Hydrothermal Processing of Pulp to Enhance its Reactivity for Viscose Process

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ABSTRACT

Hydrothermal treatment of dissolving pulp has provided a new approach to enhance the cellulose reactivity towards carbon-di-sulphide and alkali. Treated pulp shows good filterability as well as high homogeneity of cellulose xanthate solution. The results indicate that desired reduction of degree of polymerisation (D.P.) from any starting level is possible and high quality viscose is produced from hydrothermal treated pulp at CS_2 charge of as low as 17-20% based on cellulose. Other benefits demonstrated with hydrothermal treated pulp include lower concentration of alkali in steep lye and in final viscose. The hydrothermal processing of dissovling pulp can be useful to tackle the problems of environmental danger associated with viscose process.

The main effect of hydrothermal treatment is lowering of average degree of polymerization (D.P.) and increased accessibility of chemicals due to enhanced reactivity. The depolymerization and enhanced reactivity of pulp showed dramatic improvement in homogeneity of viscose solution at reduced chemical consumption.

INTRODUCTION

Since last many years, the viscose rayon industries have been trying various ways to minimise the chemical inputs in the process. The main aim of these efforts is both economic and environmental. Some efforts on these lines include the use of additives[1-3], double steeping[4], high energy electron treatment[5-11], enzyme treatment[12,13] etc.

Besides chemical purity of dissolving pulp, the reactivity of cellulose, towards chemicals is utmost important parameter in making derivatives of cellulose for value added industrial products like rayon, carboxymethyl cellulose, cellulose carbamate etc. The reactivity of cellulose for chemical processing depends on the structural levels of cellulose molecules[14], fibre morphology, crystalline/amorphous region as well as chemical purity. Many chemical pulps with high purity are not suitable for viscose process specially due to their poor affinity for alkali and CS_2.

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In recent years successful attempts have been made to enhance cellulose reactivity by high energy electron processing of pulp[5-11], but hydrothermal treatment has not been tried yet. Present work unravels the effect of hydrothermal (H.T) treatment of dissolving pulp to increase its reactivity for viscose process.

A significant influence of activation of pulp by hydrothermal treatment is perceptible. Most of the pulps respond well to hydrothermal treatment and a high quality of viscose can be produced at 20% or low CS_2 charge on cellulose basis. Additional advantages are that such pulp needs less alkali concentration in steep lye, low aging time and less alkali in final viscose. The depolymerization and enhanced reactivity of cellulose caused by hydrothermal treatment show marked improvement in viscose quality and reduction on environmental load due to low consumption of chemicals. In present work it has been illustrated that the hydrothermal treatment produces similar results as high energy electron processed pulp. The H.T. treatment is simple, convenient and less cost intensive.

EXPERIMENTAL

Materials

Following wood pulp of commercial grade were taken for this study:

1. Hemlock soft wood sulphite pulp (Ketchikan-120).

2. Southern pine soft wood pre-hydrolysed sulphate pulp (Buckey V-60).

3. Eucalyptus hard wood flash dried kraft pulp (Grasim-F.D).

HYDROTHERMAL TREATMENT

Commercial grade dissolving pulps were treated hydrothermally under high pressure and temperature. The optimal conditions were determined for different pulps which depend on initial degree of polymerization, type of pulp and final D.P. of cellulose required.

The pulp was taken in a autoclave suitable for high temperature and pressure with predetermined quantity of water so as to get 1:4 to1:5 pulp to water ratio. The temperature of system was raised to desired level and pulp was treated at maximum temperature for certain period. The depolymerization of treated pulp depends on pH, maximum temperature and time at maximum temperature. These parameters were optimised for each pulp. After completing the hydrothermal treatment the excess water was removed by pressing the pulp and then it was dried. The usual maximum temperature for hydrothermal treatment ranges from 120-165°C for 2-4 hours depending on type of pulp and degradation needed.

