

# The Behaviour of Cellulose Molecules During Oxidation Reactions and its Effect

V. R. Parthasarathi\*

*Cellulose  
Oxidation  
Carboxyl groups  
Carbonyl groups  
Periodic acid  
Nitrogen Tetraoxide  
Nitrogen Pentoxide  
Chlorine dioxide  
Covalent bond  
Hydrogen bond  
Colour reversion  
Strength properties*

*Even under the most controlled conditions, cellulose is oxidized during pulping and bleaching processes. The effects of oxidation, specially the extensive ones, are generally harmful to the properties of pulp and paper. But there are cases where oxidation has proved to be beneficial. It brings out high brightness without hampering the pulp and paper properties. The cases discussed here are of those oxidizing agents which show some specificity in their oxidation reactions. The discussions are based on cellulose morphology and the mode of reactions the cellulose undergoes. The article further discusses the effect of oxidation of cellulose on the colour reversion and strength properties of pulp and paper.*

## Introduction

All existing Vegetable fibres contain cellulose in their constituents in large proportion but like any other biological products, they contain many other non-cellulosic constituents as well. As such, the exact composition of vegetable fibres cannot be correctly spelt out due to various difficulties.<sup>1</sup> Whenever, the composition of a fibrous raw material is specified, it in fact, includes both cellulose, hemi-cellulose and other non-cellulosic products like lignin, extractives etc. The specie containing only cellulose, as its sole constituent, is non-existent so far. The aim of modern pulping is to isolate cellulose in its most purest form, from the other constituents, composited with it. In doing so, the cellulose is made to undergo many chemical changes and during this process, the cellulose in

itself gets oxidized. So far, till date, the complete isolation of cellulose, from the pulping raw material has never been achieved.

## Cellulose

The term cellulose denotes only that part of the carbohydrate which is resistant to certain chemical reagents to which other carbohydrates are not. The most precise definition is to use the prefix like Cross-Bevan cellulose and alpha ( ) cellulose etc. so as to distinguish it from the non-cellulosic carbohydrates, some of which like cellulose show resistance to certain chemical reagents. It is best distinguished by its behaviour towards alkali and acid. As stated, the total cellulosic content is called "Hollo-cellulose", which contains the total carbohydrates both cellulose and non-cellulose

like hemi-cellulose, the name hemi-cellulose being so given to show its heterogeneity. Drawing clear boundaries between cellulose and hemi-cellulose and then the exact quantitative determination has been a difficult analytical problem, since the most resistant hemi-cellulose is retained in the cellulose residue, even at the severest of isolating conditions and the degraded cellulose fractions appear in the recovered hemi-cellulosic fraction. A further difficulty in defining cellulose as a carbohydrate based on glucose is that glucomannan, a non-cellulosic homopolymer is also a carbohydrate, based on glucose. Also the methyl uronic acid which is not a carbohydrate in the strict sense is still included in the carbohydrate fraction.

Cellulose, formed by the so called photosynthesis, a compli-

\*Research Chemist, Pulp and Paper Research Institute Jaykaypur-765 017 Dist. Koraput Orissa.

