A novel approach for determining the reactivity of dissolving pulp based on the COD method

CHEN GONG, SHI YU, LIU YAN-ZHAO, NI JIAN-PING, YANG XIAO-BO, AND TIAN CHAO

ABSTRACT: A novel approach for determining the reactivity of dissolving pulp according to the chemical oxygen demand (COD) of water has been discussed. First, a sample of dissolving pulp was subjected to mercerization and xanthation in order to obtain dissolved cellulose fractions. Next, the fractions were digested with a testing solution as applied in COD procedures. Finally, the resulting liquid was rapidly tested by ultraviolet-visible spectrophotometry (UV-Vis). By quantifying the absorbance of Cr^{3+} at a wavelength of 600 nm, the reactivity of dissolving pulp was indirectly calculated. The results measured by this novel COD method correlated well with the most accepted Fock test results with less than 10% relative difference. Meanwhile, this newly developed COD method required less time-consuming procedures as compared to the Fock test.

Application: This novel COD method presents an alternative approach for determining the reactivity of dissolving pulp in laboratory or industrial applications.

Dissolving pulp has been widely used for manufacturing artificial textile fibers (Viscose or Lyocell), cellulose acetate, carboxymethyl cellulose, and other cellulose derivatives [1-3]. The reactivity of dissolving pulp as measured by the Treiber viscose filterability test [4] and the Fock test [5] has been used to determine the amount of active hydroxyl groups on the backbone of the cellulose chains available to be substituted by derivatization reagents such as carbon disulfide (CS_2) [6-8].

The filterability test has been commonly accepted in the viscose rayon industry for quick comparison of dissolving pulp's quality. The sample is prepared by submerging a specified amount of pulp into a solution of sodium hydroxide (NaOH) and CS_2, and then transferring the suspension to custom-made filtration equipment. By measuring the filterability of the viscose fraction in a customized screen, the reactivity of dissolving pulp is determined. This filterability test is not particularly reproducible and it is difficult to use with samples that cannot be filtered through the screen.

The Fock test has been developed based on the simplified viscose process for the purpose of accurately quantifying the reactivity [9-11]. The sample is first mixed with NaOH and excess CS_2 as xanthation; the regenerated cellulose is then precipitated out of the solution by adding sulfuric acid and oxidized by potassium dichromate ($K_2Cr_2O_7$); after titration of the residual $K_2Cr_2O_7$ in the solution with standard sodium thiosulfate solution ($Na_2S_2O_3$), the reactivity of cellulose fibers is back-calculated and determined as the percentage of dissolved cellulose (shown in the following equation). The original Fock test is not consistent due to its relatively large variations influenced by testing conditions [13-14]. With optimized experimental parameters, the modified Fock test is well established for reactivity testing, with less than 5% standard deviation among replicates.

$$\text{Dissolved cellulose (\%)} = \frac{\left\{v1c1-\left(v2c2\times\frac{100}{40}\right)\times\frac{1}{6}\right\}\times M\times\frac{1}{4}\times\frac{100}{10.4}}{m}\times 100$$

where:

M is molecule weight of glucose unit (162 g/mol)

m is oven dried weight of pulp sample, g

v_1 is volume of $K_2Cr_2O_7$ added (0.01 L)

c_1 is concentration of $K_2Cr_2O_7$ solution (1/6M)

v_2 is volume of consumed $Na_2S_2O_3$, L

c_2 is concentration of $Na_2S_2O_3$ solution (0.1 N)

$\frac{100}{40}$ is 40 ml diluted sample taken out from 100 ml volumetric flask and titrated

$\frac{1}{6}$ is each dichromate ion consumed six thiosulfate ions

$\frac{1}{4}$ is each glucose unit consumed four dichromate ions

$\frac{100}{10.4}$ is 10 ml sample (equal to 10.4g) taken out from the 100 g viscose liquid

Despite its quantitative precision and relatively good stability after modification [15], the Fock test requires a series of complex and time-consuming procedures. In the xanthation step, the excess CS_2 was added into the sample to ensure

that all active hydroxyl groups on the backbone of the cellulose chains were substituted by CS_2 [6-8]. In the following step, the residual CS_2 has to be completely released by standing for 15~20 h before oxidation to avoid over-estimation of reactivity caused by unreacted CS_2 [16]. Also, before the oxidation step, the sample needs to be acidified by adding 68 wt% sulfuric acid and reacting for 1 h. Then, the sample was oxidized with excess $K_2Cr_2O_7$ for another hour, in which the reflux devices were applied to maintain the boiling temperature of the oxidation reaction without losing samples. Therefore, it is desired to have a more efficient and applicable approach to determine the pulp reactivity.