CHARACTERIZATION OF HYDROTHERMAL TREATED PULP

The hydrothermal treated pulps were analysed using standard methods for their important constituents like alpha cellulose[15], hemicellulose, rayon yield[16], copper number[17], cellulose viscosity[18], freeness[19], etc. Cellulose degree of polymerization (D.P) was calculated from following formula:

D.P $= 1000 \log (\eta) - 400$

Where η $=$ Viscosity of 1% cellulose in cuprammonium solution at 20°C

PREPARATION OF ALKALI CELLULOSE

Alkali cellulose was made by conventional sheet steeping method in Emil Blaschke machine. The concentration of sodium hydroxide in steep lye was varied from12% to 22% containing 20-25gpl hemi cellulose which is normally present in commercial steep lye due to re-circulation of solution. Steeping was carried out for 40 minutes at 20-22°C. After Steeping the excess of sodium hydroxide solution was drained off and the sheets were pressed to get desired press weight ratio (normally 2.70 to 2.80). The pressed sheets were further shredded in a sigma blade shredder to get a fluffy mass of alkali cellulose. The desired degree of polymerization was achieved by aging the alkali cellulose under controlled conditions of time and temperature.

XANTHATION AND DISSOLUTION

Aged alkali cellulose was treated with carbon-disulphide (CS_2) in a dry churn under vacuum. The CS_2 charge was varied from 11-30% on cellulose basis for H.T treated pulp and 15 to 30% for untreated pulp. The cellulose xanthate so formed was dissolved in dilute sodium hydroxide solution at 18-20°C for 3 hours to get 9-10% cellulose and 5-6% NaOH. The

xanthate solution, commonly known as viscose was futher analysed for clogging constant value and solution viscosity (ball fall method).

CLOGGING CONSTANT OF VISCOSE (Kw)

Clogging constant value (Kw) indicates the filtering property of viscose which is the best measure of its quality from the point of view of cellulose xanthate solubility and presence of insoluble matters. These values are determined using clogging constant equation[20,21].

$$Kw = 2 \times 10^5 \left[\frac{t_2/w_2 - t_1/w_1}{t_2 - t_1} \right]$$

Where:

w_1 and w_2 = Weight of filtered viscose after filtration time t_1 and t_2 respectively, taken from the beginning of filtration.

In present case, t_1 = 20 minutes and t_2 = 40 minutes

and thus :

$$Kw = \left[\frac{t_2}{w_2} - \frac{t_1}{w_1} \right] \times 10^4$$

Clogging constant (Kw) was measured by passing the viscose through a standard filtering apparatus (2.5 litre capacity) under constant condition of pressure and filter media. Viscose viscosity was measured by falling ball method[21]. High values of Kw indicates poor viscose quality and is usually the result of slime, gels, fibres and other incompletely dissolved fibre components and impurities.

RESULTS AND DISCUSSIONS

HYDROTHERMAL TREATMENT

The hydrothermal treated pulps are analysed for their important constituents and reported in Table-1. It indicates that sulphite pulp shows higher degradation of cellulose which resulted into lower alpha cellulose, higher alkali solubilities and lower viscosity than that of kraft pulp. However the presence of higher metal ions in the F.D. kraft pulp has accelerated the hydrothermal reaction. The major effects of H.T. treatment are reduction in degree of polymerization (D.P) and increase in copper number. These effects are quite similar to that of electron beam processed pulp.

A singificant reaction observed during H.T. treatment is depolymerization of cellulose. Depolymerization caused by H.T. treatment is function of time and temperature which can be expressed by a single numerical value i.e. hydrothermal factor (H.T factor). The desired degree of polymerization can be predetermined through the adjustment of H.T factor. The hydrothermal conditions for different pulps are shown in Table-2.

HYDROTHERMAL FACTOR (H.T. FACTOR)

In kraft pulping the hydrolysis and prehydrolysis factors are quite informative to indicate the severity of pulping by single factor[22-25]. For any prehydrolysis karft pulping, there are three important cooking variables (i) maximum temperature of digester, (ii) time upto maximum temperature and (iii) time at maximum temperature. The time upto maximum temperature is usually of secondary importance if the heating up time is not very long. The initial pH of liquor is significant when acid or alkalis are used during H.T. treatment, but in present work the cooking liquor is only water and the acid generated during treatment is quite less to give lower pH to the range of 4-6. Thus maximum temperature and time at maximum temperature define the most significant variable during hydrothermal treatment.

