Isolation And Characterization Of Lignin Degradation Products From Baggase and Rice Straw

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ABSTRACT

Alkali lignins isolated from baggase and rice straw have been subjected to the oxidative degradation under high pressure and temperature using, (i) Alkaline nitrobenzene (ii) Alkaline m-dinitrobenzene and (iii) Alkaline mercuric oxide at high temperature and normal pressure.

Some of the important chemicals identified by HPLC were found to be p-hydroxybenzaldehyde, syringaldehyde, vanillin and their corresponding acids.

INTRODUCTION

Now a days, for paper making, a main raw material, Bamboo is being increasingly supplemented by various grasses and agricultural residues. Baggase and Rice straw are two potential raw materials which are being increasingly used for paper making in this region. Here soda process and Kraft process is used for the manufacture of paper in which the lignin is recovered as alkali lignin. The alkali lignin can be utilised in polymeric form or it can be further degraded to produce industrially important chemicals.

The present study aims at isolation, characterization and oxidative degradation of the lignin obtained from Baggase and Rice straw.

EXPERIMENTAL PART

I) Sample Preparation

Baggase and Rice straw were collected from local sugar industry and field respectively. It was cleaned, dried and cut into small pieces of about 5 mm size.

II) Proximate Analysis

Proximate analysis of both Baggase and Rice straw have been carried out by standard methods and all the results expressed on O.D. basis are tabulated in Table-1.

Table-1

Proximate analysis of baggase and rice straw

SR. No.	Details	% In Baggase	% In Rice straw
1.	Moisture content	9.50	10.58
2.	Ash content	1.95	09.58
3.	Cold water solubility	11.20	12.55
4.	Hot water solubility	34.80	22.50
5.	NaOH (1%) Solubility	32.80	45.00
6.	Ethanol-Benzene extraction	03.42	05.04
7.	Lignin content	28.31	21.00
8.	Holocellulose	64.30	74.00

III) Isolation of Alkali Lignin From Baggase and Rice Straw [2,3]

Identical procedures were used to isolate the lignin from both Baggase and Rice straw. Prior to the isolation of lignin, both the samples were extracted by hot ethanol-benzene (1:2).

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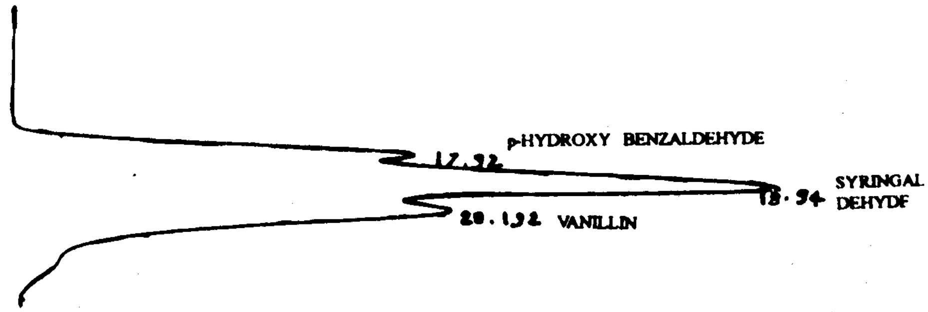
TABLE II

HPLC DETAILS OF PRODUCTS OBTAINED AFTER OXIDATIVE DEGRADATION OF ALKALI LIGNIN ISOLATED (FROM BAGGASE AND RICE STRAW)

