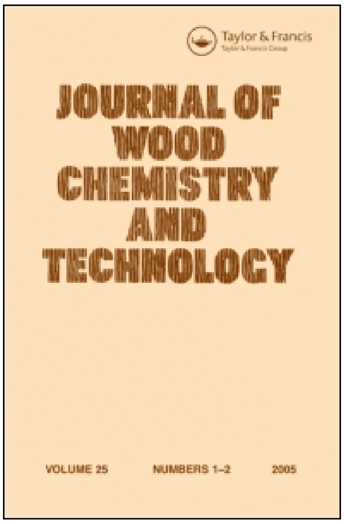

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# THE FORMATION OF GASEOUS PRODUCTS AND ITS RELATION TO PULP BLEACHING DURING THE PERACETIC ACID TREATMENT

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## ABSTRACT

When used in pulp bleaching, peracetic acid is consumed by two competitive pathways: oxidation of pulp and wasteful reactions such as decomposition. In this paper, the peracetic acid consumed in wasteful reactions is quantified by determining the gaseous products evolved. It is found that although carbon dioxide is formed under certain conditions, oxygen is the dominant product of the wasteful reactions. The oxygen formation is directly proportional to the consumption of oxidants (as peracetic acid and hydrogen peroxide) in the wasteful reactions with 2 moles of oxidant consumed per mole of oxygen formed. Therefore, the brightening efficiency during peracetic acid treatment can be characterized by correcting the measured peracetic acid consumption for decomposition. The peracetic acid brightening results for an oxygen delignified softwood kraft pulp are reported. It is found that a significant amount of peracetic acid is consumed by the wasteful reactions during the brightening. The effect of process parameters on the peracetic acid brightening efficiency is determined. It is shown for an oxygen delignified softwood kraft pulp that there is a unique relationship between pulp brightness gain and peracetic acid consumption due to the pulp oxidation irrespective of the brightening conditions.

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## INTRODUCTION

Peracids, such as peracetic acid (Pa) and monoperoxysulphuric acid (Px), have been identified as promising alternatives to chlorine containing chemicals for bleaching of chemical pulps.[1-8] Under typical peracetic acid bleaching conditions, in addition to the desirable lignin oxidation reactions, peracetic acid may be consumed by spontaneous and transition metal catalysed decomposition reactions.[9-14] Therefore, it is important to understand and monitor the peracetic acid decomposition in order to minimize these wasteful side reactions during peracetic acid bleaching.

Martin[15] and later Gonzalez-sierra[16] studied hydrogen peroxide decomposition by monitoring the gas formation during peroxide bleaching of groundwood pulps. It was found that oxygen is the only gas formed from hydrogen peroxide decomposition, and that two moles of hydrogen peroxide are decomposed per mole of oxygen formed. It was also established[16] that under typical hydrogen peroxide bleaching conditions the oxygen produced does not contribute to pulp bleaching.

Gaseous products are also formed during peracetic acid decomposition.[10-13] Kagan and Lubarsky[10] found that carbon dioxide and oxygen are the main gaseous products evolved during manganese catalysed decomposition of peracetic acid in acetic acid and water respectively. Later, Allen and Aguilo[11] confirmed that carbon dioxide is the main gaseous product generated from manganese catalysed decomposition of peracetic acid in acetic acid solution. Vrbaski and Brihta[12] investigated the cobalt catalysed decomposition of peracetic acid in an aqueous solution without pH control and claimed that oxygen was the only gas formed. However, it was found by Koubek[13] who studied the cobalt catalysed decomposition of peracetic acid at pH 5.4 in an ammonium acetate buffer, that both oxygen and carbon dioxide were formed in a ratio of about one to one. Furthermore, Koubek[13] also established that roughly 80% of the carbon dioxide formed originated from the acetate ion of the buffer.

The above authors did not extend their studies to a neutral pH range, which is optimal for peracetic acid brightening.[1,8,9,17] Furthermore, the relationship between the gas formation and efficiency of peracetic acid brightening has never been examined. In this paper, the relationship between gas formation and peracetic acid consumption is determined for typical peracetic acid brightening conditions. Subsequently it is attempted to relate the gas formation to the brightness gain during peracetic acid treatment of an oxygen delignified softwood kraft pulp.

## EXPERIMENTAL

Peracetic acid and ultra-pure grade NaOH were purchased from Aldrich (Milwaukee, USA). The peracetic acid consists of about 34% w/w peracetic acid, 5% w/w hydrogen peroxide and 40% w/w acetic acid with the remainder being water. Reagent grade chemicals, DTPA from Fisher Scientific (Nepean, Ontario) and DTMPA from Buckman (Memphis, USA) were used in the experiments without further purification. Distilled and deionized water was used in all experiments. Its metal ion content was below the detection limits of the atomic absorption (AA) spectroscopic analysis method used in this study.

The oxygen delignified softwood kraft pulp used for peracetic acid bleaching had a 37.7% ISO brightness, a kappa number of 13.8 and a viscosity of 23.4 mPa·s. The chelation stage (Q) with 0.5% DTPA was performed at 50°C, pH 5, 2.5% pulp consistency and 30 min.

