Synthesis of useful products from bagasse lignin

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ABSTRACT

Bagasse is the main natural fiber resource in Cuba and in few other countries. Most Pulp & Paper mills using bagasse as raw material are small having capacity less than 100 tonnes/day. These small units usually do not have chemical recovery system and thus have to discharge the spent pulping liquor as effluent causing the environmental pollution which is the main problem for the pulp industry based on bagasse.

The Spent liquor constitute the main source of raw lignin available for the production of by-products. This paper deals with the development of useful products from alkaline lignin. The findings of the research work carried out in the laboratory, pilot plant and on industrial scale by pulp and Paper Research Institute "Cuba—9" and Chemical Research Center are reported.

An adhesive system based on bagasse lignin for the production of a particleboard is described. Lignin-phenol-formaldehyde (LPF) resin from industrial soda bagasse lignin was prepared. The product was evaluated in the production of particleboard.
The effect of ammoniate bagasse lignin (ABL) on the physical, physico-chemical and biological properties of compact Ferralitic Red soil and saline solonetz Solonchak soil were studied for a period of five years. In the compact soil, the ABL causes a decrease in the apparent density and an increase in available nitrogen, humus. microbial activity and improves the soil structure. In saline soil. the ABL produces an increase in the size of the aggregates and it can be washed easily.

Lignosulfonates obtained by sulfonation of alkali bagasse lignin were tested as plastifying agents in the production of Portland Cement, Oil well drilling mud and as intensifiers of clinker grinding.

Introduction

Bagasse is the main fiber resource in Cuba and in few other sugar-cane producing countries. Until now small capacity mills (<100 t/d) are predominant in the pulp industry utilizing bagasse. These small units usually do not have chemical recovery system and discharge their spent pulping liquors as effluent. This is the main environmental pollution problem of pulp industry using bagasse as raw material. These liquors constitute the main source of raw lignin available for the production of by-products. Efforts have been made to find out an economical usage of the black liquor instead of disposing it into the environment. However

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at present there is not much utilization of these liquors at large scale.

Studies were initiated to explore the possibility of using bagasse lignin for the production of useful by-products. The present paper deals with the results obtained in the utilization of bagasse lignin as an adhesive and the soil conditioner. Lignosulfonates obtained by sulfonation of alkali bagasse lignin were also tested as plastifying agents in the production of Portland cement, oil well drilling mud and as intensifiers of clinker grinding.

Experimental

Soda bagasse spent liquor was obtained from industrial soda pulping with 17% active alkali and 165°C temperature. The kappa number of the pulp was approximately 9. Liquor was collected after evaporation having the total solid content of 43%. Alkali bagasse lignin was obtained by acidification with sulfuric acid (1:1) as reported in the literature (1). Purification was done by exhaustive washing until a constant ash content was reached. Resins were prepared in 1 kg glass reactor as described in reference (2).

The evaluation of bonding capacity of resins in particleboard was done in the pilot plant. The bagasse particles were bonded with resin separetely and then were passed to form a mattress of 30 k 30 cm. This mattress was cold prepressed to reduce the thickness and then passed through hot press at a given temperature and pressure.

The capacity of the ABL as soil conditioner was evaluated in a Compact Red Ferralitic soil in experimental area of Cuban Agricultural Ministry located in Quivican, Havana, Cuba, An aleatory experimental design with two dosages of ABL (1 and 2% of weight of 20 cm layer) in 4m² plots was conducted. Each experiment was repeated three times, Corn plants were used as indicator plants and their dry weight was used as yield criterion. The effect of ABL in saline soils was studied on saline Solonchat soil with the same experimental plant described above with the addition of 3% of weight of 20cm layer but in 2 kg ceramic pots,

All the analytical method were performed in in accordance with Soil Analytical Book of Cuban Soil *Institute*. *Black* liquor from semichemical pulp process was used for the synthesis of lignosul fonates. It was filtered and concentrated by evaporation at reduced pressure. The pH was adjusted to 8 with sulfuric acid. Sulfonation was carried out with commercial Na_2So_3 in a reactor at a maximum temperature of 140°C (3). The synthesized lignosulfonates (NaLS) can be modified by treatment with $K_2Cr_2O_7$ to produce chrome lignosulfonates (CrLS)(4).

