

## SOME ASPECTS OF THE REACTIVITY OF PULP INTENDED FOR HIGH-VISCOSITY VISCOSE

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The motivation for this study was to reduce the consumption of  $C_2S$  when preparing high-viscosity viscose by pre-treating two softwood pulps with enzymes prior to the viscose stages. Reactivity was evaluated in two ways, Fock's test of the pulp and the gamma number of the viscose solution prior to regeneration. Whilst the reactivity of a pulp that had been subjected to enzyme pretreatment increased according to Fock's test, it did not increase according to the gamma number. This unexpected difference between the two reactivity tests was investigated. It was concluded that Fock's test measures the extent to which  $C_2S$  reacts with a pulp sample during a standardized test, whereas the gamma number measures the resulting degree of xanthate substitution on the cellulose backbone. The gamma number was judged to be the more relevant of the two tests, since it reflects the dissolution ability of a pulp in the viscose preparation. A higher gamma number also means that the coagulation time in the spinning process is prolonged; this is beneficial, as it can be used to increase the tenacity of the viscose fibres. Measuring the reactivity according to Fock's test, on the contrary, provides more dubious results, as the test has no undisputed correlation to the viscose preparation process.

*Keywords:* Carbon disulphide; Endoglucanase; Fock's test; Gamma number; Viscose; Xylanase

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### INTRODUCTION

Major environmental problems, especially due to the emission of carbon disulphide, are associated with the traditional viscose process. Increasingly stringent environmental legislation has therefore forced the viscose industry to employ more efficient systems for carbon disulphide recovery. This trend has also resulted in the definite closure of production units in Europe and North America. Our study has tried to investigate whether enzyme pre-treatment could be a means of reducing the consumption of carbon disulphide required for the production of high-viscosity viscose. Until the viscose industry has developed a totally new, and environmentally-friendly viscose process it is also important to investigate how the environmental impact of the current commercial viscose process can be reduced.

The main steps of the traditional viscose process are given in Fig. 1. A dissolving pulp is treated with sodium hydroxide in the mercerization step to form alkali cellulose. Carbon disulphide is then introduced in the xanthation step, where it reacts with the alkali cellulose to form sodium xanthate. The sodium xanthate is then dissolved in caustic soda

to produce a viscose solution from which cellulose can be regenerated to rayon by spinning or to sausage coating by the coagulation of a viscose sheet.



**Fig. 1.** Schematic illustration of the steps in the viscose process

In earlier studies it has been shown that some monocomponent endoglucanase enzymes significantly increased the reactivity of sulphite dissolving pulps, where the reactivity was measured according to Fock (Engström *et al.* 2006; Kvarnlöf *et al.* 2007). The proposed mechanism is that the cellulose structure is opened up by the enzyme pre-treatment, which allows the reaction chemicals greater accessibility.

Kvarnlöf *et al.* (2007) had shown that in making conventional viscose the carbon disulphide consumption can be reduced by 30% when the dissolving pulp is pre-treated with an endoglucanase. In that study the viscose quality was characterized by its filtration value,  $K_w$ .

In a study by Engström *et al.* (2006) it has been shown that the increased reactivity achieved by an endoglucanase treatment of a dissolving pulp was not only the result of a decreased degree of polymerization, and therefore it had been concluded that some other mechanism must also be involved. Consequently, it was concluded that the enzyme pre-treatment enhanced the swelling of the cellulose structure.

Recently it has been shown that enzymes can be used to give paper-grade pulps a higher reactivity, making it possible to use such pulps as a less expensive alternative to dissolving pulps for viscose production (Gehmayr *et al.* 2010). A similar study of enzyme treatment of sisal pulps indicated that such pulps were comparable to a dissolving pulp after a treatment with enzymes and alkaline extractions (Ibarra *et al.* 2010). Earlier it has been shown that the reactivity of pulps correlates with their chemical compositions. An investigation by Christoffersson *et al.* (2002) showed that pulps with more soluble hemicelluloses and more soluble low molecular cellulose were more reactive than pulps containing less soluble hemicelluloses and less cellulose of low molecular weight.

The present study investigates whether pre-treating a pulp sample with an endoglucanase or a xylanase enzyme or a mixture of both has the same effect regarding carbon disulphide consumption for high-viscosity viscose preparation as for conventional low-viscosity viscose. The hypothesis was that pre-treatment with an enzyme could open up the structure in the amorphous parts of the cellulose and that the cellulose therefore would become more reactive.

