

# **Favourable influence of anthraquinone pulping on the physico-chemical characteristics of bagasse and hardwood black liquors**

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## **ABSTRACT**

Conventional alkaline pulping processes (i.e., soda and kraft) suffer from higher cooking chemical consumption as well as lower pulp yields due to "Peeling Reaction". Presence of sulphur in the cooking liquor of kraft process also results in emission of sulphur compounds to the atmosphere. Anthraquinone would be an effective additive to improve pulp yield and reduce chemical consumption. It also holds promise in the Industry's quest for moving towards sulphur-free pulping.

Influence of anthraquinone in the pulping of bagasse and hardwoods was investigated at Seshasayee Paper and Boards (SPB). The analytical results have not only confirmed higher yields of pulp with anthraquinone but also have shown noticeable improvement in the physico-chemical characteristics of black liquors.

It is found that Soda-AQ black liquors have lower viscosities compared to soda and kraft black liquors, indicating superior mobility. The lower viscosity of soda-AQ black liquors may be attributed to lower dissolved hemicelluloses and lower molecular weight lignin fraction in the black liquors.

The study also revealed superior combustion characteristics (SVR and calorific value) of soda-AQ black liquors, due to higher lignin content and lower dissolved hemicelluloses.

An attempt was made to isolate the dissolved hemicelluloses from the black liquors for improving the rheological characteristics. The results clearly exhibited a sharp fall in the viscosity of black liquors.

The present study also re-established higher yield and better bleachability of pulps with comparable strength properties in the soda-AQ pulping of bagasse and hardwoods.

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## **Introduction**

Environmental protection and conservation of natural resources are the urgent needs of the day. Paper industry, on its part, has to move towards identifying suitable pulping process which avoids sulphur from the pulping system and at the same time improves the yield of pulp resulting in conservation of forest based raw material. Anthraquinone is a promising alternative

which can achieve the dual objectives of environmental protection and conservation of forest raw material. AQ pulping has already found acceptance in the production units of developed countries.

Investigations were carried out at SPB to evaluate the effectiveness of anthraquinone in pulping of bagasse and hardwoods.

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While a few earlier studies (1-3) have confirmed increased pulp yield and reduction in chemical consumption, no reliable information was available on the effect of AQ on the physico-chemical characteristics of black liquors from pulping of hardwoods and bagasse. The present study, therefore, addressed itself to establish these influences.

### Experimental

The pulping of bagasse and hardwoods was carried out in an experimental auto clave (CCL PULPING UNIT) after optimizing the chemical requirement to obtain a pulp of  $(14 \pm 1)$  kappa number for bagasse and  $(24 \pm 1)$  kappa number for hardwoods, using soda, soda-AQ and kraft liquors, separately. The pulping conditions are presented in Table-1.

Analysis of black liquors was carried out as per TAPPI standard (T 625 cm-85). The viscosity of black liquor was determined at 80°C, after each stage of concentration, using Brookfield Viscometer (LVT—model).

The lignin content (4) in black liquors was determined by UV spectrophotometer at a wavelength of 280

nm. Dissolved hemicellulose content in black liquors was determined according to method given by Venter (5). The physico-chemical properties of black liquors are given in Table—2.

The pulps were bleached using a three stage sequence consisting of chlorination, buffered hypo and a final hypo stage (C/EH/H). The results are presented in Table—3.

Unbleached and bleached pulps were refined in PFI mill to the freeness levels of  $40 \pm 2^\circ \text{SR}$  as per SCAN C—24:67. The hand sheets were evaluated for various strength properties as per TAPPI standard T 220 cm-88. The strength properties of unbleached and bleached pulps are recorded in Tables 4 and 5 respectively.

### Results and discussions

#### Pulping

Addition of anthraquinone (0.05% in case of bagasse and 0.1% in case of hardwoods) in soda liquor has a beneficial influence on chemical consumption and pulp yield at same kappa number, as can be seen from the data presented in Table—1.