The experimental setup was shown in Figure 1. Experiments without pulp fibres were carried out in a well-sealed 500 mL four-neck round-bottom flask immersed in a constant temperature bath. The aqueous solution containing all the required chemicals except peracetic acid was preheated to the desired reaction temperature. The reaction was initiated by addition of a concentrated peracetic acid solution to the reaction flask. The pH was kept constant with an automatic titrator by addition of 10 mol/L NaOH. Mixing was provided by a

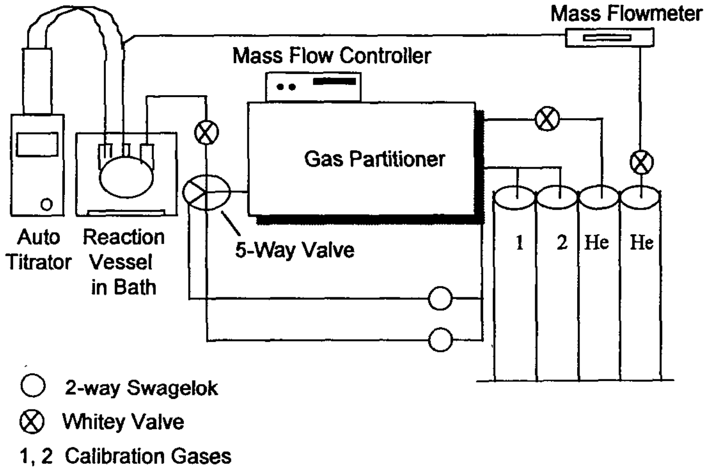


Figure 1. The Experimental Set-up for the Determination of Gaseous Products during Peracetic Acid Decomposition.

submersed 41 mm long magnetic stirrer bar driven by a magnetic drive placed underneath the constant temperature bath. Ultra pure helium was bubbled through the solution to transport the gases generated by the reactions from the flask to a gas sampling loop of a gas chromatography (Fisher model 1200 Gas Partitioner). Any leaks of the system can be detected by the appearance of nitrogen in the gas sample. The gas partitioner employs a dual-column, dual-detector chromatographic system to separate and measure the gaseous products. The first column is packed with 80-100 mesh Columpak™ PQ and the second with 60-80 mesh Molecular Sieve 13X. The flowrate of the helium transport gas was controlled by a mass flow controller (Model Edwards 825). The gas in the sampling loop was injected at predetermined time intervals into the gas partitioner for analysis. Samples of peracetic acid solution were also withdrawn with a syringe, weighted and analysed following the iodometric method developed by Greenspan and Mackellar.[18]

The volume concentrations of oxygen and carbon dioxide in the helium gas stream are related to the different gas flow rates as:

$$[O_2](\%) = \frac{100F(O_2)}{F(O_2)+F(CO_2)+F(He)} \qquad (1)$$

$$[CO_2](\%) = \frac{100F(CO_2)}{F(O_2)+F(CO_2)+F(He)} \qquad (2)$$

where $F(O_2)$ and $F(CO_2)$ represent the volumetric flowrates of oxygen and carbon dioxide respectively generated by the reaction solution, and F(He) is the helium flowrate. By solving Equations (1) and (2), one can calculate $F(O_2)$ and $F(CO_2)$ as:

$$F(O_2) = \frac{F(He)\cdot[O_2]}{100-[O_2]-[CO_2]} \qquad (3)$$

$$F(CO_2) = \frac{F(O_2)\cdot[CO_2]}{[O_2]} \qquad (4)$$

By integrating the flowrates of $O_2$ and $CO_2$ from time $t_1$ to $t_2$ the volume of $O_2$ and $CO_2$ evolved during time interval of $t_1$ to $t_2$ can be determined. The volume of $O_2$ and $CO_2$ evolved was then converted into moles using the ideal gas law. The molar quantities of peracetic acid and hydrogen peroxide consumed were calculated from the difference in the concentrations of peracetic acid and hydrogen peroxide at determined times $t_1$ and $t_2$.

Peracetic acid brightening of pulp was conducted in a 1000 mL four-neck round bottom flask at 0.5 and 1.5 % consistency, with mixing provided during the course of brightening by a mechanical stirrer. Again ultra pure helium was bubbled through the suspension to carry the gaseous products out of the reaction. However, now all the gas was collected in a 10 L Tedlar gas sampling bag. The helium gas flow rate was kept around 50 mL/min with the mass flow controller. The total gas volume collected was measured by water displacement and the gas

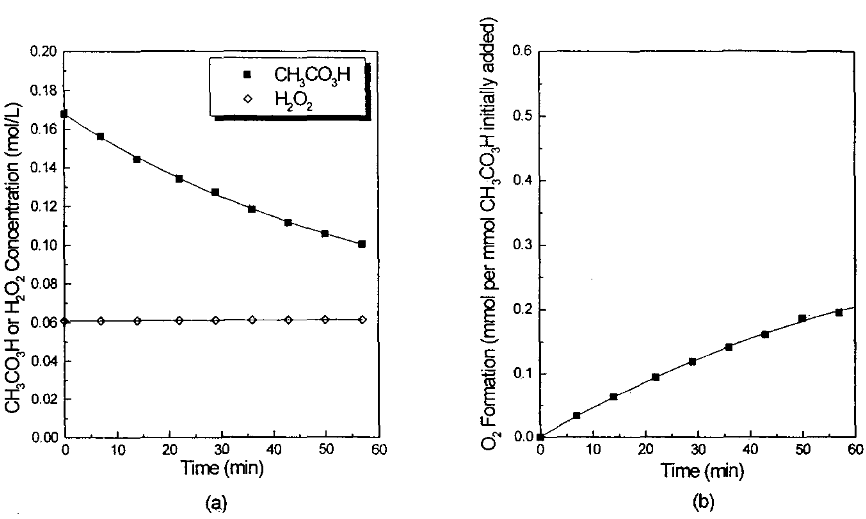


Figure 2. The Formation of Gaseous Products and the Consumption of Peracetic Acid at 25°C, pH 8.2, F(He) of 100 mL/min and with 0.5 g/L DTMPA Addition.

composition was determined by analysis with the gas partitioner. After the peracetic acid treatment, the pulp was thoroughly washed with deionized water and made into handsheets. Samples of the spent liquor were withdrawn and titrated for the residual peracetic acid and hydrogen peroxide concentrations.

Pulp brightness, viscosity and kappa number were determined in accordance with TAPPI methods T452 om-92, T230 om-89, and T236 cm-85, respectively.