cated bio-chemical synthesis, is a simple structure of long chains of glucose units joined by 1:4-B-glucosidic bonds. It is largely in crystalline (para crystalline gluccan) form in most vegetable plants and in some animal tissues as stated early. Reactions of cellulose with metallic sodium in liquid ammonia as well as the acetylation and methylation shows that there are three hydroxyl groups capable of undergoing reaction.<sup>3</sup> Acid hydrolysis of methylated cellulose yielded quantitative amount of 2,3,6-trimethyl glucose, apart from a small quantity of 2,3,4,6-tetra-methyl glucose.<sup>4</sup> This indicates the presence of three hydroxyl groups in 2,3,6 position whereas the 1,4,5 positions are blocked out for the end monomer where the 4-hydroxyl group is present. But the amount of 4-hydroxyl groups attached to the non-reducing groups is very meagre, about 0.7–0.8% in the total hundreds/thousands of hydroxyl groups.<sup>4a</sup> The acetylation of cellulose produces a crystalline octoacetate of cellubiose, the dimer of glucose and which when further hydrolysed gives glucose. This concludes that cellulose is a dehydrated polymer of glucose units. The hydrolysis of cellulose, with the enzyme "Emulsin" proves that it is a glucosyl-B-glucoside. Further elucidation proves that cellubiose is actually a 4-0-glucopyranoside. It was also a common belief that the only type of linkage that exists between the inter-glucose units, to say precisely, in the cellulose unit is that of 1-4-B-D-glucosidic bonds (cf. 1-4-A-D-glucosidic bondage of starch). But a serious challenge to conclude as above (that the only bond is that of

1-4-B-D glucosidic form in cellulose) comes from the results of kinetic energy released during the acetylation and subsequent hydrolysis of cellubiose, cellutriose and other cellulosic polymers to glucose. It is still being believed that apart from 1-4-B-D-glucosidic bonds, the inter-glucose units in cellulose may be linked by some other types of bond.

### Reactions of Cellulose

The structure and morphology of cellulose is that certain molecules undergo readily certain type of reactions. This is more in the case of addition and substitution reactions. Still more striking is the intramolecular reactions, which the glucose unit of the cellulose undergo.

To say accurately, in a cellulose unit different glucose unit undergo different chemical reactions, which may or may not be the same for two subsequent glucose units.

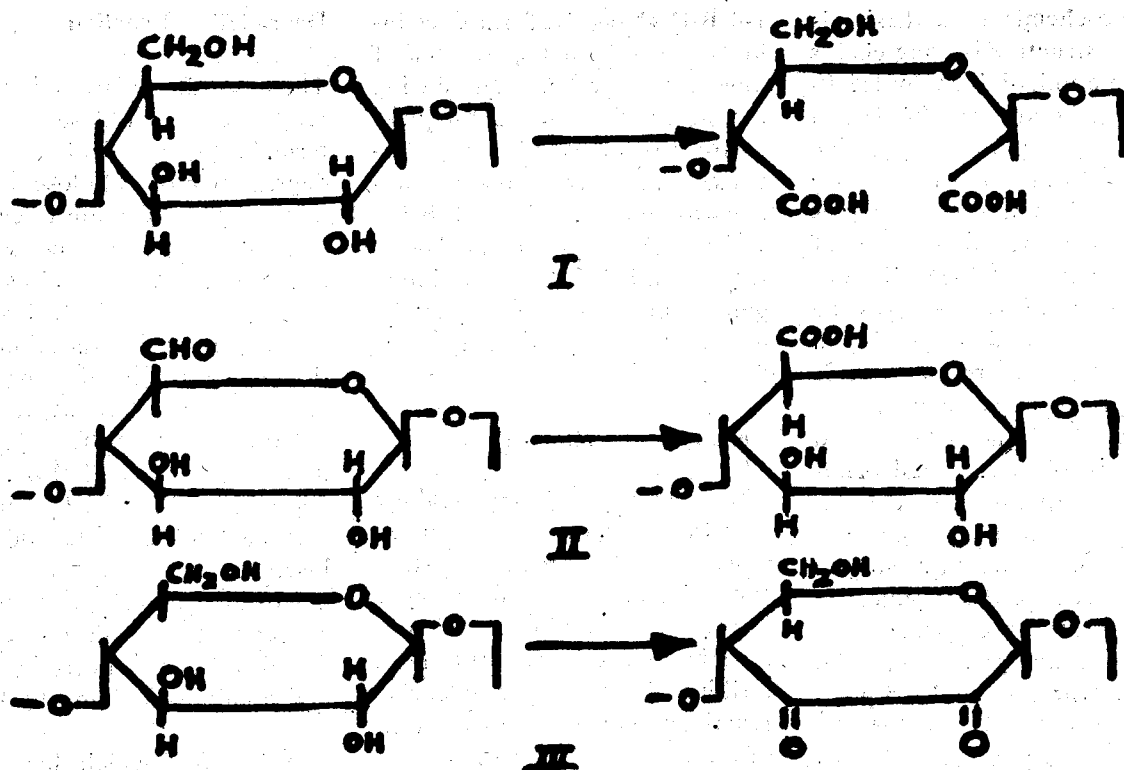
Like all other carbo-hydrates, the cellulose molecule is capable of reacting at its hydroxyl and acetal groups and as well as at the aldehydic end-groups. The reaction especially acetylation, followed by hydrolysis is also possible in case of certain hemi-celluloses.