The end-product for this study was sponge cloth towels, and the gamma number is the most important quality parameter for such viscose grades. The gamma number is defined as the number of xanthate groups per 100 anhydroglucose units (AGU). The theoretical maximum esterification corresponds to a gamma number of 300%, i.e. a degree of substitution of 3 per AGU in the cellulose. The gamma number is reduced as a result of the xanthate groups splitting whilst the viscose is “ripening”. This reduction is rapid initially and levels off after a period of time. During the ripening phase the xanthate

groups are also being rearranged between the positions of the glucose units (Schwaighofer et al. 2010) as well as between cellulose chains (Fischer et al. 2005). A high gamma number gives the viscose a slow and controlled regeneration rate which leads to high-tenacity fibres and gives the sponge cloths an even porosity structure. For sponge cloth production, the gamma number should be neither too high nor too low. A mill that desires to produce high viscosity viscose typically aims at having a gamma value of 70 to 73 %. A higher gamma number (>80 %) could lead to poor coagulation that, in turn, leads to low quality sponge cloth towels being produced in the manufacturing process. A lower number (<50 %) could, conversely, cause too rapid a regeneration of the cellulose and possibly result in a sponge cloth with low levels of elasticity and absorbency. It should also be noted that a low degree of polymerization of the cellulose results in poor strength of the viscose products. The focus was thus to find a treatment that increased the gamma number, while reducing the degree of polymerization as little as possible.

## EXPERIMENTAL

### Materials

The commercial spruce/pine dissolving pulp, manufactured by two-stage sodium sulphite cooking had a limiting viscosity number of 540 dm<sup>3</sup>/kg after TCF-bleaching. The brightness was 92 % ISO, and the  $\alpha$ -cellulose content was 91%.

**Table 1a.** The Carbohydrate Content of the Initial Kraft Pulp and the Initial Sulphite Dissolving Pulp

Xylanase (AXU/g pulp)	Alkali extraction	Endo-glucanase (ECU/g pulp)	Cellulose (%)	Glucmannan (%)	Galactan + Arabinan (%)	Xylan (%)	Total hemicellulose (%)
Initial kraft pulp(0)	No	0	82.9	8.1	0.7	8.3	17.1
Initial dissolving pulp (0)	No	0	96.0	2.4	0.1	1.5	4.0

**Table 1b.** The Carbohydrate Content of the Enzyme-treated Pulp Samples Prepared from the Dissolving Pulp\*

Xylanase (AXU/g pulp)	Alkali extraction	Endo-glucanase (ECU/g pulp)	Cellulose (%)	Glucmannan (%)	Galactan + Arabinan (%)	Xylan (%)	Total hemicellulose (%)
0	No	0	96.2	2.3	0.1	1.4	3.8
0	Yes	0	98.0	1.6	0	0.4	2.0
10	No	0	96.4	2.3	0	1.3	3.6
10	Yes	0	98.0	1.6	0	0.4	2.0
100	No	0	96.4	2.3	0	1.3	3.6
100	Yes	0	98.2	1.4	0	0.4	1.9
100	Yes	4.5	98.0	1.6	0	0.4	2.0

\* The enzyme treatment was done with xylanase (10 AXU/g pulp and 100 AXU/g pulp) with or without a following alkaline extraction. In one case endoglucanase also added (4.5 ECU/g pulp).

The dissolving pulp was provided by Domsjö Fabriker AB in Sweden, and had been dried and cut into sheets at their mill. Södra Cell AB in Sweden provided the commercial northern (TCF) bleached softwood kraft pulp with a limiting viscosity number of 627 dm<sup>3</sup>/kg, consisting of 70% spruce and 30% pine and with an ISO brightness of 86%. This pulp had been dried and cut into sheets at Södra Cell AB.

The enzymes used for pre-treatment were a monocomponent endoglucanase preparation (Fiber Care R<sup>®</sup>) and a xylanase preparation (Pulpzyme HC<sup>®</sup>), both provided by Novozymes AS in Denmark. The enzyme activity was determined by the manufacturer and expressed in Endo Cellulase Units (ECU) per unit mass of material as 4500 ECU/g (for the endoglucanase enzyme), and in Active Xylanase Units (AXU) per unit mass of material as 1000 AXU/g (for the xylanase enzyme).