## RESULTS AND DISCUSSION

### The Formation of Gaseous Products During the Decomposition of Peracetic Acid

The result of gas formation and decomposition of peracetic acid at pH 8.2 and 25°C with 0.5 g/L DTMPA present was presented in Figure 2. The flow rate of helium was 100 mL/min and the mixing speed was 400 rpm. It was established[9] that the disappearance of peracetic acid under this condition is mainly due to the spontaneous decomposition, as illustrated in Equation (5):

$$2\ CH_3CO_3H \longrightarrow 2\ CH_3CO_2H + O_2 \qquad (5)$$

Figure 2b shows that $O_2$ is the only gas generated in the system at this condition. The experiments were repeated at helium flowrates of 70 and 300 mL/min, and stirring speeds of 200 and 800 rpm. It was found that the oxygen formation is not affected by the helium gas flowrate or the mixing speed. This means that there are no significant transport limitations for the release of oxygen from the reaction system.

By plotting the peracetic acid consumption against the oxygen formation in Figure 3, it can be seen that the molar ratio of peracetic acid consumed and the $O_2$ formed is quite close to 2 stipulated by Equation (5). Similar experiments at pH of 7.0 and 6.0 under otherwise the same conditions confirmed the above conclusions that only oxygen is generated and that the stoichiometry of the peracetic acid consumption to the oxygen formation is very close to 2.

It was found[10-13,19] that trace amounts of transition metal ions, such as cobalt, manganese, copper and iron catalyse the decomposition of peracetic acid. Among these metals, manganese is the main catalytic species responsible for enhanced peracetic acid decomposition during pulp bleaching.[9] Therefore, for an aqueous solution of equilibrium peracetic acid the relationship between the peracetic acid decomposition and the gas formation was examined in the presence of 0.75 ppm Mn(II) without the addition of DTMPA at pH 8.2 and 25°C (Figure 4). As expected, the presence of Mn(II) enhanced the disappearance rates of both peracetic acid and hydrogen peroxide (Figure 4a). Similarly, the $O_2$ formation was also increased with the addition of Mn(II). It was further confirmed that the sum of the number of moles of peracetic acid and

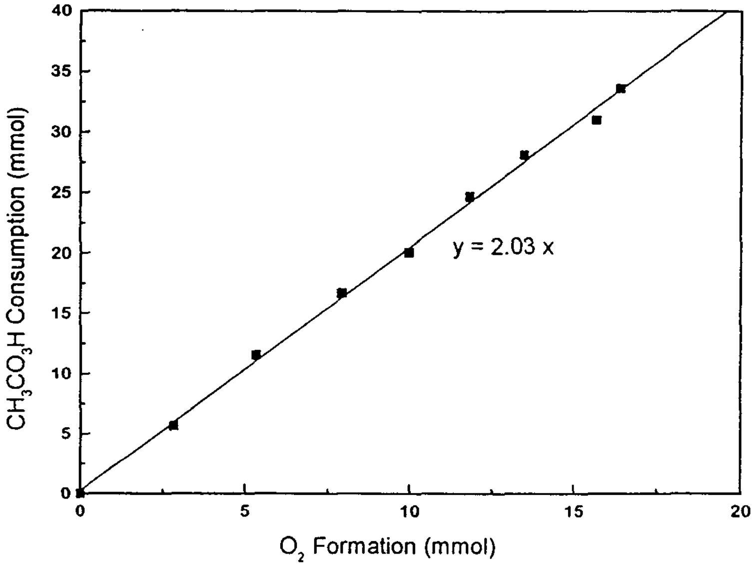
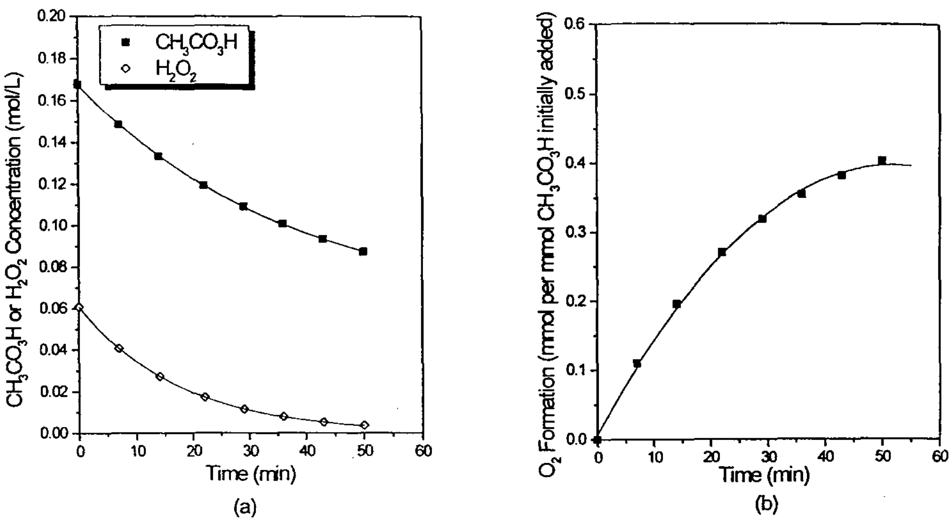


Figure 3. The Stoichiometry of the Peracetic Acid Consumption and the Oxygen Formation at 25°C, pH 8.2, F(He) of 100 mL/min and with 0.5 g/L DTMPA Addition.



(a) (b)

Figure 4. Gas Formation and the Consumption of Peracetic Acid in the Presence of 0.75 ppm Mn(II) and at 25°C, pH 8.2, F(He) of 100 mL/min.

hydrogen peroxide consumed was twice that of the number of moles of oxygen formed.

