Optimization of the enzymatic activation of a dissolving pulp before viscose manufacture

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ABSTRACT: As a continuation of an earlier enzymatic study on a dissolving pulp before viscose manufacturing, a new set of experiments were carried out with the best-performing enzyme from that study, Carezyme(R). The intention was to optimize the enzyme treatment so that the subsequent viscose process could be carried out with the lowest possible demand for chemicals in the etherification stage. The study focuses on pulp yield, reactivity, viscose viscosity (measured as ball-fall time), and the filter clogging value of the viscose.

Application: Mills could use the enzyme optimized in this study for treatment of dissolving pulp before viscose production to reduce production costs and associated environmental consequences.

Most of the cellulose produced in the pulp industry is used for paper and board products, but a substantial part is also used for making regenerated cellulose and cellulose derivatives [1]. Currently, the worldwide production capacity for viscose fibers from cellulose is about 3 million tons per year, and the major industrial process used is the viscose rayon method [2]. Other methods, such as the Lyocell method, are still in a minority position compared with the conventional rayon method. The viscose rayon method, where carbon disulfide (CS2) is used as an etherification agent, is the oldest commercial process. It was developed in 1891 by C.F. Cross, C. Beadle, and E.J. Bevan [3].

Since the raw material in viscose production is cellulose, which is renewable, viscose processes can be assumed to have a bright future. However, the environmental effects of the viscose rayon process must be reduced, particularly with regard to CS_2 emissions. The use of higher-reactivity pulps could reduce the demand for CS_2 in the viscose process.

In a conventional viscose process, pulps of relatively high degree of polymerization (DP) are used. This requires a pre-aging step to reduce the DP to a lower level more suitable for the viscose production process.

New research has indicated that an enzymatic modification of cellulose could increase its solubility in alkaline solvents. This is of interest for subsequent viscose production, as it suggests that the consumption of CS_2 in the viscose process can be reduced. An enzymatic treatment would make it possible to increase pulp reactivity and to simplify the production of the viscose dope solution. Hopefully, the pre-aging time could thus be considerably reduced. Attempts to develop a process to dissolve the enzymatically treated pulps directly have shown little progress [4,5]. The reason for the lack of success with different types of purified cellulases could be that the mechanisms involved are still not fully known.

The possibility of using enzymatically modified pulps is an important option for the development of a viscose process with lower sulfur emissions. Further goals include the development of a totally CS_2-free process. In this study, we have used the best-performing enzyme preparation, the mono-component endo-glucanase Carezyme, identified in earlier studies [6]. In this study, the enzymatic treatment conditions were optimized, and the viscose dope preparation of the enzymatically treated pulp was studied. The study could be a valuable indication of how well the enzyme-treated pulp would behave in a viscose production environment.

EXPERIMENTAL

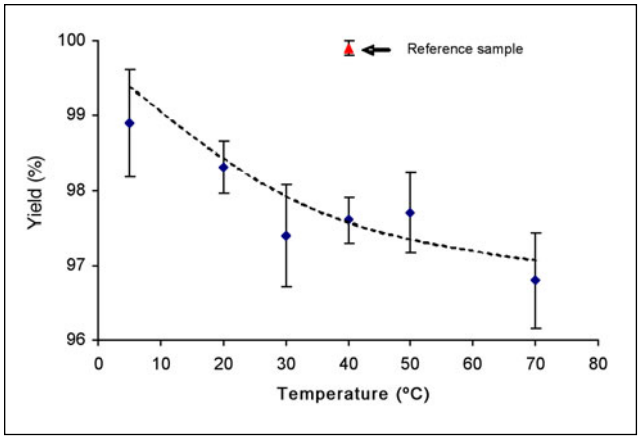
Pulp and enzyme

A bleached sulfite spruce dissolving pulp from a northern Swedish pulp mill with a viscosity of 490 dm^3/kg (15 cP), R_{18} > 94%, and an ISO brightness of 92% was used in all the trials. The analyses were performed in accordance with SCAN CM 15:99 for viscosity, SCAN-C 2:61 for R_{18}, and SS-ISO 2470 for brightness.