The chemicals used were sodium hydroxide (NaOH) (purity 99 % from VWR International) and carbon disulphide (CS<sub>2</sub>) (purity ≥99% from SIGMA-ALDRICH).

## Methods

### *Laboratory viscose method*

The mercerization step was performed in a stainless steel vessel. The pulp sheets were cut into 1x1 cm pieces, and 25 g, measured as oven dry pulp, was added to the vessel together with 800 g of 18% (w/w) sodium hydroxide solution at 45 °C. The mixture was continuously stirred and kept at a constant temperature for 20 min. The resulting slurry was poured into a pressure vessel and placed into a pneumatic machine, and a pressure ranging between 69 and 74 kg/cm<sup>2</sup> was applied for 120 s. In order to remove access liquid from the alkali cellulose cake forming inside the vessel, vacuum was applied at the top and at the bottom of the vessel. The weights of the alkali cellulose cakes were between 63.0 and 64.5 g.

The alkali cellulose cakes were divided into smaller fragments by hand and then put into a mechanical shredder, where the alkali cellulose was shredded for 30 min to obtain an alkali cellulose fluff.

The preparation of viscose through xanthation of alkali cellulose was done in a laboratory glass reactor, modified especially for this type of reaction, as described by Treiber *et al.* (1962).

A sample of 50 g of the alkali cellulose was then transferred to a laboratory glass vessel. A stirrer was mounted in the vessel before the closing lid was attached. Vacuum was applied to the vessel, and then it was transferred into a water bath (28 °C). The stirrer was set for 120 rpm. The calculated amount of carbon disulphide was charged with a syringe through a membrane into the vessel. Simultaneously the temperature of the water bath was raised to 32 °C.

After 2.5 h the vessel was taken out from the water bath and the formed xanthate was transferred into a steel vessel. Sodium hydroxide solution was poured over the xanthate so that the final viscose solution had a chemical composition of 9.5 % cellulose and 8.8 % sodium hydroxide. The steel vessel was immediately connected to a cooling system, and the dissolution of the xanthate was performed during continuous stirring for 3 h at 5 °C.

After 3 h the stirrer and cooling system was shut off, and the viscose was allowed to ripen in the same steel vessel covered with Parafilm<sup>®</sup> for 16 h.

*PFI-mill treatment*

PFI-mill treatment of the pulps was performed according to ISO 5264-2.

*Enzyme treatment*

The endoglucanase enzymatic step was performed in a glass beaker. The pulp sheets were cut into 1x1 cm pieces, and 25 g of oven dry pulp was added to the beaker together with 475 g of deionised water. The beaker was placed into a water bath and tempered to 45 °C under continuous stirring. A calculated amount of enzyme with known concentration was added to the pulp slurry in the beaker. The pulp slurry was continuously stirred and kept at constant temperature for various times. The enzyme-treated pulp was then dewatered to a dryness of approximately 30%. In the following mercerizing step the extra water in the enzyme treated pulp was accounted for and compensated with an extra adding of sodium hydroxide to the mercerization steel vessel.

The xylanase enzymatic step was performed in plastic bags in a water bath at 60 °C for 2 h, testing three different enzyme charges (0, 10, and 100 AXU/g pulp). The calculated amount of xylanase was added to a phosphate buffer solution (11 mM  $\text{NaH}_2\text{PO}_4$  and 9 mM  $\text{Na}_2\text{HPO}_4$ ) and then added to dry pulp to get 3% pulp consistency. The pH was set to 7 (the optimum pH as described by the enzyme manufacturer Novozyme AS, Denmark). After the enzymatic treatment the enzyme was denaturated with hot deionised water (90 °C) and filtered through a Büchner funnel. In order to remove the xylan from the enzymatically treated pulps an alkali extraction was performed with 9% NaOH solution at room temperature for 1 h and at 4% pulp consistency. The pulp samples were then washed with deionised water and filtered through a Büchner funnel until the filtrate reached a pH of 5 and a pulp dryness of approximately 30%.

*Reactivity according to Fock*

A pulp sample of 0.50 g, calculated as oven dry pulp, was transferred into a 100 mL Erlenmeyer bottle with a glass stopcock and a magnet. Then 50 mL sodium hydroxide (9% w/w) and 1 mL carbon disulphide were added, and the bottle was sealed with the stopcock. The mixture was continuously stirred with the magnetic stirrer for 3 h. The mixture was then transferred into a round flask and deionised water was added to obtain a total weight of 100 g. The round flask was sealed with a stopper and was vigorously shaken to obtain a homogenous solution. 40 mL of the solution was then centrifuged at 6000 rpm for 5 min. Then 10 mL of the liquid phase was transferred to a 100 mL beaker and neutralized with 3 mL sulphuric acid (20% w/w). The mixture was left to de-gas for 15 to 20 h at 25°C.

