Nitrogen-Centered Activators of Peroxide-Reinforced Oxygen Delignification

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In an effort to augment the efficiency of an oxygen delignification stage, we examined the effectiveness of various heterocyclic aromatic nitrogen compounds as possible activators of such a stage. It was shown that a variety of such compounds may act as activators in the presence of hydrogen peroxide, improving the delignification efficiency of oxygen delignification. Among the group of activators examined, 1,10-phenanthroline was found to be the most potent. Injecting the activator in the middle of the delignification stage (simulating a two-stage process) was shown to provide most of the benefits. The optimum injection time was found to at 30 min from the onset of the delignification. At the optimal charge of 1,10-phenanthroline (0.3%), the delignification was improved by 18%. While the presence of copper ions was found to further improve the efficiency of the activating system, this was accompanied by an extensive carbohydrate degradation.

Introduction

Environmental restrictions coupled with market pressures have forced the pulp and paper industry to explore alternatives to chlorine-based bleaching practices for the production of bleached kraft pulp. Oxygen and oxygen-based chemicals, such as peroxide, ozone, and peracids, have been considered as leading candidates for chlorine replacement in pulp bleaching. A market bleached pulp can be successfully produced by applying oxygen, peroxide, and ozone as bleaching agents, so-called totally chlorine-free (TCF) bleaching; however, these bleaching agents are not as effective as chlorine.

Oxygen is capable of removing up to 50% of the residual lignin in the unbleached pulp. Beyond this point, a loss of pulp strength may occur. Industrially, it would be extremely beneficial to extend the conventional oxygen treatment to beyond 50% residual lignin removal without extensive carbohydrate depolymerization. This would decrease bleach chemical demand, ensuring the viability of the process with significant environmental benefits.

Several methods of enhancing the delignification efficiency of oxygen have been reported:

A two-stage oxygen delignification process, in which the oxygen and alkali charges are split between two separate oxygen stages, was shown to increase lignin removal by oxygen.[1] Pulp pretreatment prior to the oxygen delignification stage, by which the reactivity of the residual lignin toward oxygen is enhanced, allowed for a substantial increase in the delignification efficiency of oxygen.[2−11] A two-stage oxygen delignification process with an interstage pulp treatment, where the pulp is activated prior to the second oxygen stage, has also been recommended.[12−17] In this process, the reactivity of the residual lignin in the second oxygen stage, as well as the efficiency of the second oxygen stage, is increased, and subsequently the overall lignin removal by oxygen is increased.

Activation and catalysis of oxygen is another pathway aimed at improving the efficiency of oxygen delignification. The addition of catalysts and activators, such as polyoxometalates,[18−24] metalloporphyrins,[25] and other mostly transition-metal-based catalysts, was shown to improve lignin removal and/or the selectivity of the oxygen delignification process.[26−28]

Hydrogen peroxide was also shown to promote the delignification efficiency of oxygen. Combining the effects of oxygen and peroxide was first reported in the 1980s.[29−31] Addition of oxygen and hydrogen peroxide to the alkaline extraction stage resulted in reduced K numbers and improved viscosities. Addition of hydrogen peroxide to the oxygen delignification stage has also been examined.[32−34] This peroxide-reinforced oxygen delignification process can increase the degree of delignification of the oxygen stage by up to 60%.

Heterocyclic aromatic nitrogen compounds, such as polypyridines, have been studied as activators or catalysts of oxygen and peroxide delignification. It was reported that the addition of 1,10-phenanthroline can significantly improve the lignin removal of the oxygen pulping process on wood.[35−37] Because wood contains transition metals, such as iron or copper, it was proposed that the mechanism of the action of phenanthroline may depend on the formation of iron− or copper−phenanthroline complexes. Polypyridines were shown to increase the reaction rate of alkaline hydrogen peroxide.[38] The addition of polypyridines to the peroxide bleaching stage had a considerable effect on brightness gains.