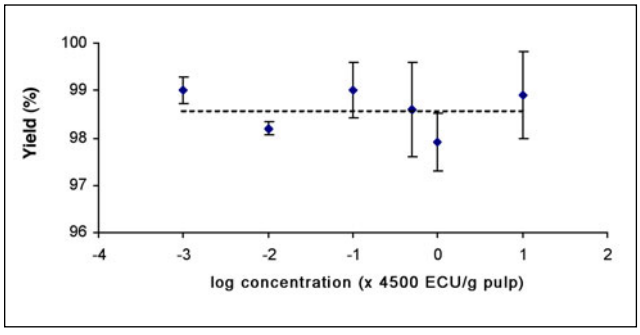
Carezyme 4500 L (4500 ECU[CP]/g, where ECU[CP] = endocellulase units of Carezyme product; Novozymes, Bagsværd, Denmark) is a liquid preparation that can be used under neutral to moderately alkaline conditions and at temperatures ranging from 15°C to 65°C.

Sample preparation and enzyme treatment conditions

The pulp samples were cut into squares (~1 cm^2) and dropped into a beaker



1. Yield of enzyme-treated pulp as a function of temperature. The reaction time was 2 h, and the enzyme concentration was 4500 ECU/g pulp.



2. Yield of enzyme-treated pulp at different enzyme concentrations. The reaction time was 2 h, and the temperature was 40ºC.

with distilled water, and the mixture was adjusted to pH 8 by sodium hydroxide (NaOH). The pH was not varied in the different tests because the value used is convenient for the viscose manufacturing process. The beaker was then immersed in a water bath for temperature conditioning. The pulp sample was homogenized to a slurry with a mechanical stirring device. The enzyme was then added to the slurry and the stirring rate was set to 150 rpm for the entire reaction time. To enable optimization of the pulp yield, pulp viscosity, and pulp reactivity, the following ranges were examined: 4.5–45,000 ECU/g pulp, 30°C–60°C and 0–24 h reaction time.

After the enzyme reaction was stopped by washing with hot water, the sample was filtered (G3 glass filter crucible, pore size: 40-100 µm), and dried at 105ºC, except for the viscose preparation samples, which were filtered and air-dried overnight.

Determination of yield and viscosity of enzyme-treated pulp

The yield was determined by dividing the weight of the residue in the crucible after pulp washing by the initial sample weight. The viscosity of the washed and dried samples was determined in accordance with SCAN CM 15:99. The reference samples were taken from the pulp sheets and were treated in the same way.

Reactivity of the pulp after enzyme treatment

To determine how well the pulp had responded to enzyme treatment, its reactivity was determined using Fock's method of reactivity [7] which is described by Kvarnlöf et al. [6]. The reference samples were taken from the pulp sheets and were treated in the same way.

Viscose preparation of the enzyme-treated pulp

The viscose was prepared and the samples characterized according to a method developed by Treiber et al. [8].

RESULTS AND DISCUSSION

The Carezyme enzyme was developed for use in the laundry industry, where it provides color care, softening, cleaning, and whitening of the textiles [9]. This was the best enzyme type for pulp activation, according to Kvarnlöf et al. [6].

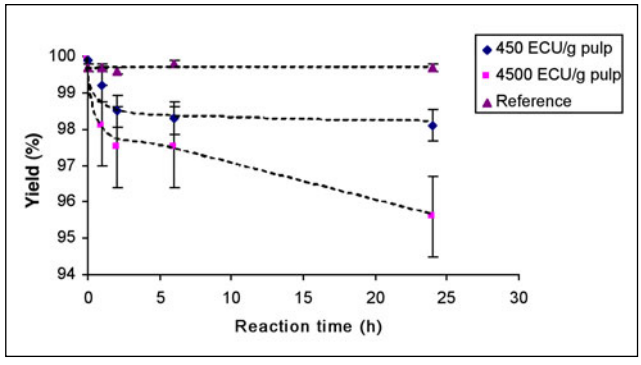
The initial step in this study was to determine the conditions at which the enzyme was most efficient. The parameters of interest were temperature, reaction time, and enzyme concentration. The aim was to maintain a high pulp yield, reduce the pulp viscosity, and increase the pulp reactivity.

The results suggest that samples treated at lower temperatures have slightly higher yields than samples treated at higher temperatures (**Fig. 1**). The error bars in this and other figures denote the standard deviations of the data.

