Physico-Chemical Properties of Spent Liquors From Pulping of Agricultural Residues and Their Influence on Chemical Recovery Operation

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ABSTRACT

Considering the increasing cost of cooking chemicals and severe pollution problems, small pulp mills will have to have suitable chemical recovery system. For design & development of economic process equipment and also for smooth monitoring of chemical recovery operation it is important to know the behaviour of spent pulping liquors, particularly, during evaporation and combustion stages. Though some data is available on some of the properties but not much of the information relating to the rheological properties, polymeric nature of organic components in the spent liquors and combustion characteristics is available. In the present studies an attempt is made to collect the scientific data on these properties. Two of ihe commonly and widely used agricultural residues namely rice straw and bagasse have been selected for these studies. Studies include influence of nature of organic components lignin macromolecules. in particular, on the rheological properties of the spent liquors and rate of thermal decomposition With the help of Simultaneous Thermal Analyser, data relating to pyrolysis and combustion behaviour of black liquors has heen collected. The other important physico-chemical properties studied are foaming index, viscosity, etc. Studies on polymeric nature using gel-chromatographic technique show how the rheological properties are closely related with the polymeric nature of organics.

Studies on chemical, physico-chemical and thermal preperties clearly indicate that spent liquors from pulping of agricultural residues differ substantially when campared to those of wood black liquors. The data will be of immense help in design and selection of equipments for chemical recovery system for mills using non-woody raw materials.

INTRODUCTION

Today number of small mills based on agricultural residues like rice straw, bagasse, etc. are contributing over 30% to the total paper produced in our country. Due to lack of suitable process technology for the recovery of cooking chemicals none of these mills are equipped with chemical recovery systems. Conventional recovery system, involving evaporation and incineration of spent pulping liquors followed by lime causticization of dissolved smelt, suffers severe set back due to the fact that spent liquors from pulping of agricultural residues differ substantially compared to wood spent liquors[1,2] Some data is available on the properties of spent liquors from pulping of agricultural residues[3,4] However not much of information, relating to the influence of chemical composition on the physico-chemical properties, is available. Spent liquors from agricultural residues show high viscosity and poor burning characteristics[5]. Koorse, etal[6] have discussed the importance of physico-chemical properties like viscosity, boiling point rise, specific heat, etc. on the behaviour of black liquors during evaporation and combustion. Further they have pointed out that for design and development of equipments of economic size it would be important to have the knowledge of these physico-chemical properties. Kubes[7] has Pointed out that recovery furnace operation, to a large extent, is influenced by the quality of the black liquor. Spent liquor produced in most of the small pulp mills have very low soilds concentration ranging from 2-4%[8]. Evaporation of such low concentration black liquor calls for enormous steam enery requirement .Silica present in the black liquor is one of the negative factor for efficient concentration of black liquors.

In the coming years, it is envisaged that more number of small mills are likely to come up and development of equipment, suitable for handling the spent liquors from non-woody plant fibers, is an immediate challenge before engineers and scientists.

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The present paper discusses the physico-chemical properties of spent pulping liquors from two of the commonly used agricultural residues namely bagasse and rice straw. An attempt has also been made to investigate the possible reasons for abnormal behaviour of these spent liquors.

EXPERIMENTAL

Raw Material : Rice straw was procured from local farms and bagasse from a nearby mill in the form of bales. Stalks of straw were cut intc 1-2" length. For the Present studies wet depithing of bagasse was carried out mechanically by passing the wet bagasse through a disc refiner at a high clearance to loosen the pith followed by screening on the vibratory screen using 0.3 mm slot width screen. Depithed bagasse was taken for the studies.

Black Liquor Preparation : For black liquor preparation rice straw and bagasse were cooked in the laboratory 25 litre tumbling digester at 160° C by soda process. The active alkali charge was 10% and 12% for rice straw and bagasse respectively. A constant H-factor was maintained for all the pulping experiments.

Black Liquor Analysis: Chemical analysis of spent liquors(Table–1 & 2) both prepared in laboratory and those collected from mills were carried out according to the procedures mentioned in **TAPPI - Standard Method T-625.** Elemental Analysis was carried out on Hereus CHN-O Rapid Analyser.