Recently, a new efficient delignifying system consisting of copper complexes and peroxide in an aqueous solution has been reported.[39,40] The system is based on the reaction of Cu(II) and peroxide in the presence of

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various copper coordinators, such as derivatives of pyridine. While low K numbers for bleached pulps were obtained, severe fiber damage was apparent with the accompanying substantial viscosity losses.[41] In actuality, the recent literature pertaining to the activation and catalysis of peroxide and oxygen delignification of chemical pulps has recently been thoroughly reviewed.[42]

In view of the variety of efforts to activate oxygen delignification to date, this research was carried out with the aim of ascertaining and understanding the effectiveness of various heterocyclic aromatic nitrogen compounds, including polypyridines and phenanthrolines, as possible activators of oxygen delignification. In addition, the effect of metal ion addition on the performance of these activating systems was also examined. A new approach, injecting the activator in the later phases of oxygen delignification (simulating a two-stage process), was also examined and optimized.

Experimental Section

Black spruce kraft pilot-plant pulp of a K number of 29.9 and a viscosity of 42 mPa·s was used in this series of experiments.

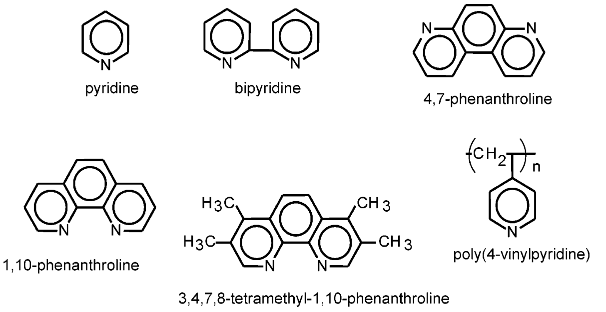
The pulp was chelated at 2% consistency using a charge of 0.5% diethylenetriaminepentaacetic acid (DTPA; oven dry basis, throughout this paper) for 30 min at 50 °C. The pulp was brought to the desired consistency using distilled and deionized water, followed by acidification to pH 4.5 (dilute sulfuric acid) prior to the addition of the chelant (in the form of a 4 g/L solution). Finally, the pulp was thoroughly washed with deionized water.

Oxygen delignification was carried out with 25 g of oxygen-delignified pulp samples in a specially designed kettle reactor. The temperature of the bleaching experiments was 90 °C, and the pulp consistency was 10%. The NaOH charge was 2.5%, and the charge of $MgSO_4$ was 1%. When the activator was injected in the middle of the stage, additional charges of NaOH (1%) and $MgSO_4$ (0.5%) were applied to aid solubilization and to compensate for the dilution effect the added water would have on the overall delignification. This excess charge was arrived at by a series of preliminary experiments where a certain amount of water was added in the middle of the delignification, seriously disrupting the process. By adding incrementally increased charges of NaOH, we arrived at the conclusion that an addition of 1% NaOH was necessary to compensate for the effect of dilution. A somewhat better approach to this would have been to run the control and the activated experiments at similar initial pH values.

The desired charges of NaOH and $MgSO_4$ were mixed with the pulp samples in a Hobbart mixer, and the mixture was then transferred to polyethylene bags. The samples were preheated to the required temperature in a microwave oven. The preheated pulp samples were then placed in the reactor and preheated to the target temperature, and mixing at 10 rpm commenced. Approximately 15 min was allowed for the temperature to equilibrate, and then the reactor was pressurized with oxygen at 100 psig.

Chemical injection during the delignification was carried out via an injection chamber. At the desired time, the injection chamber was attached to a pressure kettle reactor. After approximately 15 s (so as to equilibrate the pressure in the reactor and injection chamber), an oxygen pressure of 70 psig was applied. The chemical solution was injected by the flow of oxygen through the injection chamber.

