RAPID ESTIMATION OF GAMMA NUMBER OF VISCOSE BY UV SPECTROPHOTOMETRY

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ABSTRACT

Viscose process is the most important method for industrial cellulose dissolution. The degree of substitution (DS) is an important parameter in cellulose derivatives, and it is usually expressed as a gamma number (γ No.).

In this work, viscose was prepared from eucalyptus and cotton linter dissolving pulps. Two methods were used for by-product separation: coagulation method (CM, reference) and ion exchange method (IEM). Similar γ Nos. were obtained with both methods for viscoses from cotton linters.

The molar absorptivity of cellulose xanthate at 303 nm (ε_{303nm}) was determined by, firstly, measuring the absorbance of different purified viscoses and, subsequently, drawing a linear regression with the values obtained.

The purification efficacy of IEM was analyzed from the UV peaks obtained in the range of 220-380 nm of the original and purified viscoses. The disappearance of the absorption of the main by-product, sodium trithiocarbonate, was observed.

Finally, with the ε_{303nm} mentioned above and the absorbance measurement of the purified viscoses, their γ Nos. were determined using a spectrophotometric method (SM). This would indicate that UV spectrophotometry could be used to estimate this parameter in a quick and easy way, which is decisive for the use of viscose in regenerated cellulose products.

Keywords: cotton linters, eucalyptus, gamma number, UV spectrophotometry, viscose.

INTRODUCTION

Cellulose is the most abundant natural polymer on Earth. Its physical, mechanical and chemical behavior - including its insolubility in most solvents- is due to the numerous inter and intramolecular hydrogen bonds of its macrostructure. The industrial dissolution methods are N-methylmorpholine N-oxide (NMMO) and viscose. The latter is the predominant one, with an annual worldwide production of 3.5 million tons (Bywater, 2011).

The dissolving pulps used for the preparation of viscose have high cellulose content (90%-98%), low content of hemicelluloses, extractives and minerals, and little residual lignin. They are also characterized by high brightness, uniform molecular weight distribution, and a high degree of polymerization (DP). They require an aging step to reduce the DP to the optimal working level. The pulp is swollen in concentrated NaOH to form alkali cellulose (AC), and then the AC is aged until the appropriate DP is reached. Then, it is treated with carbon disulfide (CS_2) to obtain a solid metastable intermediate, cellulose xanthate, which is finally dissolved in diluted NaOH solution to form viscose. The molded products are obtained when the substituents are released and the high purity cellulose is regenerated.

One of the parameters which determines the physical and chemical properties of the cellulose derivatives is the degree of substitution (DS) (Conaway, 1938). For viscose, it is defined as the number of xanthate groups per anhydroglucose unit of the cellulose.

In order to test the uniformity of the xanthation or to locate leaky reactors, it is necessary to determine the total sulfur, the sulfur in cellulose xanthate and in the by-products formed during the process of viscose (sodium trithiocarbonate and sodium sulfide). Therefore, for this type of analyses, reliable and fast methods of determination are needed. (Barthelemy, 1945)

The concentration of cellulose xanthate in viscose can be expressed as a percentage of carbon disulfide or as the γ No., which is 100 times the DS of cellulose. The γ No. is frequently used for research on viscose because it is an indicator of the variation of the composition. The viscose continuously changes

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its DS and the distribution of the xanthate groups in the cellulosic chain over time. (Schwaighofer, 2011)

The exact determination of the total sulfur and the sulfur of the by-products is obtained by oxidizing the sulfur to sulfate and determining it gravimetrically as barium sulfate (Barthelemy, 1945). As this procedure requires skill, space and a long period of time, it is not usually performed, and rapid volumetric techniques are preferred. Barthelemy and Williams (Barthelemy, 1945) describe a technique, used in this work as a reference for determining the γ No. of viscose, in which the total sulfur, in the presence of sodium zincate, is converted quantitatively into zinc sulfide, which is then titrated in an acid medium with a sodium thiosulfate solution. Similarly, the sulfur of the by-products is determined after separating the cellulose xanthate by coagulation and precipitation using saturated sodium chloride. The sulfur of the cellulose xanthate is determined from the difference between the total sulfur and the sulfur of the by-products.