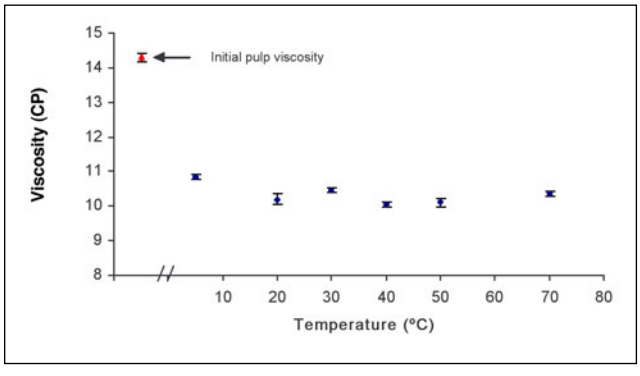
There is apparently an optimum temperature between 40ºC and 60ºC, as reported by the manufacturer for tests on carboxy methyl cellulose (CMC) [13]. The somewhat higher yield at 5°C to 20ºC was probably the result of the relatively low activity of the enzyme at these temperatures.

The enzyme is an endoglucanase type of cellulase, which means that it primarily attacks the cellulose chains internally, resulting in a lowering of the viscosity by chain cleavage. The main reason for the relatively small loss in yield, regardless of temperature, is probably that there was very little attack on the ends of the cellulose chains, which would mean that few soluble sugars were formed [10]. The same trend can be seen in **Fig. 2** for the tests at different enzyme concentrations. Although the highest enzyme concentration was 10,000 times the lowest concentration, there is no significant difference in yield loss.

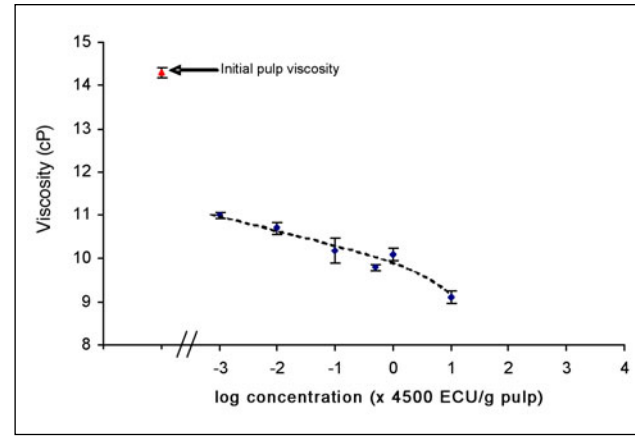
A set of experiments was also performed with different enzyme reaction times. The enzyme concentration was 450 or 4500 ECU/g pulp. As shown in **Fig. 3**, the reaction time had only a small influence on the yield. This influence was higher at 4500 than at 450 ECU/g pulp charge. For the reaction times



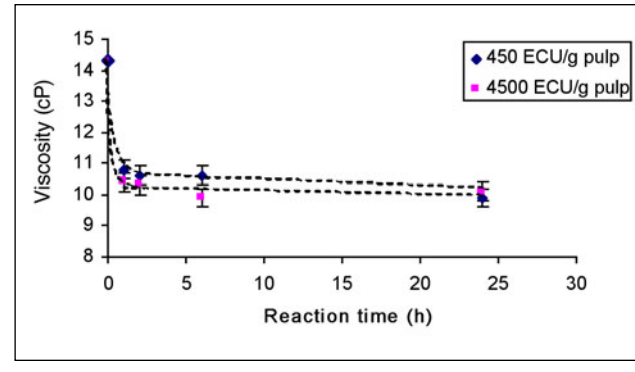
3. Yield of an enzyme-treated pulp treated at two enzyme concentrations and for different times. The reaction temperature was 40°C.



4. Pulp viscosity after enzyme treatment at different temperatures. Reaction time: 2 h. Enzyme concentration: 4500 ECU/g pulp.



5. Pulp viscosity after treatment at different enzyme concentrations. Reaction time: 2 h. Reaction temperature: 40°C.



6. Pulp viscosity vs. reaction time in the enzyme stage at 450 and 4500 ECU/g pulp. Reaction temperature: 40°C.

of practical interest, i.e. ≤ 6 h, the pulp yield loss was about 2%.

The reason for the clearly lower yield of the sample treated at the higher enzyme concentration for 24 h could be that in this case the enzyme had time to degrade very small cellulose fragments that normally would not be attacked to any great extent during a shorter period. The enzyme would then produce a larger amount of soluble sugars that would be removed by washing. Since more enzyme molecules are available at the higher concentration, it is more likely that they will find and attach to the small cellulose fragments. This yield change is, however, rather small, indicating that there exist only a few cellulose fragments that can be degraded into soluble sugars by the enzyme.