Dialysis of Black Liquor: Black liquor (50 ml) from rice straw and bagasse were dialysed separately in cellulose membrane pouch, sealed at the both end, for72 hours against 2 liters of 0.1 M bicarbonate-alkali buffer with two charges of buffer. Subsequent dialysis was carried out against distilled water with four charges. From the material balance amount of material passing through the membrane was estimated.

Gel Filtration: Black liquor sample equivalent to 25 mg T.S. free from suspended matter was charged to 1 cm x 55 cm column of Sephadex -G-25. This charge was eluated through column by bicarbonate-alkali buffer and 2 ml eluate fractions were colleted after every ten minutes. Absorbance of each fraction at 280 nm was measured using Spectronic UV–21–D.

Physico—Chemical Properties:

Colloidal Stability: Colloidal stability was determined from the solids concentration at which spent liquor started giving precipitate during concentration in rotary vacuum flash evaporator.The. precipitation point was clearly visible.

Viscosity Measurement: Spent liquors were concentrated upto 35 to 55% solids range in a vacuum flash evaporator and viscosity was measured at dfferent solids concentration at 80 ± 0.1°C using Brookfield RVT Model Viscometer. Viscosity values for 45 & 55% solids concentration were obtained from viscosity curves.

Foam Coefficient: Foaming characteristics of spent liquor was assessed by determining the foam coefficient Kf and foaming index according to the method based on the principle described by Braginskii (9). Schematiclay-out of the apparatus used for determining the foam coefficient is illustrated in Fig–1.

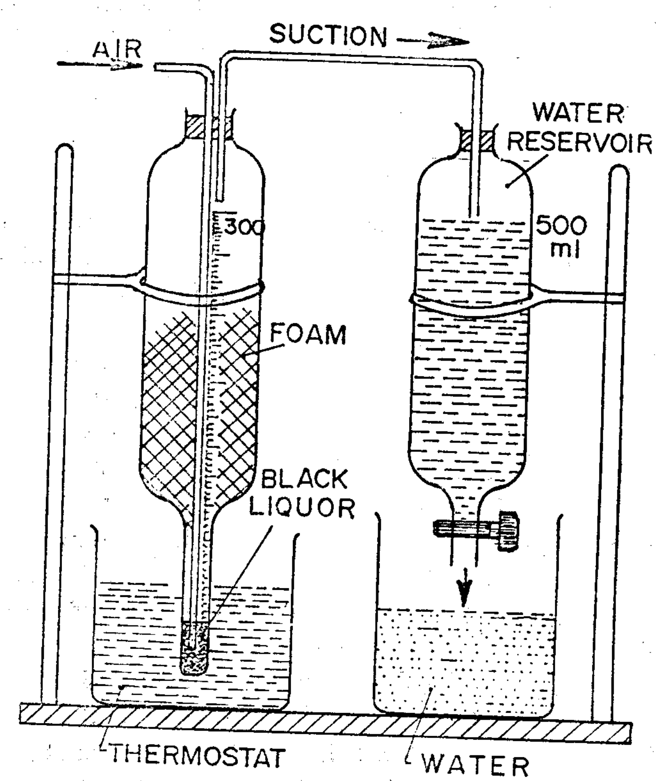

FIG. 1—APPARATUS FOR MEASURING FOAM INDEX

Foam coefficient was calculated using following formula–

$$Kf = \frac{Vf}{V}$$

Where, Vf = Volume of foam

and V = Volume of spent liquor taken for test (10 ml)

$$\text{Foam index} = \frac{V_1}{V} \times 100$$

Where, V_1 = Volume of spent liquor converted into foam.

Swelling Volume Rato (SVR) : SVR value of spent liquor was measured according to the method followed by Oye, etal[10].

Calorific Value : Calorific value of spent liquor was determined according to the **TAPPI – Standard Method T-605** used for the analyses of coal.

Integral Procedural Decomposition Temperature (IPDT):

Thermogravimetric Analysis (TGA) of the spent liquor was carried out using STA-781 Simultaneous Thermal Analyser. The conditions maintained were as below :

Sample weight	—	10–15 mg
Temperature rise	—	20°C/minute
Thermocouple	—	Pt/Pt : Rh 13%
Atmosphere	—	Air

The IPDT of the spent liquor was calculated from thermogravimetric (TG) curves based on the formula given by Wandalt[11].

$$IPDT = \frac{Ac}{At}(Tf - Ti) + Ti$$

Where, Ac = Area under the curve.