Samuelson and Gärtner (Samuelson, 1951) published a method for separating the cellulose xanthate from the by-products using an ion exchange resin. The ions of the by-products, which are small and divalent, are strongly adsorbed; while the ions of cellulose xanthate, which are too large to diffuse into the resin phase, are easily separated from the anionic resin. After the separation procedure, the xanthate sulfur is directly determined by the volumetric method mentioned above.

The viscose is a typical multicomponent system for spectrophotometrical analysis, but the instability of trithiocarbonate in dilute aqueous solution is a serious limitation for this kind of methods (Rahman, 1971). Therefore, it is necessary to remove the by-products of the viscose for an accurate determination of xanthate.

Rahman (Rahman, 1971) proposed a spectrophotometric method for a rapid determination of γ No. The technique involves purifying a sample of viscose using anionic resin, separating the purified solution by filtration, and washing it with distilled water. Then the absorbance of an aqueous dilution of the purified solution is measured at 303 nm, wavelength in which the cellulose xanthate absorbs strongly. The disadvantage of this procedure is that it is very difficult to find calibration patterns for this method; hence it can be used only for a quick estimation of γ Nos.

The UV spectrum of viscose shows three absorption peaks: at 332, 303 and 226 nm. According to the literature (Tunc, 1969; Rahman, 1971; Dux, 1957), they correspond to the contributions of the following main components in viscose: sodium trithiocarbonate (332, 303 and 226 nm), cellulose xanthate (303 and 226 nm) and sodium sulfide (226 nm).

The spectrum also shows an isosbestic point at 363 nm. This phenomenon is caused by the reaction of the trithiocarbonate with the oxygen dissolved in the solvent, which results in trithio percarbonate (Rahman, 1971).

The aim of this work is to determine the possibility of obtaining a rapid estimation of the gamma number of viscose by UV spectrophotometry. The viscoses were prepared from cotton linters and eucalyptus dissolving pulps. The pulps were previously characterized and the influence of their characteristics was analyzed on the viscoses obtained.

Two methods were used for the separation of the by-products in viscose: the method of coagulation (CM, reference) (Barthelemy, 1945) and the ion exchange method (IEM) (Samuelson, 1951). The values of the γ Nos. obtained were compared between the different methodologies, and the purification efficacy of IEM was analyzed using UV spectrophotometry. Moreover, the γ No. of viscoses purified with the anionic resin, i.e. without by-products, was determined using a spectrophotometric method (SM) (Rahman, 1971). This technique would permit a fast and simple estimation of γ No., without the need of determining the total sulfur and the sulfur of by-products by titration, so its applicability for routine monitoring in industrial processes could be feasible.

MATERIALS AND METHODS

Raw materials
Eucalyptus dissolving pulp (EP) and cotton linters dissolving pulp, filter grade, (CLP) were used. The latter was the reference pulp.

Characterization of the pulps
The following analytical techniques were used: alpha-, beta- and gamma-cellulose (TAPPI T203 cm-99); alkali solubility with 10wt.-% and 18wt.-% NaOH aqueous solutions, called S10 and S18 respectively (TAPPI T235 cm-00); ash (TAPPI T211 cm-02); extractives (TAPPI T204 cm-97) and intrinsic viscosity in cupriethylenediamine (CUEN). Viscosimetric average degree of polymerization (DP_V) (Marx-Figini, 1987).

Preparation of viscose
The first step in the preparation of viscose consists in treating the pulp with 18wt.-% NaOH aqueous solution to obtain alkali cellulose (AC). The excess alkali in the swollen pulp is removed by pressing until the weight of the residual AC is approximately 4.25 times the weight of the originally dry pulp. The treated pulp undergoes an aging process to control and reduce the DP. Then, the aged AC reacts with CS_2, which is added in a concentration determined according to the amount of cellulose in AC (Fischer, 2003). Finally the solid cellulose xanthate is dissolved in 6wt.-% NaOH aqueous solution to form the solution of viscose. (Whistler, 1963)

The fine-tuning of the technique was performed with the reference pulp, cotton linters.