Although the present work is concentrated only with hydrothermal treatment at high temperature and pressure, it is similar to the work of Brasch[25] which was based on the assumption that the temperature coefficient was 3/10°C temperature rise in prehydrolysis stage. The preliminary work on hydrothermal treatment of pulp also showed that the hydrolysis rate is higher than two and therefore it is assumed that in case of H.T. treatment the hydrolysis rate is approximately three fold per each 10°C rise in temperature. It is thus possible to calculate the relative rate of hydrolysis during H.T. treatment for any desired temperature by following equation[25]:

$$\text{Relative rate} = 3^{(t-100)/10}$$

Where t is the temperature in .°C

Table-1 Chemical analysis of original and H.T treated pulp

Parameters	Units	Ketchikan- 120 Original	Ketchikan- 120 H.T treated	Buckey V - 60 Original	Buckey V - 60 H.T treated	Flash Dried Original	Flash Dried H.T treated
α Cellulose	%	92.8	91.9	94.7	94.4	94.6	93.6
β Cellulose	%	4.7	5.3	4.1	4.2	3.6	4.3
γ Cellulose	%	2.5	2.8	1.2	1.4	1.8	2.1
S_{10}*	%	10.8	17.2	6.2	7.1	6.6	8.0
S_{18}*	%	7.0	8.2	3.5	3.4	3.7	3.6
$S_{21.5}$*	%	6.3	7.0	3.1	3.4	3.5	3.7
Pentosans	%	1.8	1.7	1.7	1.6	2.8	2.7
Copper No.	---	1.1	2.4	0.6	0.9	0.6	1.1
Resin & Fats (Alcohol + Benzene)	%	0.31	0.30	0.23	0.22	0.33	0.31
Ash	%	0.053	0.032	0.073	0.066	0.073	0.068
Silica	ppm	40	28	38	32	146	134
Iron	ppm	8	6	18	15	44	36
Calcium as CaO	ppm	60	66	86	92	140	120
Viscosity T-206	Cp	16.4	7.9	10.8	7.7	10.6	6.8
Degree of polymerization	D.P	815	498	637	486	625	432
Freeness	°SR	13.0	13.5	10.3	11.3	14.5	14.9

* S_{10}, S_{18} & $S_{21.5}$ = Solubility of pulp in 10%, 18% & 21.5% NaOH solution respectively at 25°C