It has been known that the chemical oxygen demand (COD) test can be used for quantifying the amount of organics in water [17], and it measures the concentration of oxygen corresponding to the $K_2Cr_2O_7$ consumed by the dissolved substances and suspended matter in the water sample [18]. The COD value in the sample is proportional to the increase in the absorbance of Cr^{3+} (reduced from $K_2Cr_2O_7$) at a wavelength of 600 nm ± 20 nm; thus, the COD value is quantified by measuring absorbance of Cr^{3+}. Inspired by that idea, we adapted the COD test for determining the reactivity of dissolving pulp.

In contrast with quantifying the dissolved substances and suspended matter in the water sample in the conventional COD test, the pulp reactivity measures the dissolved cellulose fraction in alkaline solution after xanthation. The soluble fraction can be precipitated out of the solution through acidification of viscose dope. Therefore, the resulting suspension can be reacted with $K_2Cr_2O_7$ and quantified by measuring the ultraviolet-visible spectrophotometry (UV-Vis) absorbance of Cr^{3+} after an appropriate calibration. To further establish this method, the effects of testing conditions were investigated along with the replicate testing to improve the accuracy and precision of this COD method. Also, this developed COD approach was compared with the commonly applied Fock test to validate its applicability to evaluate dissolving pulp reactivity.

EXPERIMENTAL

Chemical and materials

The chemicals used in the experiment, including sodium hydroxide, carbon disulfide, sulfuric acid, potassium dichromate, sodium thiosulfate, silver sulfate, mercury sulfate, and potassium hydrogen phthalate were all analytical-grade, purchased from Aladdin Chemicals Co. Ltd. (Shanghai, China). A sodium hydroxide solution (9 wt%) was used for the pulp mercerization and xanthation. The commercial dissolving pulps used in the present study were kindly provided by a variety of manufacturers in China.

Apparatus

A temperature controllable water bath with shaking function (ZN-17-HSY-B, Gaodeyiqi; Jintan, China) was used for the sample mercerization and xanthation procedures. A smaller size of temperature controllable water bath (XT5018-GP18-D61, Xutemp; Hangzhou, China) was used for the degassing procedure. A centrifuge (Thermo Scientific Heraeus Multifuge X1R; Waltham, MA USA) equipped with four 50-ml tubes was used to remove the non-dissolvable substances from the viscose dope. A COD digestion instrument (5B-1, LIANHUAKEJI; Bejing, China) was used for sample preparation before UV-Vis test. A UV-Vis spectrophotometer (UV-1800, Shimadzu; Kyoto, Japan) equipped with 10-mm quartz cuvettes was used for the spectroscopic measurements.

Procedures of sample preparation, reaction, and measurement

The xanthated sample was prepared according to the modified Fock test [15]: 0.5000 g of the dissolving pulp was added into a 50.00 ml of sodium hydroxide solution (9 wt%) for the mercerization (at 25±0.1°C for 10 min under constant shaking) to obtain an alkali cellulose suspension. Then, the alkali cellulose was xanthated by reacting with carbon disulfide solvent (1.30 ml) at 25±0.1°C for 3 h in the constant temperature shaker (250 rpm).

Once the xanthation was finished, the mixture was diluted with distilled water to obtain a total weight of 100 g. After vigorous shaking by hand, less than 30 ml of the mixture was transferred into a 50-ml tube and centrifuged at 4000 rpm for 15 min to separate the reacted cellulose (i.e., dissolved) from the unreacted cellulose.