Characterization of viscose
The quality of the viscoses obtained was evaluated using the following analytical techniques: content of cellulose (Cellulose, %); total alkali (Alkali, %) (Whistler, 1963); filter clogging value

(Kw): is an evaluation parameter of the quality of viscose and, indirectly, of the pulp used regarding its ability to form gel particles (Treiber, 1962); total carbon disulphide, carbon disulphide as by-products and gamma number (Barthelemy, 1945).

Carbon disulphide as xanthate was determined using three techniques: the method of coagulation (CM, reference) (Barthelemy, 1945), the ion exchange method (IEM) (Samuelson, 1951), and the spectrophotometric method (SM) (Rahman, 1971).

Analysis of the presence / absence of by-products

UV spectra of the original viscoses were initially performed in the range of 220-380 nm. These viscoses were prepared from both pulps with a dose of 25% of CS_2, and afterwards purified using anionic resin. The spectra were performed again in the same wavelength range.

Estimation of the molar absorptivity of the cellulose xanthate

The viscoses were prepared from CLP with different doses of CS_2 and purified with the anionic resin. From the purified solutions, different dilutions were prepared and their absorbances at 303 nm were measured to estimate the molar absorptivity of the cellulose xanthate.

RESULTS AND DISCUSSION

The most important requirements for the dissolving pulp to be used in the preparation of viscose are: high purity, evaluated as content of α-cellulose content, and low content of hemicelluloses, ashes and extractives. (Kvarnlof, 2006)

Table 1 shows the characteristics of the different pulps. The results show that the CLP chosen as reference material has the specifications of filter grade (Xuelong, 2002). Moreover, EP and CLP have similar features. Both pulps meet the requirements to be used for the preparation of viscose. They both have high purity, due to their high percentage of α-cel and to their low content of hemicelluloses (γ-cel). They also have a low content of extractives and degraded cellulose (β-cel).

The characteristics of the viscoses prepared from CLP and EP with different doses of CS_2 are shown in **Table 2**. The viscoses obtained

Table 2. Characteristics of the viscoses obtained with both pulps

Dissolving pulp	Dose of CS_2 (%)	Cellulose (%)	Alkali (%)	Kw
CLP	29	6.02	7.30	<100
	25	6.28	7.40	<100
	21	5.92	7.61	<100
	17	5.84	7.37	<100
EP	25	6.27	7.73	<100

Table 3. γ No. obtained from viscoses of cotton linters

Dose of CS_2 (%)	Ripening time (days)	CM		IEM	
		$CS_{2\,xant}$ (%)	γ No.[a]	$CS_{2\,xant}$ (%)	γ No.[a]
29	7-15	1.43	51	1.51	53
	19-27	0.97	35	1.06	38
25	7-15	1.25	46	1.23	45
	19-27	1.06	39	1.10	40
21	7-15	1.32	47	1.22	44
	19-27	1.13	41	1.06	38
17	7-15	1.24	45	1.25	46
	19-27	1.14	42	1.08	39

[a] γ No.=(213*$CS_{2\,xant}$(%))/Celullose (%)
CM: method of coagulation. **IEM**: ion exchange method.

from both pulps and with differing doses of CS_2 are similar regarding their contents of cellulose, total alkali and filter clogging value. The latter is a parameter which determines the quality of the solution of viscose. Sixta *et al.* (Sixta, 2004) classified the quality of the viscose considering Kw as a function: Very Good (0-300), Good (300-500), Fair (500-800), Poor (800-1500) and Unacceptable (>1500). Based on this classification and on the Kw obtained, all the viscoses prepared showed very good quality.

To analyze the efficiency of the separation of by-products, in both methods CM and IEM, the γ No. of the viscoses prepared from CLP with different doses of CS_2 and different ripening times was determined. **Table 3** shows the results obtained and they

Table 1. Characterization of both pulps

Dissolving pulp	α-cel (%)	β-cel (%)	γ-cel (%)	Alkali solubility			Ash (%)	Extractives (%)	$[\eta]$ [b] (ml/g)	DP_v [c]
				S_{18} (%)	S_{10} (%)	R_{10} [a] (%)				
CLP	97.0	2.3	0.6	1.8	4.9	95.1	0.12	0.14	548	1349
EP	95.6	3.5	0.9	1.9	5.8	94.2	0.09	-	438	1004