Table-2 Critical conditions for hydrothermal treatment

Pulp	Initial Viscosity Cp	H.T. conditions Max. temp. °C	H.T. conditions Time hr.	pH of liquor Initial	pH of liquor Final	Viscosity of H.T treated pulp Cp
100% Eucalyptus Kraft F.D (Grasim)	12.0	140	3	7.9	4.6	7.5
" "	12.0	160	2.5	6.8	4.5	6.8
Mixed Hardwood Kraft (Grasim)	13.0	140	3	7.6	4.6	6.5
" "	13.0	160	3	8.0	4.5	5.5
Softwood Kraft (V-60)	11.0	140	3	7.5	5.1	7.8
Softwood Sulphite K-120	16.4	140	3	8.0	5.1	8.5
" "	16.4	145	3	7.8	5.0	7.9
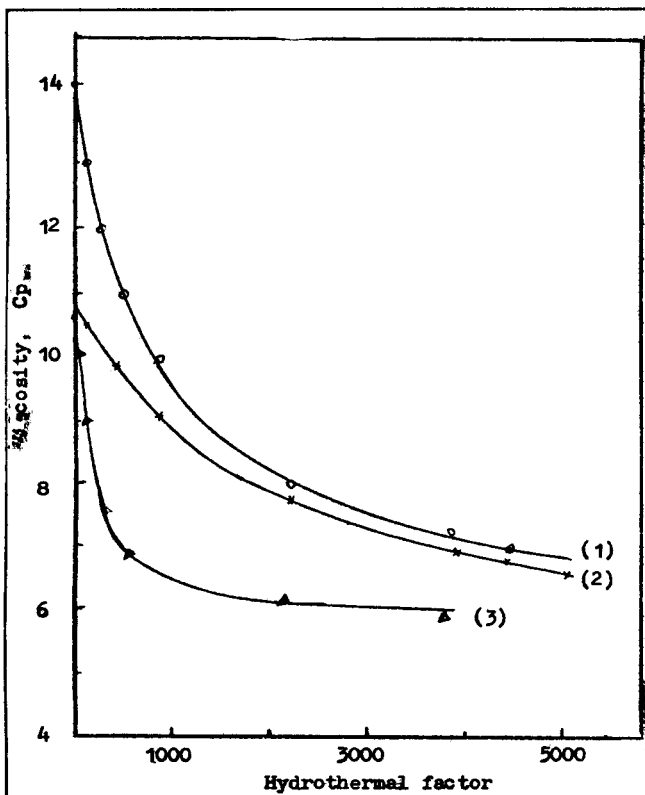
Fig. 1- Dependence of cellulose viscosity on hydrothermal factor (1) K-120, (2) V-60, (3) F.D.

Fig. 2- Viscose clogging constant (Kw) as function of CS$_2$ charge (Eucalyptus kraft pulp, F.D.)

This equation can be used to calculate hydrothermal reaction factor by multiplying relative rate to time at maximum temperature and is denoted here as H.T. factor.

The severity of hydrothermal treatment is shown in Fig. 1 by plotting H.T. factor versus cellulose viscosity. The data shows that the reduction of viscosity depends on H.T. factors.

CARBON DISULPHIDE REDUCTION

In viscose industries, the concentration of carbon disulphide (CS$_2$) during xanthation of alkali-cellulose is usually kept high (30-35% on cellulose) to get good quality of viscose having low clogging constant (Kw). Cost of CS$_2$ and environmental impact have made several attempts to reduce amount of CS$_2$ needed to prepare good filterable viscose. Electron processing of pulp has previously been shown as one of the means to achieve this objective. It has now been demonstrated in present work that the reduction of CS$_2$ by 30-40% of conventional dose is possible when viscose is prepared from H.T. treated pulp. However eucalyptus flash dried pulp did not
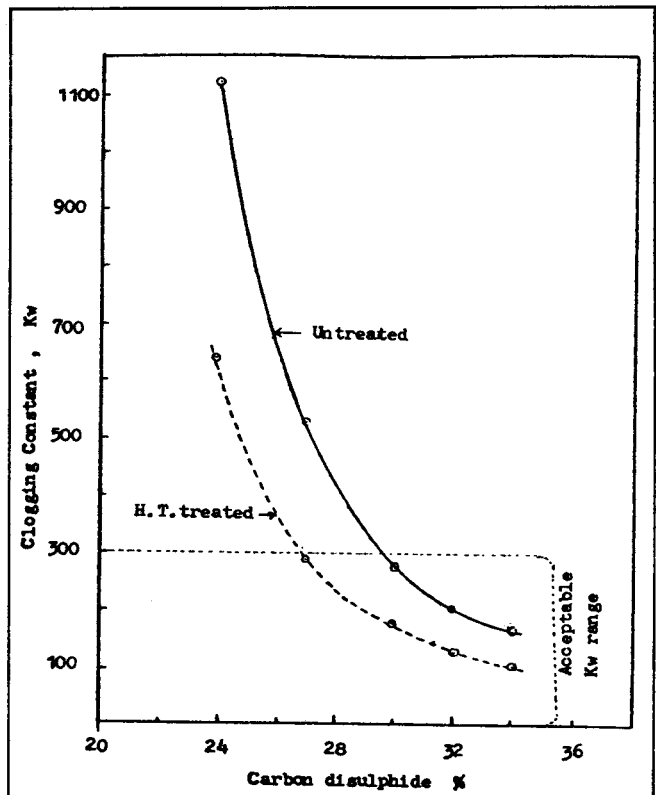
respond well to H.T. treatment to enhance its reactivity (Fig. 2). The probable cause for this may be the flash drying system causing hard fish eye formation and presence of higher metal ions impurities besides crystalline nature of wood fibres. Table-3 shows some critical results of viscose Kw at various level of CS$_2$ for different dissolving grade pulps treated hydrothermally.