Kagan and Lubarsky[10] and later Vrbaski and Brihta[12] identified the stoichiometry of the manganese catalysed decomposition of peracetic acid in an aqueous solution as:

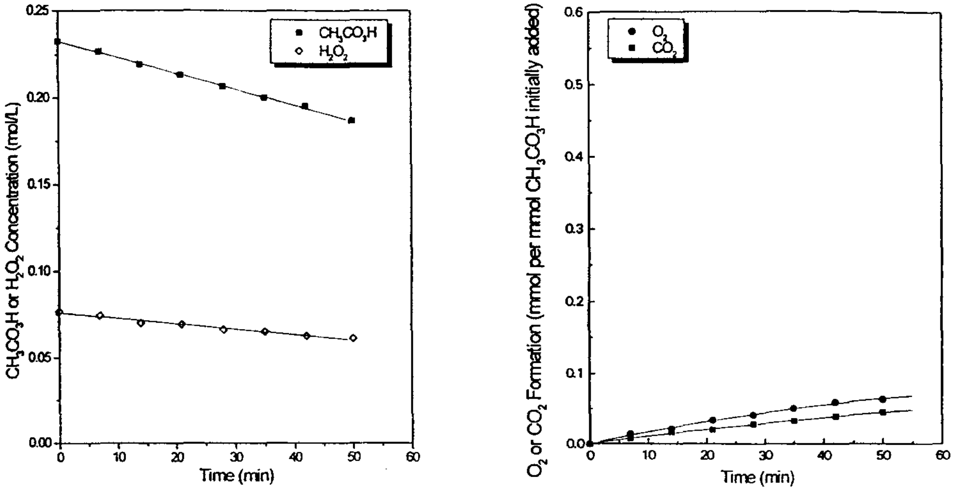
$$2CH_3CO_3H \xrightarrow{M^{n+}} 2CH_3CO_2H + O_2 \qquad (6)$$

McDonough[14] and later Evans and Upton[20] reported that the reactions of peracetic acid and hydrogen peroxide were catalysed by transition metal ions. The overall reaction was reported as[20]:

$$CH_3CO_3H + H_2O_2 \xrightarrow{M^{n+}} CH_3CO_2H + H_2O + O_2 \qquad (7)$$

Furthermore, it was established[9] that there is also an oxidation-reduction cycle in the reaction system with the addition of $Mn^{2+}$. The overall stoichiometry of the oxidation-reduction cycle is the same as Reaction (7). As is evident from Reactions (5), (6) and (7), the molar ratio of the consumption of oxidants and the formation of oxygen is always 2 consistent with the experimental evidence.

The effect of pH on the formation of gaseous products in the presence of 0.75 ppm $Mn^{2+}$ was further investigated by decreasing the pH from 8.2 to 5.0. As shown in Figure 5a, the disappearance rates of both peracetic acid and hydrogen peroxide are much slower at pH 5.0 than at pH 8.2. This is due to the fact that the reaction rates of Reactions (5), (6) and (7) are all decreased at a lower pH [9]. Figure 5b shows that both oxygen and carbon dioxide are generated at pH 5.0. Further experiments showed that the formation of $CO_2$ is increased by the addition of acetic acid in the presence of $Mn^{2+}$. This is in



(a) (b)

Figure 5. Gas Formation and the Consumption of Peracetic Acid in the Presence of 0.75 ppm Mn(II) and at 25°C, pH 8.2, F(He) of 70 mL/min.

agreement with the earlier result by Kagan and Lubarsky[10] as well as that of Allen and Aguilo [11] that carbon dioxide is the main gaseous product from the manganese catalysed decomposition of peracetic acid when it was carried out in an acetic acid solution. In addition, it was reported[13] that both carbon dioxide and oxygen are the gaseous products when the cobalt catalysed decomposition of peracetic acid was performed in an ammonium acetate buffer of pH 5.4. As will be shown below, the present experimental evidence as well as that reported in literature support that carbon dioxide is the further oxidation product of acetic acid, rather than a direct product from the decomposition of peracetic acid.

In the previous section it was shown that two moles of the oxidants, peracetic acid and hydrogen peroxide, are consumed per mole of oxygen generated. Therefore for the experiments at pH 5.0 described above, the amount of oxidant consumed was corrected for the oxygen formation according to the

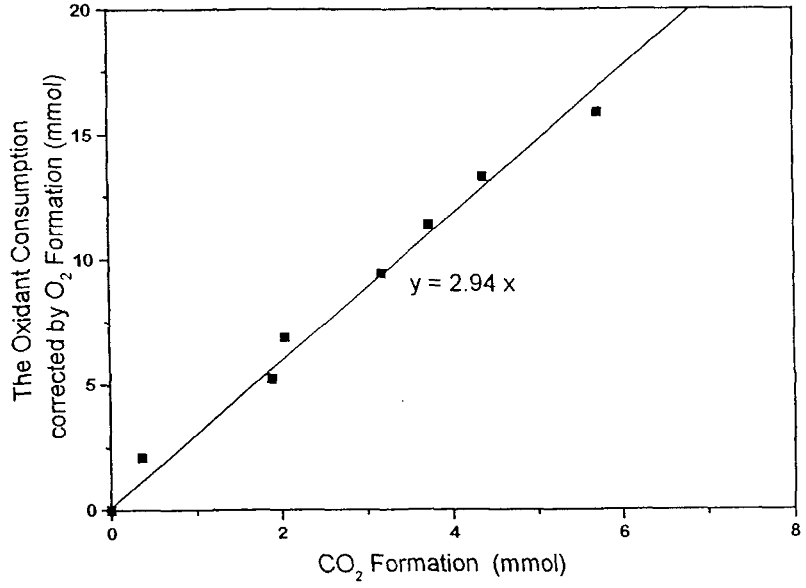


Figure 6. The Stoichiometry of the Peracetic Acid Consumption and Carbon Dioxide in the Presence of 0.75 ppm Mn(II) and at 25°C, pH 5.0, F(He) of 100 mL/min.

