A STUDY OF VISCOSE QUALITY BY REDUCTION OF KNOTS IN SLURRY AND ALKALI CELLULOSE

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In the viscose process, the consumption of carbon disulphide (CS_2) during the xanthation stage is largely affected by the presence of knots in the slurry and alkali cellulose. Knots are hard patches of cellulose, present in the pulp or generated during the processing of pulp in the viscose making process. A novel method for qualitative and quantitative detection of knots is described in the present work. Reducing the number of knots in alkali cellulose (alkcell) has resulted in an increase in the ripening index (RI) of the viscose solution from 9.5 to 13.0. It was also noted that the reduction in the number of knots in the slurry and alkcell led to reduced CS_2 consumption by 4%. It was further observed that the gamma number of the viscose solution did not change significantly with a lower number of knots and lower CS_2 addition, thus a lower consumption of CS_2 was sufficient to achieve better penetration in the alkcell.

Keywords: knots, CS_2 consumption, viscose, bulk density, hard patches, ripening index

INTRODUCTION

Regenerated cellulose fibers are always in focus due to their superior and unique performance in textile and other applications, such as disposable medical products, packaging materials and artificial membranes.[1,2] Of all regenerated fibers, rayon is the most widely used one. Its preparation starts by steeping of dissolving grade pulp with caustic soda, which causes swelling of the pulp to form alkali cellulose (alkcell).[3] After achieving the desired depolymerization in the maturing drum, the alkcell is derivatized by carbon disulphide in the xanthation process. The product thus formed is dissolved in dilute alkali, regenerated back by spinning in an acidic bath and then drawn through spinnerets to obtain fibers with desired properties. The critical quality parameters of viscose fibres, such as fibre tenacity, denier and elongation, are not only determined by the process conditions, but also largely impacted by the properties of the raw materials.

The major raw material in the viscose process is pulp. Most of the properties of viscose are determined by the quality of the pulp used.[4,5] Pulp is derived from different wood sources and processed using different techniques into dissolving grade pulp. Hence, the reactivity of different pulps varies significantly. It is also reported that mechanical treatment, such as grinding and pulp refining, creates additional accessible surfaces in the compact cellulose structure and increases reactivity of a kraft-based dissolving pulp.[6,7] Improving the accessibility of pulp for mercerization and xanthation has been a key approach to improve the reactivity. Another approach to improve the reactivity has been to reduce the knots in the slurry and alkcell. Knots are unwanted, large, dark aggregates of wood fibres, formed during the preparation of dissolving pulp.[8,9] Knots are screened off from the pulp, sent back to the digester and re-cooked, so that their fibres are not wasted. However, traces of knots trapped in the pulp still remain in the final pulp sheets. It has been reported that knots are inherently present in the pulp.[10] Researchers have attempted to reduce the number of knots in the pulp formation step itself.[11] However, traces of knots are always present in the pulp. Knots can be reduced or eliminated in the later stages as well, such as in steeping and shredding. Based on our initial observations of the process in a commercial viscose production plant, it appears that a significant amount of knots continues to be present in alkcell at different process steps, as knots are generated during the processes of pulp to slurry/alkcell conversion. The effect of knots on fibre properties has been also highlighted by Bhagwat and Koutu.[12] However, deeper understanding of the effect of knots during various steps of the viscose making process and their impact on the ripening index (RI) and filterability index (kw) of the viscose solution is still necessary.

On the one hand, a homogeneous slurry, as well as alkcell preparation, with low levels of knots is critical to obtain a high quality viscose solution, as this ensures that the alkali penetrates fully and uniformly the cellulose mass during the slurry preparation stage. On the other hand, further steps should also be controlled to minimize the generation of knots. A knot-free alkcell has reduced bulk density and facilitates better penetration of CS_2 during the xanthation reaction. In the present study, attempts have been made to obtain a deeper insight into these aspects. However, the quantification of knots was the first challenge, as currently available methods provide limited information. The sieve method currently practiced provides a measure of total knots, while a better understanding may emerge while measuring the knot sizes as well. Hence, as part of the study, a new method was developed for qualitative and quantitative measurement of the knots in the slurry and alkcell. The method developed was used to map the occurrence of knots across the different process steps. Subsequently, process parameters, such as impeller speed during steeping and shredder sieve size, were optimized to minimize the amount of knots in the slurry and alkcell in a lab-scale viscose process set-up. The effect of these modifications on the properties of the viscose solution, such as RI and gamma number, was studied.