The hydroxyl groups reacts with the addition, substitution and oxidation reagents and the acetal groups undergo hydrolysis in acid as well as in alkaline media. The aldehydic end-groups can be reduced to alcohol, oxidized to carboxyl groups or rearranged under the influence of alkali to form either an alcohol or carboxyl group.

### Degradation Reaction

The term, degradation, in special reference to cellulose is a vague term. In the chemical sense, the degradation of cellulose actually means its conversion to carbon-dioxide and water, contrary to that of the photosynthesis. But this extreme reaction is never allowed during degradation reactions. The intermediate products of cellulose, by the degradation reaction may be either hydrocellulose or oxycellulose. The degradation especially in the low molecular models of cellulose, found to take place in the glucosidic bond position and consequent degradation can be found to occur both in acidic and alkaline medium. (fig.)

The reaction which has got no preference for either the acid or alkali it has been found that the reaction is faster at acidic pH. The hydrolytic degradation of a long chain polysaccharide such as cellulose is therefore influenced by oxidized groups even though only a few monomers are present. The heterogeneous oxidation reaction on cellulose can be carried out with any halogen hypohalite (XOX'). The pH is more important in this reactions. The reaction rate at various pH with various oxidants such as dichromate, nitrogen dioxide/pentoxide, periodate chlorite and hypoiodate also varies. The resulting product, the oxy-cellulose, or better called oxidized cellulose has varying amounts of oxidized groups in it, which is mainly dependent on the various oxidant as already stated. Apart from it, the mode of reaction, the pH at which the reaction is carried out is also an important factor.



1. Periodate-chlorite oxidation.
2. Scoured cotton
3. Citrus pectin
4. Aliglunic acid

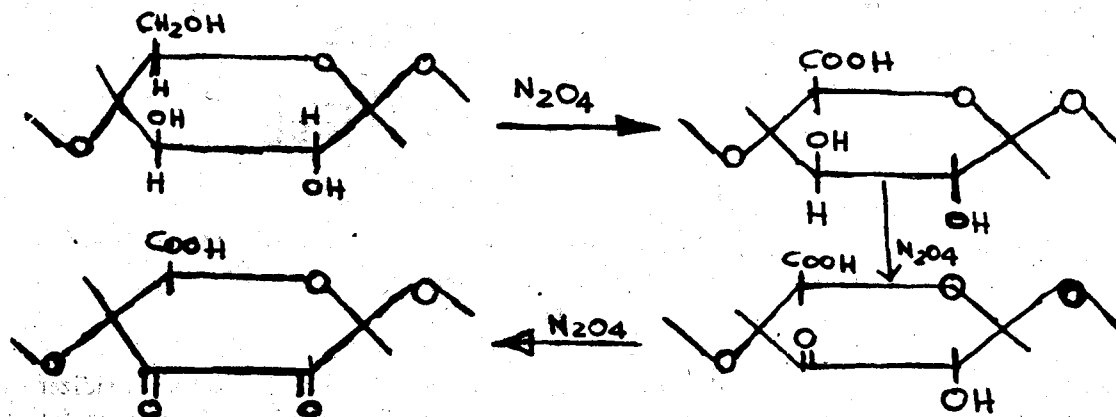
5. Nitrogen dioxide/Pentoxide Oxycellulose
6. Glucoro nolactone.