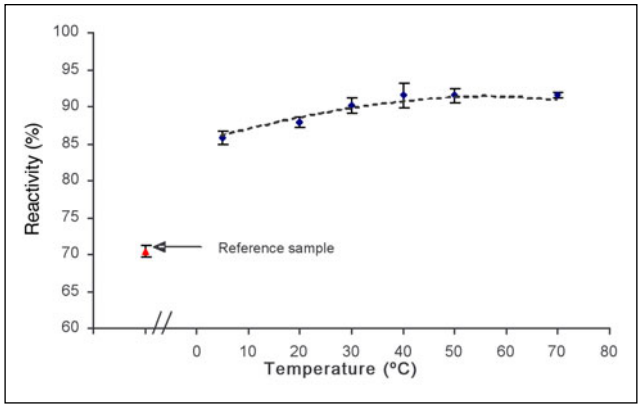
The influence of the enzyme treatment temperature on pulp viscosity is shown in **Fig. 4**, where it is evident that temperature had no effect between 5°C and 70°C. A low temperature is thus sufficient for the enzyme treatment.

The viscosity seemed to drop to a value of about 10 cP, regardless of the temperature. The reason for this is probably that the enzyme primarily attacks amorphous regions of the cellulose, as do most endoglucanases, and when the accessible cellulose is degraded, the enzyme is unable to attack the more crystalline parts of the cellulose matrix. This could mean that there is no or very little substrate accessible for the enzyme to depolymerize further.

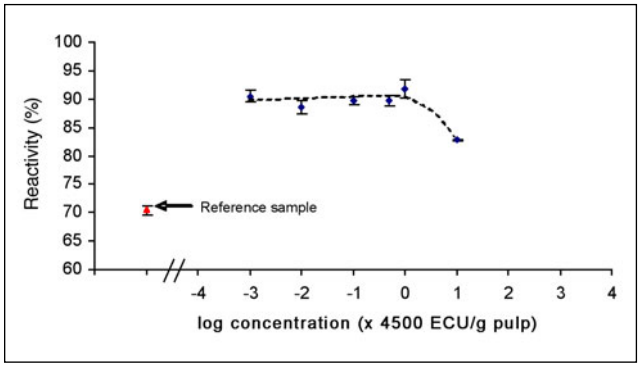
The pulp viscosity was slightly influenced by the enzyme charge, as shown in **Fig. 5**, but the incremental effect of an additional change was so small that a dosage higher than 4.5 ECU/g pulp would not be worthwhile. Thus, the minimum viscosity which it was possible to achieve by enzyme treatment was about 10 cP.

A slight decrease in pulp viscosity with increasing enzyme concentration can, however, be seen in Fig. 5, which may be due to contamination of the Carezyme solution with other enzymes. The concentration of these impurities would increase with increasing dose of the Carezyme solution.

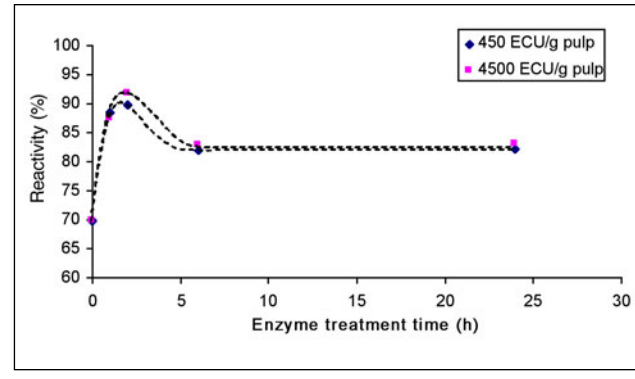
The influence of the time of enzyme treatment is shown in **Fig. 6**, at enzyme concentrations of 450 and 4500 ECU/g pulp. The full effect on viscosity was achieved within 2 h, re-



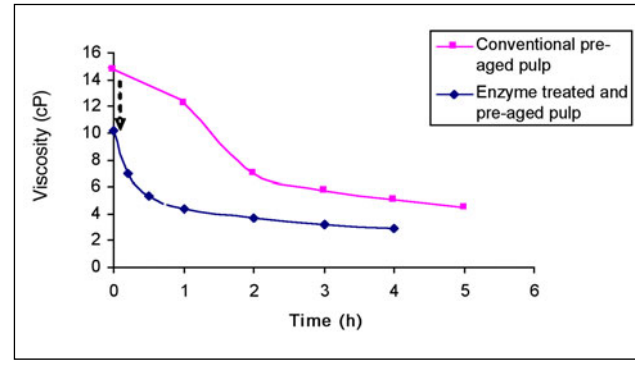
7. Reactivity according to Fock's test [7] after enzyme treatment at different temperatures. The enzyme concentration was 4500 ECU/g pulp.