At = Total area of the rectangle

Tf = Final attained temp. on total decompostion

Ti = Initial temp. at which weight loss started.

RESULTS AND DISCUSSION

a) Chmical Composition: Properties of spent pulping liquors, to a large extent, are influenced by the type of raw material processed, condition maintained during pulping and the quality of resultant pulps. Spent liquors from pulping of agricultural residues dffer substantially with the spent liquors from pulping of conventional raw materials like bamboo and woods. Not much of the data on the chemical composition of spent liquors from agricultural residues is available. Even if available they are scanty and efforts have not been made to correlate the chemical composition with physico-chemical properties of these spent liquors.

At the first instance, comprehensive chemical analysis of spent liquors collected from the small pulp mills was carried out to observe the extent of variation in the chemical composition. Table-1 gives the typical chemical composition of the spent liquors collected from the mlls based on bagasse and rice straw.

The results in Table–1 clearly show that mill spent liquors had solid concentration ranging from 4 to 8%. There was a wide variation in the residual alkali content which ranged from 0.1 to 7 g/l. Spent liquors from bagasse and rice straw had significant quantities of silica. In one of the spent liquor from rice straw the silica content was as high as 13%. The elemental composition and calorific values which are influenced by the amount of organics, showed variation with the organic matter content. They also differ substantially from the black liquors from wood & bamboo,with respect to low solids concentration, low level ofresidual alkali and high proportion of silica. In absence of wet cleaning method theae is a likelihood of carry–over of significant proportion of silica from the mud adhering to the raw material.

b) Chemical Composition of Laboratory Black Liquors: Black liquors from rice straw and bagasse were produced in laboratory for detailed chemical anaysis and study of polymer and physico-chemical properties. Chemical analysis of these black liquors is given in Table–2. For comparison,analysis of mixed hardwood black liquor is also included along with these results.

Black liquors produced in the laboratory showed marked variation in the chemical composition compared to mill black liquors. Solids contents in laboratory black liquor were on higher side. However laboratory black liquors showed low levels of residual alkali.The organic matter and carbon contents were on higher side for labor atory black liquors, presumably due to more dissolution of lignin during cooking.

Table—1

ANALYSES OF MILL BLACK LIQUORS

Particulars	Raw Material		
	Mill–1 Rice straw	Mill–2 Rice straw	Mill–3 Bagasse
pH	9.9	8.8	4.8
Total solids, % w/w	6.87	3.89	8 10
Suspended solids, mg/l	1215	1210	180
Organics, %, w/w	69.87	66.64	67.65
Inoaganics, %, w/w	30.12	33.36	32.35
Residual Active Alkali (RAA) as NaOH, g/l	0.64	0.08	7.23
Total Alkali, (T.A.) as Na_2O, g/l	11.32	7.59	18.50
Silica content, (SiO_2), %, w/w	12.85	3.66	3.76
Elemental Analysis			
Carbon, %, w/w	34.2	—	30.10
Hydrogen, %, w/w	4.8	—	4.15
Nitrogen, %, w/w	1.3	—	1.11
Oxygen, %, w/w	42.2	—	45.14
Sodium, %, w/w	17.50	18.50	19.50
Calorific value, Cal/g	3528	3195	2932

(—) Data not available.

Table—2

ANALYSES OF LABORATORY BLACK LIQUORS

Particulars	Raw Material		
	Rice Straw	Depithed Bagasse	Mixed Hardwoods
Pulping			
Chemical dosage, AA as NaOH, %	10	12	22
Sulphidity, %	Nil	Nil	25
Pulp yield, %	50	55	44.6
Chemical composition of spent liquor			
pH	10.8	11.8	10.9
Total solids, % w/w	8.36	8.68	20.9
Suspended solids, mg/l	1580	386	—
Organics, % w/w	77.2	70.1	68.4
Inorganics, as NaOH, % w/w	22.8	29.9	31.6
Residual Active Alkali (RAA) as NaOH, g/l	0.96	0.96	11.7
Total alkali (TA) as Na_2O, g/l	12.70	15.96	44.2
Silica contents (SiO_2), % w/w	3.57	2 05	—
Elemental Analysis			
Carbon, % w/w	36.25	38.87	39.8
Hydrogen, % w/w	4.46	4.37	5.2
Nitrogen, % w/w	1.39	0.42	Nil
Oxygen, % w/w	41.64	37.91	35.5
Sodium, % w/w	16.26	18.43	16.8
Sulphur, % w/w	Nil	Nil	2.7

(—) Data not available.

