

Improvement in the Fock test for determining the reactivity of dissolving pulp

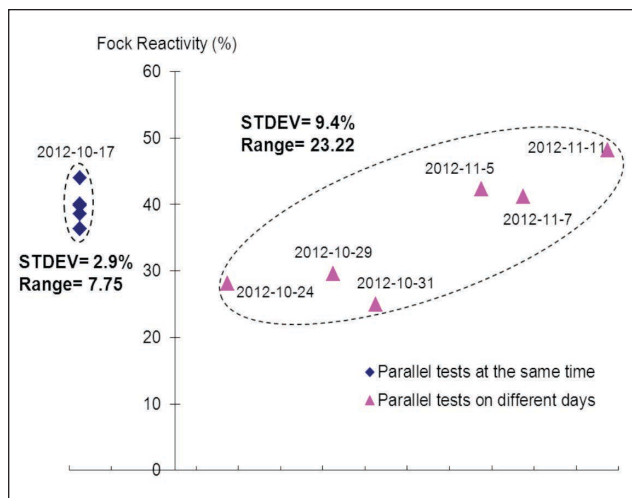
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ABSTRACT: The Fock test is widely used for assessing the reactivity of dissolving pulp. The objective of this study was to modify the method to improve the repeatability of the test. Various parameters that affect the repeatability of the Fock test were investigated. The results showed that Fock reactivity is dependent on testing conditions affecting the xanthation between cellulose and carbon disulfide, such as the moisture content of the pulp sample, sodium hydroxide (NaOH) concentration, xanthation temperature, carbon disulfide dosage, and xanthation time. The repeatability of the test was significantly improved using the following modified testing procedure: air dried sample in the constant temperature/humidity room, xanthation temperature of 66°F (19°C) in a water bath, xanthation time of 3 h, NaOH concentration of 9% (w/w), and 1.3 mL carbon disulfide.

Application: The improved Fock test can give good repeatability in the reactivity test of dissolving pulp in research and development (R&D) laboratories and production lines.

Dissolving pulp is the raw material for manufacturing rayon and many other cellulose derivatives. As an important quality parameter, reactivity (sometimes referred to as accessibility or processability) is used to represent the reactivity of dissolving pulp toward carbon disulfide in the downstream processing plants. More specifically, it is used to assess the reactivity of the hydroxyl groups on glucose units of cellulose chains toward carbon disulfide [1,2]. The increased reactivity of dissolving pulp implies improvements in the quality of cellulose products, and may lower the required dosage of carbon disulfide [3,4], an expensive and toxic chemical in the rayon industry.

Several methods have been developed to determine the reactivity of dissolving pulp. The most popular one, the Fock test, was reported in 1959 [5]. In this method, the dissolving pulp sample is mixed with sodium hydroxide and excess amounts of carbon disulfide to form a solution of cellulose xanthate. Cellulose is regenerated from this solution in the presence of sulfuric acid, and its quantity is determined to obtain the percentage of reacted cellulose (known as the Fock reactivity). Evidently, the Fock test is a simplified viscose process on a laboratory scale [6,7]. Compared with other methods, such as iodine sorption [8], water retention value [9], phosphitylation and quantitative ^{31}P nuclear magnetic resonance (NMR) spectroscopy [10], and viscose filter value (which is commonly used in the viscose rayon industry, but complex and requires special equipment), the Fock test is easy to handle under conventional laboratory conditions [7,11]. The Fock test generally has been accepted in assessing the



1. The poor repeatability of the Fock test performed on the same dissolving pulp sample but at different dates. Conditions: Tests were conducted according to the method described by Kvarnlöf (2007) and Östberg et al. [15].

reactivity of dissolving pulps produced from various raw materials by either acid sulfite or pre-hydrolysis kraft processes [10,12].

However, Fock test results have not been consistent. In a study by Christoffersson [13], the Fock reactivity results conducted in the same laboratory under the same conditions, at the same time, varied from 56.9% to 64.7%, and the standard deviation was 13% for parallel tests conducted at different times (Fock reactivity results varied from 33.3% to 57.6%).

Sample ID	Raw Material	Producing Method	Intrinsic Viscosity (mL/g)
A	Hardwood	Pre-hydrolysis kraft	680
B	Hardwood	Pre-hydrolysis kraft	650
C	Softwood	Sulfite	1046

1. Characteristics of dissolving pulp samples used in this study.

This poor repeatability was also seen in our study (**Fig. 1**), which was carried out on the same sample, following the same procedure, but on different days. This is no doubt unacceptable for both research work and quality control in the production line.