Chart 1. Nitrogen-Centered Potential Activators Applied in the Oxygen Delignification Trials



After a total of 60 min of reaction time, the reactor pressure was released and the pulp sample was discharged and thoroughly washed with distilled water.

Standard handsheets were then made, and brightness (standard E.1), K number (standard G.18), viscosity (standard G.24P), and *z*-span tensile strength (standard D.37P) measurements were carried out using standard Pulp & Paper Technical Association of Canada procedures.

Results and Discussion

Originally, the idea of introducing an activator during an oxygen delignification stage was based on the fact that the efficiency of oxygen decreases in the later stages of the process. The introduction of an activator at that point would generate a more powerful oxidative system, which may then compensate for the lower reactivity of the residual lignin. This phenomenon was confirmed by an initial experimental curve for our oxygen bleaching system, where it became apparent that a rapid K number reduction, during the early stage of the process, decreased with time. During the second half of the process, only a marginal K number reduction was observed. Our approach was to perform two oxygen ministages, separated by the injection of the activating system, within a single oxygen delignification stage. For this “two-in-one” oxygen bleaching stage, we examined certain nitrogen-centered activators in the presence of hydrogen peroxide as potential activating systems aimed at increasing the oxidizing power of oxygen during the later stage of oxygen delignification and increasing the overall efficiency of the delignification process.

Comparison of the Efficiencies of Different Potential Activators. A number of different potential N activators were examined as potential activators for oxygen delignification, as shown in Chart 1.

A literature search when coupled with our preliminary tests indicated that activators of this type cannot work efficiently without the presence of hydrogen peroxide. The pertinent data and rationale for this effect will be expanded upon in a subsequent part of this paper. A comparison of the delignification efficiencies for various activators (Figure 1) showed that, with the exception of 1,10-phenanthroline and pyridine, no other compound from this group of activators can significantly improve the delignification efficiency of oxygen or peroxide-reinforced oxygen. In several cases, the K number reduction is even lower than that of the peroxide-only control counterpart. This finding, however, is not in agreement with the work of Jaschinski and Patt, in which they demonstrated that bipyridyl and

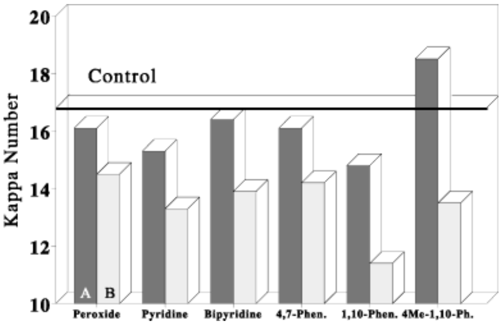


Figure 1. K number reduction of activated oxygen-delignified pulp. The control line was obtained from oxygen delignification without activator addition. A comparison of different N-centered activators added at the onset of the stage (A, activator charge = 0.033 mmol/g of pulp) or injected after 30 min of reaction time (B, 0.017 mmol/g). See the Experimental Section for more details. Pyridine charges were doubled, to maintain an equimolar charge of nitrogen. Temperature: 90 °C. Retention time: 60 min. Pressure: 100 psi. NaOH: 2.5%. $MgSO_4$: 1%. Injection: NaOH, 1%; $MgSO_4$, 0.5%; H_2O_2, 1%. Activator charges are as described previously.

tetramethyl-1,10-phenanthroline were also reported to be efficient at improving peroxide-reinforced oxygen delignification.[38] This discrepancy could be explained by different reaction conditions (higher temperature and longer reaction time) and also by the amount of peroxide present in the two sets of delignification experiments (4% compared to 1% in our experiments). It was surprising to find tetramethyl-substituted 1,10-phenanthroline being inefficient (actually, decreasing the effect of peroxide) as compared to unsubstituted 1,10-phenanthroline. The proper mechanism of action of phenanthroline/peroxide in pulp bleaching is not yet accounted for. Consequently, the logical explanation offered for the difference is the effect of the actual methyl group. 4,7-Phenanthroline was also inefficient in improving the efficiency of peroxide-reinforced oxygen delignification. The inactivity of this phenanthroline is likely caused by the location of the heterocyclic nitrogen within the phenanthroline.