EXPERIMENTAL

Materials

Hardwood pulp, prepared by the kraft method and supplied by Sappi, USA, was used for experiments. Commercial grade NaOH, used for the preparation of caustic lye (supplied by S.D. Fine Chem) and LR grade CS_2 (supplied by Finar Chemicals Ltd., India) were used for the xanthation reactions.

Preparation of slurries and alkcell with lower and higher amounts of knots

Pulp sheets were shredded in a pulp shredder under predetermined conditions. A slurry of alkcell was prepared in a pulper of 9 L capacity, maintaining jacket temperature at 50 °C and stirring at variable speed to achieve 'good' and 'bad' slurries – with a lower and higher amount of knots, respectively. The finely shredded pulp was mixed with 18% lye in a pulper at 50 °C to prepare the slurry. The slurry with a higher amount of knots was obtained by using a pulper speed of 100 rpm, while the slurry with a lower amount of knots was obtained by using a speed of 1400 rpm. The time of pulping was the same – of 20 min. Details of the slurries are tabulated in Table 1. For achieving different grades of alkcell, the slurry was prepared by the method described for the preparation of good slurry. This slurry was then pressed through a hydraulic press at 90 bar pressure to obtain the alkcell cake. Alkcell was then shredded in a shredder, rotating at 2000 rpm, to obtain a fluffy mass to accelerate the xanthation reaction. This is the second step wherein knots are generated. Alkcell with a higher knot amount was prepared by shredding through a 12 mm sieve, while that with a lower knot amount was prepared by shredding through a 10 mm sieve. Hence, two different grades of alkcell were obtained by using good slurry. The alkcell with a higher knot amount was termed as 'bad' alkcell, while that with a lower knot amount was denoted as 'good' alkcell.

Quantification of knots in slurry and alkcell

A fixed quantity of slurry (or alkcell) was weighed for % cellulose and was dispersed thoroughly in distilled water. The mixture was filtered through 40 μm nylon filter cloth to obtain a thin film of cellulose. The film was dried by heating it in an oven at 100 °C. The film was placed on a wooden box with an aperture of 6 cm diameter and illuminated from below by a 200 W incandescent bulb. Images of the film were taken by a 16 MP digital camera. The captured images were then processed by IC Capture software (Infoanalytics Software Solution; Version: ParX) for quantification of the knots in the images. Figure 1 shows the steps involved in the processing of the images for determining the number of knots. The number of knots over a specified area was thus quantified by the image analyzer. The initial evaluation of the samples made with different amounts of knots in the slurry could be successfully differentiated, indicating the suitability of the method for distinguishing the 'good' slurry, with less than 10 knots, from the 'bad' slurry, with more than 30 knots on the film.

Experimental method for viscose solution preparation

Slurries with different knot levels were prepared at a lab scale, by changing the impeller speed, while keeping the rest of the parameters constant (described above). The slurry thus obtained was pressed and shredded to form crumps of alkcell. The shredded alkcell was kept in an oven at 50 °C until the desired degree of depolymerization was achieved. It was then fed into the xanthater and CS_2 was added under vacuum and allowed to react at 29 °C and 15 rpm impeller speed.