The supernatant was saved for degassing treatment as follows: 1.60 ml of supernatant was pipetted into a 50-ml tube. Then, 0.48 ml of 20 wt% sulfuric acid and 17.92 ml distilled water were added to make up the total volume of 20 ml and the weight was recorded. Subsequently, the tube with open cap was put into a water bath to evaporate the remaining CS_2. Once the evaporation was finished, the tube was refilled with distilled water to make up to the originally recorded weight. This prepared sample was saved for UV-Vis testing later.

Testing solution preparation

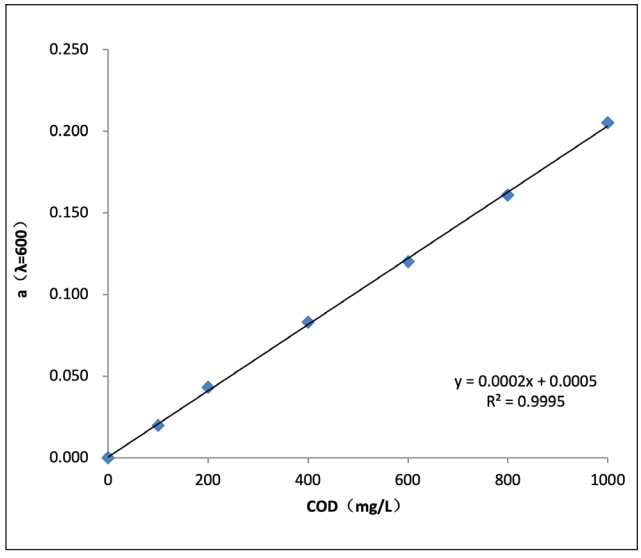
Testing solution preparation [18] included:

Silver sulfate-sulfuric acid aq: 1 g of silver sulfate was dissolved in 100 ml sulfuric acid (density 1.84 g/ml) to make silver sulfate-sulfuric acid aq with concentration of 0.01 g/ml.

Mercury sulfate aq: 125 g mercury sulfate was dissolved in 500 ml 17 wt% sulfuric acid to make mercury sulfate aq with concentration of 0.25 g/ml.

Potassium dichromate aq: solid potassium dichromate was put into an oven (105°C ~120°C) until reaching constant weight; 24.5154 g potassium dichromate was dissolved in 500 ml distilled water and added with 17 wt% sulfuric acid to the level of 1000 ml volumetric flask.

Testing solution: prepared by mixing a), b) and c) solutions at a ratio of 12:2:1 for later use according to the COD test standard.



1. The standard curve of absorbance and chemical oxygen (COD) value of sample.

Standard curve preparation

Potassium hydrogen phthalate was used as standard reagent. It was first dissolved in distilled water to make a 0.02 mol/L solution, then 2 ml, 4 ml, 8 ml, 12 ml, 16 ml, and 20 ml of potassium hydrogen phthalate solution were pipetted into six 100-ml volumetric flasks, respectively, making up to the level by adding distilled water. Testing solutions were pipetted into the 7 series of tubes (7.5 ml in each tube), then filled with 2.5 ml of 6 different concentrations of potassium hydrogen phthalate—one with 2.5 ml distilled water as reference. The COD values of these concentrations of potassium hydrogen phthalate were 0 (as reference), 100 mg/L, 200 mg/L, 400 mg/L, 600 mg/L, 800 mg/L, and 1000 mg/L.

After boiling the 7 tubes in the COD digestion instrument at 165°C for 15 min and cooling down in a dark place, the absorbance values of the prepared samples were measured by the UV-Vis spectrophotometer under the wavelength of 600 nm.

The standard curve, shown in **Fig. 1**, was made by plotting the COD value as the x-axis, and the absorbance of potassium hydrogen phthalate (at different concentrations, subtracting the absorbance of reference) as the y-axis, showing a strong liner correlation (R^2=0.9995).

