## Phenol Sulhonates Are The Accelerators In Delignification Process.

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#### ABSTRACT

Casurf is a non-ionic bio-degradable surfacatant , basically it is a sulphonated product of cardanol used as penetrating aid in pulping.. It is the desire of every one of us here to maximize efficiencies and productivity of whatever system we operate today. However our effort to fine tune existing operation or conservation of resources can only make a marginal impact on overall performance. In MHW (Mixed hard Wood) pulping process, digester additives on a regular basis improved the hard wood pulp productivity. Active alkali reduction, knots generation and cost reduction were noticed in addition to absorbing the cost of the additive. Sulphonated product of caradanol (penta-decadienyl phenol) i.e. Casurfact as a digester aid, it improves the liquor penetration and diffusion into the chips by their surface active property has been far more successful with regards to improving the pulping efficiency. The hydrophilic-liphophilic water soluble additive improves the pulping. Their unique wetting mechanism of the chips alkali penetration into the chips is the key to efficient pulping.

The work presented in this paper was intended to identify the potential penetrating power of casurf and various surfactants both individually and in combination in Kraft pulping. The main objective of this paper is to judge the effectiveness of casurf in R & D Lab by various control cooks and with the addition of casurf at constant cooking conditions using autoclave bomb digester. The results that followed indicated Kappa number reduction by 20 to 18% (2 units), pulping rejects reduced by 1.5% to 0.9%, Screen yield increased by 4.4% to 5.0% over the control cook. The reduction in AA, increase in yield favors the deliginification in kraft pulping, lower in total solids higher organic solids in black liquor and significant changes in RAA, viscosity and hemi-cellulose show favorableness in the chemical recovery process.

#### Introduction

The Mysore Paper Mills Ltd, produces 300 TPD Newsprint and 100TPD cultural paper and have sugar mill of 2500 TPD sugar cane crushing capacity. Newsprint is produced from mechanical pulp and cultural paper from chemical pulp. Mechanical pulp is a high yield pulp and is obtained from semi-chemical process i.e CSRMP (Cold soda refined mechanical pulp) and chemical pulp from Kraft process. Hard wood, pinus and bagasse are the raw materials used in MPM.

To meet global competitiveness, improving the productivity of hard wood pulp through a cost beneficial approach has been discussed. The primary objective of a total fiber management approach is to enhance pulp quality by increased efficiency of the digester. By socio-economic concern and ISO 14001 (3R) Reduce, Recycle, Reuse the wastes generated from industries are converted into

The Mysore Paper Mills Ltd. Paper Town Bhadravati-577 302 (Karnataka) valuable products. On the above concept Cashew nut shell oil was expelled from cashew nuts and which is subjected to distillation, sulphonation and used as surfactant. Non ionic biodegradable cardanol sulhonate is reddish brown viscous mass, soapy to touch sparingly soluble in water, it emulsifies on thorough shaking. It is a good surface active agent because it is hydrophilic and liphophilic in nature.

#### DELIGNIFICATION PROCESS.

During kraft pulping the surfactant reduces the strong cohesive forces between molecular surfaces. It reduce the surface tension between liquor and chips, allowing for more through wetting the chip surface and facilitating rapid penetration of liquor into the inner matrix of the chips. In case of depolymerization lignin, the alkali reacts with hydroxyl group of lignin and with redox agents diffuse out of the wood structure into the bulk liquid. The surface active action of casurf is because of linear alkyl chain attached with bulky phenol act has a liphophilic group and a SO<sub>3</sub>Na group acts has a hydrophilic group. The liphophilic group dissolves the lignin and resins in wood lamella causes ease defibrillation .The work presented in this paper was intended to identify the potential of casurf and combination with AQ both individually and in combination for kraft pulping of Acacia. The main objective was to study the effectiveness of pulping with the additives. The following results are observed.

- Reduction in % A/A of cooking liquor, Knotters and rejects in the digester.
- Improved diffusion of cooking liquors in to chips.
- Improved pulp viscosity and screen yield.
- Reduce the residual active alkali in Black liquor or improved the organic in black liquor.
- Reduction in K.No. And in increase in pulp yield can also be discussed with usage of casurf in Kraft pulping.