Lignin-Phenol-Formaldehyde (LPF) Resins :

Phenol-formoldehyde resins are used to bond particleboards which require water resistance for exterior uses. Lignin, a phenolic-type polymer, has been considered a replacement or a substitute for phenol in polyphenolic resins (5).

The introduction of lignin in the polyphenolic resins causes a deterioration of the resin properties restricting the utilization of lignin in large quantities. Lignin adhesives typically require longer press times, higher press temperatures and have poorer water resistance than pure phenolic resins. (5)

Recently, it was proved (6) that industrial soda bagasse lignin possess a greater number of reactive sites towards alkali catalyzed electrophilic substitution reactions and a comparable reactivity than phenol toward formaldehyde. For these reasons, it is expected that soda bagasse lignin would prove to be a good substitute of phenol in phenol formaldehyde resins.

Taking into account the reactivity of bagasse lignin and the procedures reported in literature (7), a synthesis method for the production of lignin-phenol formaldehyde (LPF) resins was developed (8). Using this process three different types of lignin-phenol - formaldehyde resins were prepared. The content of isolated lignin and black liquor were different for each resin as illustrated below :

A—Resin made with only black liquor
B—Resin made with black liquor and isolated lignin
C—Resin made with only isolated lignin

The main properties of these resins are given in Table-1. For comparison, the properties of commercial phenolic resin (PF-4) are also presented (9). There are not much differences in the properties of the resins and all the value ssatisfy the requirements for the production of bagasse particleboard.

There are evidences that lignin compounds can be used as conditioners having advantages over other compounds (II). A summary of the results obtained over three years using bagasse lignin in the melioration of compact and saline soils are presented.

Ammoniated bagasse lignin (ABL) was obtained using bagasse lignin isolated from spent pulping liquor. A valuable property of ABL is that the conditioners with various pH values and active mass can be obtained from it. This makes it possible to use ABL on soils having very different properties (12).

a) Compact Soils

The action of ammoniated bagasse lignin (ABL) on Ferralitic Red Compact soil in plot scale confirm the results obtained in the loboratory (13). The organic matter increases proportionally toABL dosage. This effect is more pronounced in the depth of 0—10 cm (Table—3). The same trend is observed with the variation of total nitrogen which is an important reserve for the plant nutrition.

The application of ABL to soil increases total Carbon, fundamentally in humic carbon which is in agreement with ABL dosage. Also, there is an increase in H/F relation (13) which reflects that during the crop cycle the ABL was partially biodegraded and finally produced humic molecules by condensation.

It can be noticed that ABL increases the stability of soil agregates while the soil structure is also improved The product has a high remainder power and promotes the soil fertility. This result is corroborated by the yield obtained in corn harvest (Table-4).

In agreement with the variation of humic compounds, a significant increase in the bacterial biomass takes place when the ABL is applied to the soil. At four months the minimal dosage of ABL (1%)gave significantly higher values than the control (Table-5). However, at 9 and 16 months the dosages of 2 and 3% ABLre sulted in significant increase in bacterial biomass and in the global biological activity as is shown by the enzymatic activity of the deshidrogenaze enzyme in the soil.

Table-3 Organic Matter Content in Soil Treated withABL

Treatment	Depth (cm)	Org. Matter %	Total N %	C(h+f) %	C(h) %	H/F
Control	0-10	2.45	0.106	0.29	0.11	0.6
	10-20	2.53	0.112	0.38	0.09	0.3
	0-10	3.12	0.136	0.37	0.27	2.7
I (1%)	10-20	2.86	0.118	0.35	0.26	2.9
II (2%)	0-10	3.43	0.138	0.46	0.32	2.3
	10-20	3.13	0.121	0.34	0.32	2.1

Table—4 Yields of the Corn (Dry Matter)

Treatment	Dry Matter (kg)
Control	5.66
I(1%)	7.38
II(2%)	9.12

Table-5 Changes in Becterial Biomass, an Activity of DHA with ABL Application

Treatments	Time to Sampling					
	4 Months		9 Months		16 Months	
	B.b	DHA	B.b	DHA	B.b	DHA
0	0.68	2.3	0.73	2.4	0.78	10.6
I	0.84	4.9	1.44	4.8	1 41	10.5
II	0.75	2.5	2.04	6.8	1.95	12.1
III	0.60	2.0	1.67	5.5	2.64	20.5