[a] R_{10}=100-S_{10}. [b], [c] $[\eta]$= Intrisic viscosity, DP_v= Viscosimetric average degree of polymerization (Marx-Figini, 1987)
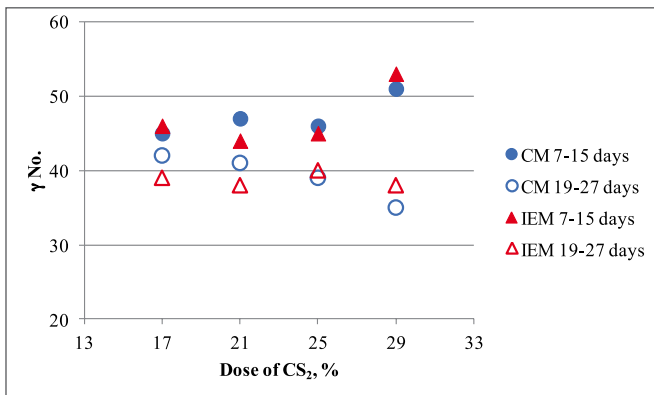
Figure 1. Gamma number *vs.* dose of CS$_2$

are compared in **Figure 1**. It can be seen that the values of γ No. obtained from the anionic resin method (IEM) and the ones obtained from the reference method (CM) are similar.

The differences observed can be attributed to possible errors in determining the concentration of xanthate because the total purification cannot be ensured with the anionic resin used for this assay.

After preparing it, the viscose undergoes an aging process in which the substitution becomes more uniform and the sulfidation continues, which generates more by-products as the γ No. decreases (Lewin, 2007). Figure 1 shows the decrease of γ No. over time, which is higher for the viscose with a dose of 29% of CS$_2$.

To confirm the presence of the main components of viscose, i.e. cellulose xanthate, sodium trithiocarbonate and sodium sulfide,
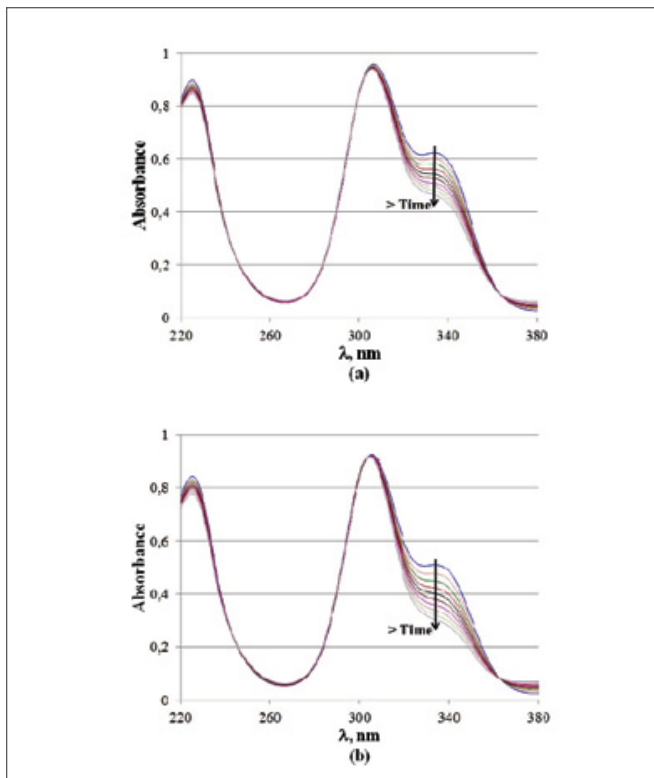