Next, 20 mL of sulphuric acid (68% w/w) and a magnet were added to the beaker, and the mixture was left to mix with a magnetic stirrer for 1 h. The mixture was transferred into a round flask, and 10 mL of potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) (1/6 M) was added. The mixture was then boiled with reflux for 1 h to oxidize. The mixture was then left to cool until it reached room temperature, before being transferred into a 100 mL measuring cylinder and diluted to the 100 mL mark with deionised water. Then 40 mL was transferred to a beaker and 5 mL of potassium iodide (KI) (10% w/w) was added. The iodine produced in the beaker was titrated with sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ) (0.1 M), using starch (Thyodene) as an indicator. The reactivity was calculated based on the

amount of non-reduced Cr<sup>6+</sup> that remained after the oxidative reaction between potassium dichromate and cellulose.

#### *Limiting viscosity number*

The limiting viscosity number was measured according to ISO 5351-1:2004.

#### *Carbohydrates*

The carbohydrates were measured according to SCAN-CM 71.

#### *Gamma number*

The gamma number was determined by performing spectrophotometric measurements of viscose dissolved in sodium hydroxide (Rahman 1971).

The gamma number of the viscose solution was measured after 16 h of ageing. Approximately 1 g of viscose was taken for analysis. The exact weight was noted. The viscose was dissolved in 50 mL sodium hydroxide solution (1% w/w de-aired with nitrogen gas for 30 min, 25°C) during 30 to 40 min in a 250 mL beaker with a magnetic stirrer. The dissolved viscose was then transferred to a 100 mL measuring cylinder and diluted to the 100 mL mark with sodium hydroxide solution (1% w/w de-aired with nitrogen gas for 30 min, 25°C). The measuring cylinder was shaken vigorously, and 5 mL of the solution was immediately transferred to a 100 mL Erlenmeyer bottle containing 1.8 g anionic exchanger (Amberlite, IRA-402). The anionic exchanger was allowed to affect the solution for 10 min. The solution was then separated from the anionic exchanger by washing it with deionised water through a glass funnel containing a filter paper, into a 250 mL measuring cylinder. The cylinder was filled to the mark with deionised water and was then shaken vigorously. The absorbance was measured at 303 nm (UV-160 1PC, visible spectrophotometer, Shimadzu) and with deionised water as reference.

The gamma number is given in per cent where 100% corresponds to a degree of substitution of 1 (Barthelemy and Williams. 1945). The gamma number was calculated using the formula below:

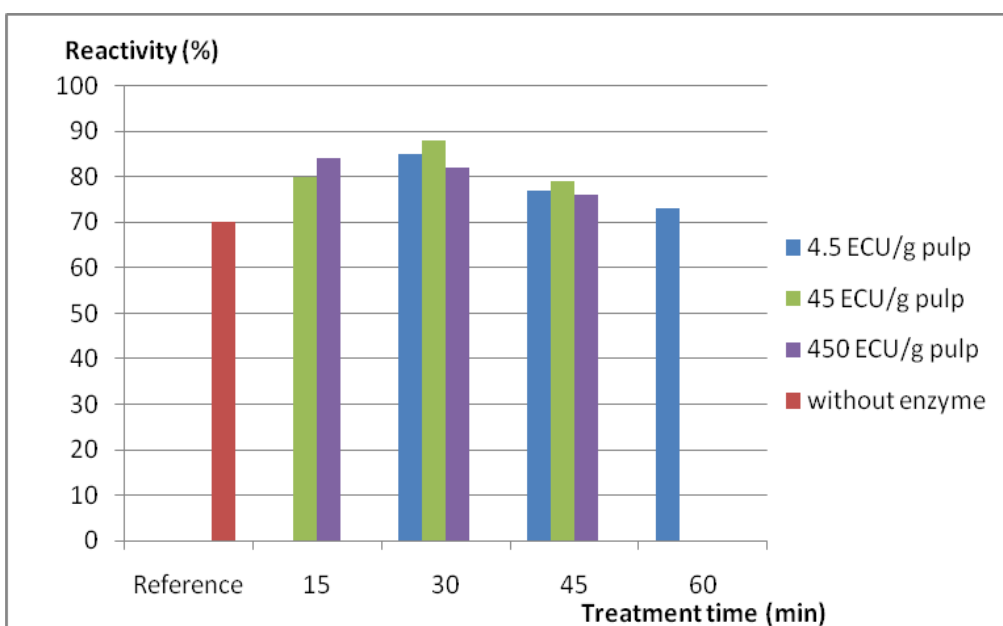
$$\gamma = \frac{A_{303} \times 546.48}{\text{sample weight} \times \% \text{ cellulose}} \quad (1)$$

