Dissolving Grade Pulping Operations : Case Studies

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Major use of dissolving grade pulp is in Viscose rayon industry. Industrial grade pulps are used for many other purposes and particular example is melamine grade. The problems associated with dissolving grade pulp usage are pulp reactivity at different steps of viscose processing. Viscose filterability is major area of problems. This paper deals with pulp manufacture by two major processes and viscose rayon Processing and associated problems there in.

Brief History

Pulps for the manufacture of cellulose derivatives are referred to as Dissolving Grade Pulps. Productions of Dissolving grade pulps call for special attention and technical expertise from raw material selection, to the final stages of bleaching of pulps/viscose and rayon manufacture. Basically dissolving grade pulping is a chemical concept of obtaining cellulose in its purest form from wood or any cellulose material. This cellulose is morphologically in fibre form similar to paper making pulp, but chemically in its purest form for chemical conversions.The importance of dissolving grade pulp is its higher brightness than paper grade pulps, its higher alpha cellulose content than regular pulps and its lower impurities than paper grade pulps.The ideal dissolving grade pulp is regarded as the pulp, which has high alpha content., very low pentosans content and less calcium and mineral impurities. It is certainly important that degree of polymerization (chain length of cellulose molecules) shall be uniformly distributed in good quality dissolving grade pulps.This dissolving grade pulp is being used in India for the manufacture of filament yarn (Rayon), Staple fibre or foı extruding in film form (cellophane).

The pulping process followed by South India Viscose and A.P.Rayons have been discussed here with inherent advantages and disadvantages with regard to pulp quality and process limitations. South India Viscose Ind. used to produce considerably good quality dissolving grade pulp due to unifom wood quality, relative ease of processing / bleaching of finished pulp. Pulp produced by South India Viscose had market reputation as chemically active pulp with easily filterable viscose properties. The process description of South India viscose with our mill experience is described herewith.

Case Study

SIV Industries Ltd is an integrated plant having facilities

Table 1 Analysis of Important Wood Species and Standards

Particulars	Unit	SIV Norms	Blue Gum Eucalyptus globulus	E. Hybrid Eucalyptus tereticornis	Grandis E.grandis
Moisture	%	30.0	30	30	30
Basic Density	GM/CC	0.60	0.53-0.58	0.53-0.64	0.40-0.45
Benzene Extract	%	0.50	0.30-0.50	0.18-0.46	0.20-0.40
Alcohol Extract	%	2.50	1.40-1.80	2.70-4.90	1.20-2.00
Cold Water Extract	%	1.20	0.10-0.80	0.10-1.39	0.20-0.60
5% NaOH Extract	%	5.00	5.0-6.5	3.6-6.2	4.5-5.5
Pentosans	%	20.0	17.5-19.5	13.5-17.5	16.5-18.0
Lignin Max.	%	30.0	25.5-27.5	30.5-34.9	28.0-31.0
C&B Cellulose (by difference)	%	40-43	41-43	36.5-43.5	40.0-43.0
Ash	%	0.40	0.50	0.35-0.55	0.20-0.30
CaO	%	0.10	0.10	0.01-0.09	0.06-0.08

Note: C&B Cellulose expressed in this analysis actually represents possible pulp yield as finished product and alpha content.

for manufacture of wood pulp, Viscose Staple fibre and Rayon filament yarn along with important auxillaries like Sulphuric Acid and Carbon-disulphide off internal use. The mill opted for Acid Sulphite process with calcium base. Even though base recovery is not practiced, it recovers all the spent liquor to produce lignosulphonates as by-products and to generate steam energy in the chemical recovery type boiler. Even though material of construction to handle the spent liquor is SS 316 Ti make to withstand the pH conditions, process of concentration, combustion are similar to kraft mill chemical recovery plant except that no soda recovery plant exists.

The mill considers wood raw material as cellulosic input for a chemical industry and takes care from wood selection onwards. It adopts W.H.DORE wood analysis method. In this method analysis for C&B cellulose denotes pulp yield as final product and helps to carry material balance in each stage similar to chemical industry (wood balance). Characteristic analysis figures of regular wood species with standards are shown in Table 1.

