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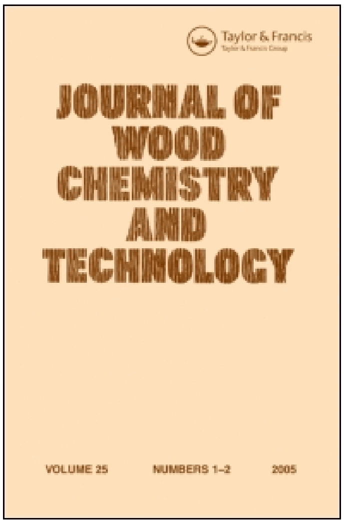

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KRAFT CELLULOSE OXIDATION BY RUTHENIUM TETROXIDE

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ABSTRACT

Ruthenium tetroxide (formed by reaction between either $RuCl_3$ or RuO_2 and NaOCl) was used in catalytic amounts to oxidize bleached kraft pulp cellulose. The effects of pH, ruthenium concentration, and the co-oxidant were studied at room temperature in aqueous medium. It was shown that oxidation of cellulose by this system produced oxycellulose containing both carbonyl and carboxyl groups. In addition, it was demonstrated, that side reactions in alkaline medium strongly accelerated the degradation of cellulose.

INTRODUCTION

Cellulose is highly susceptible to oxidizing agents. The extent of the degradation depends on the nature of the reagent and on the conditions under which oxidation occurs. The majority of non-selective oxidizing agents introduce carboxyl as well as carbonyl groups at different positions of the β-anhydro-D-glucose units according to the conditions of reaction[1].

The stability of oxidized celluloses containing carbonyl groups is very dependent on the alkalinity of the oxidizing solution. Generally, when the oxidation of cellulose is not carried out under very mild temperature and low alkalinity levels, there is a degradation and cleavage of macromolecular chains.

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In this study, bleached kraft softwood pulps were oxidized with a relatively new system using ruthenium tetroxide. Ruthenium tetroxide is a strong oxidizing agent capable of oxidizing aldehydes to acids, alcohols to aldehydes or ketones, olefins to aldehydes, amides to imides and ethers to esters[2,3]. It has been used to introduce ketonic groups on polysaccharides[4,7].

Ruthenium tetroxide can be formed by the reaction of either hydrated ruthenium dioxide or ruthenium trichloride with aqueous sodium hypochlorite or Caro's acid (peroxysulfuric acid)

$$RuO_2.2H_2O + 2NaOCl \quad RuO_4 + 2H_2O + 2NaCl.$$

The oxidation of sugars or alcohols to ketones has been described as follows[8,9].

$$RuO_4 + 2RR'CHOH \quad RuO_2 + 2H_2O + 2RR'CO.$$

In an alkaline oxidizing medium, the ruthenium can exist as uncomplexed ruthenate (RuO_4^{2-}), perruthenate (RuO_4^{-}) and ruthenium tetroxide (RuO_4). At higher hydroxide concentrations (6M) perruthenate is reduced rapidly by water to ruthenate in the presence of hypochlorite.

Arendt et al.[9] have studied the oxidation of low-crystallinity cellulose using ruthenium tetroxide in water solution. They claimed that complete transformation of all the primary alcoholic groups ($-CH_2OH$) into carboxylic groups (-COOH) was accomplished.

RESULTS AND DISCUSSIONS

Oxycellulose is obtained from cellulose by an oxidizing procedure that introduces carbonyl and/or carboxyl groups anywhere in the molecules. Depending on the pH, the oxidizing agents can cause oxidation of the hydroxyl groups to aldehyde, ketone, and carboxyl groups, as well as cause depolymerization of the cellulose.

Oxidation of pulp using Caro's acid as the oxidant led to a small increase in the aldehyde content without appreciable degradation of the cellulose (see Table 1). Concentrations of oxidant above $17,5 \times 10^{-3}$ mol/l did not cause further increases in the number of carboxylic and carbonyl groups formed.

In Table II, the result of oxidation using ruthenium dioxide in small concentration (1 mg RuO_2/g pulp) in combination with Caro's acid ($17,5 \times 10^{-3}$mol/l) is shown. The aldehyde concentration increased slightly with a decrease in pH from 5 to 2. In addition, using Caro's acid in combination with ruthenium dioxide resulted in a threefold increase in aldehyde concentration (from 16,5 meq to 49,0 meq) at the same conditions. Simultaneously, the degree of polymerization decreased by about 40% and the resultant oxycellylose showed predominantly reducing character.