Table—1. Pulping Data Of Bagasse And Hardwoods

Particulars	Units	Bagasse			Hardwoods		
		Soda	Soda-AQ	Kraft	Soda	Soda-AQ	Kraft
Moisture content	%	76.5	76.5	76.5	29.0	29.0	29.0
Fibre to pith ratio	—	3.80:1	3.80:1	3.80:1	—	—	—
Active alkali charged as NaOH	%	21.0	16.0	16.0	24.0	18.5	18.5
AQ dosage on OD raw material	%	—	0.05	—	—	0.1	—
Material to liquor ratio	—	1:6	1:6	1:6	1:3	1:3	1:3
Cooking temperature	°C	170	170	170	170	170	170
H-Factor	—	385	385	385	1622	1622	1622
Total unbleached pulp yield	%	52.3	56.5	54.4	47.2	53.0	50.5
Screened rejects	%	Nil	Nil	Nil	Nil	Nil	Nil
Screened pulp yield	%	52.3	56.5	54.4	47.2	53.0	50.5
Unbleached pulp kappa number	—	13.0	13.0	14.0	23.0	23.0	25.2

The chemical requirement gets reduced by 5% (from 21 to 16) as compared to soda pulping of bagasse (kappa number  $14 \pm 1$ ) with an increase in pulp yield by 4.2%. Similarly, reduction in chemical requirement by 5.5% (24 to 18.5) and improvement in pulp yield by 5.8% are observed in case of hardwoods (kappa number  $24 \pm 1$ ). The chemical requirement remains the same when compared to kraft pulping of bagasse and hardwoods.

### Black Liquor Properties

The physico-chemical properties of black liquors from bagasse and hardwoods are given in Table—2.

It is observed from the results that soda-AQ black liquors from bagasse and hardwoods exhibit improved mobility and combustion characteristics when compared to soda and kraft liquors.

Table—2. Black Liquor Characteristics Of Bagasse And Hardwoods

Particulars	Units	Bagasse			Hardwoods		
		Soda	Soda-AQ	Kraft	Soda	Soda-AQ	Kraft
pH	—	12.8	12.5	11.8	12.9	12.2	11.5
Total solids	gpl	118	102	117	233	223	231
R.A.A. as Na <sub>2</sub> O at 200 gpl	gpl	14.4	10.8	8.5	8.7	4.5	4.4
Solids level							
Organics content	%	64.9	70.8	68.8	67.0	70.2	69.6
Calorific value	cal/g	3240	3490	3380	3450	3860	3680
Swelling volume ratio	ml/g	8	9	9	37	44	38
* Viscosity at 80 °C (Brookfield) at solids level of	cps						
	56%	2250	1750	1600	98	58	87
	61%	6900	5200	6400	580	265	480
	65%	—	—	—	1940	1520	1700
Lignin content (UV spectroscopy, 280 nm W/W)	%	26.66	53.15	45.71	24.4	48.92	45.44
Hemicellulose content of black liquor (W/W)	%	9.7	6.9	9.3	4.8	2.9	4.7