Bagasse and rice straw black liquors differed with respect to suspended solids, silica and organic matter. Rice straw black liquor showed higher suspended solids arising out of parenchyma cells, silica and organic matter compared to bagasse black liquor. Despite higher organic residue the rice straw black liquor showed less carbon due to the fact that the black liquor contained more of carbohydrate degradation product which have low carbn values. This is supported by the fact that rice straw had 5% lsser pulp yield compared to bagasse.

Due to higher material liquor ratio, the solids concentration of bagasse and rice straw black liquors was on very much lower side compared to wood black liquor. On mill scale operation, where material to liquor ratios are still higher due to significant quantities of condensate carried with the steam, more dilute black liquors are obtained. Total solids concentration in black liquor is an important factor which determines the requirements in thc evaporation operation of chemical recovery system. Every efforts should be made to produce the black liquors with higher solids concentration. According to Pant, etal (12) it is possible to save substantial proportion of energy with every 1% rise in solids concentration.

Residual alkali is an important process variable and it is necessary to ensure that black liquor contains certain minimum alkali level. Reduction in alkali level would lead to colloidal instability resulting in precipitation of organic compounds during concentration (13). Thus the mill black liquor distinctly differ from the black liquors produced in the laboratory.

C) Elemental Analysis: Estimation of carbon content in black liquor is considered important in terms of heating values of black liquors. Determination of organic matter does give some idea of the fuel value of black liquors, but the carbon content and subsequent heating values would depend, to a large extent, on the ratio of dissolved lignin to carbohydrate and lignin degradation products (14). Agricultural residue, straws in particular, produce spent liquors which contain less lignin resulting in low carbon values. Rice straw black liquor had lower carbon content compared to bagasse and wood black liquors.

d) Physico–Chemical Properties : Physico–chemical properties such as colloidal stability, foaming tendency, viscosity (flow behaviour) are important and study of these properties helps to understand the behaviour of black liquor during evaporation and combustion operations of recovery system. These paysico–chemical properties are influenced by chemical and polymeric nature of organic constituents in the black liquors.

Foaming Tendency : All the black liquor contain significant proportion of organic acid salts and have tendency to produce the foam. The foaming tendency is influenced by the amount of these orgnic acids and the pH of the black liquors. Foaming and entrainment are common problems of evaporator causing liquor losses, corrosion and scale formation. Table—3 shows the forming characteristics of rice straw and bagasse black

Table—3

PHYSICO-CHEMICAL PROPERTIES OF SPENT LIQUORS

Particulars	Raw Material		
	Rice Straw	Depithed Bagasse	Mixed Hardwoods
Foam index, at Initial solids, at 32°C and			
pH 11 0	18.0	10.0	19
10.0	15.0	10.0	—
9.5	15.0	10.0	—
Foam Coefficient at Initial solids, at 32°C and			
pH 11.0	20.0	5.0	6
10 0	14.0	5.0	—
9.5	12.0	5.0	—
Colloidal stability Precipipitation point at, % solids	27	N.P.*	37
Brookfield viscosity, m Pa. Sec at 80°C at % solids,			
35	32**	422	—
40	43	794	—
45	—	1260	—
55	—	—	123

*No Precipitation

**Precipitates above 32%. Viscosity could not be determined above 45% T.S. due to precipitation.

liquors at different pH values. For efficient pulp washing and black liquor evaporation it is necessary to have increased understanding of the various factors influencing the foaming tendency of black liquors. Foam index is the percentage volume of the black liquor converted into foam and foam coefficient is the percentage ratio of volume of the foam to the volume of black liquor taken for test. Rice straw black liquor showed relatively higher foam index and foam-coefficient values compared to bagasse black liquor. Higher foaming tendency in rice straw black liquor might be attributed to higher proportion of organic acids in rice straw spent liquor which was confirmed by Kulkarni, etal[15]. Bagasse black liquor produced lesser degree of foam.