By optimize the casurf dosage with and without and by varying temperature, time of cooking and dosage of A/A in a bomb digester. The cooking efficiency judge by the addition of casurf and otherd different surfactants like Anthroquinone and lignosulphonates have been discussed. The results have been also evaluated and discussed in the lab such as K.No, RAA, yield and % rejects.

#### **EXPERIMENTAL**

Chemical pressure cooking experiments were carried out in the laboratory by using autoclave bomb digester. It consists of 6 bombs, each of 2.5 litrs capacity rotating in an electrically heated polyethylene glycol; bath. Chemical doses were added so as to get Kappa number in the medium range of 20+/-2 Pulping studies were performed at constant A/A of cooking liquor, temperature, time and chips liquor ratio with a charge of 300 g acacia wood chips in each auto-clave bombs.

A control experiment was also run simultaneously in each set. The surfactant solutions like casurf AQ and Lignosulphonates were added in to cooking liquor and thoroughly mixed before transferring into the bombs. After charging the bombs with chips and liquor they were selected and placed in the oil bath. The initial temperature of the oil bath was 60°C, 60 minutes to reach 165°C, and maintain 120 minutes at constant temperature 165°C. At the end of the cooking process the bombs were removed and quenched in the water tank to depressurize and remove the bottom lid and collect the black liquor for further analysis. After thorough washing, squeezing the pulp on 3mm mesh for determine the knotters. The pulp was screened on 0.25-mm slot width screen to evaluate screen yield, Kappa Number, brightness and digester rejects. Black liquor was analyzed for total solids, free active alkali, organics and viscosity.

The casurf is optimized at a dose of 0.05, 0.1, 0.5, 1.0% w/w of fiber individually and by combination of 0.05% AQ with 0.10% casurf.

The cooking conditions used for pulping and its variable parameters have been discussed in detail in the following various tables.

# KRAFT PULPING CONDITIONS OF ACACIA WOOD

Acacia chips taken (10% moisture)......300g......270g (OD) Cooking liquor A/A17% Sulphidity. 15% Bath ratio......1:3.5 Cooking temperature 165+/-5°C Time to temperature 165°C-----60min Time at cooking temperature--120 min. Pressure 8-9 KSC

#### CHARACTERISATION OF PULP AND BLACK LIQOUR.

Kappa Number is the main characteristic of pulp in a measure of lignin content i.e. degree of delignification. It is determined by reactions of pulp samples with in acidified potassium permanganate solution according to TAPPI test method T-236. Yield was calculated as pulp (O.D basis) produced per 100g of chips (O.D) as per TAPPI standard method T-210 Rejects and uncooked materials were determined by drying in an oven at  $105^{\circ}C$ 

Total solids in the Black Liquor were measured gravimetrically after removal of water and other non-aqueous volatile materials according to TAPPI standard methods T-650. Viscosity at different solid content was determined using L.V. Brookefield digital viscometer. Other black liquor parameters like RAA, organic, were determined as per TAPPI test methods T-625. All the experiments were performed in duplicate and repeated to optimizing the casurf. The average values are reported here with.

**RESULTS AND DISCUSSIONS.** 

#### Table no. 1

**Kraft pulping**; 17% A/A, 15% Sulphidity, Bath ratio 1:3.5, Temp, 165oC, Time 60+120 min, Using different penetrating aids.