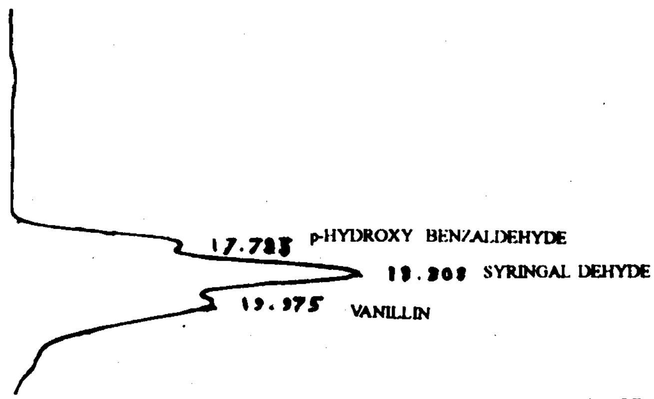
OXIDIENT USED	A LKALI LIGNIN SOURCE	STANDARD/ SAMPLE. [TOTAL QUANTITY INJECTED (μ.g.)]	RETENTION TIME OF IDENTIFIED COMPONENT (Min).	ASSIGNMENT (NAMES OF CHEMICALS DETECTED).	PEAK AREA RECORDED BY INSTRUMENT	QUANTITY OF COMPONENT INJECTED/ DETECTED in (μ.g.) AREA BASIS.	% OF THE DETECTED COMPONENT FROM SAMPLE	CHROMATO GRAM. FOR REFER-ENCE.
NITRO BENZENE	BAGGASE	STANDARD (Mix.) [60]	17.92 18.94 20.14	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANILLIN.	81200 290888 194353	15.00 25.00 20.00		FIG - 1.1
		SAMPLE [40]	17.78 18.808 19.975	p-HYDROXY BENZALDHYDE SYRINGALDEHYDE VANILLIN.	37137 133461 90447	06.859 11.4642 09.3069	17.00 28.65 23.50	FIG - 1.2
NITRO BENZENE	RICE STRAW	STANDARD (Mix.) [300]	16.89 18.73 20.05	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANILLIN.	741705 2329203 1230625	100.00 100.00 100.00		FIG - 2.1
		SAMPLE [40]	16.30 18.68 20.05	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANILLIN.	2216 40843 130505	00.30 01.75 10.60	00.75 04.38 26.51	FIG - 2.2
m-DINITRO BENZENE	BAGGASE	STANDARD (Mix.) [60]	17.92 18.94 20.19	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANILLIN.	81200 290888 194353	15.00 25.00 20.00		FIG - 1.1
		SAMPLE [20]	17.817 18.73 20.07	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANTILLIN.	15067 73348 51935	02.78 06.30 05.34	13.50 31.50 26.50	FIG - 1.3
MERCURIC OXIDE	BAGGASE	STANDARD (Mix.) 3 ACIDS. [10]	38.46 41.70 43.80	p-HYDROXY BENZOIC ACID SYRINGIC ACID VANILLIC ACID.	14848 99650 190886	02.00 04.00 04.00		FIG - 1.4
		SAMPLE [40]	38.35 41.71 43.80	p-HYDROXY BENZOIC ACID SYRINGIC ACID VANILLIC ACID.	44728 329191 657286	06.02 13.20 13.73	12.04 26.40 27.46	FIG - 1.5
MERCURIC OXIDE	RICE STRAW	STANDARD (Mix.) [300]	16.89 18.73 20.05	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANILLIN.	741705 2329203 1230625	100.00 100.00 100.00		FIG - 2.1
		SAMPLE [40]	16.27 18.77 20.10	p-HYDROXY BENZALDEHYDE SYRINGALDEHYDE VANILLIN.	12742 34425 133602	01.72 01.48 10.46	04.30 03.70 27.14	FIG - 2.3

Fig. 1



HPLC OF MIXTURE OF p-HYDROXY BENZALDEHYDE, SYRINGALDEHYDE AND VANILLIN (SANDARD SAMPLES)

FIG - 1.1



HPLC OF PRODUCTS OBTAINED BY OXIDATIVE DEGRADATION OF ALKALI LIGNIN FROM BAGGASE USING ALKALINE NITROBENZENE

FIG - 1.2

Extractive free sample, along with the aqueous sodium hydroxide (15%) was cooked in a digestor at 128 psi for two hours. The contents were filtered and black liquor was acidified to obtain crude lignin. It was then reprecipitated from dioxane and water.

IV) Oxidative Degradation of Lignins Isolated from baggase and Rice Straw using various oxidants.