Figure 2. UV spectra of viscose: (a) cotton linters; (b) eucalyptus
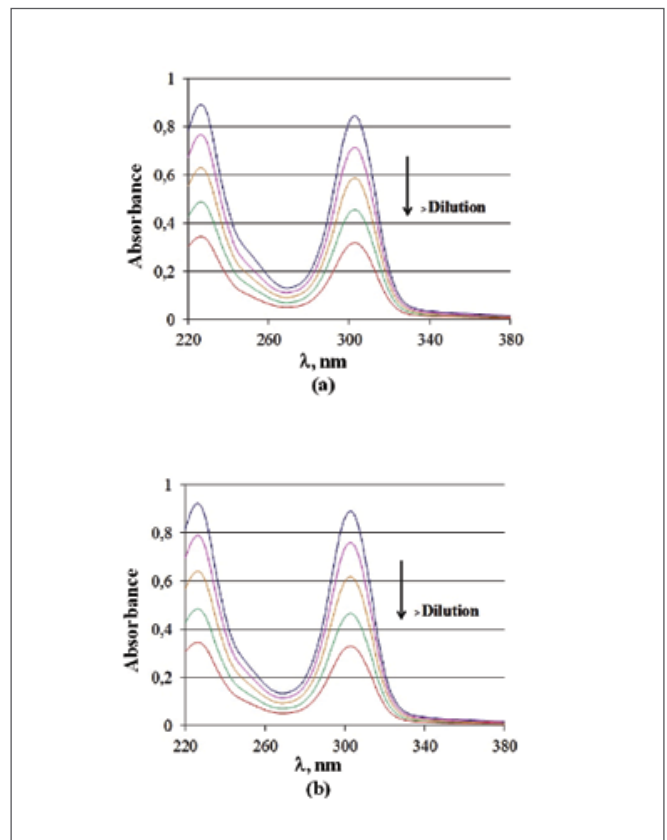

Figure 3. UV spectra of purified viscose: (a) cotton linters; (b) eucalyptus

UV absorption spectra of the viscoses obtained from both pulps and at a dose of 25% of CS$_2$ were performed at intervals of 2 minutes and in the range of 220-380 nm. The spectra obtained are shown in **Figure 2**. Both spectra show three absorption peaks: at 226, 303 and 332 nm, corresponding to the three main constituents. It should also be noticed the isosbestic point at 363 nm and the decrease of absorption of trithiocarbonate in the three wavelengths over time, which is attributed to the instability of this by-product in dilute solutions.

Subsequently, these viscoses were purified with anionic resin and the UV spectra were performed again, in order to evaluate the effectiveness of the resin in the separation of the by-products. In both spectra (**Figure 3**) the absorption peaks of cellulose xanthate are observed at 226 and 303 nm. They clearly show the absence of the absorption peak at 332 nm and of the isosbestic point corresponding to the trithiocarbonate, which confirms the absence of this by-product in the purified viscose.

To obtain a rapid method for estimating the content of cellulose xanthate using UV spectroscopy, a molar absorptivity value of the cellulose xanthate is required. To obtain an estimation of the molar absorptivity value (ε), dilutions from CLP viscoses with differing doses of CS$_2$ and purified by anionic resin were prepared. The absorbance of each dilution was measured at 303 nm and at different viscose maturation times. Finally, the corresponding $\varepsilon_{303\ nm}$ for each viscose was obtained from the

Table 4. Spectrophotometric data of viscoses of cotton linters

Dose of CS₂ (%)	Ripening time (days)	C_{xant} (Mother solution) (10^{-4} mol/L)	Absorbance					$\varepsilon_{303\,nm}$ (L/mol.cm)
			Dil 5	Dil 4	Dil 3	Dil 2	Dil 1	
29	7-15	8.13	0.280	0.399	0.514	0.630	-	14037
	19-27	5.59	0.212	0.298	0.380	0.474	0.579	15418
25	7-15	6.63	0.245	0.350	0.448	0.553	0.648	15059
	19-27	6.21	0.253	0.358	0.456	0.564	0.668	16474
21	7-15	6.58	0.238	0.337	0.427	0.529	0.628	14600
	19-27	5.71	0.203	0.284	0.380	0.472	0.553	14801
17	7-15	6.70	0.251	0.351	0.451	0.565	0.647	15024
	19-27	5.77	0.220	0.314	0.410	0.501	0.592	15730

linear regression of each graph 'Absorbance *vs.* Concentration of xanthate'. **Table 4** shows the data obtained.