Accordingly, the objectives of this study are to identify the reasons for the poor repeatability of the Fock test and to develop an improved testing procedure that will provide acceptably repeatable results. To accomplish those objectives, the testing conditions affecting the xanthation of cellulose, such as the sodium hydroxide (NaOH) concentration, xanthation temperature, carbon disulfide dosage, and xanthation time, were systematically studied. Then, an improved Fock test procedure, which gave acceptable repeatability, was proposed and verified.

EXPERIMENTAL

Determination of Fock reactivity

Table I lists characteristics of the three commercial dissolving pulp samples provided for this study by different mills in Canada. For xanthation and regeneration of cellulose, 0.50 g of pulp sample (calculated as oven dry [o.d.] pulp) was weighed and placed in a 250 mL Erlenmeyer flask with a stopper. After 50 mL NaOH solution was added, this flask was placed in a shaker, submerged in a water bath, and shaken for 10 min. As soon as the carbon disulfide was added, the flask was sealed with plastic paraffin film and continued to be shaken at 250 rpm for several hours at the specified temperature. When the time was up, deionized water was immediately added to the flask to give the solution a total weight of 100 g. After a vigorous shake, the solution was transferred to a tube with stopper and centrifuged at 5000 rpm for 15 min to separate dissolved cellulose from unreacted cellulose. Then, 10 mL of the supernatant was pipetted into a 100 mL flask and neutralized with 3 mL sulfuric acid of 20% (w/w). The cellulose was regenerated for 15-20 h and degassed to remove carbon disulfide (CS₂).

For measurement of the dissolved cellulose, 20 mL sulfuric acid (H₂SO₄) (68% w/w) was added to the 100 mL flask and the suspension was shaken for 1 h to acidify the regenerated cellulose. Thereafter, a 10 mL potassium dichromate (K₂Cr₂O₇) solution (1/6 M) was added to the flask and the mixture was reboiled for 1 h, during which the oxidation took place. When

the mixture was cooled to room temperature, it was diluted into a 100 mL volumetric flask and 40 mL of this solution was transferred into a 250 mL Erlenmeyer flask. As soon as 5 mL potassium iodide (10% w/w) was added, the solution was titrated with sodium thiosulfate (0.1 N) using starch as the indicator. The volume of consumed sodium thiosulfate was recorded to obtain the percentage of cellulose that reacted with carbon disulfide, according to the following Eq. (1):

Dissolved cellulose (%) =

$$\frac{\left\{v_1c_1 - \left(v_2c_2 \times \frac{100}{40}\right) \times \frac{1}{6}\right\} \times M \times \frac{1}{4} \times \frac{100}{10.4}}{m} \times 100 \quad (1)$$

where, M is the molecule weight of glucose unit (162 g/mol), m is the o.d. weight of the pulp sample (g), v_1 is the volume of K₂Cr₂O₇ added (0.01 L), c_1 is the concentration of K₂Cr₂O₇ solution (1/6 M), v_2 is the volume of consumed Na₂S₂O₃ (L), c_2 is the concentration of Na₂S₂O₃ solution (0.1 N), ($\frac{100}{40}$) means 40 mL diluted sample is taken out from 100 mL volumetric flask and titrated, ($\frac{1}{6}$) means each dichromate ion consumes six thiosulfate ions, ($\frac{1}{4}$) means each glucose unit consumes four dichromate ions, and ($\frac{100}{10.4}$) means 10 mL sample (equal to 10.4 g) is taken out from the 100 g viscose liquid.

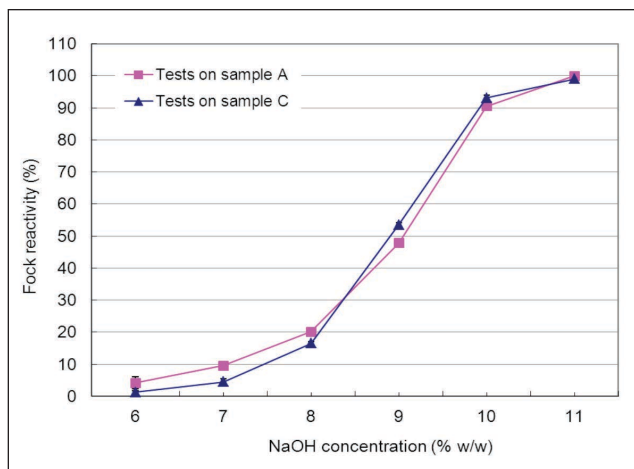
RESULTS AND DISCUSSION

Effect of testing conditions

The NaOH concentration plays an important role in viscose rayon production. Before xanthation, dissolving pulp is first mercerized using a 10%-20% NaOH solution in an independent step to form alkali cellulose [16-18], which then reacts with carbon disulfide [13,15]. For the Fock test, the mercerization, the xanthation, and the dissolution of cellulose are carried out in the same step. In the literature, various NaOH concentrations were adopted by different researchers, including 8% w/w [19], 9% w/w [15,20], and 90 g/L [6,11]. To determine the effect of the NaOH concentration on the Fock reactivity, Fock tests on two pulp samples with various NaOH concentrations were conducted; **Fig. 2** shows the results.