Colloidal stability and Flow behaviour concentrated black liquors: For an efficient and smooth operation of evaporator units it is necessary that the black liquors should be colloidally stable and free flowing. Colloidal instability of black liquors and the reasons for this colloidal instability was investigated and discussed by Kulkarni, etal[13]. It has been observed that low pH values, higher proportion of high molecular weight lignin macromolecules and the presence of organic acid salts in significant proportion are the reasons for colloidal instability of spent liquors. Due to the colloidal instabillty some of the black liquors have a tendency to produce precipitate during concentration. Results in Table—3 show the rice straw spent liquor was unstable colloidally and started precipitating at about 27% solids concentration. Rice straw black liquor was much more unstable colloidally even when compared with mixed hardwood black liquor. Bagasse black liquor, on the other hand, was colloidally stable. Some of the experiments conducted have revealed that when more pith is carried with bagasse then the resulting black liquor is colloidally unstable, presumably due to increased proportion of organic acid salts.

Flow behaviour of concentrated black liquors measured in terms of viscosity is an important parameter controlling pressure drop, heat and mass transfer rates, mixing rates, etc. Knowledge of the flow behaviour is desirable for piping design, selection of pumps and estimation of power costs. Viscosity results (Table—3) show a vide variation for rice straw and bagasse black liquor. Bagasse black liquor exhibited very high viscosities at solids concentration over 35%. Rice straw black liquors although had lower viscosity upto 30% but concentration beyond 35% was dfficult due to heavy precipitation. Mixed hardwood black liquor, on the other hand, had very low viscosity compared to bagasse black liquor.

e) Thermal Properties: Table—4 shows the results of thermal praperties like calorific value. swelling volume ratio (SVR) and integral procedural decomposition temperature (IPDT). Calorific value is an important property which gives an estimate of the amount of heat of combustion. Calorific value is largely influenced by the carbon content. Rice straw black liquor showed very less calorific value despite higher organic residues compared to bagasse black liquor. This is attributed to the less carbon content.

Table—4

THERMAL AND POLYMER PROPERTIES OF BLACK LIQUORS

Particulars	Raw Material		
	Rice Straw	Depithed Bagasse	Mixed Hardwood
Thermal Properties:			
Calorific Value, cal/g	3341	3744	2990
Swelling volume ratio, ml/g	6.2	15.5	13 0
IPDT, °C*	535	589	430
Polymer Properties:			
Dialysis, % loss (a)	74.9	81.0	65.2
Gel Filteration High/low Molecular weight ratios	1.2	1.6	1.4

*IPDT—Integral Procedural Decomposition Temperature.

(a) Dialysis in cellulose membrane having critical mol. wt. of about 3500

Swelling Volume Ratio (SVR) is an empirical and semi-quantitative method to assess the burning characteristics of the black liquor. The swelling process is similar to the cooking of the coal. Black liquor combustion involves three main steps-drying in which water is evaporated, volatile burning involving pyrolysis and gaseous combustion and finally char burning in which solid char surface is burnt. It is the second step in which the black liquor. residue gets swollen. More the swollen volume better is the rate of thermal decomposition. It has been established by Kulkarni, etal (13) that this property is influenced by the thermo-plasticity of organic matter in black liquor. Rice straw black liquor showed lower swelling volume ratio compared to bagasse and mixed hardwood black liquors. Although properties like calorific value and SVR do give information relating to burning characteristics, but these properties do not give the precise combustion behaviour. Recently the thermo-analytical techniques like differential ther-mal analysis (DTA), thermo gravimetric analysis (TGA) have been widely used to understand the combustion behaviour of organic substances. Typical TGA curves for rice straw and bagasse black liquors are illustrated in Fig—2. Integral procedural decomposition temperature (IPDT) is one