Table 1
Pulp and process conditions for obtaining low and high amounts of knots in the slurry

Knot amount	Pulp form	Pulp particle size	Mixing time
Low	Ground	<4 mm	05 minutes
High	Shredded	8-10 mm	05 minutes

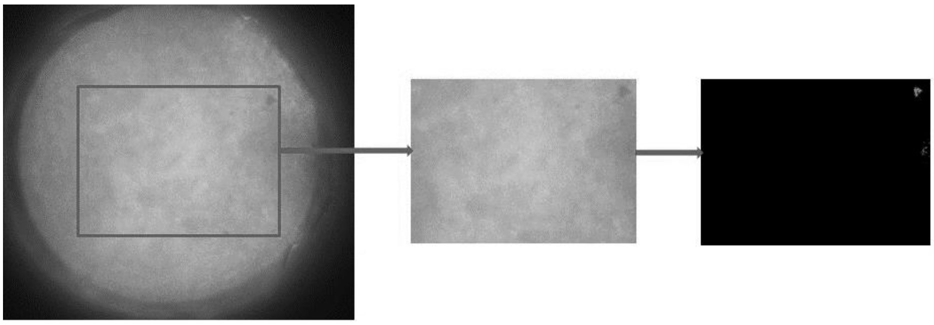

Figure 1: Pictorial representation for assessing the amount of knots

After the xanthation was completed, vacuum was released by purging nitrogen gas. A predetermined quantity of return lye was then added to the xanthate and dissolution was carried out at 3-5 °C, and 100 rpm for 2 h. The temperature was then increased to 5-10 °C and maintained at the same level for 16 h to complete the ripening. The composition, the viscosity (by ball fall, BF) and the ripening index (RI) of the viscose solution were assessed after 18 h.

Viscose solutions were prepared from the slurry and alkcell with different knot levels, with the addition of two different amounts of CS_2 in xanthation. One set, with 35% CS_2 addition on cellulose basis, represents the commercial viscose solution method[13] and the other one, to which 31% CS_2 was added on cellulose basis in the xanthation, represents the lowered CS_2 level. All the viscose solutions prepared were examined for the regular viscose properties of RI, corrected filterability index (cKw), and gamma number. To collect further information, additional methods were developed and used to determine xanthate sulphur, percentage of by-products in the viscose solution.

Analysis of viscose solution

Determination of gamma number by UV method

Viscose samples were analyzed by a UV spectrophotometer for evaluating the total sulphur content, by-products and gamma number. For this analysis, 1 g of viscose solution, after ripening, was diluted in 1% lye and the absorbance at 303, 332 and 363 nm was recorded. The peaks at 303 and 332 nm correspond to the xanthate sulphur, while the peak at 363 nm corresponds to sulphur by-products. This method was described by Lanieri *et al.*[14]

Determination of RI by Hottenroth method

The ripening index or coagulability of the viscose solution was measured by the ammonium chloride ripeness number, which is the quantity (in mL) of 10% aqueous solution of ammonium chloride required to cause the commencement of coagulation of 20 grams of viscose solution diluted in 30 mL of water.[15]

Determination of filterability index

The filter value or clogging value was measured by a filter apparatus, as described by Treiber.[16] The apparatus consists of a steel cylinder of known filter area, open at both ends. Compressed air of 2.1 kg/cm^2 was passed through the cylinder containing the viscose solution. The bottom of the cylinder was packed with filters of specific mesh sizes for filtration of the viscose solution. The filter clogging value was calculated by the following equation:

$$K_w = \frac{2 \times \left[\frac{t_2}{m_2} - \frac{t_1}{m_1}\right] \times 10^5}{t_2 - t_1} \quad (1)$$

where t_1 and t_2 are the filtration time in min (20 and 40 min), respectively, m_1 and m_2 are the weight of viscose solution in grams, filtered after 20 min and 40 min, respectively. The filter clogging value (K_w) calculated was then adjusted for viscosity. Then, the corrected filter clogging value (cK_w) was reported and used for further comparison. The formula for cK_w is as follows, where η is the ball fall time in seconds for a viscose solution:

$$cK_w = K_w \times \left[1 - \frac{(\eta - 55)}{100}\right] \quad (2)$$

RESULTS AND DISCUSSION

The present study focuses on understanding the effect of slurry and alkcell quality, in terms of amount of knots, on the properties of the viscose solution. Knots are formed during the pulping process or may be generated later at intermediate steps during the preparation of the viscose solution. As suggested in the literature, knots are an important quality parameter of alkcell, which has significant effect on the quality of fiber.[12] However, a systematic study of its influence in the xanthation reaction has not been fully addressed in the literature. The study aims to understand the contribution of the knots formed during different stages of the viscose process on the xanthation reaction.