Alkali lignins isolated from Baggase and Rice straw were independently Oxidized by various oxidants (Under similar conditions for both the sources) such as (a). Alkaline nitrobenzene (b). Alkaline m-dinitrobenzene and (c). Alkaline mercuric oxide. The details are as under.

Oxidative degradation by nitrobenzene [4,5,6]

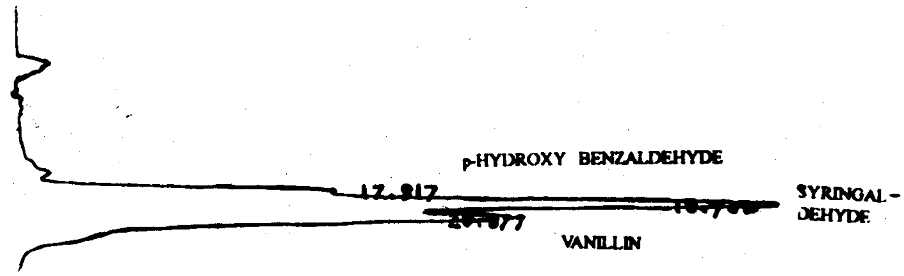
Alkali lignin was dissolved in aqueous sodium hydroxide (2N) and to it was added, nitrobenzene. The mixture was heated in Autoclave at 180°C, (Pressure 10 kg/cm^2) for two hours. After cooling, the organic liquid phase was completely removed. The alkali layer was acidified.

The aqueous suspension was extracted with chloroform. Removal of chloroform produced light brown solid. It was analysed by HPLC [7,8]. The findings are expressed through chromatograms fig. 1.1, fig 1.2, Table-II and fig.2.1. fig.2.2, Table-II respectively.

Experimental Details of HPLC

The brief information regarding the HPLC analyses is as under. However further individual details are given in Table-II.

Fig. 1.3



HPLC OF PRODUCTS OBTAINED BY OXIDATIVE DEGRADATION OF ALKALI LIGNIN FROM BAGGASE USING ALKALINE m-DINITROBENZENE

FIG - 1.3

1) Instrument used - Shimadzu-SPD-6-AV. With recorder, chromatopac -C-R-6-A Shimadzu.

2) Detector - UV detector set at 275 nm.

3) Solvent system - Water-acetic acid-n-butanol in a Ratio (342:1:14) V/V.

4) Column - C 18 Shim - Pac-CLC-ODS (M). 4.6 mm x 25 cm.

5) Flow rate - 0.5 ml/min.

6) Chemicals - All Solvents were EMERCKglass distilled and standards were SIGMA/ FLUKA HPLC GRADE.

7) Qualitative analysis - The peaks obtained in the - standard mixture were identified by the comparison of retention time with individual standards, retentation time under the same conditions.

8) Quantitative analysis - This was carried out by - taking into account, the quantity of standard injected, the quantity of sample injected and their proportional area under the peak as recorded by the instrument.

Oxidative degradation by m-dinitrobenzene

Identical oxidation was carried out using m-dinitrobenzene in place of nitrobenzene. Here, HPLC results for alkali lignin obtained from Baggase and Rice straw are shown in chromatograms fig 1.1, fig 1.3 Table-II and fig 2.1, fig 2.3, Table-II respectively.

Oxidative degradation by mercuric oxide[9]

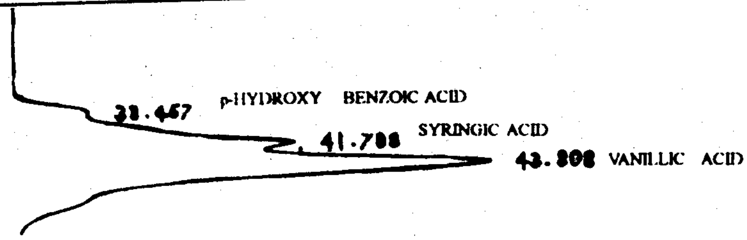
Alkali lignin (Baggase) along with a suspension of mercuric oxide and aqueous sodium hydroxide (2N) was refluxed for six hours. It was filtered. Filtrate was acidified and the resulting suspension was extracted with chloroform. Removal of chloroform produced a brown solid. Its HPLC analysis is represented through chromatograms Fig 1.4, Fig 1.5 and Table-II.

