.98 in urea treated lignin, ammonified lignin, nitric acid treated lignin and nitric acid/ KOH treated lignin respectively and gain remarkably higher( 270.77 %) in nitric acid/ KOH treated lignin. The reduction in methoxyl group and increase of carboxyl and phenolic group clearly bring out that the lignin is converted into humus. The aliphatic hydroxyl group decreased from 5.20 to 2.71(47.89) in nitric acid/ KOH treated lignin, however the reduction in case of urea treated lignin(37.70), ammonified lignin(40.00), nitric acid treated lignin(43.08) was also quite high. The loss in aliphatic hydroxyl group indicates that the side chains of the lignin are undergoing aromatization.

#### IV. CONCLUSION

The above said findings reveal that the lignin is very slow biodegradable compound but when added with nitrogen it turns to a palatable substance for microbes and as such, get transformed to humus substances. The humus is the most active, useful and essential substance for a fertile soil since it increases water holding capacity, improve soil structure and porosity and acts as a store house of nutrients besides beneficial physiological effects. It is, therefore, possible to use modified black liquor lignin obtained after pulping of wheat straw as soil conditioners to enhance the fertility of soil. This will help in solving problem of discharge of black liquor on the one hand and ameliorate the soil conditions on the other hand.

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