The formation of oxycellulose by oxidation using hypochlorite solutions is presented in Table III. Concentrations of oxidant varied from 1,42 to 4,26 g/l, expressed as Cl_2. The small increase of carboxylic groups and the copper number is related to the decrease of degree of polymerization (at pH = 11 and room temperature).

Table IV shows the results of oxidation of bleached kraft pulp by the system $RuCl_3$/NaOCl. In this case, the reactants were added in the order:

$$(RuCl_3 + NaOCl) + H_2O + Pulp.$$

TABLE I

OXIDATION OF BLEACHED KRAFT PULP BY MONOPERSULFURIC ACID (CARO'S ACID).

Caro's Acid mol · l^{-1}	$\overline{DP}_v$	$-COOH$ meq. / 100 g. of cell.	$-CHO$ meq. / 100 g. of cell.
———	944	3,6	2,0
$8,8 \cdot 10^{-3}$	936	3,6	2,2
$17,5 \cdot 10^{-3}$	898	3,8	16,5
$35,0 \cdot 10^{-3}$	880	4,6	14,6
$88,0 \cdot 10^{-3}$	892	4,1	16,7

Reaction time, 120 min.
Starting pH, 2,0

TABLE II

OXIDATION OF BLEACHED KRAFT PULP BY RUTHENIUM DIOXIDE / CARO'S ACID.

Caro's Acid mol · l^{-1}	$\overline{DP}_v$	pH	$-COOH$ meq./100 g. of cell.	$-CHO$ meq./100 g. of cell.	Copper number
———	944	—	3,6	2,0	0,7
$^{**}17,5 \cdot 10^{-3}$	580	2,0	6,5	49,0	4,0
$17,5 \cdot 10^{-3}$	501	5,0	7,0	43,0	3,9

**Equivalent to 1,24 $g \cdot l^{-1}$ of Cl_2.
Reaction time, 120 min.
Starting concentration of RuO_2, 1 mg/g of pulp.

TABLE III

OXIDATION OF BLEACHED KRAFT PULP BY SODIUM HYPOCHLORIDE.

Conc. NaOCl $g \cdot l^{-1}$ of Cl_2		$\overline{DP}_v$	$-COOH$ meq./100g. of cell.	Copper number
initial	final			
—	—	1050	4,3	0,8
1,42	1,35	1020	5,0	0,8
2,84	2,45	940	5,2	0,9
4,26	3,73	900	5,8	1,0

Starting potential , 1060 mv
Starting pH , 11,0
Reaction time , 60 min.

TABLE IV

OXIDATION OF BLEACHED KRAFT PULP BY $RuCl_3$ / NaOCl.

Conc. NaOCl $g \cdot l^{-1}$ of Cl_2		$\overline{DP}_v$	$-COOH$ meq./100g. of cell.	Copper number
initial	final			
—	—	1050	4,3	0,8
1,42	0,99	298	14,4	8,8
2,84	1,71	289	25,0	8,9
4,26	2,70	240	26,6	11,5

Starting concentration of $RuCl_3$, 1 mg/g of pulp.
Starting pH , 11,0
Reaction time , 60 min.

The data in Table IV show that the copper and carboxyl numbers increased and the degree of polymerization decreased with increasing concentration of NaOCl. The data indicates rather severe degradation of the cellulose. In addition, the carboxyl number is probably lower than the true value due to lactone formation[11]. Metallic ions may have contributed to the drastic decrease (up to 75%) of the $\overline{DP}_v$[12,13]. However, the main cause of the cellulose degradation would be expected to be elimination reactions of the oxycellulose in the alkaline medium[14] because carbonyls are β to the glycosidic linkages. Secondary oxidation of the oxycellulose by the oxygen from the air would not be expected to have a large effect on the degradation.

The effect of $RuCl_3$ concentration on the pulp oxidation is shown in Figure 1 and Table V. Higher $RuCl_3$ concentrations led to an increase of the oxidants perruthenate and ruthenium tetroxide (Figure 1) and a decrease of $\overline{DP}_v$ (Table V) but did not necessarily increase the concentration of carboxyl and carbonyl groups.