Evidently, the Fock reactivity of dissolving pulp is very sensitive to the NaOH concentration in the xanthation step, especially in the range of 8%-10%. Based on these results, the NaOH concentration needs to be controlled precisely to minimize the testing error, and a specified NaOH concentration must be given for the Fock test to compare the results from different researchers.

Cellulose mercerization is essential for xanthation, by which the cellulose is swollen and alkali cellulose (Na-cellulose) is formed. The swelling degree of cellulose or transition from cellulose to Na-cellulose is dependent on the concentration of NaOH. At low NaOH concentrations, usually below 10%, the cellulose swelling or transition of cellulose increases significantly with increase in the NaOH concentration; at high NaOH concentrations, the transition to Na-cellulose will reach



2. Effect of sodium hydroxide (NaOH) concentration on the Fock reactivity. Conditions: Air-dried pulp sample of 7.5% moisture, 66°F (19°C) xanthation temperature, 1.3 mL carbon disulfide (CS₂), 3 h xanthation time.

the plateau, but the swelling of cellulose may decline [1,21].

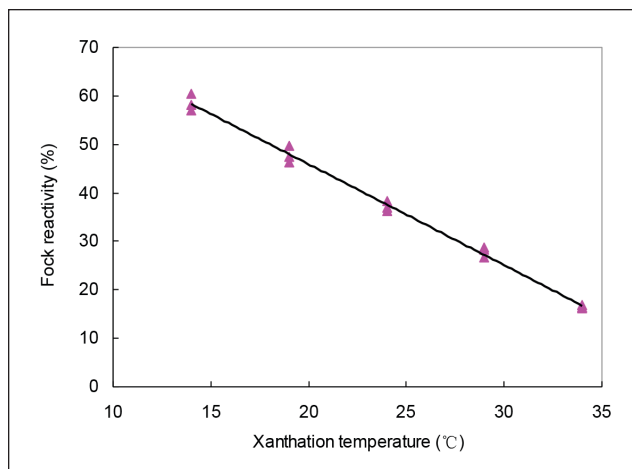
Any processing conditions that can introduce variation in the NaOH concentration during the xanthation process should be minimized. Variation in the moisture content of the pulp samples, for example, can result in testing errors. To illustrate the effect of moisture brought in from the pulp sample, a set of experiments was conducted on the same pulp sample (sample B), but with different moisture contents (Table II).

The results in Table II support the conclusion that the Fock reactivity of a pulp sample with lower moisture content is significantly higher than that of the same pulp sample with higher moisture content. In fact, it can be calculated that under the conditions studied, for the air dried sample (moisture content of 7.5%) and the sample with 73.66% moisture content, the additional moisture led to a 0.23% decrease in the NaOH concentration, which is then responsible for the much lower Fock reactivity for the 73.66% sample. Figure 2 also shows that at an NaOH concentration of 8%-10%, a small change in the NaOH concentration can cause a big change in the Fock reactivity. For this reason, pulp samples for the Fock test should be conditioned in the constant temperature/humidity room for 24 h, allowing a constant moisture content to be obtained.

Sample Status	Moisture Content of Sample (%)	Fock Reactivity (%)
Air dried	7.50	51.53
Wet	54.18	45.62
Wet	73.66	38.24

Conditions: 9% w/w NaOH concentration, 66°F (19°C) xanthation temperature, 1.3 mL CS₂, 3 h xanthation time.

II. Effect of the moisture content of pulp sample on Fock reactivity.



3. Effect of xanthation temperature on Fock reactivity. Conditions: Air-dried sample A of 7.5% moisture, 9% w/w NaOH concentration, 1.3 mL CS₂, 3 h xanthation time.