Effect of slurry knots on viscose solution quality

Two slurries, a 'bad' slurry and a 'good' one, differing in the amount of knots were prepared as described above. The slurries were analyzed as regards the number of knots, by the method described in the experimental part. Images of the 'bad' and 'good' slurries are shown in Figure 2. The number of knots was determined by software, and a number of knots below 10 was considered indicative of a 'good' slurry, while above 30 was considered as 'bad' slurry.

The properties of the viscose solutions prepared under different process conditions from the slurries, at the lab scale, are tabulated in Table 2. It can be observed that, in the case of the viscose solutions made with 35% CS_2, the RI is higher for the 'good' slurry than for the 'bad' one. This is also reflected in a higher xanthated sulphur value, indicating better xanthation at lower knot levels. A similar trend is also observed in the case of 31% CS_2.

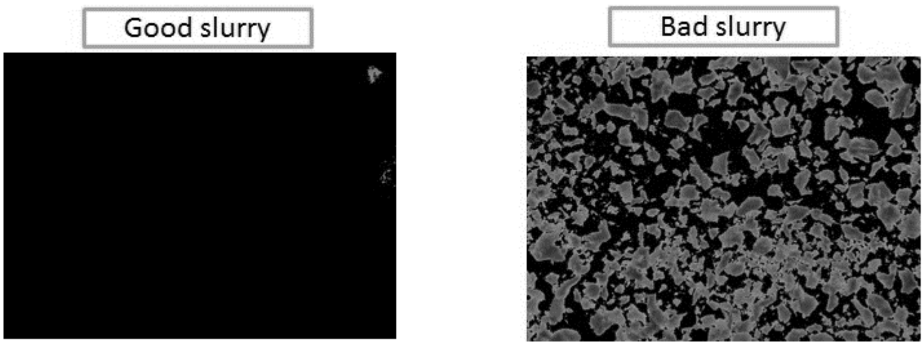

Figure 2: Optical images of 'good' and 'bad' slurries

Table 2
Experimental results for different slurry quality

Slurry quality	CS_2, %	RI	BF	CKw	By-product, %	Xanthate sulphur, %	Gamma number
Bad	35	13	80	43	1.03	1.84	50.33
Good	35	15.5	67	56	0.93	2.03	55.52
Bad	31	08	82	92	0.84	1.63	44.38
Good	31	12	57	73	0.84	1.69	46.99