RESULTS AND DISCUSSION

Most of the results of the present work have been presented in Fig-3. The proximate analysis of the Baggases and Rice straw found to contain about 28% and 21% lignin (O.D. basis). However 18% and 15% of the lignin (O.D. basis) could be isolated, and as seen from the fig-3, around 64% of the total lignin from Baggase and 71% from Rice straw could be isolated from Rice straw. Alkali lignin has a great significance as it is recovered from black liquor produced by the soda process, which is one of the major process having commercial importance.

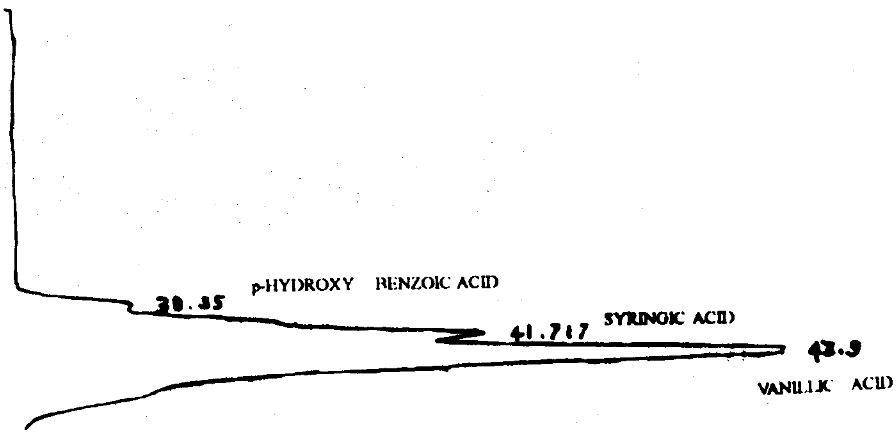
As seen from the fig-3, it is clear, that oxidation by nitrobenzene could produce around 18.5% of the lignin to a low molecular compounds. However the extent of degradation of lignin by m-dinitrobenzene and mercuric oxide was found to be 13% and

Fig.1.4 & 1.5



HPLC OF MIXTURE OF p-HYDROXY BENZOIC ACID, SYRINGIC ACID AND VANILIC ACID (STANDARD SAMPLES)

FIG - 1.4



HPLC OF PRODUCTS OBTAINED BY OXIDATIVE DEGRADATION OF ALKALI LIGNIN FROM BAGGASE USING ALKALINE MERCURIC OXIDE

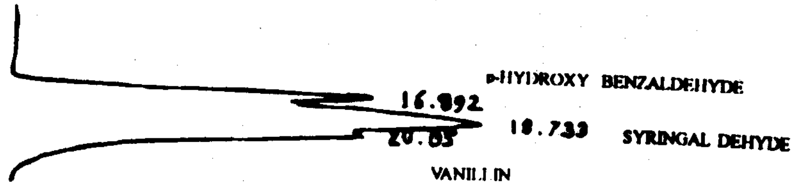
FIG - 1.5

to be more potent oxidant for this purpose than rest of the two.

It can also be pointed out that, after oxidation of alkali lignin (Baggase) by nitrobenzene, about 69.02% of chemicals could be identified (on degraded lignin basis). In case of oxidation by m-dinitrobenzene and mercuric oxide, 72.10% and 65.00% of the chemicals could be identified. It is further noted that oxidation by nitrobenzene and m-dinitrobenzene produced p-hydroxibenzaldehyde, syringaldehyde and vanillin. Their individual quantities in the same order, in case of alkaline nitrobenzene oxidation was 17%, 28%, 23% and 13%. oxidant 26% respectively. However, when oxidant was mercuric oxide, it produced p-hydroxybenzoic and, syringic acid and vanillic acid. Their proportion was found to be 12%, 26% and 27% respectively on the degraded lignin basis.