Fig. rate of oxidation to  $\text{CO}_2$  for various oxidized cellulose (for carboxyl groups).

The secondary hydroxyl on carbon 2 and 3 may be oxidized to ketone carbonyls, which are usually present to some extent in most of the oxidized cellulose. The primary hydroxyls (C6) at carbon 6 position ( $-\text{CH}_2\text{OH}$ ), are converted to aldehydic carbonyls ( $-\text{CHO}$ ), which is further oxidized to carboxylic acids, the so called uronic acids. Whatever may be oxidant employed, almost every one of them produces a certain amount of ketone, aldehydes and carboxyl groups. Ring scission usually occurs during the oxidation reaction. The most com-

mon type of scission (though there are others) is the splitting between 2 and 3 carbons to produce two aldehydic groups on these carbons which may further be oxidized to carboxylic groups. There are other reactions which are negligible and also of practically no importance. The difficulty with any oxidizing agents (leaving one or two) is that none is specific in their oxidizing reactions that too with cellulose. But this rule for cellulose cannot be applied strictly to hemicellulose, which contains certain type of groups which are very specific

in their reactions. Those oxidants which are specific in their oxidation reaction towards cellulose are periodic acid, nitrogen dioxide/nitrogen tetroxide/nitrogen pentoxide. The conversion of the primary alcohol to carboxylic acid via an intermediate aldehydic formation is the main reaction with nitrogen tetroxide/nitrogen pentoxide. ( $\text{N}_2\text{O}_4/\text{N}_2\text{O}_5$ ). But during this reaction apart from Carboxyl group formation, introduction of carbonyl groups at 2 and 3 carbons also take place.<sup>5</sup> (fig.)



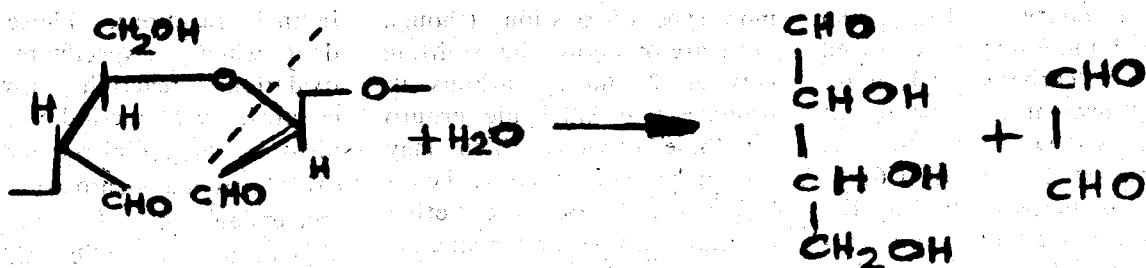
The periodate oxidation of  $-\text{glycols}$  studied by Malaparade and the subsequent hydrolysis which yielded formic acid showed that in each molecule of a linear polymer made up of D-glucose units linked from  $\text{C}_1$  to  $\text{C}_4$ , the non-reducing groups produced one formic acid and the reducing groups two.<sup>6</sup> No formic acid will be produced from the intermediate chain units. Measurement of the formic acid liberated gives an idea of the chain length, although the amount of formic

acid produced depends on the formic ester formed and its rate of hydrolysis.

In periodate oxycellulose the  $\text{C}_2$  and  $\text{C}_3$  carbon which are converted to dialdehyde which on hydrolysis yielded to glyoxal which was identified as bis-phenyl hydrozone and D-erythrose.<sup>7</sup> The confirmation of D-erythrose was carried out by its conversion to D-erythro uronic acid. The medium of oxidation is periodate in bromine water.