The effect of pH variation (Table VI) on carboxyl and carbonyl groups formation and the degree of polymerization was negligible in the range pH 10-12. In all cases, the copper numbers and carboxylic group concentrations were quite high, indicating extensive degradation of the pulp.

The reaction between the cellulose and ruthenium tetroxide is not specific and radical reactions and oxidation can occur at more than one point in the monmeric units.

When the oxidation by sodium hypochlorite solution is carried out at high pH, the carbonyl groups formed are rapidly oxidized to carboxyls. At pH 7 the formation of carbonyl groups is considerable

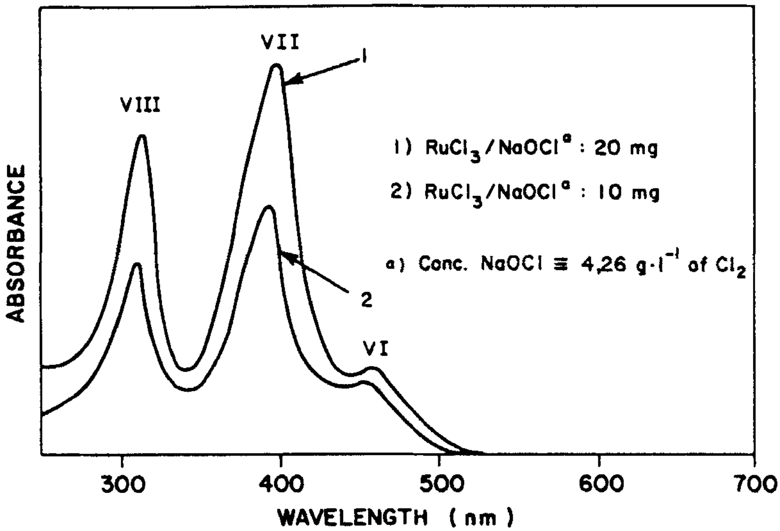


Figure 1. The effect of $RuCl_3$ concentration on Ru^{6+} Ru^{7+} and Ru^{8+} formation.

TABLE V

EFFECT OF $RuCl_3$ CONCENTRATION ON BLEACHED KRAFT PULP OXIDATION.

Conc. NaOCl $g.\cdot l^{-1}$ of Cl_2		$RuCl_3$ mg.	$\overline{DP}_v$	$-COOH$ meq./100 g. of cell.	Copper number
initial	final				
—	—	—	1050	4,3	0,8
4,26	2,34	10	240	26,6	11,5
		20	210	25,1	10,9
2,84	1,61	10	285	25,0	8,9
		20	235	22,9	7,6
1,42	0,82	10	298	14,4	8,8
		20	250	16,8	7,3

TABLE VI

EFFECT OF pH ON OXIDATION OF BLEACHED KRAFT PULP BY $RuCl_3/NaOCl$.

Conc. NaOCl $g.\cdot l^{-1}$ of Cl_2 initial	final	Potential mv initial	final	$\overline{DP}_v$	pH	-COOH meq./100 g. of cell.	Copper number	Solubility in % solution NaOH
4,25	2,81	1060	1020	270	12,0	21,0	10,8	31,2 %
4,25	2,70	1060	1000	240	11,0	26,6	11,5	30,9 %
4,25	2,73	1060	990	241	10,0	18,3	11,6	31,0 %
4,25	2,44	1060	960	230	9,0	13,4	9,8	28,7 %

Starting concentration of $RuCl_3$: 1 mg / g of pulp.
Solubility of pulp in sodium hydroxide (1 %).

faster than their oxidation which results in the persistence of carbonyl groups[15].

The treatment of cellulose with $RuCl_3/NaOCl$ follows a complex mechanism difficult to explain. Extensive oxidation of carbonyl to carboxyl groups does not appear to take place.

Figure 2 shows the results of infrared spectroscopy examination of oxycellulose prepared by using $RuCl_3/NaOCl$ system. The absorption band at 1640 cm^{-1} represents the water as well as hydrated carbonyl vibration[16,17]. On the other hand, the absorption band at 1740 cm^{-1} represents C = 0 vibration which may be attributed mostly to carboxylic groups in our case.