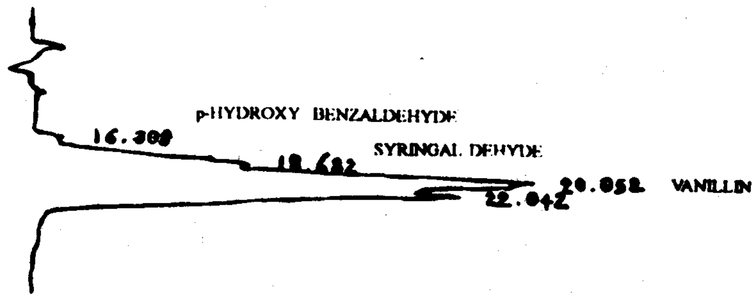
Similarly the extent of oxidative degradation of alkali lignin (Rice straw) by nitrobenzene and mercuric oxide was found to be 10% and 5% respectively. In both the cases similar chemicals, such as p-hydroxy benzaldehyde, syringaldehyde and vanillin were identified. Their respective formation in case of alkaline nitrobenzene oxidation was found to be 0.75%, 4.3% and 26.5% in case of oxidation of alkali lignin by mercuric oxide, the identified chemicals were same i.e. p-hydroxy benzaldehyde, syringaldehyde and vanillin and their relative formation (on degradation on degraded alkali lignin basis) was found to be 4.3%, 3.7% and 27.14% respectively.

Fig.2



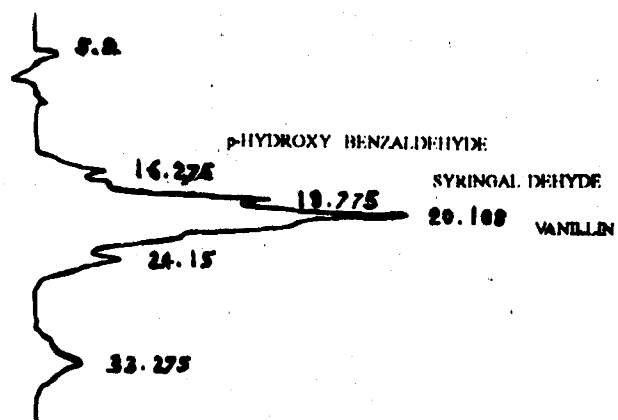
HPLC OF MIXTURE OF P-HYDROXYBENZALDEHYDE, SYRINGALDEHYDE, VANILLIN (STANDARD SAMPLES).

FIG - 2.1



HPLC OF PRODUCTS OBTAINED BY OXIDATIVE DEGRADATION OF ALKALI LIGNIN OF RICE STRAW WITH ALKALINE NITROBENZENE.