Xanthation temperature

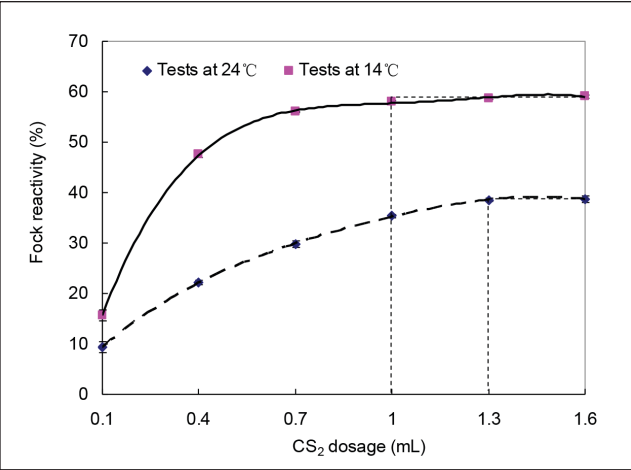
In the study by Fock in 1959 and most of the related studies by other researchers [4,6,7,11], the xanthation step in the Fock test was performed at room temperature. Because room temperature may fluctuate significantly, it can cause inconsistency in the testing results. Figure 3 shows that the Fock reactivity differed from 58.50% to 16.45% when xanthation temperature was varied from 55°F to 93°F (13°C to 34°C).

Several reasons might be responsible for the significant decrease in the Fock reactivity as the temperature increases: 1) the boiling point of carbon disulfide is only 115.3°F (46.3°C) and, therefore, more carbon disulfide loss might occur at a higher temperature through evaporation; 2) sodium hydroxide can swell cellulose to a higher degree at lower temperature [16,21-23], which facilitates the diffusion of carbon disulfide inside the cellulose structure; 3) xanthation is an exothermic reaction [16]; and 4) in the xanthation system, more byproducts will be produced when the xanthation temperature increases, which competes for the consumption of carbon disulfide with the xanthation reaction [16,24-26].

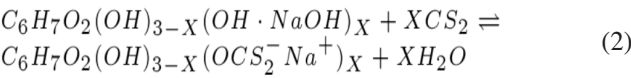
Similar results were reported by other researchers, though with various purposes. In a study by Rassolov and Finger [28], a sharp decrease in the maximum degree of esterification of cellulose at high xanthation temperature was observed. Stepanova et al. [25] found that a higher xanthation temperature would lead to an increase in the formation rate of sulfur-containing byproducts and simultaneously reduce the amount of carbon disulfide consumed in the xanthation of cellulose.

Carbon disulfide dosage

Based on the stoichiometry of Eq. (2), one can calculate that about 0.6 g of CS₂ would be required for xanthation of 0.5 g dissolving pulp, with the assumption that all of the three hydroxyls on the glucose unit are xanthated (about 50%-70% of the hydroxyls can be practically xanthated [16,27]).



4. Effect of CS₂ dosage on Fock reactivity. Conditions: Air-dried sample A of 7.5% moisture, 9% w/w NaOH concentration, 3 h xanthation time.

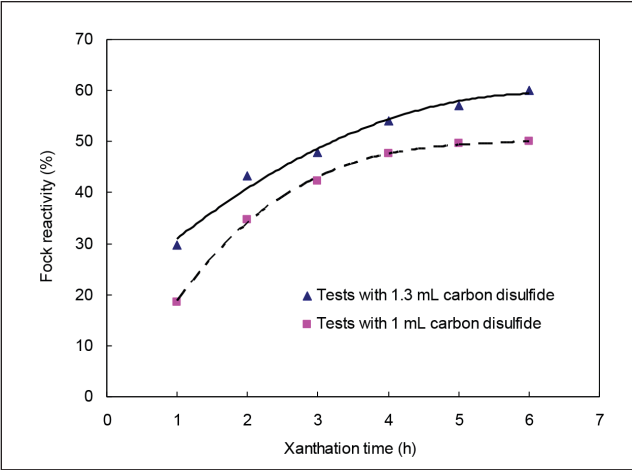


Thus, 1 mL of CS₂ (equal to 1.26 g), suggested in the Fock test published in 1959, seems to be in great excess for the Fock reactivity test. More recently, however, the dosage of CS₂ in the xanthation step was increased to 1.3 mL [6,7,11], while others still used 1 mL of CS₂ [14,15,20]. **Figure 4** shows the effect of CS₂ dosage on Fock reactivity.

At 75°F (24°C), the Fock reactivity reached a plateau at the CS₂ dosage of 1.3 mL (Fig. 4), and a lower CS₂ dosage than 1.3 mL would yield a lower reactivity; at 57°F (14°C), 1 mL of CS₂ would reach the plateau. Moreover, a much higher Fock reactivity was obtained at 57°F (14°C) than at 75°F (24°C), which is consistent with the results in Fig. 3.