Fig. 3 shows the Kw values determined at various CS$_2$ concentration for viscose prepared from hydrothermally treated and untreated hemlock soft wood sulphite and southern pine soft wood kraft pulp. In these experiments, Kw values below 300 are considered within acceptable working range, while values above 300 reflect a poor quality of viscose. From Fig. 3, it is evident that viscose prepared from untreated pulp at a concentration of 28-30% CS$_2$ gives good clogging constant (Kw) values. As the CS$_2$ content decreases the Kw values increase indicating marked drop in filterability. Contrary, the Fig. 3 indicates that when H.T treated pulp was used, acceptable clogging constant (Kw) were obtained at 15-20% CS$_2$ concentration. Thus the treated pulp requires about 30-40% less CS$_2$ than untreated pulp.
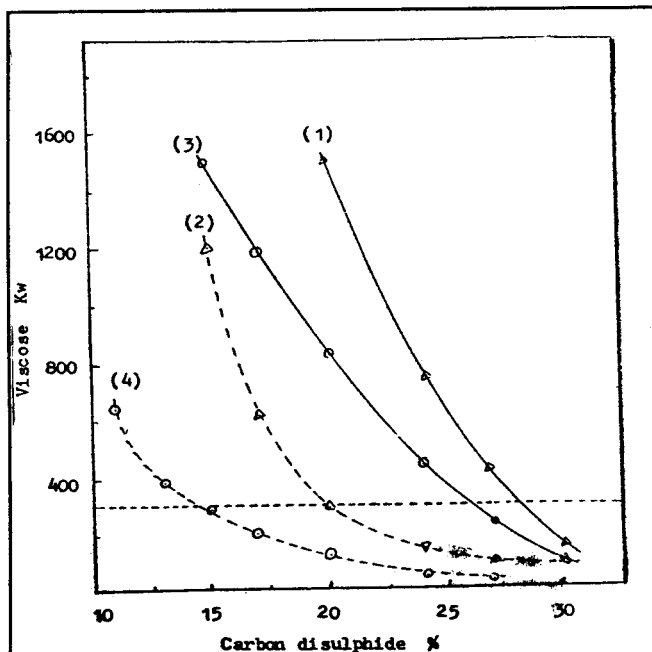
Fig. 3- Kw values as function of CS2 charge for soft wood pulp. (1) V-6 untreated, (2) V-60 H.T. treated, (3) K-120 untreated, (4) K-120 H.T. treated

This low requirement of CS_2 will obviously reduce the hazardous emission as well as cut down the production cost of fibre.

REDUCTION OF NaOH CONCENTRATION IN STEEP LYE

In the manufacture of rayon fibre by viscose process, the first step is the mercerization of pulp to prepare alkali cellulose and is known as steeping. In conventional process the concentration of sodium hydroxide in steep lye is usually 18-19%. This concentration is necessary for getting sufficient swelling of cellulose and desired rate of degradation during aging of alkali cellulose. Lower alkali concentration (10-12% NaOH) shows maximum swelling but alkali cellulose prepared from such solution would result into a very long aging time for oxidative degradation. In H.T. treated pulp the cellulose D.P. can be achieved to any desired level and thus the time required for alkali-cellulose aging can be shortened or eliminated. Thus lower alkali concnetration in steep lye may be used with H.T. treated pulp, which shows higher swelling and low alkali in alk-cell. This low alkali in alk-cell causes lower by-product formation during xanthation and leaves more CS_2 available for main xanthation reaction.