The addition of activators by injecting them during oxygen delignification after 30 min from the onset of the reaction (the B series in Figure 1) showed significantly improved K number reduction for every activating system when compared to activation by the addition of an activator at the beginning of the oxygen delignification stage. The potency of injecting the activator after 30 min is further demonstrated by the fact that better delignification efficiencies were apparent, despite the fact that only half of the amount of the activator was used (0.017 mmol/g) as opposed to the amount of the activator (0.033 mmol/g) when introduced at the onset of the reaction. The efficiency patterns remained the same, with the best K number reduction figures being obtained with the injection of 1,10-phenanthroline (K = 11.4; 62% delignification; Figure 1). Pyridine (K = 13.2; 56% delignification) was the only other compound that showed an improvement of the K number reduction when compared with the addition of peroxide (K = 14.8; 51% delignification). However, the effect was less pronounced when compared to that of 1,10-phenanthroline.

It is apparent from this set of experiments that the injection of the activating system during oxygen delignification augments the efficiency of oxygen delignification. Furthermore, the efficiency of this form of activation is superior to that from addition of the activator at the beginning of the delignification stage. On the basis of the demonstrated efficiencies, 1,10-phenanthroline (containing two heterocyclic nitrogens) and pyridine (containing one heterocyclic nitrogen) were chosen as representative members of these activators for a more detailed investigation of the factors and parameters affecting their efficiency.

Table 1. Effect of the Different Components of the Activating System on the Overall Efficiency of Activated Oxygen Delignification[a]

injection	K	brightness [% ISO]	viscosity [mPa·s]
control O_2 delignified	16.8	35.9	26.7
H_2O	18.4	34.0	
NaOH, $MgSO_4$	15.0	38.4	31.6
NaOH, $MgSO_4$, H_2O_2	14.8	45.0	28.0
NaOH, $MgSO_4$, 1,10-phenanthroline	14.8	37.8	26.0
NaOH, $MgSO_4$, H_2O_2, 1,10-phenanthroline	11.4	49.9	24.8
NaOH, $MgSO_4$, Cu^{2+}	13.2	38.8	12.1
NaOH, $MgSO_4$, Cu^{2+}, 1,10-phenanthroline	12.0	40.8	10.8
NaOH,$MgSO_4$, Cu^{2+}, H_2O_2, 1,10-phenanthroline	10.9	40.4	9.5

[a] Initial K number: 29.9. Retention time: 60 min. Temperature: 90 °C. Pressure: 100 psi. NaOH: 2.5%. $MgSO_4$ and H_2O_2: 1%. Injected 1,10-phenanthroline charge: 0.6%. Cu^{2+}: 200 ppm. Charges are based on oxygen-delignified pulp.

Effect of Metal Ions and Hydrogen Peroxide. The use of 1,10-phenanthroline as a catalyst of alkaline oxygen pulping has been described by Germer and coworkers.[35−37] The mechanism of action of phenanthroline for oxygen pulping described by this team proposed the participation of heavy-metal ions present in the wood.[36] More specifically, phenanthroline acted as a ligand, coordinating with metals in the pulp to form complexes capable of activating oxygen during the delignification process. Similarly, in recent years, a new potent delignification system based on coordinated transition-metal (Cu) compounds has been described.[39−41] The later system, however, requires hydrogen peroxide or other organic peroxides as an essential component for activity. Heterocyclic nitrogen compounds (pyridine derivatives) were tested for their efficiency as coordinators for this system. Pyridine or polypyridine-based compounds have also been reported to be able to activate hydrogen peroxide delignification in the absence of the transition metals, i.e., chelated pulps.[38]

During this effort, an attempt was made to compare the ability of phenanthroline to activate oxygen delignification in the presence of hydrogen peroxide and/or copper ions. The activation system we examined was introduced 30 min after the beginning of the oxygen delignification stage.