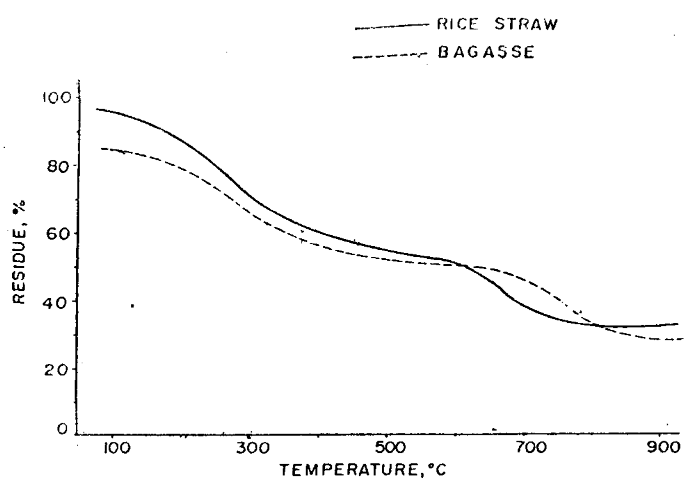

FIG. 2 THERMO GRAVIMETRIC CURVES

such parameter which indicate the temperature at which half of the material is burnt. Both rice straw and bagasse black liquors showed higher IPDT values, compared to wood black liquor, indicating resistance to burning. Bagasse showed IPDT value higher than that for rice straw indicating that bagasse black liquor is relatively more difficult to decompose thermally. Resistance to thermal decomposition is attributed to higher proportion of higher molecular weight organic components[13].

f) Polymer Properties : Black liquor is a complex colloidal aqueous solution containing polymeric substances like lignin and hemicelluloses. Polymer properties of orgonic matter, lignin macromolecules in particular, are closely linked with black liquor properties. Properties like viscosity, colloidal stability and thermal decomposition are closely related to the polymeric nature of organic matter. Lignin constitute the main organic component in the black liquor. During pulping, part of the lignin is dissolved as small molecules but major part is solubilized as large colloidal macromolecules. Molecular size of these lignin macromolecules depends on the nature of lignin and conditions employed during pulping.

In the present study techniques like dialysis in cellulose membrane and molecular sieve charomatography (gel filtration) were employed to understand the polymer-properties. Results of some of these findings are given in Table—4. It was observed that bagasse black liquors showed less permeable fraction compared to straw black liquor indicating higher molecular weight fractions in bagasse black liquor, This is further supported by gel filtration studies. The gel filtration curves are illustrated in Fig.—4 & 5.

Bagasse spent liquor had higher proportion of high molecular weight lignin fractions compared to straw. The ratio of high to low molecular weight fractions was higher in the case of bagasse black liquor. After dialysis the low molecular weight fraction disappeared and only high molecular weight peak appeared (Fig.-3 & 4) Dialysis and gel filtration studies clearly indicate that higher viscosity of bagasse black liquor is attributed to high molecular weight lignin fractions. Further studies in these directions would be essential for black liquors from different raw materials.

CONCLUSION

1. Black liquors from small pulp mills differ substantially compared to wood black liquors in respect of chemical composition, particularly residual alkali, total solids and carbon content.