Cooking Process

It uses batch cooking in conventional stationary / vertical digesters of SS 316 Ti make and cooking is carried in similar way as kraft pulping. However cold blowing is done at the end. Total cooking cycle is about 16 hours. Maximum temperature is 140 °C. However due to inherent gas pressure, the digester pressure will be about 8kg/sq.cm maximum.

Cooking liquor: Calcium bi-sulphite cooking liquore with total SO_2 = 5%, AND TOTAL CaO = 1.4% Cooking temperature maximum = 138 °C.

Cooking cycle = about 10 hours. About 7 hours to reach maximum temperature of about 140 °C and residence time at 140 °C for 2.5 hours to 3.0 hours. Cook end point is measured by cooking / spent liquor colour, cooked pulp 'k' number/sieber number and pulp viscosity. Pulp viscosity and 'k' number are carefully controlled in cooking process. Digester pressure is relieved at the end of cooking and residual SO_2 is recovered for re-use. Wash liquor from Brown stock washer end is used for rinsing and washing of cooked chips in digester and spent liquor collected is sent to evaporator plant and boiler plant.In Acid sulphite pulping process, cooking liquor of above composition with calcium base slowly penetrates and forms soluble component of calcium ligno-sulphonate with lignin in wood. Hence de-lignification is done first and then the acidity of cooking liquor at the particular temperature level of 140 degrees centigrade in final stages of cooking helps for depolymerization of cellulose chain and removal of pentosans/hemicelluloses etc by acid hydrolysis reaction. Thus in this end point is critical to control degradation of cellulose to desired level.

Digester Cycle

Preparation = 15 minutes

Chip Charging = 1 hour 45 minutes

Closing = 15 minutes

Intial temperature = 45 °C.

Final temperature = 140 °C.

Time to reach maximum temperature = 7 hours
Residence time at maximum temperature = 2.5 - 3.0 hours

Liquid displacement = 1 hour 45 minutes

Degassing time = 15 minutes

Discharging the pulp = 1 - 3 hours

Total cycle in general = 16 hours.

Table 2 Characteristics of Unbleached Pulp - SIV

Particulars	Unit	Standard Norms	Values	
			Blue gum + Wattle blend	E.Hybrid 85% + Pinus 15% blend
Viscosity (Snia Method)	cp	40-60	35 - 65	18 - 26
Sieber Number (Snia method similar to 'k' number)	No	18 - 22	18 - 22	20 - 26
Alpha Cellulose	%	88 - 89.5	89 - 90	88 - 89.5
Pentosans	%	6.0 - 7.0	55 - 7.0	5.5 - 7.0
Resins	%	0.40 - 0.60	0.35 - 0.60	0.40 - 0.70
Unbleached Pulp Yield	%	44 - 45	42 - 44	40 - 43

• Sieber number is conventional expression of 'k' number given by Snia Viscosa, Italy from correlation chart. Analysis procedure is 'k' number only and it is 2.8 - 3.2 times more than 'k'number. This is adopted for better control of value during cooking because of higher numerical value.

From Digester to Brown stock washers of three stage, the process is similar to paper industry with the application of Pressure knots, pressure screens, centricleaners and brown stock washers of counter current washing system. Even DD Washers are also in consideration for process. Characteristics of cooked/ unbleached pulp with standard norms are shown in Table 2

Bleaching Process

As this acid sulphite pulps are of low 'K' number with low bleach requirement, simple C-E-H sequence is sufficient to produce brightness up to 90+ units. However Hypo chlorite stage is split to three stages with monitoring of pulp viscosity at every stage and dosing of hypo accordingly (controlled bleaching with viscosity monitoring).