The constant 546.48 is derived from the dilution factors, the molecular weight of glucose and the molar extinction coefficient (Dux and Phifer. 1957). In this investigation a molar extinction coefficient of 14822 was used.

The cellulose content of the viscose was determined by spreading 2 g of viscose into a thin film between two glass plates. The plates were then pulled apart and placed in hydrochloric acid (42 mL/L, 25°C) until the cellulose films loosened from the plates. The films were then washed with water to remove the acid and after pressing they were washed with acetone and pressed again. The films were finally dried at 105 °C to a constant weight, and the cellulose content was determined as the total weight of the dry sample.

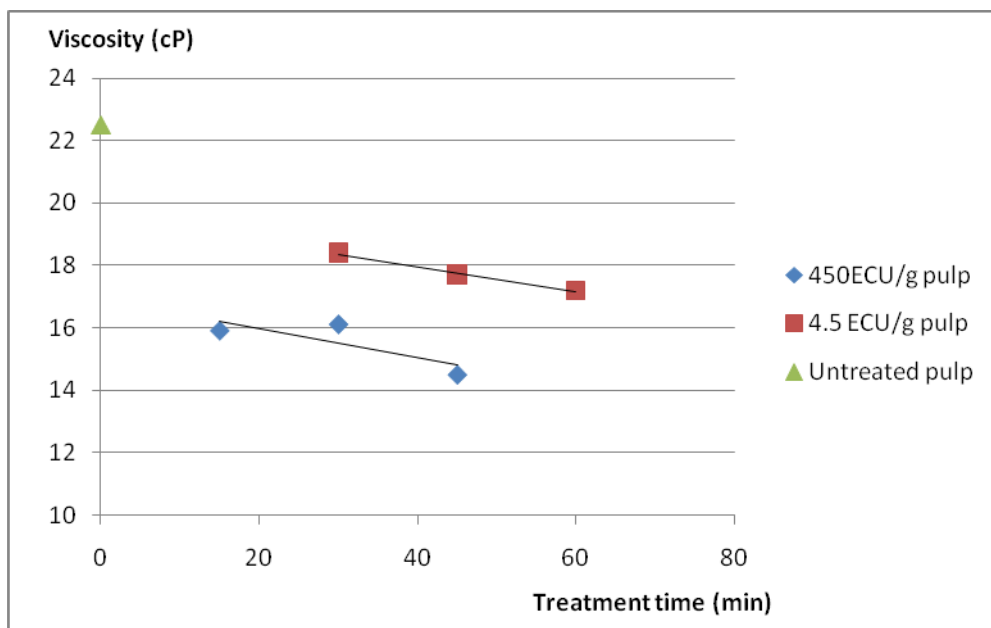
## RESULTS AND DISCUSSION

The sulphite dissolving pulp was used to produce viscose, and the influence of an enzymatic pre-treatment prior to the viscose preparation was initially evaluated. Thus, the pulp was first treated with different amounts of enzymes in order to investigate the effect of the enzyme charge on the reactivity (Fock's test). The results are shown in Fig. 2. It can be seen that by increasing the enzyme charge from 4.5 ECU/g to 45 ECU/g pulp, slightly higher pulp reactivity was obtained. However, a 10 times higher enzyme charge reduced the reactivity compared to the case of the 45 ECU/g pulp. This probably means that if the enzyme charge was too high or the enzyme treatment was too long the cellulose structure started to collapse and the pulp reactivity decreased. However, the final reactivity of all enzyme-treated pulp samples increased if compared to the reference pulp sample that had not been pre-treated with enzymes.



**Fig. 2.** Reactivity of the enzyme-treated (Fiber Care R<sup>®</sup>) sulphite dissolving pulp as a function of treatment time. Three different concentrations of endoglucanase were used: 4.5, 45, and 450 ECU/g pulp.