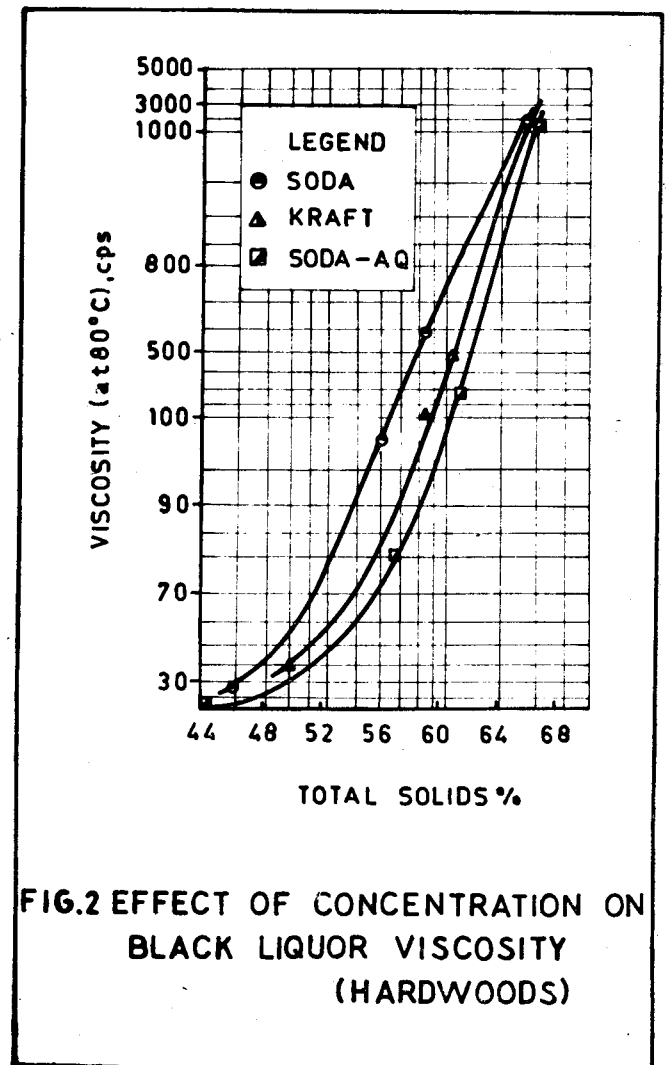
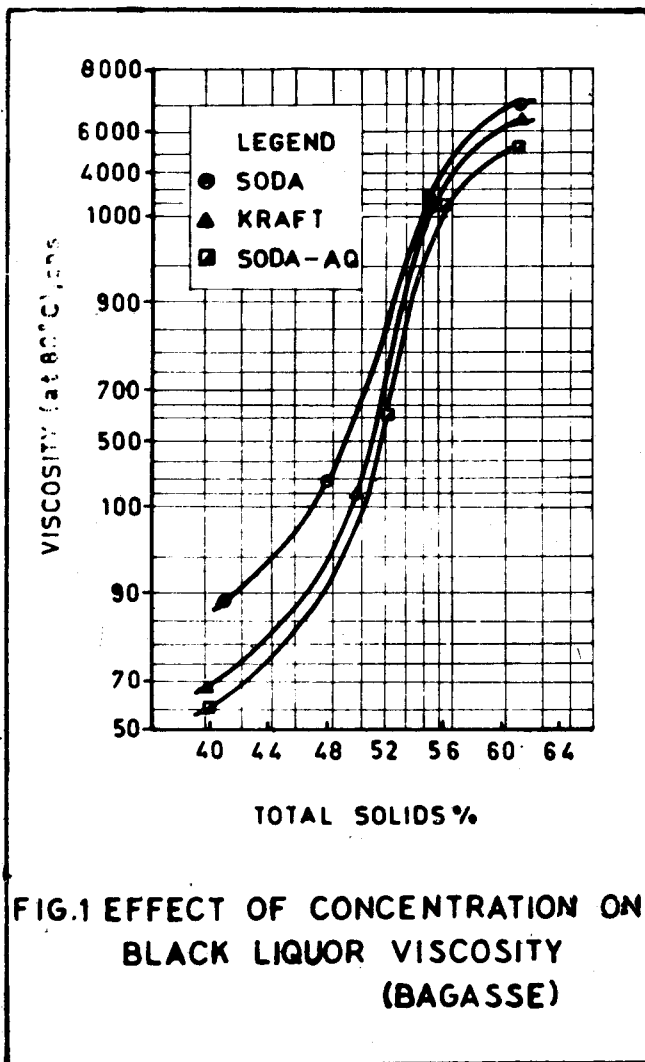
\* at R.A.A. level of 8.5 gpl (as Na<sub>2</sub>O) for bagasse black liquor  
at R.A.A level of 4.4 gpl (as Na<sub>2</sub>O) for wood black liquor