Final pulp is treated with 1% SO_2 water for removal of calcium and other mineral impurities with pulp which will effect the viscose quality unless otherwise removed from the pulp. It is not possible to remove absolutely fee from these mineral impurities, but by ion exchange method at low pH conditions, with retention of SO_2 water part of calcium ions and hardness with pulp is reduced considerably. Final pulp after bleaching and acidification processing are analyzed for its characteristics. Ideal characteristics of dissolving grade pulps produced by SIV for various applications are shown in Table 3. In Table 3 A, dissolving grade pulps from other sources analyzed by SIV method are shown. General specifications of various purposes of dissolving grade pulps shown in Table 4

Viscose Preparation, Various Steps

The Industries is having facilities to handle dissolving grade pulp in sheet form and slurry form both. Rayon grade pulp is mostly used in sheet form. Where as VSF Grade pulp (Staple fibre grade) is either used in sheet form or used as slurry to reduce de-watering time and energy for drying. Some mills produce pulp in crumbles for easy handling by flash drying process. In either case alkali cellulose is prepared and pressed to the press ratio of 1:2.7/2.9

In VSF and in Rayon grade treatments, the conditions applied are little bit modified due to specific requirements of viscose quality and yarn characteristics. Alkali cellulose is aged as slow aging in case of rayon grade and fast aging in case of VSF to meet the process requirements and dP norms (degree of polymerization). Xanthation of alkali cellulose is carried in simplex vessels (reactors) under controlled conditions of vaccum, temperature and time with churning facilities. Viscose is filtered in three stages by mechanical/auto cleaning pressure filter devices and by pad and frame filter in final stage. The quality of pulp plays a major roll in quality of viscose and its filterability. Further viscose is aged to drop viscosity to desired level and spun in suitable spinnerates under controlled spin bath temperature and salt concentration conditions. In general for producing viscose staple fibre spinnerettes containing 23,000 holes of 70 micron opening is used to produce tow, where as in case of rayon filament yarna

Table 3 Characteristics of Bleached Pulp - SIV

Particulars	Unit	SIV - Rayon Grade Pulp	SIV - VSF Grade Pulp
Brightness	%	90 - 91	87 - 90
Viscosity (Snia Method)	CP	28 - 32	16 - 22
Alpha Cellulose	%	90.5 - 91.5	90-91
Beta Cellulose	%	5.0 - 6.0	5.5 - 6.5
Gamma Cellulose	%	3.0 - 4.0	2.5 - 3.5
Resins	%	0.25 - 0.35	0.3 - 0.4
Pentosans	%	3.5 - 4.5	4.0 - 5.0
10% Soda Solubility	%	10-11	10 - 12
18% Soda Solubility	%	5-6	5.0 - 6.5
7.14% Soda Solubility	%	12 - 14	12.5 - 14.5
21.5% Soda Solubility	%	3.5-45	4.5 - 5.5
Copper Number	No.	1.3 -1.6	1.3-17
Ash Max	PPM	400-600	1500
CaO Max.	PPM	150-250	1000
Acid Insolubles (as silica)	PPM	60	60
R203 (Aluminium oxide + Iron Oxide)	PPM	60	60

Table 3A Characteristics of various dissolving grade pulps, Analyzed by SIV method

Particulars	Unit	AP. Rayons	Century Pulp	Kechikan Pulp	Russian Pulp
Alpha Cellulose	%	94+/- 2	92+/- 1	93+/-1	94.6+/-
Beta Cellulose	%	3.5-4.7	2.5	3.7	3.6
Gamma Cellulose	%	2.3-2.4	4.0	—	—
Viscosity (Snia Method)	CP	17-22	19	29	30
7.14% Soda Solubility	%	6.6-7.4	9.1	8.0	9.5
21.5% Soda Solubility	%	1.8-3.2	—	3.84	—
Pentosans	%	3.8-7.7	4.9	2.42	—
Resins	%	0.28-0.32	0.33	0.30	—
Copper Number	No.	0.98	—	—	095
10% Soda Solubility	%	6.7-9.5	8.05	—	8.06
18% Soda Solubility	%	4-6	4.5	—	4.59
Copper Number	No.	0.98	—	—	0.95
Ash Max.	PPM	560-600	555	460	160
CaO Max.	PPM	73-126	101	210	55
Acid Insolubles (as silica)	PPM	82-146	105	24	55
R203 (Aluminium oxide + Iron Oxide)	PPM	105-186	145	63	80
Brightness (Photovolt)	%	80.6-84.1	84.5	88	91.5
Specks/sq. meter	No	60	—	20	20
Absorption of 17.5% NaOH	%	514-556	—	532	—
Expansion in !7.5% NaOH	%	432 - 500	—	467	—
Sheet Thickness	mm	0.9-1.0	—	1.01	0.89
Apparent Density	gm/cc	0.824	—	—	0.64
Rayon Yield(calculated)	%	97.5-98.2	96.9	—	—