The enzyme treatment of the pulp samples reduced the limiting viscosity number, which meant that the cellulose chain length became shorter due to the enzymatic reactions. This is shown for two enzyme charges in Fig. 3. It can be seen that a higher enzyme charge and a longer reaction time both led to lower viscosity. A reduction in the limiting viscosity number is obviously a problem when producing viscose grades intended for high-strength products, as strong viscose products require relatively long cellulose chains.



**Fig. 3.** The viscosity of the sulphite dissolving pulp versus the treatment time for two concentrations of endoglucanase (4.5 and 450 ECU/g pulp)

Thus, the results in Fig. 2 and especially in Fig. 3 suggest that relatively low enzyme charges combined with a relatively short treatment time are favoured when producing high-viscosity viscose. This combination of conditions increased the pulp reactivity from 70 to about 85%, as can be seen in Fig. 2. However, the most important parameter in this investigation was the gamma number, and therefore more experiments were carried out to ascertain whether the gamma number also increased if the pulp was pre-treated with an enzyme prior to viscose preparation more experiments were carried out.

Gamma numbers obtained as a function of the carbon disulphide charge with or without an enzyme pre-treatment are shown in Table 2. As can be seen, the gamma number increased slightly when the carbon disulphide charge increased. However, it can also be seen that if an enzyme pre-treatment was used the gamma number of the viscose decreased. Thus, it seemed that the accessibility of the cellulose in the following sulphidation stage was decreased slightly by the enzymatic pre-treatment.

**Table 2.** Gamma Numbers of Viscose made from Endoglucanase-treated Sulphite Dissolving Pulp with Different Carbon Disulphide Charges\*

Enzyme concentration (ECU/g pulp)	CS <sub>2</sub> (%)	Gamma number (%)
0	53	53
0	45	50
4.5	53	48
4.5	48	48
4.5	43	44

\* Enzyme treatment conditions: 15 m, 45°C, 5 % pulp concentration (4.5 ECU/g pulp)



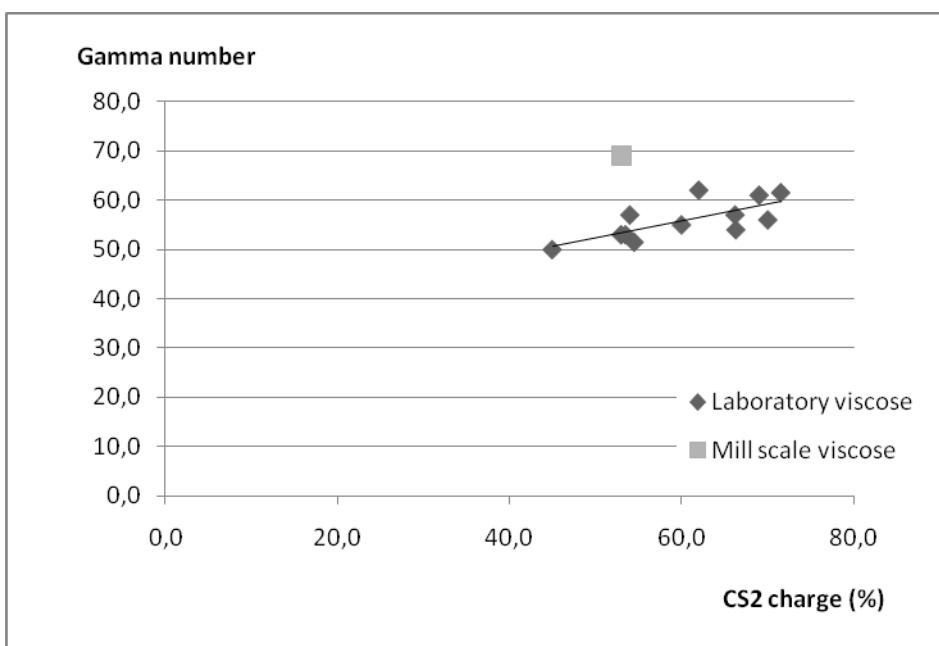
In Fig. 2 and Table 3 the reactivity of the pulp according to Fock increased with increased enzyme pre-treatment time up to 30 min. However, the gamma number on the other hand was reduced by the same enzyme treatment. A conclusion that can be drawn from Tables 2 and 3 is that an increase in pulp reactivity according to Fock appeared not to correlate to a corresponding increase in the gamma number of the viscose solution.