8. Reactivity according to Fock's test [7] with different enzyme doses in the pulp slurry. Reaction time: 2 h. Reaction temperature: 40°C.



9. Reactivity according to Fock's test [7] vs. enzyme treatment time with 450 and 4500 ECU/g pulp. Reaction temperature: 40°C.



10. Pulp viscosity as a function of time with and without a prior enzyme treatment. The arrow indicates the depolymerization due to the enzyme treatment.

gardless of the enzyme charge.

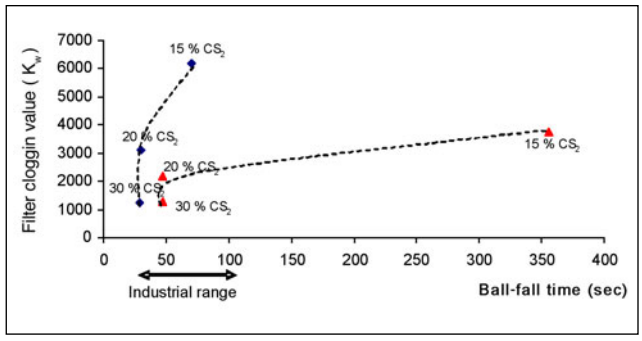
Figure 7 shows that the reactivity determined according to Fock's method increased with temperature between 5°C and 40°C, but that there was no change in reactivity above 40°C.

Figure 8 shows that the reactivity according to Fock's test [7] was essentially independent of enzyme dose in the range from 4.5 to 4500 ECU/g pulp. At 45,000 ECU/g pulp, on the other hand, the reactivity was significantly reduced. The results showed that an enzyme dose of 4.5 ECU/g pulp was sufficient to achieve high reactivity. The poor result with 45,000 ECU/g pulp could be due to steric hindrance because the enzyme molecules are too numerous relative to the substrate, making it more difficult for the enzyme molecules to attach to and react with the cellulose chains.

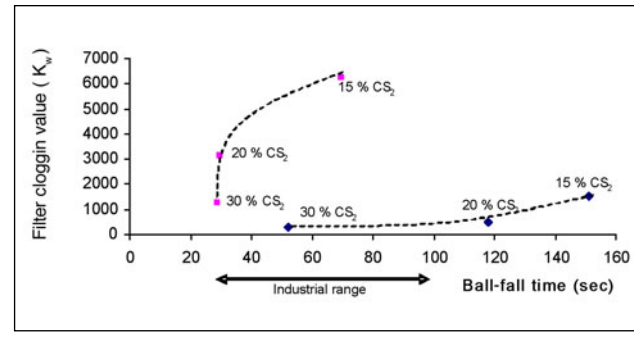
Figure 9 shows that the enzyme treatment time should not be too long and that the optimum time was about 2 h. With a longer reaction time, reactivity was reduced, possibly due to an agglomeration of cellulose molecules and fibrils, leading to lower accessibility and thus reduced reactivity.

When producing viscose, it is important that the cellulose chains not be too long, i.e., that the viscosity of the pulp not be too high. A viscosity of 4.5–5 cP in the pulp prior to sulfidation is usually recommended, and an enzyme treatment with Carezyme alone is therefore insufficient. A so-called "pre-aging" stage is therefore recommended. The influence of such a pre-aging stage after the enzyme treatment is shown in **Fig. 10**. The figure shows that a fairly short (≤1 h) retention time after enzyme treatment is sufficient to reach the desired viscosity. The effectiveness of this short pre-aging time is probably due to a more open structure in the cellulose matrix as a result of the enzymatic treatment, which makes it easier for the oxygen-based radicals to attack and depolymerize the cellulose chains. In a viscose mill with no enzyme stage, the retention time in the pre-aging step is usually 4-5 h, which is much longer than the pre-aging stage required after enzyme treatment.

A good parameter for evaluating a viscose dope made by carbon disulfide treatment of pulp is the filter clogging value, K_w. This value is determined from the amount of viscose that



11. Filter clogging value K_w vs. viscosity of viscose (ball-fall time). The triangles represent viscose from enzyme-treated pulp and the diamonds represent viscose from non-enzyme-treated pulp.