Table 4 Characteristics of dissolving grade pulps

Particulars	Unit	Low Alpha Wood Pulps	high Alpha Wood Pulps	Linter	Cotton	
		Textile Rayon	Cello-phane	Tyre cord	Tyre cord	Pulp For Tyre Cord & Film
		Normal Viscosity	Low Viscosity	Normal Viscosity	Low Viscosity	
Alpha Cellulose	%	89.0-92.0	87.0-91.0	94.0-96.0	93.5-95.3	98.0-99.0
Beta Cellulose	%	3.0-5.0	50-7.0	2.0-3.0	2.0-3.0	1.0-1.5
Gamma Cellulose	%	3.0-6.0	3.0-5.0	1.5-3.5	2.0-4.0	0.0-1.0
10% KOH Solubility	%	10-17	13 .0-20.0	6.0-10.0	6.0-10.0	15-40
Ether Extract	%	0.1-0.30	0.1-0.30	0.05-015	0.2-0.10	0.05-0.10
Ash	%	0.04-0. I3	0.05-0.13	0.04-0.08	0.04-008	0.01-0.03
Silica	%	0.005-0.02	0.003-0.02	0.004-0.02	0.004-0.02	0.01-0.03
Calcium	%	0.01-0.05	0.01-0.05	0.01-0.03	0.01-0.03	0.01-0.03
Iron	PPM	5-15	5-15	5-15	10-20	10-20
Cuprammonium Viscosity (ACS Method)	CPS	250-700	100-200	250-700	75-125	250-350

varied quality of spinnerettes having 12 to 48 holes are used depending on denier requirements. The fine thread coming out of the spinnerette is drawn out continuously and is wound in a spinning pot rotating at 7000 rpm. During the draw of filament, streth and twist are given to add strength. SIV is having 59 spinning machines with each having 200 spindles. The yarn is collected in the form of cake. The two produced in VSF plant is uniformly cut into required staple length according to market requirements. This staple fibre is suitable blend for cotton in making fabric for textile industry. Rayon is directly used for weaving of fabric.

Further treatments after regeneration of cellulose in staple fibre or filament yarn/cake form are processes involved are CS2 recovery, de-sulphurization, bleaching, washing, finishing and drying operations in systematic way. Either rayon yarn in cakes or staple fibre in bales, it is conditioned in specific temperature and humidity conditions before delivering in to market. Market specifications for Rayon Filament yarn and Viscose Staple Fibre as per SIV Norms are shown in Table 5 and Table 5A respectively.

APR Industries Ltd- Case Study

Now the plant has crossed 300 tonne perday in production level per day and also improved considerably in pulp quality compared to earlier days. The mill is having more flexibility in raw material selection due to inherent advantages of process. Unlike in Acid sulphite process, wood selection is not much problem for pre-hydrolysis kraft pulping and hence the mill was able to use all mixed hardwood varieties and eucalyptus together.

Pre-Hydrolysis Stage

In this stage either steam or water is used to soften the wood and to hydrolyse unwanted pentosans and hemi-celluloses with wood chips. This also helps to make the further cooking easy and less time consuming. As a criteria for extent of pre-hydrolysis needed, it is practiced to match the color of pre-hydrolyzed liquid, its pH and specific gravity. BOD and COD are other criteria to indicate extent of organics removed from wood chips as pre-treatment.