### Mobility Characteristics

A marked difference is observed in the viscosity of black liquors from soda, soda-AQ and kraft processes when the solids content in black liquors is increased. This behaviour is exhibited by both bagasse and hardwood black liquors. The soda-AQ black liquors had consistently low viscosity values at the same level of concentration (and at same RAA levels) exhibiting better rheological properties, when compared to soda and kraft black liquors. The results in Table-2 show that at a total solids level of 61% (W/W), the viscosity of soda-AQ bagasse black liquors at 80°C is 5200 cps compared to 6900 cps of soda and 6400 cps of kraft

black liquors. Similarly, in the case of hardwood black liquors at a total solids level of 65% (W/W), the viscosity of soda-AQ black liquors at 80°C is 1520 cps compared to 1940 cps of soda and 1700 cps of kraft black liquors. The effect of concentration on black liquor viscosities of bagasse and hardwoods is illustrated in Figures 1 and 2.

From the figures, it may be noticed that soda-AQ black liquors from bagasse and hardwoods register lower viscosity compared to soda and kraft black liquors. The superior behaviour of soda-AQ black liquors from bagasse and hardwoods is attributed to lower dissolved hemicellulose content in black liquors.



The dissolved hemicellulose content in soda AQ black liquors from bagasse is 6.9 % (W/W) compared to 9.7% in soda and 9.3 % in kraft black liquors. Similarly, the hemicellulose content in soda-AQ black liquor from hardwoods is 2.9% (W/W) compared to 4.8% in soda and 4.7 % in kraft black liquors. This data clearly indicate that anthraquinone plays an important role in the reduction of hemicelluloses in black liquors.

The lower viscosity of soda-AQ black liquors may also be due to lower molecular weight lignin fractions present in black liquor (6). However, this fact not confirmed by the authors due to non-availability of testing facility at the mills.

### Combustion characteristics

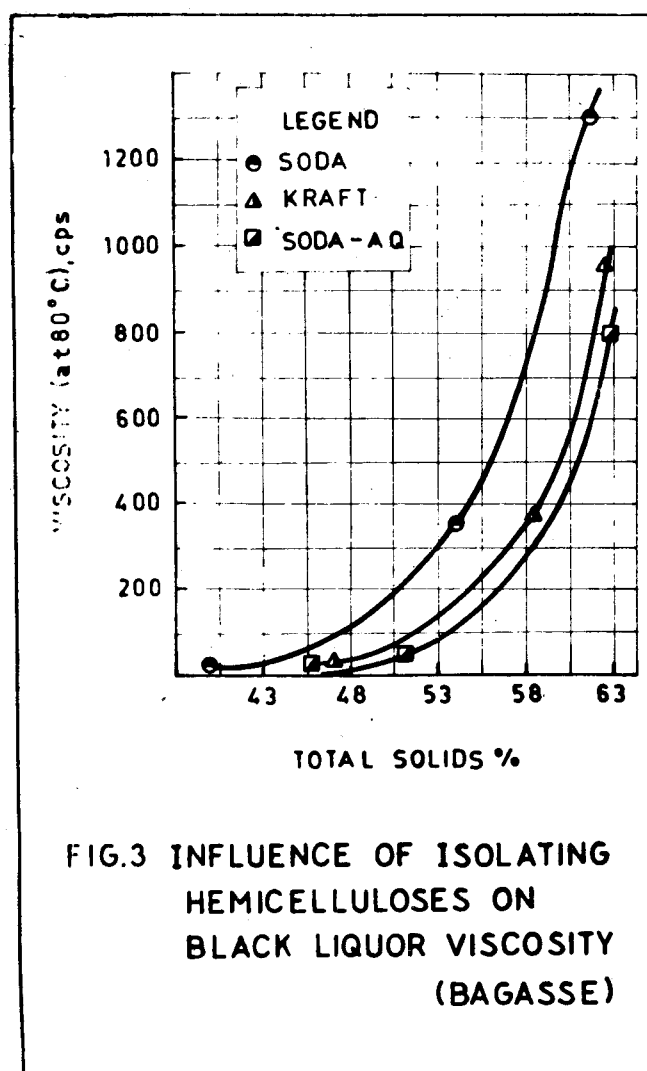
From the data of Table.2, it is observed that soda AQ black liquors from bagasse have higher organics content (70.8 %) and higher calorific value (3490 cal/g) compared to that of soda and kraft black liquors. The same trend is observed in case of hardwood soda AQ black liquors from hardwoods (44 ml/g compared to 37 to 38 ml/g of soda and kraft) confirm of better combustion properties. In case of soda-AQ black liquors from bagasse, there is no appreciable change in swelling volume ratio when compared to soda and kraft black liquors (SVR : 8 to 9 ml/g) in all the black liquors). The lignin content in black liquors from soda-AQ bagasse pulping (53.15% W/W) is more compared to lignin content in soda (36.69 %) and kraft (45.71 %) black liquors. In case of soda-AQ hardwoods also, the black liquor has higher lignin content (48.92% W/W) when compared to soda (24.4%) and kraft (45.44%) black liquors. This clearly indicates that anthraquinone, promotes the rate of delignification during pulping thus improving the combustion properties of black liquors.