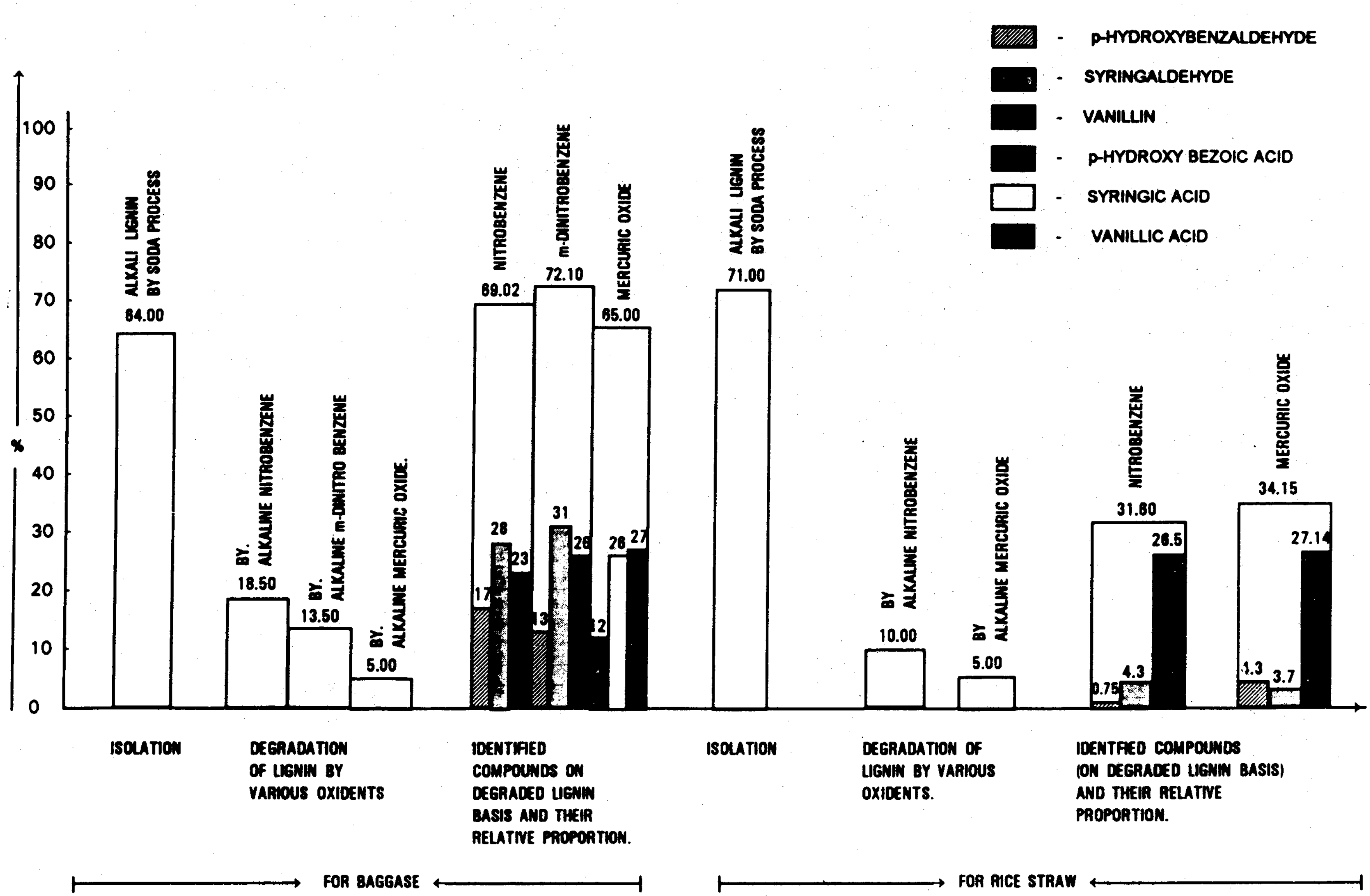
FIG - 2.2



HPLC OF PRODUCTS OBTAINED BY OXIDATIVE DEGRADATION OF ALKALI LIGNIN OF RICE STRAW WITH ALKALINE MERCURIC OXIDE.

FIG - 2.3

FIG-3.
OXIDATIVE DEGRADATION OF ALKALI LIGNIN ISOLATED FROM BAGGASE AND RICE STRAW.



From results it appears that the nitrobenzene is the best oxidant and with its use alkali lignin can lead to the formation of value added products such as vanillin in particular.

Although the yield of these chemicals is not exceptionally high, but considering the huge quantity of black liquor in the paper industries, the organic technology of this carries a great potential and hence needs more attention and exploitation.

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REFERENCES

1. TAPPI standards
2. Marshall, H.B. Brauns, B.L. and Hibbert, H., can J. Res 13 B, 103 (1935)
3. Plugian, M., Ind. Eng. Chem. 32, 1399 (1940)
4. Bicho, J.G. Zavarian E., and Brink D.L. Tappi 49, 218 (1966)
5. Kavanagh K.R. and pepper J.M., can J. chem. 33, 24 (1955)
6. Pearl I.F., J.Am. chem. soc. 64 1429 (1942)
7. Sarkanen K.V. and Ludwig C.H. Lignins, occurrence, formation, structure, and reactions Wiley, Interscience, New York, Sydney, London. Toronto P.444. (1964)
8. Hartley, R.D. and Hazel Buchan., J. Chromatog 180, 139-143 (1979)
9. Cymbaluk N.F. and Neudoerffer T.S.J. Chromatogr 51167 (1970)