The spectrum of oxycellulose highly oxidized by $NaClO_2$ exhibits a considerably more intense band at 1740 cm^{-1}. The absorption is due to carboxyl originally present in the oxidized cellulose, aldehyde groups that have been oxidized to carboxyl groups as well as any ketone groups presents in the original oxidized cellulose. It seems

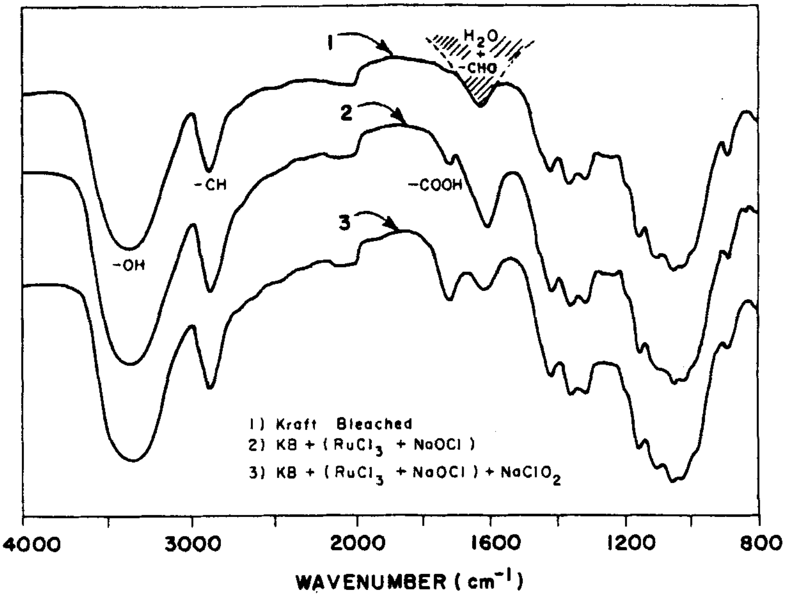


Figure 2. Bleached Kraft Pulp Oxidation.

that there is a lower concentration of free (non-hydrated) aldehyde groups. Ruthenium tetroxide oxidized cellulose samples were treated with hydroxylamine. The IR spectra did not show any absorption in the carbonyl stretching region. The samples were subsequently acid washed to regenerate free carboxylic acid. The IR spectra were unchanged.

The infrared spectrum shows that aldehyde groups were formed. The effect of the presence of Mg^{2+} on the cellulose oxidation is presented in Table VII. The protective effect of the Mg^{2+} during the pulp oxidation by $NaOH/O_2$ system has been described[18]. Unfortunately, under our conditions, the protective effect of Mg^{2+} against depolymerization is absent.

The results of the recycling and reuse of the oxidation reaction medium are presented in Table VIII. It is clear, that the system

TABLE VII

EFFECT OF Mg^{2+} ON DP DURING OXIDATION USING $RuCl_3$/NaOCl SYSTEM.

Conc. NaOCl g.·l^{-1} of Cl_2		$MgCl_2$	$\overline{DP}_v$	-COOH meq./100 g. of cell.	Copper number
initial	final				
2,84	1,71	—	285	25,1	8,9
2,84	1,70	1%	281	23,6	8,8

Starting concentration of $RuCl_3$: 1 mg/g of pulp.
Concentration of $MgCl_2$: 1 % (w/w) of pulp.

can be reused at least once without adjusting the concentration of oxidants only if the lower efficiency is acceptable. Nevertheless, there is a decrease of oxidative efficiency, as shown by the comparison of the results in Table IV and VII for the initial concentration of 2.8 g/l of chlorine. This can be explained by the formation of perruthenates and disappearance of ruthenium tetroxide after the first pulp oxidation[19].

The formation of different reaction products in our system during the oxidation is shown in Figure 3 after the successive oxidations. It can be seen that the ratio of Ru VII (perruthenate) to RU VIII (ruthenium tetroxide) concentration increases from one step to the other.