Kraft Pulping

After pre-hydrolysis kraft pulping is similar to conventional wood pulping. However it is monitored on 'H' factor digester pre-set conditions to meet the wood

Table 5 Rayon Filament Yarn Properties

Characteristics	120/28 Bright	120/40 Bright	150/36 Bright	300/44 Bright	450/90 Bright	100/40 Bright
Denier	120+/- 4%	120+/- 4%	150+/- 4%	300+/-4%	400+/- 4%	100+/-4%
Twist / Meters	70-74	70-74	70-74	80-83	80-85	70-74
Conditioned Tenacity gms/denier	1.65-1.75	1.65-175	1.65-175	175-1.85	170-1.80	1.65-1.80
Wet Tenacity gms/denier	0.70-0.80	0.70-0.75	0.70-0.80	0.80-0.90	0.75-0.85	0.75-0.80
Conditioned Elongation %	18-21	18-21	18-22	20-22	22-26	18-21
Wet Elongation %	22-27	22-27	21-29	25-29	28-32	22-26
Direction of Twist	S	S	S	S	S	S
Number of Filaments	28	40	36	44	90	40
Moisture Regain Maximum %	13	13	13	13	13	13
Normal Weight of each Cone in Kgs	1.8-1.9	1.8-1.9	1.8-1.9	1.8-1.9	1.8-1.9	1.8-1.9

- 1. All tests are carried out under standard Atmosphere of 65+/-2% RH, and Room Temperature of 20+/-2 Deg. Centigrade.
- Tenacity and Elongation are Base on Pendulam type Tester and not Instrom Tester.

Table 5.A Viscose Staple Fibre Properties

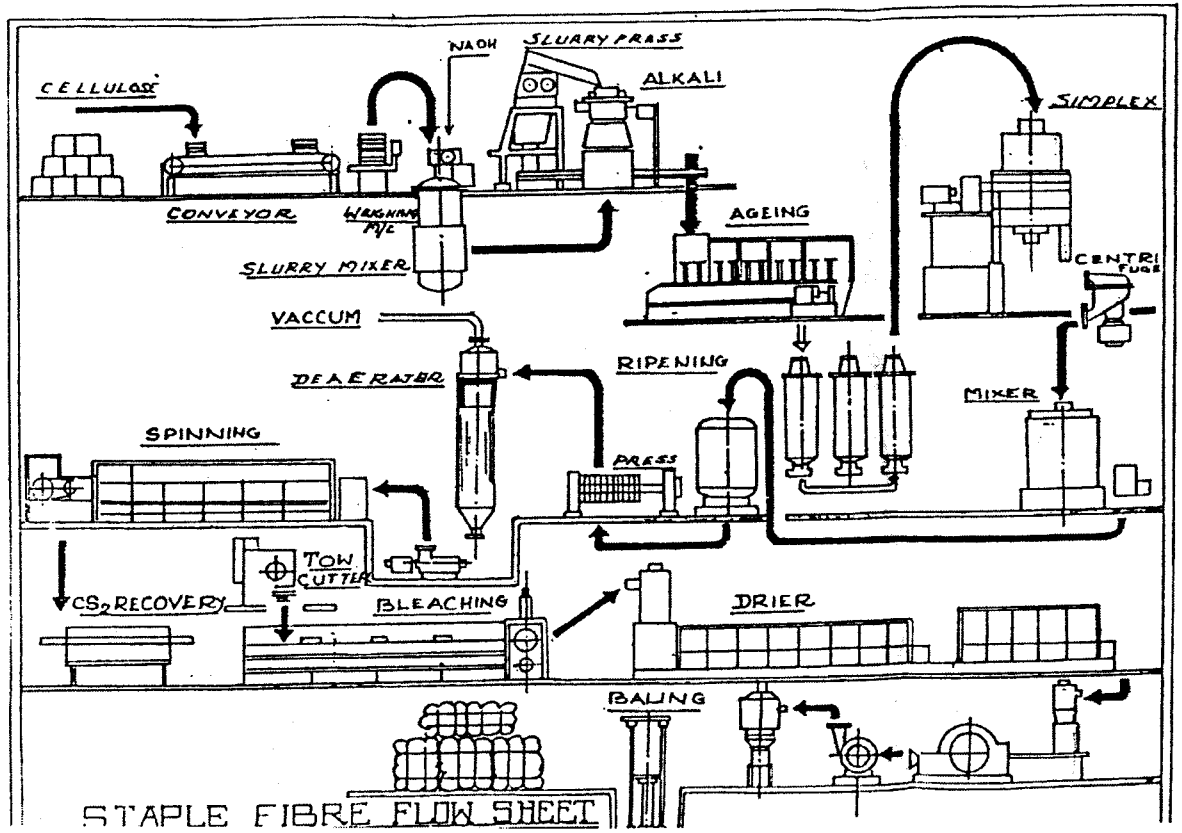
Viscose Stape Fibre	Unit	1.5 Denier Bright	1.2 Denier Bright	1.5 Denier Colour Black
Denier	GMS	1.5 +/- 0.005	1.2 +/- 0.005	1.5 +/- 0.005
Conditioned Strength	gms/ denier	2.4 +/- 0.1	2.5 +/- 0.1	2.35 +/- 0.1
Conditioned elongation	%	18.5 +/- 1.0	185+/-1.0	18.5 +/- 10
Wet Strength	gms/ denier	1.4 +/- 0.1	1.4+/-01	135 +/- 0.1
Wet elongation	%	20.5 +/- 1.0	20.5 +/- 1.0	20.5 +/- 1.0
Finish	%	0.25+/- 0.05	0.25+/- 0.05	0.25+/- 0.05