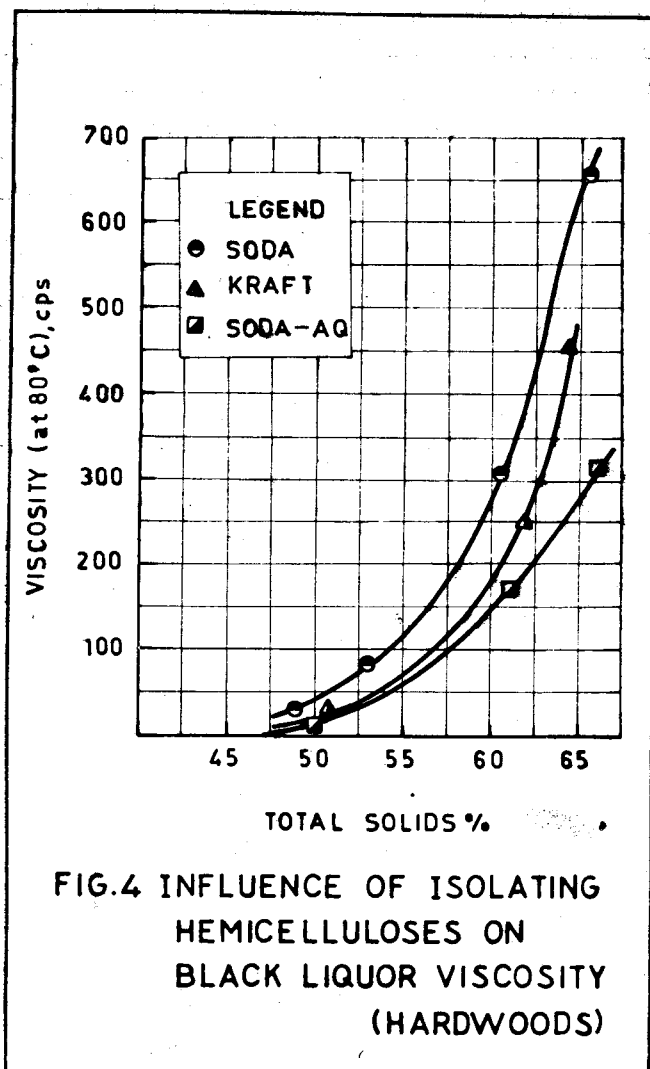
### Influence of dissolved hemicellulose on black liquor viscosities

Viscosity of concentrated black liquors has a profound influence on the efficiency of recovery system, in particular, on evaporation section. The rheological

properties of black liquors, which depend on the nature of dissolved lignin and carbohydrate polymers, are made more favourable by the addition of anthraquinone during pulping. The dissolved hemicellulose content in black liquor is found to be on the lower side when anthraquinone is added in pulping, favouring superior mobility characteristics.

Figures 3 and 4 show the viscosity of soda, soda-AQ and kraft black liquors bagasse and hardwoods, at various solids concentration after hemicellulose separation. The data clearly show that removal of hemicelluloses results in substantial decrease in viscosity of black liquors.