Spectral measurement

The 7.5 ml testing solution was mixed with 2.5 ml of prepared sample (labeled as sample I), while the blank sample II was prepared by mixing 7.5 ml testing solution with 2.5 ml of distilled water. After boiling these two tubes in the COD digestion instrument at 165°C for 15 min and cooling down in a dark place, the absorbance values of the prepared samples (subtracting blank sample) in the visible region were measured with the UV-Vis spectrophotometer under the wavelength of 600 nm. With the absorbance and standard curve, the COD reactivity of dissolving pulp was calculated as follows:

$$\text{COD Reactivity (\%)} = \frac{\frac{A\times V_2}{8\times a\times 1000}\times 6.85\times \frac{M}{V_1\times 1.04}}{1000\times m}\times 100\%$$

where:

A is absorbance of the prepared samples I subtracting blank sample II

a is slope of standard curve, 0.0002

8 is 1/2 oxygen mole mass, g/mol

6.85 is 1 mmol of ½ oxygen equals to 6.85 mg cellulose

V_1 is volume of viscose fraction before dilution, ml

V_2 is volume of viscose fraction after dilution, ml

1.04 is density of viscose fraction, g/ml

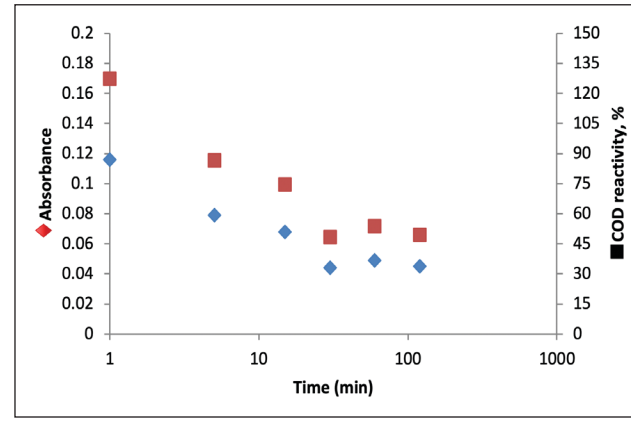
M is total weight of viscose fraction, g

m is oven dried weight of sample, g

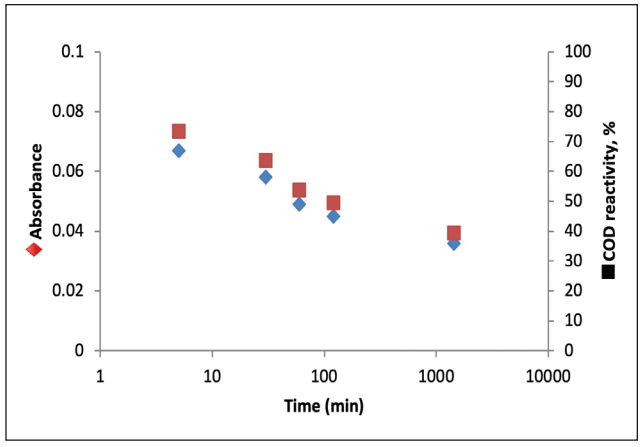
RESULTS AND DISCUSSION

Effect of testing conditions—Degassing time

According to the modified Fock test [15], the dissolving pulp was first reacted with 9 wt% NaOH for mercerization and then with CS_2 for xanthation. As mentioned in the previous section, the unreacted CS_2 could be removed by evaporation at room temperature overnight (commonly 15-20 h). If the CS_2 was not completely removed, a high value of pulp reactivity would be determined due to the residual CS_2 [7,16]. In the present method, CS_2 degassing time was highly shortened by heating the test tube in the boiling water bath and refilling the tube with distilled water to the original solution weight afterwards. Under this circumstance, CS_2 can be rapidly removed while the concentration of regenerated cellulose solid is retained. Here, we examined the proper heating time to ensure that all remaining CS_2 was removed for the accuracy of the test. As the heating time of the sample solution was increased from 1 min to 2 h, the absorbance value first declined and then went flat—same as the COD value (shown in **Fig. 2**). This trend implied that the remaining CS_2 was completely removed after 30 min heating, leading to a stable COD value. Therefore, we chose 30 min as the degassing time to make sure the sample solution without extra CS_2 remained for the following oxidation reaction.