2. Straw black liquor is colloidally unstable and difficult to concentrate beyond 35% solids concentration.

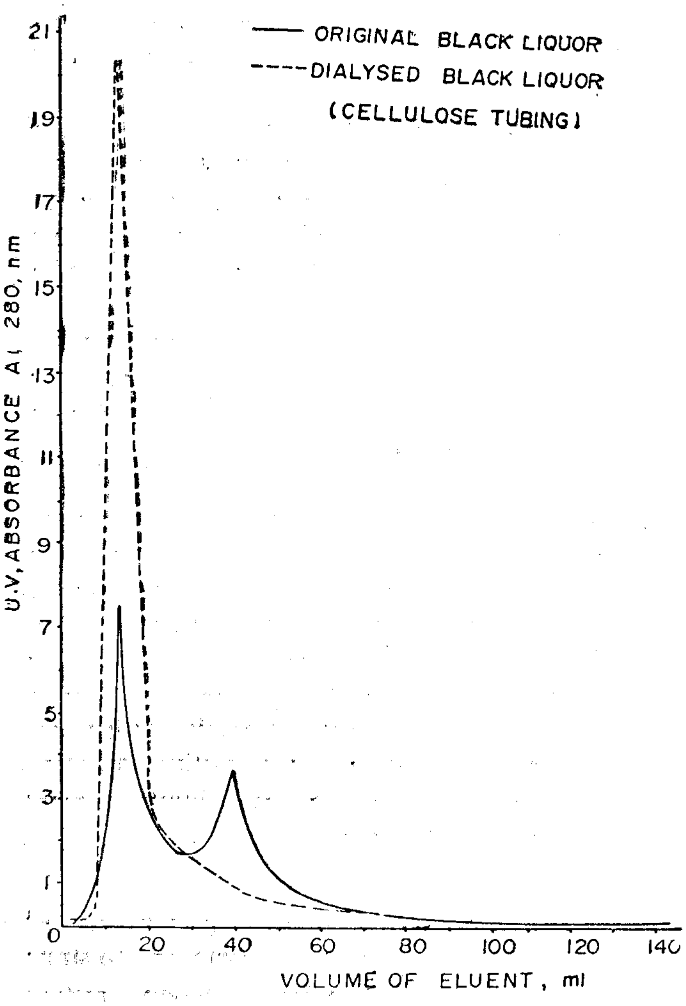

FIG. 3—GEL CHROMATOGRAPHY OF RICE STRAW BLACK LIQUOR.

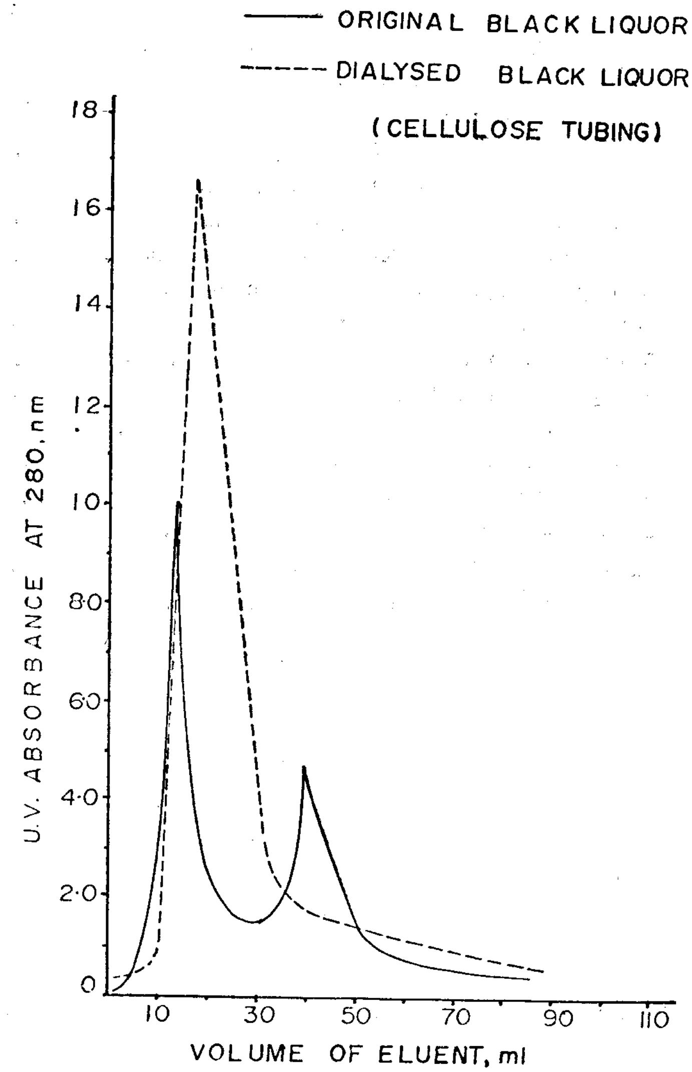

FIG. 4, GEL CHROMATOGRAPHY OF BAGASSE BLACK LIQUOR.

3. Bagasse black liquor exhibited very high viscosities compared to wood black liquors.
4. From thermo-gravimetric analysis studies, it is observed that straw and bagasse black liquors are resistant to thermal decomposition and burn slowly.
5. Studies on polymer properties clearly indicate that high viscosity and lower rate of thermal decomposition of bagasse black liquor are attributed to the presence of higher proportion of high molecular weight lignin fraction.

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