To study the effect of metals on the performance of the activating system, the metal content of the pulp was reduced by a chelation stage prior to oxygen delignification. The activating system consisted of an N activator, hydrogen peroxide, alkali, and $MgSO_4$. The effect of each of these components on the resulting delignification was thus examined in detail. An additional set of experiments was also designed to examine the effect of the presence of copper ions on the activation and oxygen delignification efficiency.

The data of Table 1 show the K number, brightness gains, and viscosity obtained when adding each component of the activating system. To simulate and study the effect of consistency change that accompanies the addition of the activator, 25 mL of water in the absence of any additives was injected into the system. Lowering the consistency and thus decreasing the alkali concentration were found to have a negative effect on the efficiency of delignification. The addition of the extra oxygen in the middle of the stage was found to have no effect on K reduction. Injection of extra alkali together with $MgSO_4$ improved the K number reduction by approximately two K units. Injection of hydrogen peroxide with extra alkali showed a slight decrease in the K number but a significant increase in brightness gains. A low level of metals in the prechelated pulp was found to prevent hydrogen peroxide from decomposing and consequently improving delignification. The low peroxide decomposition was also reflected in increased brightening effects (45.0% ISO).

Injecting 1,10-phenanthroline showed an improvement in the K number reduction identical with that of peroxide (K = 14.8), but the brightness gains were not significant. The addition of hydrogen peroxide together with 1,10-phenanthroline showed a dramatic increase in both delignification and brightness gains. A K number of 11.4 and a brightness of about 50% ISO can be achieved by this activating system. Consequently, it was confirmed that N activators do not efficiently activate oxygen delignification in the absence of hydrogen peroxide.

The injection of copper (Cu^{2+}) ions in the oxygen delignification stage together with extra alkali was found to improve the K number reduction without brightness gains. An activating system consisting of copper ions with 1,10-phenanthroline was found to further decrease the K number, with a slight increase in brightness. Injecting copper ions, 1,10-phenanthroline, and hydrogen peroxide resulted in the greatest decrease in the K number (10.9). These data correlate with the findings of Messner and co-workers, who reported that an activating system consisting of peroxide, copper ions, and polypyridine as a coordinating center is capable of efficiently activating oxygen delignification.[41] However, an examination of the viscosities of the bleached pulps showed that the presence of Cu^{2+} ions in the oxygen bleaching system also activates carbohydrate degradation. For all of the experiments with Cu ions present, the viscosity dropped from approximately 30 mPa·s (control) to the level 10−12 mPa·s.

It was thus concluded that for the Cu/peroxide/phenanthroline combination, while capable of efficiently activating oxygen delignification, its low selectivity precludes it from being a viable activation system. In contrast, the combination of hydrogen peroxide/1,10-phenanthroline was found to activate oxygen efficiently and selectively. The efficiency of the K number reduction was only slightly lower (11.4 to 10.9 with Cu^{2+}), while the pulp viscosity remained at an acceptable level (24 mPa·s) and the brightness gains increased significantly (40−50% ISO with Cu^{2+}). One may thus conclude that the presence of copper ions not only increased carbohydrate degradation but also increased degradation of hydrogen peroxide.

Effect of 1,10-Phenanthroline and Pyridine Charge. As shown in Figure 2, using 1% NaOH and 0.5% $MgSO_4$ charges and injecting them together with the various activator charges showed a marked decrease in the K number for charges of 1,10-phenanthroline up to 0.3%. Higher activator charges resulted in only a marginal K number decrease. It is apparent that even the injection of small charges of the activator may cause significant improvements in the K number reduction; however, a level of 0.3% of the activator seems to be optimal for the K number reduction. At this charge, the delignification efficiency of oxygen delignification was found to be increased by 11% compared to its control counterpart (1% peroxide-reinforced oxygen delignification) or by 19% compared to a conventional oxygen delignification stage. Similar trends were also observed for pyridine; however, its efficiency was lower than that of phenanthroline. At the optimal charge of pyridine (0.25%), the delignification efficiency was improved by 5% in the presence of H_2O_2 or by 13% compared to a conventional oxygen delignification stage.