The reaction is initially fast and subsequently proceeds at a slower rate. This is because of the formation of carbonyl and carboxyl groups simultaneously and then the formation of carboxyl groups proceeds further. This, rather, resembles the reaction of acid hydrolysis over cellulosic periodate and results in accession of periodate over the entire structure.

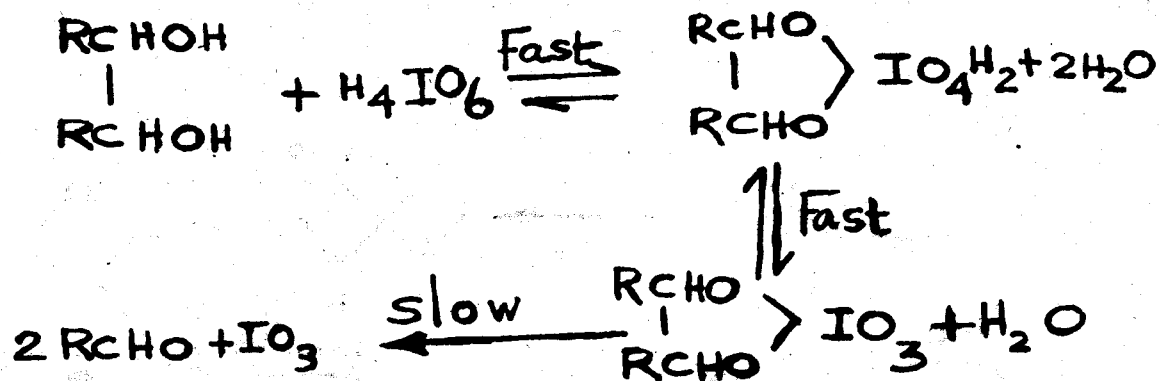
The mechanism is as given below.<sup>8</sup> (Fig.)



I

The second school of thought over this is, the oxidation

followed by the hydrolysis of -glycols.



II

Chlorine dioxide in contrast to most other oxidizing agents is found to be little reactive towards cellulose, an observation which was made use in the non-degradative bleaching of pulp.

Although the oxidation on cellulose produces carbonyl groups in most of the oxidizing reactions, the kinetic studies on the types of carbonyl groups formed, show that there is wide variation in the products, and most peculiar is the variation that occurs within the same molecule, which depends on the reaction conditions. The hypochlorite oxidation at pH7

produces five types of carbonyl groups and three types at pH 10. The periodate oxidation of cellulose produces 6 (six) types of carbonyl groups. The oxidation rate and oxidation potential values of these carbonyl groups formed show that only five of the eight types of carbonyl groups that formed during the hypochlorite oxidation at pH7 and 10 resembles with these carbonyl groups. The general trend in hypochlorite oxidation is that maximum rate of carbonyl groups are formed in acidic pH whereas the carboxylic groups are more in alkaline range. In all cases hypochlorous acid is considered

as the active oxidizer during the hypochlorite oxidation. The introduction of carbonyl group in no way stops the alkaline hydrolysis of glucosidic bond position as 6-OXO and 2OXO group are in the B-position to the glucoside bond at C<sub>4</sub> position and the 3-OXO group is at C<sub>1</sub> position. Obviously it is native to consider oxidation as a simple type of reaction. Moreover unlike other oxidation reactions, it is not as simple as it is considered to be. Nevertheless by specifying the conditions closely and choosing satisfactory parameters for the criterion level of oxidation, the illeffects of oxidation on the

paper property may be to some extent controlled.

### Yellowing/colour Reversion

The permanence of paper is its capacity to retain certain properties especially folding endurance and its original colour over a long period.<sup>9-10</sup> Colour reversion and folding endurance are mainly due to the hydrolytic and oxidative changes involved. Both carbonyl and carboxyl groups are involved in this sensitization.