**Table 3.** Pulp Reactivity according to Fock and the Gamma Number of Viscose Solution for Endoglucanase-treated Sulphite Dissolving Pulps\*

Enzyme treatment time (min)	Enzyme concentration (ECU/g pulp)	Reactivity according to Fock (%)	Gamma number (%)
Reference	0	76	55
1	4.5	76	47
15	4.5	88	51
30	4.5	89	48

\* Conditions used: 53% CS<sub>2</sub>, 4.5 ECU/g pulp.

The correlation between the gamma number and the C<sub>2</sub>S charge for some laboratory viscose samples and one mill-produced viscose sample is shown in Fig. 4.



**Fig. 4.** The gamma number versus the carbon disulphide charge for viscose prepared from sulphite dissolving pulp on laboratory and industrial scales. The dissolving pulp used was identical in both cases.

As can be seen, the gamma number increased slightly with increasing carbon disulphide charge, but the correlation was relatively weak. It can also be seen that none of the samples reached the corresponding level obtained in industrial production. Thus, there seemed to be a difference between small, laboratory-scale experiments and large,

industrial-scale production. The difference could be due to several factors, such as a difference in mixing efficiency (industrial mixing seemed to be better than laboratory mixing) or a difference due to the varied volume/surface ratio, etc. Thus, the results indicated that it is easier to obtain a high gamma number on an industrial scale than on a laboratory scale.

### Influence of Pre-Treatment with Xylanase

It was also investigated whether the gamma number of the viscose solution could be influenced by pre-treating the starting pulp with an enzyme that mainly reacts with xylan (i.e. a xylanase). The results are shown in Table 3. First of all it can be seen that a xylanase pre-treatment had no influence on the limiting viscosity number of the pulp. This could be expected, as xylanase reacts specifically with xylan that has a low DP. The limiting viscosity number is mainly a function of the much higher DP of the cellulose molecules, and these were not affected by the xylanase.

It can also be seen in Table 4 that, regardless of whether an alkaline stage was used after the xylanase stage, no difference was seen with respect to the limiting viscosity number or for the gamma number.

**Table 4.** Limiting Viscosity Number of a New Set of Sulphite Dissolving Pulp Samples Treated with Xylanase with or without a Subsequent Alkaline Extraction and the Gamma Numbers for Viscose Prepared from Some of the Samples\*

Xylanase (AXU/g pulp)	Alkali extraction	Endoglucanase (ECU/g pulp)	Limiting viscosity number (dm <sup>3</sup> /kg)	Gamma number (%)
0	No	0	524	62 ± 2
0	Yes	0	542	62 ± 2
10	No	0	527	-
10	Yes	0	514	63 ± 2
100	No	0	526	-
100	Yes	0	526	63 ± 2
100	Yes	4.5	443	62 ± 2

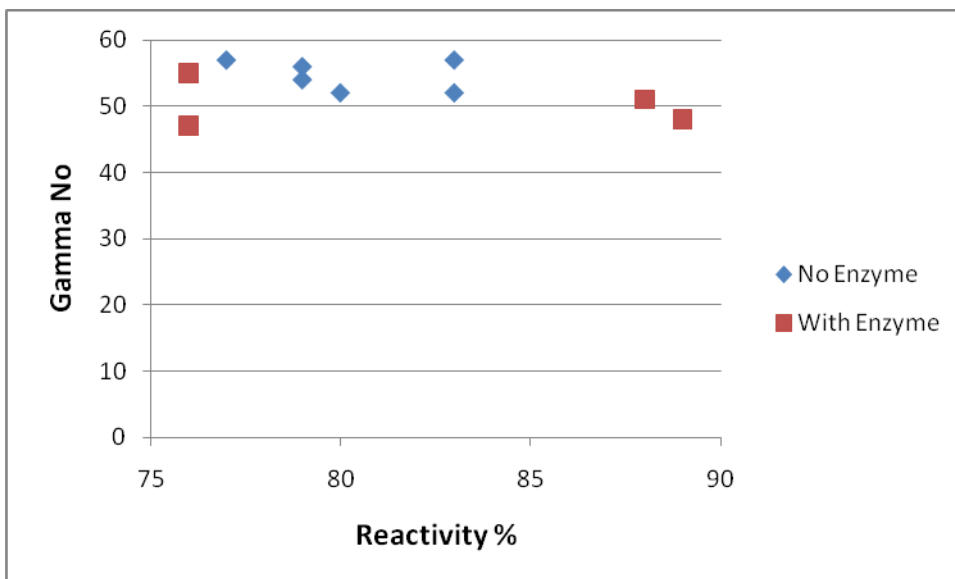
\* In one case endoglucanase was also added. Enzyme charges: 10 AXU/g pulp, 100 AXU/g pulp and 4.5 ECU/g pulp.