As it can be observed in Table 4, the values of $\varepsilon_{303\,nm}$ obtained showed some variability. It is impossible to obtain exactly the same solutions of cellulose xanthate due to its instability in diluted alkaline medium, which leads to a constant variation in the amount and in the distribution of xanthate groups in the cellulosic chains (Schwaighofer, 2011). Thus, constant values of $\varepsilon_{303\,nm}$ were not found because solutions of cellulose xanthate with differing γ Nos. were used. Probably for this reason the molar absorptivities for the cellulose xanthate found in the literature cover a wide range, for example 15900, 14790-17420 (Tunc, 1969).

To obtain the molar absorptivity for the range of the doses of CS₂ studied (17%-29%), all the values of the graphs 'Absorbance *vs.* Concentration of xanthate' were plotted together, and then a linear regression analysis was drawn. **Figure 4** shows the results.
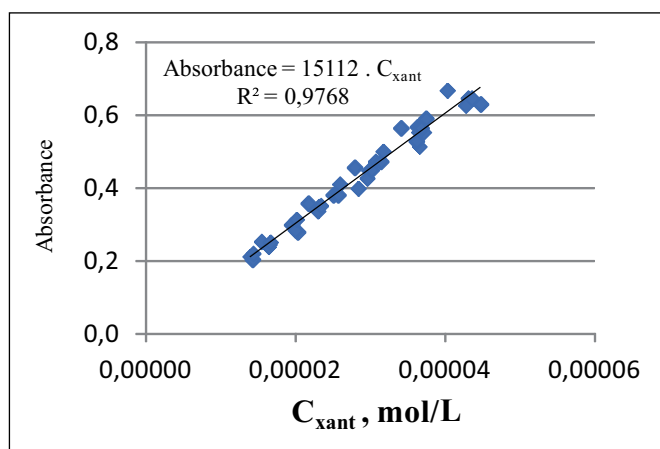
From the linear regression and using the Beer-Lambert Law, a molar absorptivity value of 15112 L/mol.cm was obtained, with a good correlation coefficient of the values. Therefore, this value is taken for the viscoses prepared by the method proposed in this paper and for the range of doses of CS₂ studied.

Finally, the possible application of the SM for a rapid estimation of γ No. was evaluated. New viscoses were prepared from both pulps, with a dose of 25% of CS₂. **Table 5** shows the results of the comparisons between the values obtained by this method and those obtained by the reference method (CM).

It was observed that, for practical purposes, the results of γ No. were similar for both methods and that the application of the molar absorptivity previously determined resulted in a very good estimation of the xanthate content in viscose and, hence, of the γ No. Therefore, this spectrophotometric determination technique would provide a very rapid and simple way of estimating the γ No. of viscose.

Figure 4. Absorbance *vs.* concentration of the purified viscoses of cotton linters

Table 5. Gamma number of the viscoses obtained from both pulps

Dose of CS₂ 25%	Ripening time (days)	CM		SM	
		$CS_{2\,xant}$ (%)	γ No.[a]	$CS_{2\,xant}$ (%)	γ No.[a]
CLP	7-15	1.41	48	1.54	52
EP	7-15	1.66	56	1.67	57

[a] γ No.=(213*$CS_{2\,xant}$(%))/Celullose (%)
CM: method of coagulation. **SM:** spectrophotometric method.

CONCLUSIONS

The eucalyptus dissolving pulp and the reference pulp -cotton linters- showed similar characteristics.

The viscoses obtained from both pulps presented similar features, even though differing doses of CS_2 were applied. The use of ion exchange resin in the IEM for the separation of the by-products in the viscose resulted in values of γ No. comparable to those obtained from the reference method (CM). It shows that with IEM it would be possible to obtain a rapid and easy procedure to determine this parameter.

The spectrophotometric analysis confirmed the ion exchange removal of the main by-product -sodium trithiocarbonate- from the viscoses prepared from both pulps.

The molar absorptivity ($\varepsilon_{303\ nm}$) of cellulose xanthate was estimated using viscoses from cotton linters with doses of CS_2 between 17% and 29%. Then, using this value, the γ No. of viscoses prepared from both pulps was obtained (SM) and the results were similar to those obtained by the reference method (CM). Therefore, this spectrophotometric method permits a rapid estimation of γ No. for routine monitoring.

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