The viscosity of soda-AQ bagasse black liquor at 61% (W/W) solids level is 5200 cps as compared to 800 cps at the same level of solids concentration, after the isolation of hemicelluloses. The same trend was also observed in soda and kraft black liquors from bagasse.

In the case of hardwood black liquors, soda-AQ liquor has a viscosity of 1520 cps at 65% solids concentration compared to 320 cps, after the isolation of hemicelluloses from spent liquor. Similar decrease in viscosity is observed in hardwood soda and kraft liquors.

#### Bleaching and Strength Properties of Pulps

Results of the bleaching experiments are given in Table-3.

From the results, it is observed that bagasse soda-AQ pulps consumed 15–20% less of total chlorine (based on O.D. unbleached pulp) when compared to soda and kraft pulps to achieve brightness level of  $76 \pm 1\%$  in three stage bleaching sequence of C/EH/H. Similarly, in the case of hardwoods soda-AQ pulps, the total chlorine consumption was 5% lower than soda pulps to achieve brightness level of  $78 \pm 1\%$  in three stage bleaching sequence. Further, the viscosity measurements (1% Cupram, 20°C) of bleached pulps indicate that soda-AQ bagasse pulp had 14% higher viscosity than soda pulp and soda-AQ hardwood pulp had

**TABLE-3 Bleaching Data of Bagasse and Hardwoods**

Particulars	Units	Bagasse			Hardwoods		
		Soda	Soda-AQ	Kraft	Soda	Soda-AQ	Kraft
Unbleech pulp kappa number	—	13.0	13.0	14.0	23.0	23.0	25.2
Total chlorine Consumed	%	4.62	3.90	5.0	8.33	7.9	8.0
Brightness of pulp (TB)	%	78.0	76.0	75.0	78.0	78.6	79.0
Bleached pulp viscosity (1% Cupram), at 20° C	cps	29.8	34.2	33.6	12.0	14.1	14.8
Bleaching losses	%	3.80	3.0	3.52	6.90	7.6	8.1

17% higher viscosity than soda pulp. This finding shows that soda-AQ pulps made from bagasse and hardwoods are easily bleachable with less chemicals and have better strength as indicated by higher viscosity.

The results of unbleached and bleached pulp strength properties are given in Tables 4 and 5.

It may be noticed that the strength properties of unbleached and bleached soda-AQ pulps from bagasse and hardwoods are comparable to unbleached and bleached soda and kraft pulps respectively indicating that addition of anthraquinone does not affect fibrillation or strength properties.

**Table—4 Strength Properties of Unbleached Pulps of Bagasse and Hardwoods at 40°SR**

Particulars	Units	Bagasse			Hardwoods		
		Soda	Soda-AQ	Kraft	Soda	Soda-AQ	Kraft
Burst factor	—	41	42	43	32	29	30
Tear factor	—	47	46	48	66	64	70
Breaking length	m	7000	7770	7640	6200	6200	6160
Stretch	%	2.9	3.4	3.3	3.2	2.5	2.6

**Table—5 Strength Properties of Bleached Pulps of Bagasse and Hardwoods at 40°SR**

Particulars	Units	Bagasse			Hardwoods		
		Soda	Soda-AQ	Kraft	Soda	Soda-AQ	Kraft
Burst factor	—	40	44	41	32	30	30
Tear factor	—	44	42	44	62	60	66
Breaking length	m	6800	6900	7000	6100	6000	6200
Stretch	%	3.2	3.7	3.6	3.2	2.6	2.8

## Conclusions

Anthraquinone has been found to be an effective chemical in soda pulping of bagasse and hardwoods for improving the black liquor properties. Soda-AQ pulping offers a definite advantage over soda and kraft processes with benefits of superior mobility and combustion characteristics of black liquors besides lower chemical requirement in pulping and bleaching, and higher pulp yields with comparable strength properties. Further, isolation of hemicellulose from black liquor results in substantial improvement in mobility characteristics.

## Acknowledgement

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