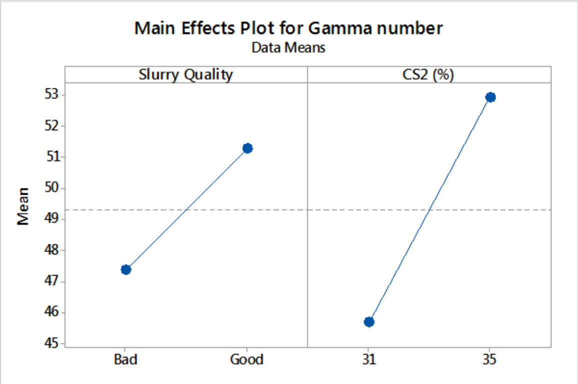

Figure 3: Main effects plot for gamma number

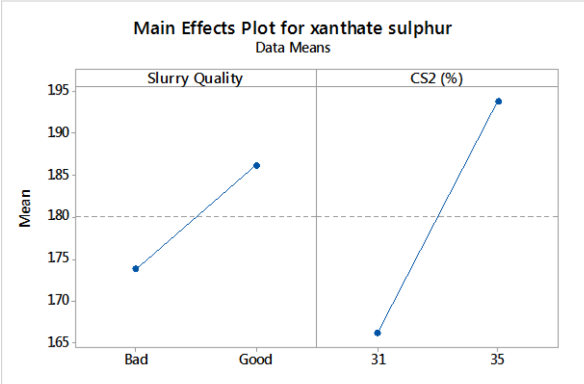

Figure 4: Main effects plot for xanthate sulphur

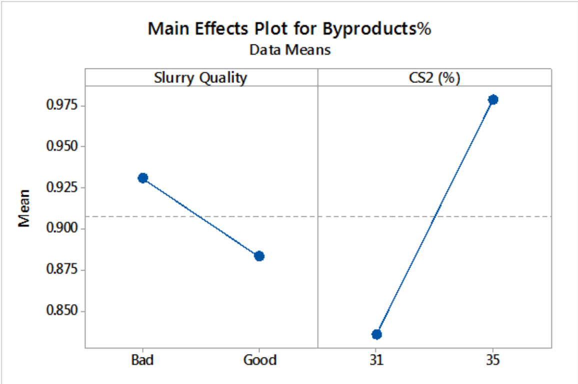

Figure 5: Main effects plot for by-products %

At 31% CS_2 addition, both ‘bad’ and ‘good’ slurries show lower RI and higher cK_w. Although only 24% CS_2 is required for the xanthation, in this case, 31% CS_2 is consumed.[17] This happens as there always exists an equilibrium between xanthated products and thio by-products, under fixed process conditions, which requires a higher concentration of CS_2 than the stoichiometric demand.[17] Hence, in the viscose solutions prepared from bad slurry, 31% CS_2 does not seem to be sufficient for the xanthation and hence RI has dropped to 8, compared to 13 under standard conditions. However, the viscose solutions made from the good quality slurry show solution properties close to those of the control sample. This is attributed to an improvement of the xanthation reaction due to a reduction in the amount of knots.

The main effects plot for good and bad slurry, at 31 and 35% CS_2 addition, is shown in Figure 3. It indicates that an increase in CS_2 dosage during xanthation increases the gamma number. Higher gamma number is due to the availability of more CS_2 to attach to the cellulose chains. It also indicates that gamma number significantly increases for good slurry quality. This is because a good slurry has a lower number of knots. Hence, the penetration of CS_2 across the alkcell is uniform, which gives proper utilization of the available CS_2 in xanthation, resulting in an increase in gamma number.

Figure 4 also illustrates this trend, *i.e.* xanthated sulphur content is higher in the viscose solution due to a higher percentage of CS_2. This can be attributed to the higher amount of CS_2 available for the reaction. However, it is interesting to note that as a higher amount of reacted CS_2 goes into the desired product, a better quality viscose solution is obtained. This is confirmed by the fact that a good slurry quality results in a higher amount of xanthated suphur than in the case of the bad slurry quality.

Figure 5 shows the main effects plot for by-products. Good slurry quality or lower CS_2 concentration are indicative of lower by-product formation. An increase in CS_2 concentration obviously increases the concentration of by-products in the final viscose solution. This indicates that it is reasonable to control the CS_2 requirement in the xanthation process through better slurry quality.