An experiment was also carried out in which a pre-treatment of the starting pulp was carried out with a mixture of endoglucanase and xylanase. It was found that the xylanase treatment had no influence on the limiting viscosity number of the pre-treated pulp, but that when the endoglucanase was added, the limiting viscosity number decreased. It can also be seen that the addition of endoglucanase to the xylanase had no effect on the gamma number of the viscose solution.

### Gamma Number Versus Fock's Test

A new set of experiments were carried out to investigate if there was a correlation between the reactivity according to Fock of the starting pulp and the gamma number of

the resulting viscose solution. The results are shown in Fig. 5. Thus, it is clear that there was no direct correlation between these two parameters. It is also seen that whether or not enzymes were used the same gamma number was obtained.



**Fig. 5.** The gamma number versus the pulp reactivity according to Fock for viscose samples prepared from the sulphite dissolving pulp at different conditions. Enzyme charge: 4.5 ECU/g pulp.

Thus, although reactivity according to Fock's test (Fock 1959) is an established indicator of the suitability of dissolving pulps for viscose preparation, it cannot, according to the results of this study, be used as the sole method of measuring pulp reactivity. Fock's test is performed on the pulp and is a small-scale test using a large excess of carbon disulphide and sodium hydroxide. It measures the yield of cellulose after the reaction and regeneration. Conversely, the gamma number is a direct measurement of the degree of substitution actually obtained on the cellulose backbone prior to the regeneration stage. From a chemical point of view it is a measure of the sulphur content of the viscose (Barthelemy et al. 1945). The reactivity of the pulp and the gamma number of the viscose solution are expected to be totally correlated, but that did not seem to be the case in the present study.

### Experiments on a Conventional Softwood Kraft Pulp

The above experiments were done on softwood two-stage sulphite dissolving pulps, and it was of interest to compare these results with the corresponding results for conventional softwood kraft pulps. The major difference between such fully-bleached pulps is found in the chemical composition of the pulps, i.e. the dissolving pulp has significantly lower hemicellulose content and higher cellulose content. The results are shown in Table 5.

**Table 5.** Viscose Results for the Conventional Softwood Kraft Pulp

Sample	Pre-treatment of pulp with endoglucanase (ECU/g pulp)	CS <sub>2</sub> charge calculated on the original pulp (%)	Gamma number (%)
1	0	25	41±2
2	0	53	64±2
3	4.5	53	76±2

As could be expected, there was a correlation between the carbon disulphide charge and the resulting gamma number, i.e. an increase of the carbon disulphide charge resulted in an increase of the gamma number. Also, treating the starting kraft pulp with 4.5 ECU/g pulp before the viscose preparation resulted in a significantly higher gamma number. This result indicated that hemicelluloses could also be esterified by carbon disulphide and not only the cellulose. Thus, the gamma number is therefore not a good measure of the amount of xanthate groups on the cellulose molecules if the pulp also contains a high content of hemicelluloses.

## CONCLUSIONS

1. The Fock reactivity of pulps increased when an endoglucanase stage was used prior to the Fock test being employed. A low endoglucanase charge (4.5 ECU/g pulp) and a short treatment time (30 min) was sufficient to obtain the maximum increase in pulp reactivity. In addition, the charge or the retention time had to be sufficiently low to avoid a severe loss in the limiting viscosity number. The Fock reactivity was unchanged when a xylanase stage replaced the endoglucanase treatment in the same position.
2. The Fock reactivity of dissolving pulps increased after a mild enzyme treatment with an endoglucanase enzyme, but the reactivity of the pulps according to Fock's test was found to be a poor indicator of the gamma number of the prepared viscose solutions.
3. The gamma number of viscose solutions was unchanged, or even reduced, when an enzyme stage was used prior to the viscose process.
4. The gamma number was found not to be selective to cellulose, and it seemed that it also measures xanthate groups in the hemicellulosic material. Both cellulose and hemicelluloses experience a certain degree of substitution in the viscose process, with the hemicellulose molecules reacting with the greater ease due to their small size.

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