Cooks	Control cook	0.1% Casurf	0.05% AQ	0.1% Lig-Sul
Kappa No.	22	20.5	20.5	21.0
Rejects%	1.5	0.8	0.8	1.1
Screen Yield %	40.0	48.5	49.8	47.8
Digester Yield %	45.5	49.4	50.6	48.9
Viscosity cps	16.0	15.0	14.5	15.1
Black	Liquor	Analysis		
RAA gpl	6.8	4.2	4.8	4.2
T.S. %	20.5	20.5	20.2	20.8
Organics%	56.0	58.6	58.9	58.0
Viscosity cps	3.8	4.1	4.2	4.1

#### Table No. 2

**Kraft pulping;** Constant dosage of penetrating aids and cooking conditions, but varies in A/A To compare control cook and with penetrating aids by varying % A/A of cooking liquor

Cooks	15% w/w Active Alkali		16% w/w A/A		17% w/w A/A	
Parameters	Control	0.1% Cs	Control	0.1% Cs	Control	0.1% Cs
Kappa No.	26	24	24	23.5	22	20.0
Rejects%	1.8	1.1	1.5	1.0	1.5	0.9
Screen Yield %	43.2	48.2	45.0	49.5	45.8	49.1
Digester Rejects %	45.0	49.3	46.5	50.5	47.3	50.0
Viscosity cps	18.0	17.5	16.0	15.8	15.0	14.5
BLACK	LIQOUR	ANALYSIS				
RAA gpl	7.8	3.8	7.5	3.8	7.0	4.0
T.S %	20.23	20.65	20.12	21.68	21.50	21.75
Organics %	46.69	56.25	47.52	57.85	55.0	58.85
Viscosity cps	4.1	3.9	4.2	3.8	3.0	3.8

#### Table. No. 3

**Kraft pulping;** Casurf optimization with 17% A/A, Bath ratio 1:3.5, Temp 165°C, but varies in duration of cooking

Cooks	Time 60+90 min		Time 60+120 min		Time 60+150 min	
Parameters	Control	0.1% CS	Control	0.1% CS	Control	0.1% CS
Kappa No.	28	25	22.2	20.5	21	19.1
Rejects %	4.5	3.8	1.8	1.0	1.1	0.8
Screen Yield%	40.5	44.5	44.1	47.8	44.7	47.7
Digester Yield %	45.5	48.3	45.9	48.8	45.8	48.5
Viscosity cps	16.2	14.5	15.8	14.1	15.2	13.8
BLACK	LIQOUR	ANALYSIS				
RAA gpl	6.8	3.8	7.1	4.5	7.2	4.2
T.S %	23.6	23.6	23.2	23.6	23.8	23.2
Organics %	54.5	56.5	56.2	58.6	56.8	58.9
Viscosity cps	4.8	4.0	4.2	3.8	4.1	3.9

Table No, 4	
Kraft pulping;	17% A/A, bath ratio 1: 3.5, Temp, 165°C
Time 60+120 m	in, but casurf dosage variation.

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Cooks	Control	0.05%	0.1%w/w CS	0.25%w/wCs	0.5%w/w CS
		CS			
Kappa No.	22	21.5	19.5	19.5	19.1
Rejects %	1.6	1.5	1.2.	1.1	0.8.
Screen yield	43.1	44.8	48.2	47.9	48.9
%					
Digester	44.7	46.3	49.4	49.0	49.7
Yield %					
Viscosity	16.8	15.1	12.8	13.8	12.6
cps					
BLACK	LIQOUR				
RAA gpl	7.8	5.5	4.6	4.8	3.5
T.S %	20.8	21.1	21.6	21.2	21.9
Organics %	52.8	54.6	58.2	57.9	58.9
Viscosity	4.1	3.8	3.4	3.5	3.5
cps					

#### Table no, 5

**Kraft pulping;** Optimization of mixed penetrating aids with17% A/A, B.R 1:3.5, Temp. 165 °C, Time 60+120 min,

Cooks	Control	0.10% CS	0.25%CS	0.05% AQ	0.10Cs+0.05AQ	0.25% LS
Kappa No,	22.5	20.1	19.8	20.4	19.5	21.2
Rejects %	1.8	1.3	1.3	1.1	0.8	1.4
Screen Yield %	44.4	47.1	47.7	48.1	48.2	47.2
Digester Yield %	46.2	48.4	49.0	49.2	49.0	48.6
Viscosity cps	15.8	14.8	13.8	13.5	13.8	14.2
BLACK	LIQOUR	ANALYSIS				
RAA gpl	7.8	4.2	4.1	3.8	3.9	4.5
T.S %	20.9	20.8	20.8	20.9	20.7	20.5
Organics %	49.8	56.8	56.9	58.4	58.7	57.8
Viscosity cps	4.8	4.1	3.9	3.6	3.8	4.1