stoichiometry of Reactions (5), (6) and (7). Subsequently the molar carbon dioxide formation was plotted against this corrected molar amount of oxidant consumed. As can be seen in Figure 6, the stoichiometry in terms of moles of corrected peracetic acid and hydrogen peroxide consumed per mole of carbon dioxide formed is approximately 3. This is consistent with the suggestion of Kagan and Lubarsky[10] that the stoichiometry of the oxidants consumed to carbon dioxide formed is 3 when manganese catalysed decomposition of peracetic acid is carried out in an acetic acid solution. Therefore, the mechanism in Figure 7 is proposed to account for the formation of carbon dioxide. The singlet oxygen, formed in Reactions (5), (6) and (7) oxidizes acetic acid to produce α-peroxide compound (I), which undergoes decarboxylation under acidic conditions,

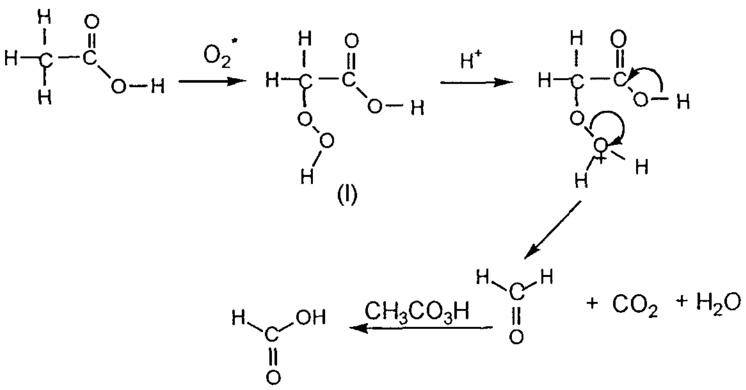


Figure 7. Plausible Mechanism of the Carbon Dioxide Formation during Peracetic Acid Decomposition.

generating carbon dioxide and formaldehyde. Subsequently, formaldehyde is further oxidized by peracetic acid to formic acid as identified experimentally by Kagan and Lubarsky.[10] Thus, the proposed mechanism satisfactorily accounts for the observed stoichiometry of the oxidant consumption and the carbon dioxide formation. In addition, it explains why a lower pH favours the formation of carbon dioxide.

## The Effect of DTPA and DTMPA on Gas Formation and Peracetic Acid Decomposition

The effect of DTPA and DTMPA addition on peracetic acid decomposition and oxygen formation at pH 8.2 was examined by adding either DTPA or DTMPA at the mid point of the reaction (at 30 min). As shown in Figures 8 and 9 respectively, there is a sharp increase in peracetic acid consumption rate when 0.02 mol/L DTPA was added with or without the addition of 0.75 ppm Mn(II) (Figure 8a). This is attributed to the fact that peracetic acid is being rapidly consumed in a reaction with DTPA as was reported earlier by McDonough.[14] He found that DTPA was rapidly oxidized

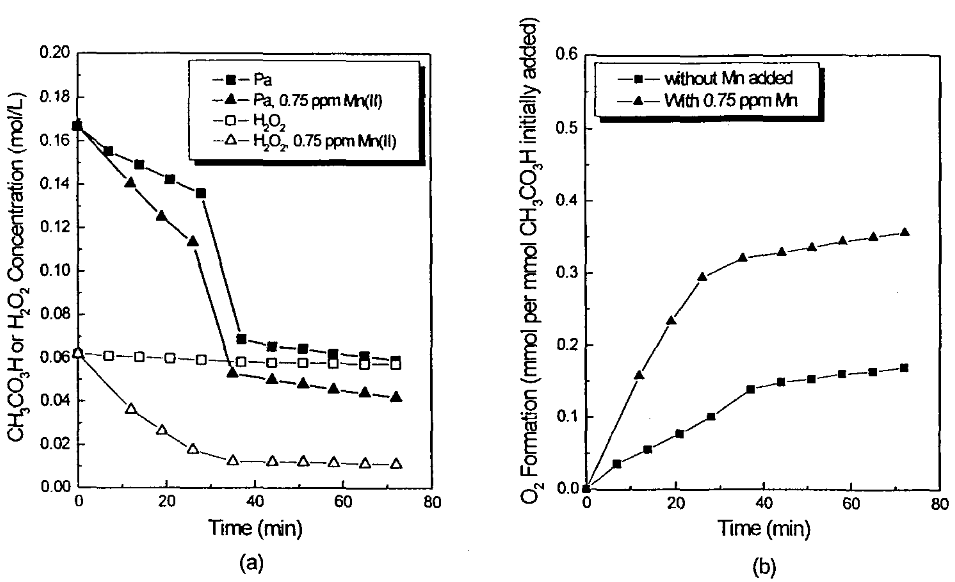
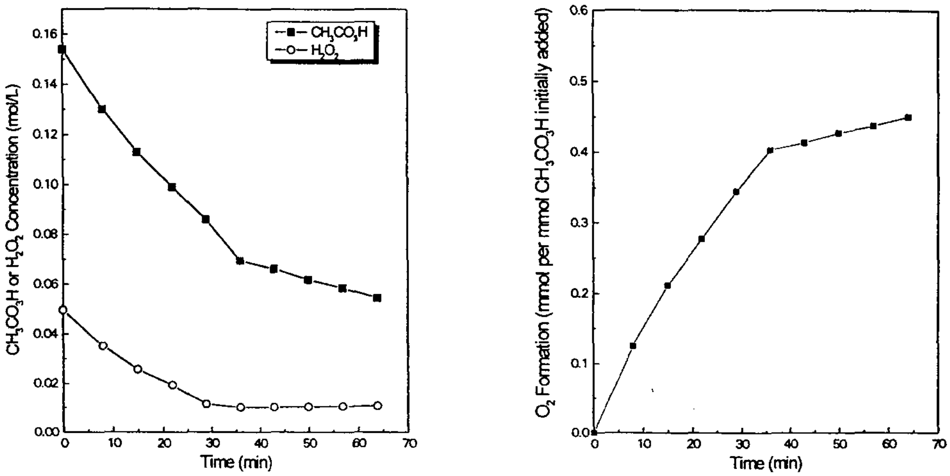