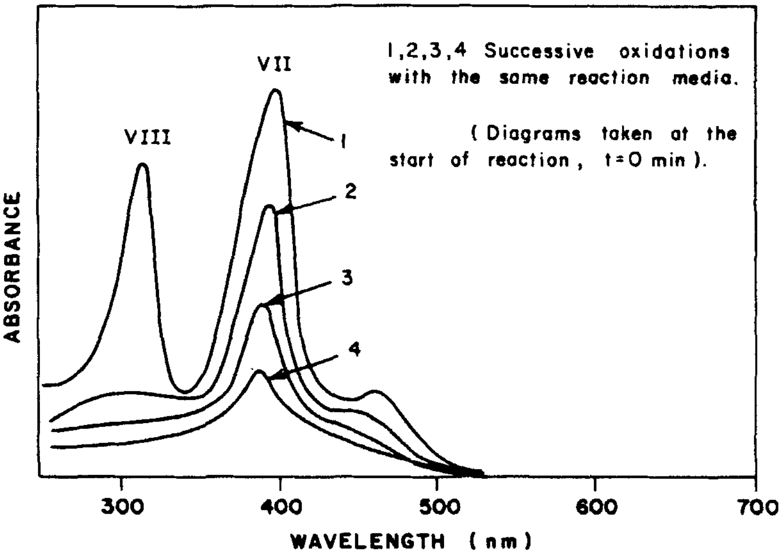
The formation of ruthenium dioxide is seen by the appearence of a black colour in the upper part of the reactor. The dimensions of the reaction vessel as well as the type of stirring play an important role in the efficiency of the reaction medium.

TABLE VIII

RECYCLE OF REACTION MEDIUM FOR OXIDATION

No	Conc. NaOCl $g.\cdot l^{-1}$ of Cl_2 initial	final	Potential mv initial	final	$\overline{DP}_v$	-COOH meq./100 g. of cell.	Copper number	Solubility in % solution NaOH
	Bleached Kraft Pulp				1050	4,3	0,8	2 %
1	4,80	2,79	1060	1000	290	20,8	9,8	31 %
2	2,79	2,38	1000	960	385	15,2	3,9	16 %
3	2,38	2,10	960	920	430	14,0	3,7	12 %
4	2,10	1,85	920	820	1000	5,0	0,8	2 %
	*4,80	2,79	1060	1000	290	20,8	9,8	31 %
	*2,84	1,71	1000	920	285	25,0	8,9	30 %
	*2,00	1,25	940	880	293	16,8	6,0	24 %

*New oxidant solution ($RuCl_3$ / NaOCl).



1,2,3,4 Successive oxidations with the same reaction media.

(Diagrams taken at the start of reaction, t = 0 min).

Figure 3. Successive oxidation of the Bleached Kraft Pulp.

CONCLUSION

It has been shown that $RuCl_3$ or RuO_2/NaOCl system can be effective in cellulose oxidation. This system, in which the oxidation in due to RuO_4 which is formed has the advantage of introducing high concentrations of carboxyl and carbonyl groups on the cellulose backbone while using only catalytic amounts of the ruthenium compound. The fact that the oxidation reaction is very fast even at low temperature and takes place in aqueous medium could be of interest for practical applications. However during the oxidation, cellulose suffers severe chain cleavage as a side reaction.

EXPERIMENTAL

Ruthenium tetroxide was formed by adding catalytic quantities of RuO_2 or $RuCl_3$ (1 mg/g of pulp) to the aqueous solution of NaOCl (0,5% of Cl_2) or Caro's acid (0,02 M). Bleached kraft pulp (spruce: 0,01% lignin; 90% brightness), 10 g (oven dried equiv.)/ liter was introduced during agitation into the oxidative solution.

The reactions were carried out at room temperature, and the pH was kept at the desired value by periodic addition of 1 M NaOH (controlled by pH meter, Horizon, model 5997). The potential of the suspension was controlled between 0.9 and 1.1 volt, since below 0.9 the RuO_2 precipitates, whereas above 1.1 volt, all the Ru is in the form Ru VIII.

Formation of RuO_4 was indicated by a color change of the reaction medium (from black to yellow). After oxidation (1 hour) the pulp was vacuum filtered and washed with 2 liters of distilled water.

Consumption of Cl_2 and H_2SO_5 during the oxidation was determined by iodometric titration.

The following standards have been used for oxidized pulp characterization: Viscosimetric average degree of polymerization,

$\overline{DP}_v$	NF-T12-005
Copper number	NF-T12-004
Carboxylic group number	T-237,su-63
Solubility of Pulp	T-212,os-76

The number of aldehyde groups were determined by the method using hydroxylamine hydrochlorine[20].

Infrared spectra of oxidized cellulose (KBr, concentration 2%) were obtained using a Model 283 P Perkin-Elmer spectrophotometer.

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