B b—Bacterial Biomass mg/g of soil
DHA—Activity of of the enzyme deshidrogenaze mg of TTF/100g of soil

b) Saline Soils:

One of the main difficulties in the washing of saline soils is the resistance to the infiltration produced by soil peptization induced by sodium in soil solution. The results obtained in washing saline soil treated with different dosages of ABL are given in Table-6. It can be seen that there is a great difference in the volume of percolated water of the treated soils in relation with the control.

Table-6. Varriation in percolate water through the saline soil treated with ABL

Treatment	Days of Washing							
	1	3	5	11	14	19	30	Total	%
Control	947	543	383	950	333	840	367	4363	34.9
ABL (1)	613	490	573	1107	707	1193	643	5326	42.6
ABL (2)	673	277	543	1314	763	1286	850	5706	45.7
ABL (3)	600	533	763	1946	773	867	739	6219	49.8

The analysis of the soil after washing showed that in all the tests using ABL, the salts content was lower than in the control. In original soil, the sodium ion is more than 20% of exchangeable cations and the content in treated soils decreases below 5% (Table—7). The Mg content also decreases while the relative calcium content increases. This demonstrates thee ffectivenessof the use of ABL (14).

Table-7 Relation between exchangeable cations after washing

Treatment	Ca	Mg	Na	K
		%		
Control	58.4	29.8	10.1	1.8
ABL (1)	66.2	27.1	5.1	1.67
ABL (2)	66.2	27.2	4.96	1.70
ABL (3)	65.0	27.9	5.5	1.65

The results of a five years study show that using ABL, it is possible to increase the number of water -stable agregates in red Ferralitic soil, reduce the salinity and content of exchangeable sodium in Solonchak soil, and increase the soil biomass, nitrogen and humus content in both soil types, Therefore. A B L., can be use as a good conditioner, meliorant and fertilizer for the soil. These results are similar to those reported by Buylov (11) using ammonium lignosulfonate.

Plastifying action in Portland cement production

The reduction of water content in raw materials used for cement production by wet process significantly contributes to reduce the fuel consumption in the kiln. The sodium Lignosulfonates act as water-reducing agent when used in the aqueous slurry cf finely divided clay used to prepare portland cement as illustrated in Table-8.

Table 8 Water Reducing Action of Sodium Lignosulfonates (NaLS) on Clay Slurry used to Prepare Portland Cement.

	Percent
Water content of clay slurry	53
Water content of clay slurry after addition of 1% NaLS	48
Reduction in water content at blank viscosity	9

Intensifier action on clinker grinding

The use of chemical additives helps increase the efficieney in clinker grinding for cement production because the molecules of such substances adsorb on to fissure of clinker grain and reduce their trituration resistance. Further more, additive molecules avoid agglomerution of fine particles formed by neutralizing insaturated valences over clinker which appear during its grinding. Lignosulfonates are products for this purpose, Table-9, indicates the considerable intensifier action of NaLS. This represents at least a 40% reduct- rndingtime.

Table-9 Intensifier action over clinker grinding for cement Production (0.08% of NaLS with respect to clinker),

	Specific	surface	(cm^2/g)
Grinding time (min.)	30	90	150
Without additive	1218	2828	3566
With NaLS	1320	3812	4221

Dispersing action over drilling mud.

The drilling of oil wells requires the circulation of a fluid called drilling mud to remove cuttings from the well bore, lubricate the drill bit, suspend the cuttings when the drill bit is stopped, and form a hydrostatic head for controlling the pressure of oil and gas in the well bore.

Lignosulfonates are employed for control of rheological properties and water loss of mud. Table-10 shows how CrLS significantly improves essential properties of mud without additives.

Table-10 Dispersnig Action on Drilling mud (1 6 % of CrLS with Respect to mud).

	Yield point ($lb/100\ ft^2$)	Gel 0/10l) b/100 ft^2)	Water loss (ml)
Without additive	24	8/35	18
With CrLS (Chrom Lignosulphonates)	6	2/8	10

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