Figure 8. The Effect of DTPA Addition on Peracetic Acid Consumption and the Oxygen Formation at 25°C, pH 8.2, F(He) of 100 mL/min and with 0.02 g/L DTPA Added at 30 min.

by peracetic acid at different pHs varying from 6 to 10 in the absence of metal ions and obtained a stoichiometry of 3 moles peracetic acid per mole DTPA. We confirmed this stoichiometry by comparing the initial quantity of DTPA added with the peracetic acid loss calculated as the difference between the total oxidant consumed and the oxidant decomposed as determined by the formation of oxygen. It is also shown in Figures 8a and 8b that the addition of 0.02 mol/L DTPA at 30 minutes leads to the decrease in the disappearance rate of peracetic acid and hydrogen peroxide as well as the formation rate of oxygen. This could be explained by the hypothesis that part of the DTPA still chelates with the metal ions but that any excess is rapidly consumed by peracetic acid.[14]

Figure 9a shows that the oxidation of DTMPA by peracetic acid is negligible as evidenced by the absence of sharp decrease in the peracetic acid



(a) (b)

Figure 9. The Effect of DTMPA Addition on Peracetic Acid Consumption and Oxygen Formation in the Presence of 0.75 ppm Mn(II) at 25°C, pH 8.2, F(He) of 100 mL/min and with 0.02 mol/L DTMPA Added at 30 min.

concentration after the DTMPA addition. The much slower rate in oxygen formation shown in Figure 9b is due to the fact that DTMPA stabilizes both peracetic acid and hydrogen peroxide.[9] Furthermore, the stoichiometry of two moles of oxidant consumed (both hydrogen peroxide and peracetic acid) per mole of oxygen formed in these experiments supports that the oxidation of DTMPA by peracetic acid and/or hydrogen peroxide can be neglected.

## The Formation of Gaseous Products and Its Relation to Peracetic Acid Bleaching

The effect of chelation, pH, pulp consistency, peracetic acid charge and reaction time on the gas formation and its relation to pulp brightening during peracetic acid treatment were studied. The results of the peracetic acid treatment of an oxygen delignified pulp are presented in Table 1. Listed are the

## TABLE 1

The Formation of Gaseous Products and its Relation to Bleaching During Peracetic Acid Treatment of An Oxygen Delignified Pulp (Initial brightness of 37.7 %ISO; initial viscosity of 23.4 mPa.s)

| **Experimental Runs** | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** |
|---|---|---|---|---|---|---|---|---|
| Samples | O | OQ | OQ | OQ | OQ | OQ | OQ | OQ |
| pH* | 7.0 | 7.0 | 7.0 | 7.0 | 5.0 | 7.0 | 7.0 | 7.0 |
| Pulp consistency (%) | 1.5 | 1.5 | 1.5 | 0.5 | 1.5 | 1.5 | 1.5 | 1.5 |
| Pa Charge (% on o.d. pulp) | 3.0 | 3.0 | 5.0 | 5.0 | 3.0 | 3.0 | 1.5 | 1.5 |
| Temperature (°C) | 60 | 60 | 60 | 60 | 60 | 40 | 60 | 60 |
| Bleaching time (min) | 120 | 120 | 120 | 120 | 120 | 120 | 30 | 120 |
| Residual Pa (% on o.d. pulp) | 0.09 | 0.3 | 0.45 | 0.5 | 1.87 | 1.51 | 0.56 | 0.04 |
| Residual $H_2O_2$ (% on o.d. pulp) | 0.05 | 0.12 | 0.06 | 0.05 | 0.39 | 0.23 | 0.19 | 0.09 |
| $O_2$ formation (mmol $O_2$ /g Pa charged) | 7.29 | 5.98 | 6.89 | 7.39 | 0.98 | 3.29 | 2.90 | 5.81 |
| $CO_2$ formation (mmol $CO_2$ / g Pa charged) | 0 | 0 | 0 | 0 | 0.69 | 0 | 0 | 0 |
| Brightness (% ISO) | 54.0 | 57.8 | 59.9 | 54.9 | 51.1 | 53.7 | 51.5 | 52.9 |
| Viscosity (mPa.s) | 20.6 | 21.0 | 20.2 | 19.9 | 22.6 | 22.3 | 22.8 | 22.5 |
| Pa consumed in pulp oxidation (% on o.d. pulp) | 0.55 | 0.77 | 0.99 | 0.58 | 0.42 | 0.55 | 0.39 | 0.47 |
| Pa consumed in wasteful reactions (% on o.d. pulp) | 2.36 | 1.93 | 3.56 | 3.92 | 0.71 | 0.94 | 0.55 | 0.99 |
| $H_2O_2$ consumed in wasteful reactions (% on o.d. pulp) | 0.43 | 0.36 | 0.75 | 0.76 | 0.09 | 0.25 | 0.05 | 0.15 |
| $\frac{\text{Pa decomposed}}{\text{Total Pa consumed}}$ (%) | 81 | 71 | 78 | 87 | 63 | 63 | 59 | 68 |
| $\frac{\text{Pa consumed by oxidation}}{\text{Total Pa consumed}}$ (%) | 19 | 29 | 22 | 12 | 37 | 37 | 41 | 32 |