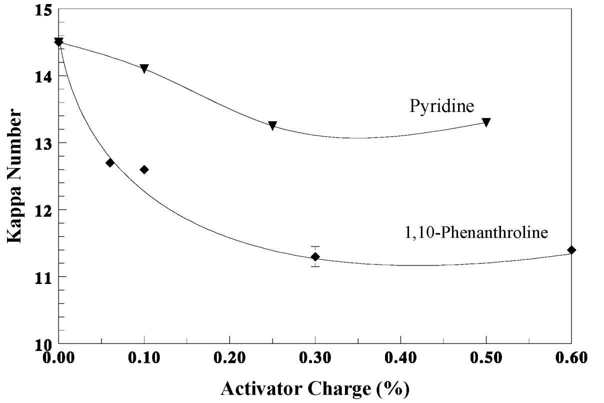


Figure 2. Effect of the activator charge on the K number reduction for black spruce kraft pulp (K = 29.9). Temperature: 90 °C. Retention time: 60 min. Oxygen pressure: 100 psi. NaOH: 2.5%. $MgSO_4$: 1%. Injection: NaOH, 1%; $MgSO_4$, 0.5%.

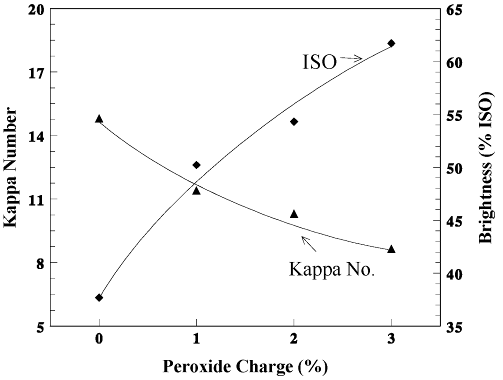


Figure 3. Effect of of the peroxide charge in the injected activator system on the K number reduction and brightness gain. O-stage conditions: temperature, 90 °C; pressure, 100 psi; NaOH, 2.5%; $MgSO_4$, 1%. Activator injection: NaOH, 1%; $MgSO_4$, 0.5%; 1,10-phenanthroline, 0.3%.

Effect of Hydrogen Peroxide Charge. Hydrogen peroxide applied during oxygen delignification has been shown to increase the delignification efficiency of such a stage,[34] and this increase is directly proportional to the applied charge. When 1,10-phenanthroline was applied in the absence of hydrogen peroxide, a very small amount (practically negligible) of oxygen activation was observed. This minor activation can be attributed to the fact that some H_2O_2 is generated during an oxygen stage as a consequence of the oxygen being reduced to water via peroxide. However, at 1% peroxide charge, the efficiency of phenanthroline (0.3% charge) was found to increase dramatically (Figure 3). The efficiency of the phenanthroline/peroxide activating

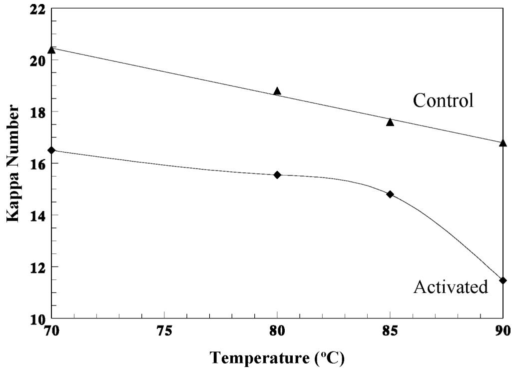
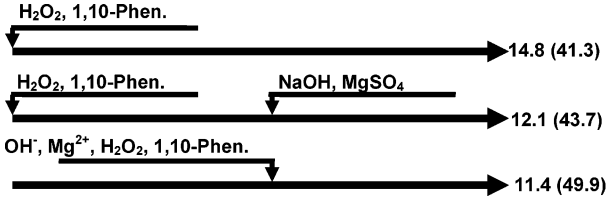