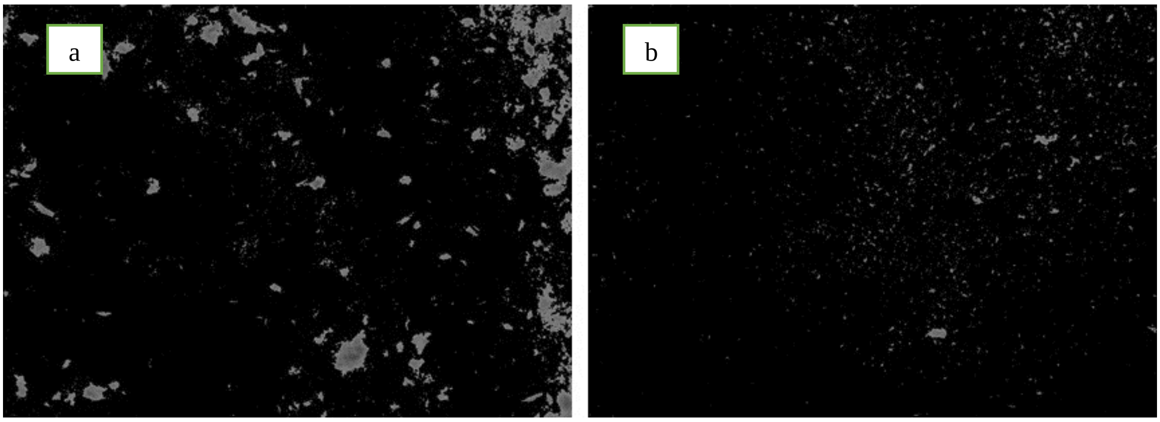

Figure 6: Optical images of a) ‘bad’ alkcell, and b) ‘good’ alkcell

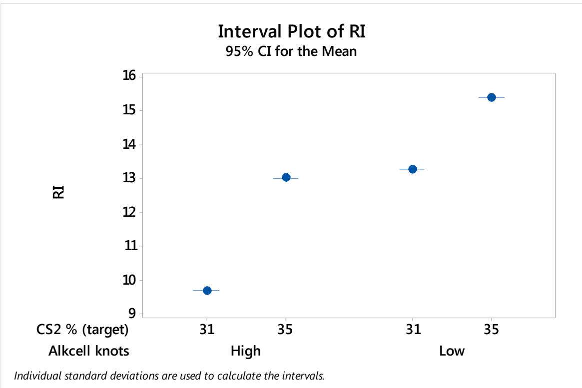

Figure 7: Interval plot of RI for ‘good’ and ‘bad’ alkcell experiments

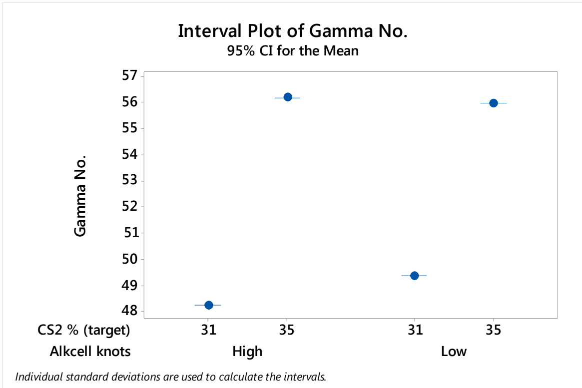

Figure 8: Interval plot of gamma number for ‘good’ and ‘bad’ alkcell experiments

Table 3
Properties of dope prepared from alkcell of different quality

Alkcell quality	% CS_2	RI	BF	CKw	By-product, %	Xanthate sulphur, %	Gamma number
Bad	35	13.0	96	50	0.95	1.98	55.5
Good	35	15.8	75	49	0.94	2.04	55.5
Bad	31	10.5	113	37	0.70	1.78	48.6
Good	31	13.5	79	50	0.81	1.90	52.0

Effect of alkcell knots on viscose properties

Alkcell with low and high knot amounts were prepared at the lab scale by controlling pressing and shredding conditions. The alkcell with a higher knot amount was denoted as ‘bad’ alkcell and the one with a lower knot amount – as ‘good’ alkcell. From each of the two prepared alkcells, a viscose solution was made using identical conditions, but adding two different levels of CS_2, 35% (control) and 31%. Images of ‘bad’ and ‘good’ alkcell are shown in Figure 6. The number of knots was determined by software and was found to be 2 for the ‘good’ alkcell (size 5-10 mm^2), and 9 for the ‘bad’ one.

The interval plots of these experiments are plotted in Figures 7 and 8 to show the major tendency and variability in the sample. The amount of knots has shown a significant effect on RI (Fig. 7).

The results of the experiments are summarized in Table 3. The listed values are the average of three repeated experiments. From Table 3, it is observed that a reduction in CS_2 adversely affects the properties of the viscose solution, such as RI, cKw and gamma number. However, the change in solution properties as a function of CS_2 addition is significantly lower in the case of the viscose solution made from ‘good’ alkcell than from the ‘bad’ alkcell. It can be also observed from Table 3 that the viscose made with an alkcell with a low knot amount and with a lower CS_2 addition matches closely the control batch, made from ‘bad’ alkcell, but with higher CS_2 addition. For these solutions, the RI number is similar, while cKw and gamma numbers are different, but within the required range for smooth spinning.