Sihtola and Nizovsky[21] in their double steeping method and Fischer and Goldberg[26] on the properties of electron processed pulp during mercerization have shown that CS_2 absorption and swelling of cellulose is high at lower alkali concentration. H.T. treated pulp also shows similar characteristics. The H.T. treated softwood southern pine kraft pulp was steeped in 12-22% NaOH to get alkali cellulose which was further treated with 30% CS_2 and viscose was prepared having 10% cellulose and 5.9% alkali. Fig. 4 shows data on the change of 1/Kw depending on the concentration of sodium hydroxide in steep lye. The lowest Kw values were obtained in the range of 14-16% NaOH in steep lye.

The viscose prepared at 30-32% CS_2 using 18% steep lye with untreated pulp (softwood kraft) shows acceptable Kw values for higher range of 5.5-6.0% NaOH, but lower CS_2 below 27% demonstrates unacceptable Kw values (Fig. 3). Contrary to this, the viscose prepared from H.T. treated pulp produces acceptable Kw values (below 300) even in the lower range (i.e. 4.8-5.2%) of NaOH with CS_2 as low as 20%. Soft wood sulphite pulp shows still better enhancement in reactivity than kraft pulp and acceptable Kw values can be obtained with CS_2 lower than 17% (Fig. 3).

As discussed earlier, the hydrothermal treatment of pulp causes two important effects i.e.
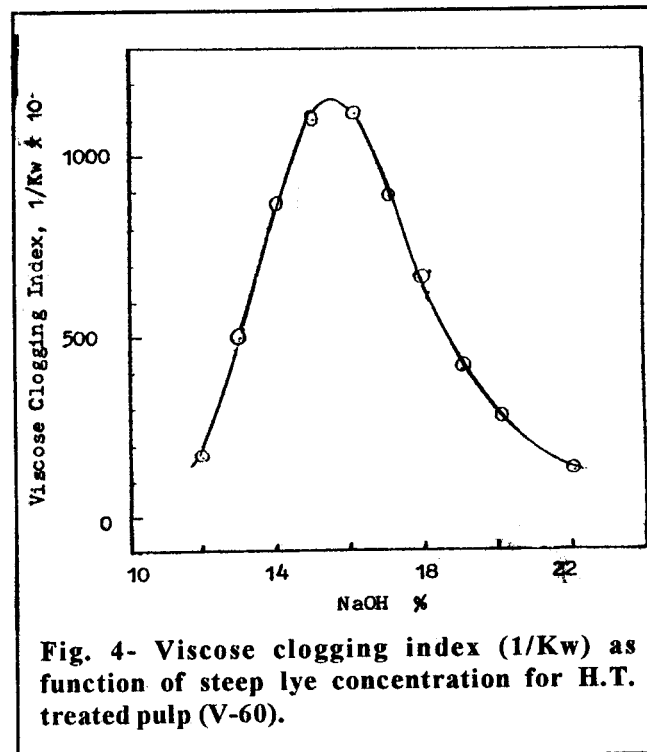

Fig. 4- Viscose clogging index (1/Kw) as function of steep lye concentration for H.T. treated pulp (V-60).

Table-3 Viscose Kw values for untreated and H.T treated pulps at different CS_2 charge

Wood Pulp	CS$_2$ Charge % (on cell)	Viscose Kw values		Reduction of CS$_2$ for acceptable Kw %
		Untreated pulp	H.T treated pulp	
100% Eucalyptus Kraft F.D	30	275	175	
" "	27	525	280	10
Mixed Hardwood Kraft	30	554	115	
" "	24	2500	265	20
Softwood Kraft (V-60)	30	152	94	
" "	20	1500	285	33
Softwood Sulphite K-120	30	80	36	
" "	16	1185	230	46

depolymerization and increased reactivity of cellulose. It can be though that H.T. treatment causes only degradation and benefits observed in Kw is from reduced D.P. To examine this view, a systematic study was carried out with hemlock soft wood sulphite pulp. The pulp D.P was reduced by degrading thermally in an oven to get same D.P. as hydrothermal treated pulp at H.T. factor 3000. The viscoses were prepared from both the pulps (i.e. thermally treated and hydrothermally treated) under identical conditions. The clogging constant (Kw) values were determined. It was observed that the H.T. treated pulp showed markable improvement in

Fig. 5- Dependence of viscose Kw and cellulose D.P. on hydrothermal factor.