12. Filter clogging values K_w from reference pulp treated in two different ways. The diamonds represent conventional viscose produced in accordance with [8], and the squares represent viscose from pulp treated as in the enzyme treatment procedure, but without enzyme.

is passed through a specified filter in a given time. The K_w value is dependent on the filter material and on the viscosity of the viscose dope [8], where the latter is usually determined by "ball-fall time." This is the time it takes for a steel ball with a diameter of 1/8 in. to fall 20 cm through a cylinder (20 mm Ø) of viscose at 20°C [11]. The lower the K_w value, the purer the viscose. In practice, a lower K_w value means that the viscose dope contains fewer unreacted alkali cellulose particles, i.e., gels, and fewer fiber residues and inorganic impurities. **Figure 11** shows the clogging values for viscose dope produced with different carbon disulfide charges from enzyme-treated and non-enzyme-treated pulps. The enzyme charge for the enzyme-treated pulp samples was 450 ECU/g pulp, the reaction temperature was 40°C, and the reaction time was 2 h.

The clogging value is lower for the viscose dopes made from the enzyme-treated pulp, which is a good indication that the reactivity is indeed enhanced by the Carezyme treatment. This could mean that it is possible to reduce the charge of carbon disulfide used to dissolve the alkali cellulose before viscose dope manufacture.

The most important conclusion of this study is that enzyme treatment can enhance pulp reactivity and thus lead to a lower requirement for carbon disulfide in viscose manufacture.

Although the clogging values are lower for the viscose from the enzyme-treated pulp than for that from the non-treated pulp, these viscoses are still not good enough from a process point of view. According to Sixta et al. [12], viscose quality can be characterized by the clogging value as very good (K_w = 0–300), good (K_w = 300–500), acceptable (K_w = 500–800), poor (K_w = 800–1500), or unacceptable (K_w > 1500). The reason for the relatively high clogging values obtained in this study was probably that the laboratory method used was not optimized for the enzyme treatment. This can be seen in **Fig. 12**, which shows data for viscose dopes produced from non-enzyme-treated pulp in the conventional way according to [8], and from pulp treated as in the enzyme treatment procedure, but without enzyme. This phenomenon will be further studied in the continuation of the project.

It is important to notice that the ball-fall time is highly dependent on the viscosity of the viscose. The DP can be calculated from the equation:

$$DP \quad 9^{*} \left(\frac{\frac{\sqrt[3]{123 \cdot BFT}}{\eta_0} - 1.033}{c * 0.0054} \right) \qquad [1]$$

where BFT is the ball-fall time, η_0 is the viscosity (in cP) of the free NaOH in the viscose, and c is the cellulose concentration in the viscose [11]. A difference between a ball-fall time of about 300 s and a value of 70 s, which are the values obtained for the enzyme-treated and the untreated samples at 15% carbon disulfide, corresponds with a difference of only 0.5 cP in viscose viscosity, which explains the wide range in observed ball-fall times.

CONCLUSIONS

This study shows that an enzyme treatment with low enzyme addition rates and low temperatures can be an effective way of enhancing pulp reactivity prior to viscose fiber production. The reaction time can also be maintained at an acceptable level. The pre-aging of alkali cellulose, which is time-consuming in conventional viscose manufacture, can be shortened as a result of the enzyme treatment of the pulp. Viscose made from enzyme-treated pulp has a lower clogging value, K_w, than viscose made from conventional pulp. This indicates that enzyme treatment could provide a way to reduce the carbon disulfide charge in viscose manufacture. **TJ**

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INSIGHTS FROM THE AUTHORS

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This research is a continuation of an earlier study that investigated a number of enzyme treatments for dissolving pulp before viscose manufacture. The best-performing enzyme from that study, Carezyme, was selected for further study. The intention was to optimize the enzyme treatment so that the subsequent viscose process could be carried out with the lowest possible demand for chemicals in the etherification stage. The use of this enzyme could reduce production costs and environmental consequences.

To cover the full range of possible enzyme treatment strategies, we used two widely differing reference charge values for most of the experimental work. A surprising discovery was that a very low enzyme charge could be as effective in most respects as a high charge.

Enzyme modification of pulp has been shown to increase pulp solubility in alkaline solution and to reduce the length of pre-aging required before viscose production. This in turn should enable viscose plants to reduce their use of carbon disulfide, a highly toxic substance used for derivatization of the cellulose before viscose dope preparation, making the viscose production process much more environmentally benign.

The next step is probably to try to optimize the viscose dope preparation in the lab for the enzymatic treated pulp. If this can be achieved, it would be possible to see the full potential of the enzyme treatment on dissolving pulp.

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