RI is higher for the viscose solution with a lower number of knots and a lower CS_2, matching the RI of the control batch. It follows form the discussion that RI is significantly affected by the number of knots. An improvement in RI in the case of the solution made from alkcell with a lower knot amount, can be attributed to the uniform distribution of CS_2, during xanthation, facilitated by the absence of hard patches (knots), which are difficult to penetrate. This, in turn, facilitates better dissolution, yielding the desired viscose solution properties. RI is a key parameter, which has to be within the specified range to ensure good spinning. Gamma number, which is indicative of the distribution of CS_2 in the xanthated product, follows the same trend as % xanthated sulphur, as shown in Figure 8. Differences are observed between the alkcell samples with high and low knot amounts at lower CS_2 addition, but not at higher CS_2 addition.

Mechanism of xanthation reaction

The mechanism of the xanthation reaction is complex, as there are many side reactions occurring along with the desired one. The desired reaction is the following:

$$Cell - OH + CS_2 + NaOH \rightarrow Cell - O - CSSNa + H_2O \quad (3)$$

However, CS_2 partly reacts with free NaOH in the alkcell, which yields Na_2CO_3, Na_2CS_3 and Na_2S as by-products:[18]

$$2CS_2 + 6NaOH \rightarrow Na_2CO_3 + Na_2CS_3 + Na_2S + 3H_2O \quad (4)$$

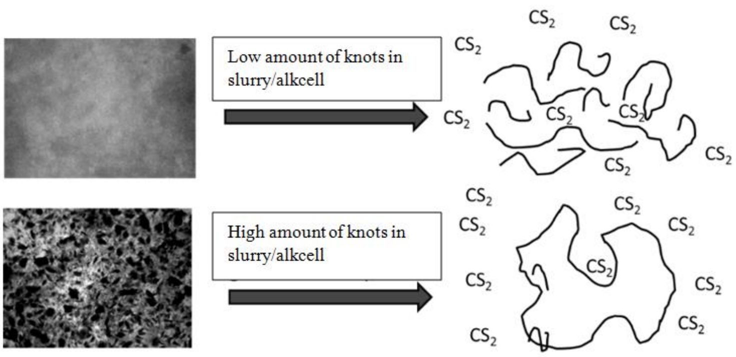

Figure 9: Pictorial representation of CS_2 accessibility to alkcell

Both reactions proceed simultaneously during xanthation. Controlling the rate of each individual reaction is key to reducing CS_2 in the xanthation reaction. From Table 2, it is observed that the conversion of the xanthated product was increased in the good slurry, while the conversion in the by-products was reduced, when CS_2 dosing was 35%. Similarly, at 31% CS_2 dosing, the xanthated product increased, though no significant decrease in the by-product concentration is noted. Similar trends are observed in gamma number. In the case of alkcell, again, the alkcell with a lower knot amount showed increased xanthate sulfur percentage and a similar gamma number trend. The diffusion of CS_2 in the alkcell is represented in Figure 9.

In a system with fewer knots, the accessibility of CS_2 to the alkcell is higher, hence the reaction with alkcell predominates. This results in a higher conversion into the desired xanthated product. However, if the amount of knots is higher in the system, CS_2 diffuses slowly towards the active sites of alkcell, because penetration through the knot walls is restricted. This provides the opportunity for CS_2 to react with NaOH, which facilitates the reaction of by-products formation. This reduces the amount of CS_2 in the xanthate, hence the gamma number value drops. In order to achieve a higher rate of xanthation, the diffusion resistance has to be eliminated or minimized. The reduction of the knot amount is one of the simplest approaches to facilitating xanthate formation, while reducing the rate/extent of by-product formation. This will not only improve the quality of the viscose solution, but also will provide an opportunity to reduce CS_2 consumption in the xanthation reaction.

CONCLUSION

Lab studies have demonstrated that the presence of knots in the slurry and alkcell has a significant impact on the quality of the viscose solution. Knots in the pulp or the ones generated during the viscose process are hard masses of cellulose into which CS_2 penetration is restricted during xanthation. This causes a reduced reaction of CS_2 with alkcell, thus requiring the use of higher quantities of CS_2 in the xanthation process. Reducing the amount of knots in the slurry and alkcell is a way to reduce CS_2 consumption, with a minimum effect on other viscose solution properties.

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