Xanthation time

The xanthation time in the Fock test was not always the same in the previous studies. For example, the xanthation time was 3 h and the CS₂ dosage was 1 mL [14,15,20], while in others, 4 h of xanthation time and 1.3 mL of CS₂ dosage were used [6,7,11]. As shown in **Fig. 5**, the xanthation time has a strong impact on Fock reactivity, especially in the first 3 h (1 mL CS₂) or 4 h (1.3 mL CS₂). The two sets of conditions (1 mL CS₂ for



5. Effect of Xanthation time on the Fock reactivity. Conditions: Air-dried sample A of 7.5% moisture, 9% w/w NaOH concentration, 66°F (19°C) xanthation temperature.

3 h versus 1.3 mL CS₂ for 4 h) also yielded different reactivity results.

Additionally, the xanthation time for the Fock reactivity to reach a plateau is much longer than the suggested 3–4 h. It was 5 h when 1 mL CS₂ was used, but no plateau was reached, even after 6 h of xanthation time when 1.3 mL CS₂ was used. For commercial viscose production, however, the xanthation time is usually 1–2 h [16,29].

The conditions for cellulose xanthation in the Fock test are very different from those for practical viscose production. The dosage of CS₂ in the Fock test is about 10 times that used in viscose production (30%–35% of the α-cellulose weight) [16], which can lead to a higher xanthation degree of cellulose [27]. In addition, in viscose production, the diffusion of CS₂ and the xanthation of cellulose are more efficient than in the Fock test, because most of the excess NaOH solution is pressed out after mercerization and the CS₂ concentration rises to a high level in a short time [16,27]. For this reason, the xanthation time is much longer in the Fock test than in viscose production.

Taking all factors into consideration, a 3 h xanthation time is recommended for the Fock test.

Fock test repeatability with modified testing procedure

Based on previous investigations, the following conditions

Pulp Sample	Fock Reactivity from Parallel Tests Performed on Different Days (%)	Standard Deviation (%)	Range
A	49.66, 48.75, 49.78, 50.71, 49.17, 47.53	1.08	3.18
B	49.62, 50.85, 52.18, 50.88, 51.53	0.95	2.56

III. The repeatability of the Fock test with the modified testing procedure.

were proposed for the Fock test:

- 1) The pulp sample is air dried in a constant temperature/humidity room.
- 2) The xanthation is conducted in a water bath at 66°F (19°C).
- 3) The dosage of CS₂ is 1.3 mL.
- 4) The xanthation time is 3 h.
- 5) The NaOH concentration is 9% (w/w).

By following these procedures, samples A and B were subjected to the Fock test on different days. **Table III** shows the results. The standard deviation of these trials was about 1% (Table III), which is much lower than that shown in Fig. 1. These results supported the conclusion that the repeatability of the Fock test is significantly improved with the modified procedure.

CONCLUSION

This study addressed the repeatability of the Fock test. The xanthation temperature of the Fock test is the most critical factor in the procedure. Room temperature was specified in the Fock test, but the actual temperature can vary significantly between different days, causing poor repeatability of the

method. Other factors, such as the NaOH concentration, CS₂ dosage, and xanthation time, can also affect the Fock test results. By air drying the pulp sample in a constant temperature and humidity room, controlling the xanthation temperature at 66°F (19°C) in a water bath, using an NaOH concentration of 9% w/w, and using the xanthation time of 3 h and CS₂ dosage of 1.3 mL, the modified Fock test can give good repeatability (the standard deviation of parallel tests performed in different days was about 1%). **TJ**

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ABOUT THE AUTHORS

A reliable and repeatable reactivity test of dissolving pulp is critical for its manufacturing processes and for R&D. For this study, we modified the Fock testing procedure so that it can give consistent testing results.

The effect of different parameters on results and their impact on the accuracy were the most difficult and key aspects of this research. A number of them were related, therefore, we addressed them by determining the effects individually.

The most interesting finding from this research was that the sodium hydroxide concentration was critical in affecting the Fock reactivity, and its repeatability.

The improved test procedure can be used by mills in monitoring their production processes. The next step is to apply the modified Fock procedure on different dissolving pulp samples from different production processes.

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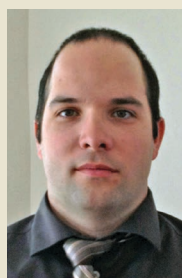
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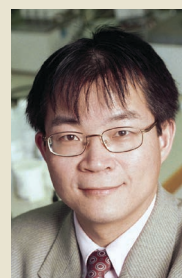
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