Kw values over thermally treated pulp. Fig. 5 shows the Kw and D.P values at various dose of H.T treatment denoted as HT factors. Better Kw value than thermally treated pulp are found even for viscose prepared from pulps treated at lower HT factors i.e. 700, 2000. These improvements in viscose Kw show clear evidence of effect of H.T treatment on improved reactivity of cellulose over and above that resulting from D.P. reduction.

Thus the hydrothermal treatment brings about the chemical and crystalline structural changes which render cellulose more accessible to acids, alkalis, carbon disulphide and certain solvents. The H.T treated pulp is not only suitable for viscose process but also for lyocell process. The structural changes have not been studied at this stage however it is pre-assumed that the amorphous area in cellulose fibre increases and makes more accessible junctures even at crystalline regions similar to high energy electron radiated pulp forming free radicals.

The viscose produced from H.T treated pulps with low CS$_2$ has series of peculiarities such as low content of by-products like Na$_2$CS$_3$ high viscosity, low maturing index etc. It is known[24] that it is not possible to get satisfactory fibre quality from a viscose in which by-porducts are absent. Obviously it is necesary to apply technological upgradation which can be able to compensate the fibre quality due to insufficient amount of by-products. In our opinion the overcoming of such bottle necks is quite possible and in fact we at our Institute have produced fibres with satisfactory quality from such a viscose.
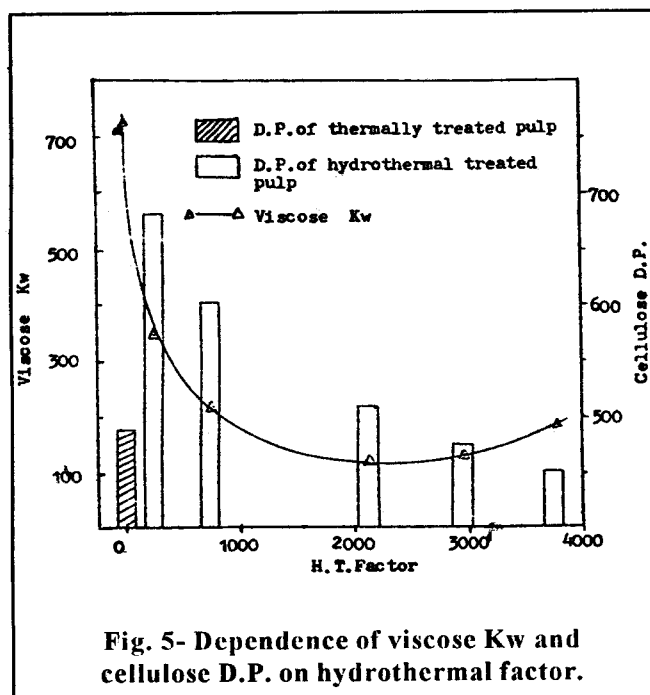
CONCLUSION

The results showed that significant improvement in cellulose reactivity can be derived from hydrothermal treatment of pulp. Several benefits were demonstrated when hydrothermal processed pulp (soft wood sulphite and kraft) were used to make viscose. These include reduction of CS_2 concentration to produce high quality of viscose, lower concentration of NaOH in steep lye and in viscose, reduction of environmental load etc. These results indicate that hydrothermal treatment provides advantages on not only to D.P reduction but also to enhance the cellulose reactivity.

The results suggest the significant economic advantages due to low chemical inputs with the use of hydrothermal treated pulp. In addition, the environmental problems associated with viscose process which are a major concern, can be coped up with permissible emission limits due to reduction in chemical demand.

ACKNOWLEDGEMENT

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