- Cutting length/staple length of fibre is as per the market requirements usually 4.5-5.0 cm
- The above tests are carried out in schopper dynamometer at 27+/-2 degrees centigrade and 65% RH

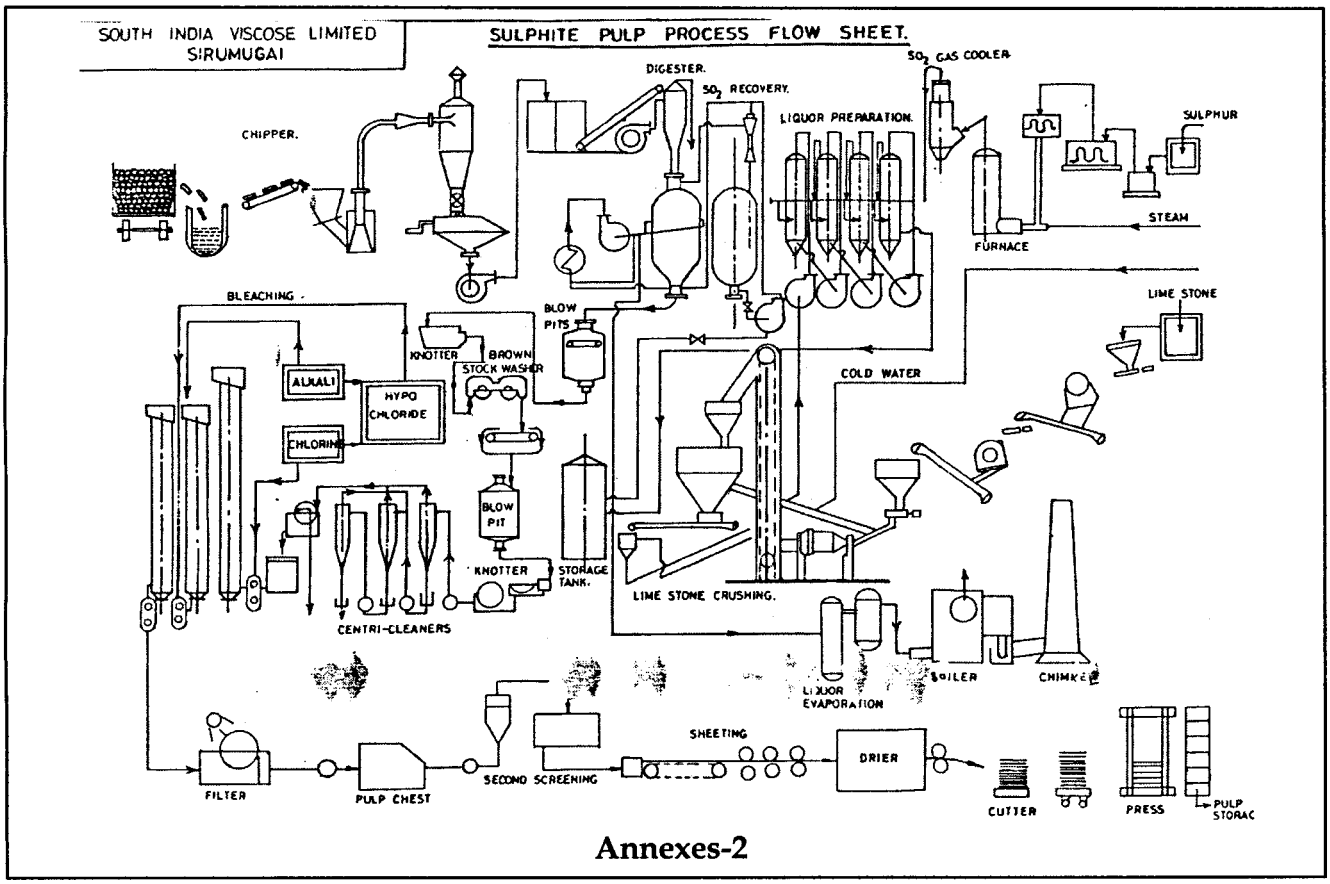
blend and to achieve desired alpha pulp quality. Pulp blowing is conventional pressure blowing only unlike in acid sulphite pulping. Chemical recovery is practiced like in paper mills. A process of anaerobic digestion of pre-hydrolysis liquor is added advantage of energy recovery. Further processing of washing, screening and bleaching are similar in both the cases. However because of higher 'K' number of pulps and its higher bleach requirements, in order to preserve pulp strength while improving pulp brightness, chlorine di-oxide bleaching is practiced in final stage followed by acidification with SO_2 water. 450-650 gsm pulp sheets are made in sheet making machine as per the market requirement.

Pulp Reactivity and Rayon Yield

Compared to acid sulphite pulp, pre-hydrolysis kraft pulp of dissolving grade is less reactive due to inherent



Annexes-1



Annexes-2

reasons. Alkali cellulose aging will take more time. However yield point of view, pre-hydrolysis kraft pulp produce higher rayon yield. On the other hand when compared to acid sulphite pulp, prehydrolysis kraft pulp loose its brightness in alkali cellulose preparation and regenerated fibre will be dull in lustre and brightness. This is the practical experience faced by many rayon manufacturers when operating both the pulps separately.

CONCLUSION

It can be seen from the details that unlike in Paper industry, in case of Dissolving grade pulping industry "CONCEPT AND APPROACH" of pulping and processing is entirely different. In this case from wood selection onwards, proper care is taken to suit the finished product requirements. This is with very much stringent in norms, when it is the case of Acid Sulphite pulping due to inherent process limitations.

A schematic sketch of process drawing for pulping and viscose staple fibre presented as Annexes - 1 & 2.

Like in a chemical industry it is practiced even wood balance, which is similar to a material balance in chemical industry or water balance/soda balance in paper industry like wise.

Due to inherent process advantages with pre-hydrolysis kraft process, industry based on this process is enjoying more freedom in selection of wood raw material.

Ultimately, however as the process involves extensive purification of cellulose in all the stages. Industry has to bear with process losses as well as related pollution problems.

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