The change of colour, i.e. colour reversion or yellowing is a function of oxidation. The most noticeable change in properties of oxidized pulp is its increased susceptibility to colour reversion, which is most unwanted. The colour reversion is more evident at higher temperatures.

The main reaction responsible for colour reversion in bleached pulp is the oxidation reaction which the cellulose undergoes during bleaching. The carbonyl groups of the cellulose are mostly responsible for this effect though other wood components may also be involved but pulps free from lignin and hemi-cellulose as in the case of bleached cotton pulps also exhibit yellowing though comparatively to a much lesser degree. This shows that carboxyl groups and therein the attached cations are also involved, as much as the carbonyl groups. The carbonyl groups take much more predominance in this reaction as shown by the reduction by borohydride or oxidation to carbonyl groups by chlorine dioxide and other oxidants. The presence of car-

bonyl groups are more harmful than that of carboxyl groups since this reaction involves the scission of the cellulose. But the argument cannot be taken as authentic because there are two opinions over this. It has been shown that the brightness stability of pulp could be improved either by the reduction of carbonyl groups by borohydride or by the esterification of carboxyl groups with propyleneoxide. The best results were obtained by combining both the reaction of reduction and esterification. There is a definite increase in carbonyl groups during peroxide bleaching. This should be responsible for a prominent colour reversion, but it is not so in this case. The reason being that the reduced end-groups are present only at the end of the chain whereas carbonyls in 2, 3, 6 position only contribute much to the colour reversion.<sup>11</sup> Although the aim should be to avoid colour reversion, this cannot be done completely. Hence effort has to be made to retain the original brightness to maximum possible extent atleast for documents and books which are meant for long time preservation or the sophisticated printings and prestige uses. The usual chlorine bleaching poses the danger of damage to the paper properties apart from colour reversion. The best solution in these cases is to carry out Ozonolysis followed by borohydrate treatment which gives the stability of colour and strength properties.

### Oxidation and Strength Properties

The wet strength of semi-blea-

ched pulp is increased with periodate and hypochlorite treatments. The periodate oxidation increases not only the dry strength but also the porosity. In hypochlorite treatment the reaction is more oriented towards delignification than oxidation. It was observed that strength properties increased during chlorination, remained constant during extraction and increased to a maximum at hypochlorite stage at 120 minutes after which the strength properties started decreasing. The kinetics of oxidation of semi-bleached pulp by hypochlorite reveals that the process is governed by two successive second order reactions in the chlorine concentrations. Energy activation has shown that at higher temperatures more than 120°C the degradation of pulp bound to occur, otherwise the hypochlorite treatment is found to increase dry strength properties but reduced porosity.<sup>12</sup> The reason for increasing dry strength properties.

In case of periodate bleaching is due to the convalance cross linking. The second school of thought over this is that the increase in strength properties in case of periodate oxidation, nitrogendioxide/pentoxide is due to the increased hydrogen bonding. The dry tensile strength is reduced even under mild oxidation and it has been observed that folding endurance decreases considerably. At higher level of oxidation the tensile strength increase but if the oxidation level goes still higher at falls back. In case of periodate bleached pulps, preservation of strength properties occurs due to hydrolysis of car-

bonyl groups to carboxyl groups through an intermediate hemiacetal.

The oxidation of kraft pulp by means of periodic acid, acid dichromate or chlorite at neutral pH increase the wet strength. The wet strength reverses when the treatment is carried out at lower pH with acid chlorite. The same happens in the case of borohydride or hydroxylamine. The change in wet strength is closely related to the carboxyl content introduced by oxidation since aldehydicarbonyls to carboxyls by acid chlorite, reduced to hydroxyls by borohydride and converted to oximes by hydroxyl amines. The effect of oxidation on pulp and paper properties may be brought out by the following linkages.

#### 1. Covalent linkages

#### 2. Strong hydrogen bonding

### 3. Oxidative cross linkages.

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