2. Effect of heating time on the spectral measurement.



3. Effect of storage period on the spectral measurement.

Effect of testing conditions—Stabilization before UV test

After the degassing procedure in this COD method, the resulting solution was digested with testing solution, and then rapidly tested with a UV/Vis. It has been known that the ultraviolet absorbance is strongly affected by the stability of the sample solution, showing various absorbance values under different circumstances [19-21]. Therefore, to improve the precision of this method, the storage period for stabilization was analyzed by recording the absorbance at different time slots (from 5 min to 24 h), using a commercial pulp sample with Fock reactivity of ~50%. As shown in **Fig. 3**, the COD reactivity value was up to 70% at the beginning, and then diminished along with the longer storage period, which is in accordance with previous studies [20-21]. The variation of absorbance may be attributed to the color change of the solution under different storage times. Also, if not completely cooled down before testing, the hot solution may generate vapor, which could lower transmittance of visible light, leading to the higher absorbance values reported [21]. The results indicated that the UV-Vis absorbance tended to stabilize after 1 h of storage, with the COD value reaching to 50%. However, a longer time (meaning over 2 h, shown in Fig. 3) would lead to a lower COD value due to the changes of Cr^{3+} influenced by environmental conditions [22-24]. Thus, 1 h of storage time was adopted for a stable ultraviolet absorbance after digesting.

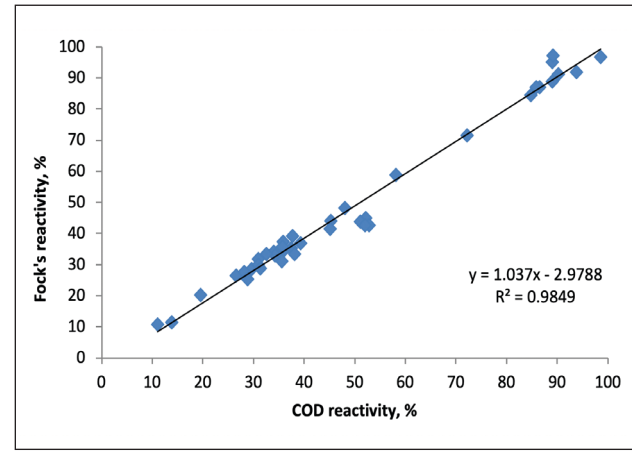
COD method repeatability and comparison with Fock test

To evaluate the repeatability of the present method, three representative commercial pulps were tested and analyzed in triplicate, as shown in **Table I**. By testing three separate measurements of each sample, within 6% of relative standard deviation (RSD) was achieved, showing practical feasibility of this method.

To explore the applicability of the present method, 41 commercial samples from various suppliers have been tested in comparison with the Fock method by applying COD reactivity as the x-axis and Fock results as the y-axis, as shown in **Fig. 4**. The reactivity of these samples fell into three main regions of 10%~30%, ~50%, and 80%~100%, which basically covered the main reactivity values for most commercial pulp samples. The results showed that the two sets of results were in a good agreement with R^2 up to 98.4%. Meanwhile, the relative difference between two testing results for the same sample was less than 10%, which indicated this COD testing method may be well applied for determining the reactivity of dissolving pulp.

No.	Reactivity, %		
	Sample A	Sample B	Sample C
1	30.8	48.3	91.1
2	28.6	53.8	91.1
3	29.7	49.4	92.2
Mean	29.7	50.5	91.5
RSD	3.7%	5.7%	0.7%