- 1. Kraft pulp of Acacia at 17% A/A with pulping additives 0.1% Casurf over control cook. K.No. reduction by 2 units Screen yield gain by 4.5% and lowering the rejects by 1.8% to 0.9% as shown in the table no. 1
- 2. Use of all the pulping additives resulted in reduction in AA requirement and reject generation and improvement in pulp yield. At constant 17% A/A charge, the K.No reduced by 22 to 20%, pulping rejects reduced by 1.8% to 0.9% with the addition of 0.25% w/w casurf. Not much variation in total solids but increase in organics, the yield increase was 4.1% over the control (no casurf) as shown in the table no.4
- 3. While cooking was carried out at the same chemical charge the Kappa number reduced by 2 to 2.5 points using higher dose of casurf

0.50% w/w of fiber. Saving in A/A, reduction in K.no, are the same as with 0.25% w/w.

- 4. Use of 0.25% and 0.1% casurf, reduced the A/A charge by 2% (18-16), pulping rejects by 1.6%to 0.8%, Screen yield gained by 43% to 49% as in both the doses are not much variation as shown in the table no.4
- 5. A net yield increase of 4.5% to 4.9%was obtained over the control cook. The K.No. Reduction by 2 points (22-20) when cooking was done at the same A/A. In combination of 0.1% w/w AQ and 0.25%W/W casurf resulted in more reduction in A/A requirement, pulping rejects, and improved in organics more improvement in pulp yield. The A/A charge reduced by 2%. The pulping rejects reduced by 1.5% and the yield increased by 4.5% over control cook as shown in

the table no. 5

- 6. Time for cooking has been also discussed in the table no.3 But more cooking time causes pulp degradation, it shows the low viscosity 13.9 using 90+150 minutes as mentioned in the table no 3.
- 7. The viscosity of the unbleached pulp was evaluated and the results have been in the table no.5 shows less degradation of pulp while on cooking using casurf.
- 8. The black liquor characteristics with and without combination of surfactant and AQ are presented in table no.5.

The reduction in Residual active alkali, improving in viscosity and organics is the major criteria for chemical and heat recovery.

#### DISCUSSIONS;

The laboratory study clearly shows that casurf and combination of casurf-AQ increase the rate of penetration and diffusion of the cooking liquor into the internal wood structure. This achieved much more uniform pulping as reflected by the lower K.no., lower percent rejects lower pulp resin content. Casurf enhances the penetration, and diffusion by wetting, emulsifying, mobilizing and dispersing resins and fatty acids occupying wood chips flow channels.

To avoid excess rejects and keep much of the yield gains from pulping with high K.No, it is highly desirable to use surfactant based digester additives. Casurf would ensure uniform penetration of cooking chemicals, allowing homogeneous pulping of chips and then by reducing knots and screen rejects when pulping to high K.no. Use of AQ and casurf combination resulted in more reduction in A/A requirement, pulping rejects and black liquor solids and more improvement in pulp yield. The AQ/ Casurf actually enhance the lignin removal by maximize the efficiency and effectiveness of cooking chemicals. The Hydrophilic-liphophilic, non-ionic biodegradable casurf would facilitate the rapid transportation of chemicals in to molecules and easy solubilisation of lignins and resin molecules.

Casurf reduces the resin content not only in the Kraft pulping but also in the dissolving grade pulp. It acts as a very good chelating agent; it also minimizes the metal ions of the pulp. Effect of metal ions by cardanol sulphonate has been also recommended for the future study.

#### CONCLUSIONS.

The reduction in active alkali charge, better yield of pulp, lower the digester rejects and reduction in Kappa number has been discussed by using optimized dosage of casurf. Cost wise AQ were more costly than casurf it may also render the better cooking additive in kraft pulping. Temperature and duration of cooking as compare with conventional kraft pulping (control) is still lower side when using penetrating aid casurf

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