** pH was kept constant during the bleaching* development of the residual amount of peracetic acid and hydrogen peroxide, the amount of $O_2$ and $CO_2$ formed, and the brightness and viscosity of the bleached pulp. The amount of peracetic acid and hydrogen peroxide consumed in wasteful reactions is calculated from the formation of $O_2$ and $CO_2$ using the appropriate stoichiometry. Since it is reasonable to assume that at the present conditions hydrogen peroxide is only consumed in wasteful reactions, i.e. does not contribute to pulp oxidation, the amount of peracetic acid consumed in wasteful reactions can be calculated from the gas formation results and the amount of hydrogen peroxide consumed. Subsequently the amount of peracetic acid consumed in pulp oxidation reactions can be calculated as the difference between the total amount of peracetic acid consumed and that consumed in wasteful reactions. Both the development of peracetic acid consumed in pulp oxidation reactions and that in wasteful reactions are given in Table 1 expressed in terms of percentage on o.d. pulp as well as of percentage of total amount of peracetic acid consumed. The results in Table 1 show that only oxygen is produced when peracetic acid brightening is performed at pH 7. However, at pH 5 (Run 5) a small amount of carbon dioxide is formed. It can also be seen that the total amount of peracetic acid consumed in wasteful reactions is much less at pH 5 than that at pH 7. These results are consistent with those obtained at the same conditions but without the presence of pulp fibres, presented in the previous sections. A surprising result of the analysis in Table 1 is that the majority of the peracetic acid is consumed in wasteful reactions, accounting for 59 to 87% of the total peracetic acid consumed. The amount of peracetic acid wasted was plotted against the hydrogen peroxide wasted for all the experiments listed in Table 1. Figure 10 shows that the molar ratio of peracetic acid wasted and hydrogen peroxide wasted is about 2. Since hydrogen peroxide is only wasted in Reaction (7) with a molar ratio of 1 between peracetic acid and hydrogen peroxide,[14] Figure 10 suggests that about half of the peracetic acid is wasted by Reaction (7) while spontaneous decomposition (Reaction (5)) and metal catalysed decomposition (Reaction (6)) are responsible for the other half of the peracetic acid wasted.

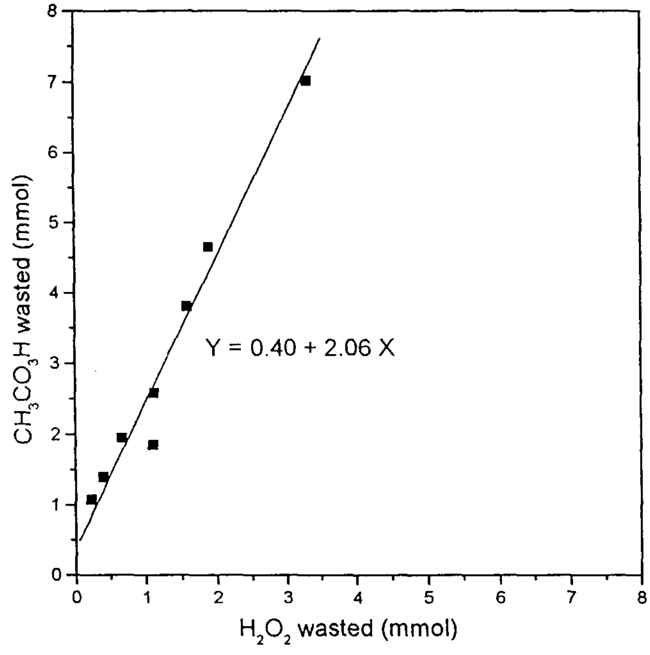


Figure 10. The Relationship Between Wasted Peracetic Acid and Hydrogen Peroxide (O or OQ Pulp, 40 - 60°C, pH 5 - 7, 1.5 - 5% Peracetic Acid Charge, 0.5 - 1.5% Pulp Consistency, 30 - 120 min).

Comparison of Run 1 with Run 2 confirms that DTPA pretreatment leads to less peracetic acid decomposition and a higher brightness gain, obviously because the DTPA chelated pulp contains less residual transition metals.[9] The effect of pH on peracetic acid brightening is seen by comparing Run 5 and 2 at pH 5.0 and 7.0 respectively. The analysis shows that a higher pH leads to more oxidation of pulp and subsequently a higher brightness gain. This is consistent with literature results[1,8,9,17] that peracetic acid brightening is more effective at a neutral pH than at a slightly acidic condition. However, a higher pH also results in less efficient use of peracetic acid since 71% of the total peracetic acid consumed was lost by the wasteful reactions at pH 7 compared to 63% at pH 5. An important result is that the data in Table 1 shows that a higher

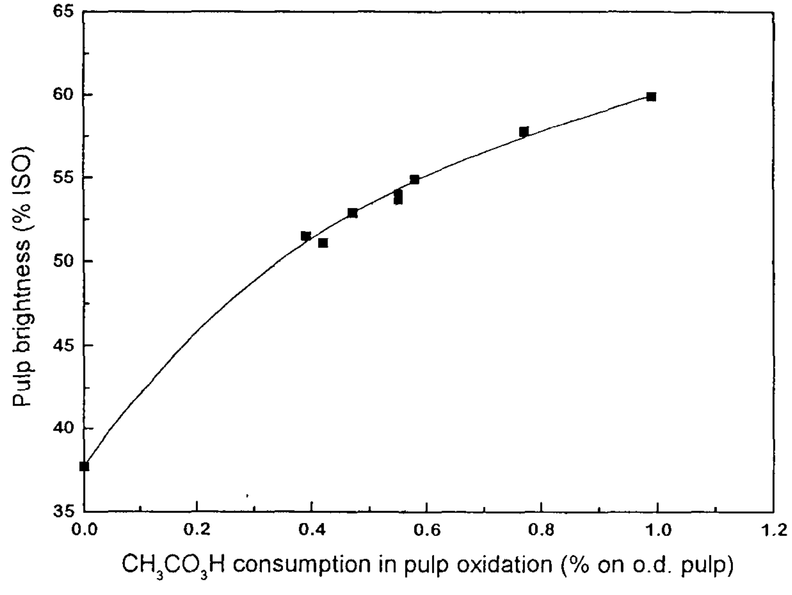


Figure 11. The Relationship Between the Peracetic Acid Consumption due to the Pulp Oxidation and the Pulp Brightness (O or OQ Pulp, 40 - 60°C, pH 5 - 7, 1.5 - 5% Peracetic Acid Charge, 0.5 - 1.5% Pulp Consistency, 30 - 120 min).