1. Precision tests of the present method for the same sample, repeatability (RSD = relative standard deviation).

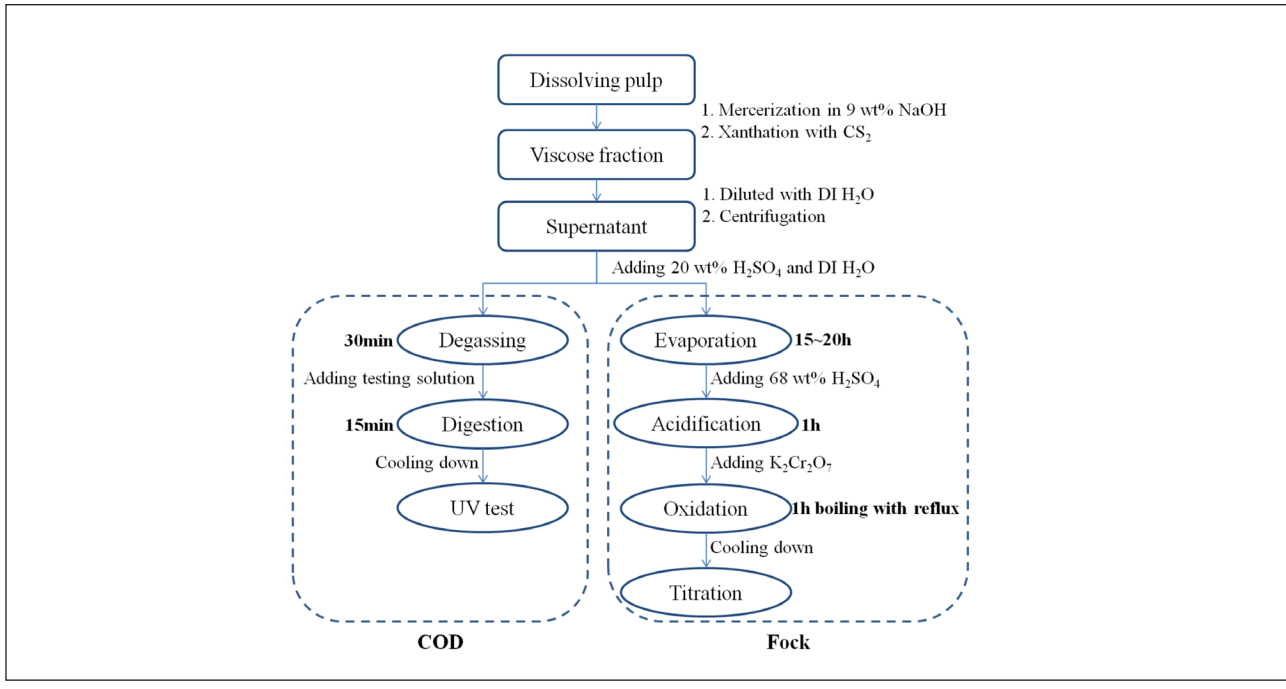


4. Comparison of the methods: Fock vs. COD.

The experimental scheme of this COD method in comparison with the Fock test is summarized in **Fig. 5**. Both COD and Fock methods need to prepare dissolved cellulose fraction in alkaline and CS_2 as viscose fraction, and then dilute the viscose fraction and centrifuge to obtain the supernatant. In comparison with the Fock test, this developed COD method required one less procedure while highly shortening the reaction time, exhibiting good potential as an alternative approach to determine the reactivity of dissolving pulp.

CONCLUSION

Here, we presented a novel COD method for determining the reactivity of dissolving pulp. The viscose fraction of dissolving pulp was first reacted with testing solution in accordance with



5. Experimental scheme: Fock vs. COD.

the COD standard and then rapidly tested by UV/Vis spectrophotometer to quantify the reactivity of pulp. By investigating the effect of testing conditions, this COD method was well established with good repeatability. The results of pulp reactivity determined by this method were in good agreement with the Fock test, while the COD method required less procedure and largely shortened reaction time than the Fock test, indicating that this COD method could be a good alternative for the analysis of pulp reactivity. **TJ**

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About this journal

ABOUT THE AUTHORS

We investigated another approach to testing the reactivity of dissolving pulp. The method we developed was based on previous testing methods, but was more efficient and applicable. The relevance and accuracy of this novel procedure was well established by comparing it with the existing Fock test and applying it to a certain amount of samples.

The developed method shows potential for both laboratory and industrial application, and it was interesting to apply the COD method for evaluating the reactivity of dissolving pulp. Mills might find it a good alternative approach for reactivity testing. Our next step is to use this method in testing additional pulp samples.

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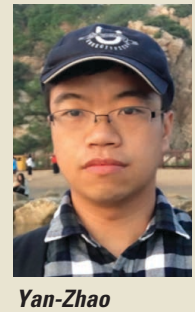
Gong


Yu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