consistency increases the pulp oxidation while the consumption of peracetic acid in wasteful reactions is slightly lower (Runs 3 and 4). Therefore a higher brightness gain and especially a higher brightening efficiency can be expected when peracetic acid brightening is performed at high consistency.

As expected a higher brightness gain is obtained at higher peracetic acid charge under otherwise the same brightening conditions (see Runs 8, 2 and 3). However, an increase in peracetic acid charge results in a significant lower brightening efficiency. This could be explained by the fact that at a higher Pa charge the reactive lignin chromophores are rapidly consumed, while the peracetic acid concentration is still high so that the wasteful reactions remain substantial. The same argument explains why the peracetic acid brightening efficiency worsens when the peracetic acid treatment is extended from 30 to 120 minutes (Runs 7 and 8).

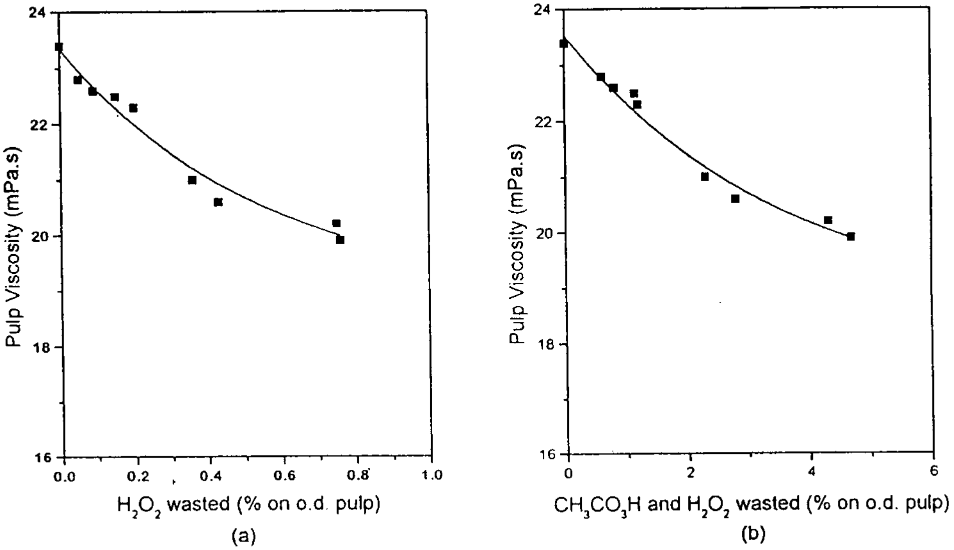


Figure 12. The Relationship Between the Pulp Viscosity and the Oxidant Consumed in Wasteful Reactions (O or OQ Pulp, 40 - 60°C, Ph 5 - 7, 1.5 - 5% Peracetic Acid Charge, 0.5 - 1.5% Pulp Consistency, 30 - 120 min).

The brightness of the peracetic acid bleached pulps were plotted against the peracetic acid consumption due to the pulp oxidation reactions for all the experiments listed in Table 1. Figure 11 shows that there is unique relationship between these two parameters, independent of the process conditions. This confirms that the peracetic acid consumption in wasteful reactions and by pulp oxidation are two completely independent phenomena.

It is evident from Figure 12a that the viscosity of the resulting pulp is closely related to the hydrogen peroxide consumption in wasteful reactions; a higher loss of hydrogen peroxide in wasteful reactions is always accompanied by a lower pulp viscosity. This may be explained by the fact that highly reactive oxygen species, such as singlet oxygen and radicals, are generated in the wasteful reactions involved hydrogen peroxide. This is in agreement with the finding by Devenyns et al.[12] that distilled peracetic acid (almost no hydrogen peroxide) is more selective than equilibrium peracetic acid in pulp delignification. Since Figure 10 shows that hydrogen peroxide and peracetic acid consumed in wasteful reactions is closely related, one can expect that the pulp viscosity loss is also closely related to oxidant (peracetic acid and hydrogen peroxide) consumed in wasteful reactions. Figure 12b shows that this is indeed the case for this oxygen delignified pulp.

## CONCLUSIONS

Oxygen is the main gaseous product produced from the decomposition of peracetic acid under typical brightening conditions, i.e. pH 7 and 60°C. One mole of oxygen is generated per two moles of oxidants (peracetic acid and hydrogen peroxide) consumed. At a relatively low pH (~5) $CO_2$ may also be formed from the wasteful reactions at a stoichiometry of 3 moles of oxidant consumed per mole of $CO_2$ released. Thus, based on the stoichiometry of formation of $O_2$ and $CO_2$ the amount of oxidant consumed in wasteful reactions can be calculated from the generation of these two gases. Furthermore, the latter information allows the determination of the amount of peracetic acid used in pulp oxidation as the difference of the peracetic acid consumed (i.e. charge minus residual) and that what is wasted. It is found that the pulp brightness gain is directly related to the peracetic acid consumption in the oxidation of pulp, independent of the process conditions. Also, the pulp viscosity loss is uniquely related to the loss in oxidant as measured by the $O_2$ and $CO_2$ generation.

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