Figure 4. Effect of the temperature on the efiiciency of the activated O-stage (injection) toward the brightness gain and K number reduction. O-stage conditions: pressure, 100 psi; NaOH, 2.5%; $MgSO_4$, 1%. Activator injection: NaOH, 1%; $MgSO_4$, 0.5%; H_2O_2, 1%; 1,10-phenanthroline, 0.3%.

Scheme 1. Comparison of Activation at the Beginning and during (at 30 min) the Oxygen Delignification Stage[a]



[a] K number and (brightness) O-stage conditions: temperature, 90 °C; total retention time, 60 min; pressure, 100 psi; NaOH, 2.5 %; $MgSO_4$, 1 %. Activator injection: NaOH, 1%; $MgSO_4$, 0.5%; 1,10-phenanthroline, 0.3%.

system increased with increasing peroxide charge, and a K number of 8.6 can be achieved at 3% peroxide charge.

Effect of Temperature. The optimum operating temperature of oxygen delignification has been established to be 90 °C (Figure 4). The objective of activation or catalysis in oxygen delignification is to increase the efficiency of the process, allowing for an enhanced degree of delignification to be obtained under otherwise identical conditions. Another approach to this may be decreasing the temperature required for a given level of delignification.

In accordance with previously reported work on the effect of temperature on oxygen delignification, the K number of the pulp after an O-delignification stage was found to linearly decrease with increasing temperature. Similarly, the efficiency of the activated oxygen delignification system was found to increase with increasing temperature, especially in the temperature regime of 70−85 °C. At the temperature interval of 85−90 °C, the effect of temperature toward enhancing delignification was even more dramatic when the activator was employed. In the presence of the activator, a temperature of 70 °C can delignify the pulp at a similar level as if 90 °C were used during an unactivated stage.

Comparison of Activation at the Beginning and during the Oxygen Delignification Stage. Industrially, it would be more feasible to introduce the activator at the same time that one adds all other bleaching chemicals, i.e., at the beginning of the stage. However, the data of Scheme 1 clearly demonstrate that the addition of the activator in the middle of the stage can produce a significantly higher K reduction number (3.4 units) and brightness gain (8.6%) than an oxygen stage activated at the beginning. Addition of extra alkali in the middle of the activated stage can reduce the K number (2.7 units), with only slight brightness improvements.

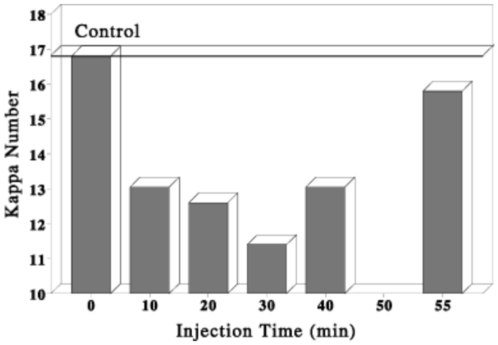


Figure 5. Effect of the activator injection time on the K number reduction. O-stage conditions: temperature, 90 °C; pressure, 100 psi; NaOH, 2.5%; $MgSO_4$, 1%. Activator injection: NaOH, 1%; $MgSO_4$, 0.5%.

During a detailed study, an injection time of 30 min was found to be the ideal instant for the introduction of the activator into the oxygen bleaching system (Figure 5). Activator injection at earlier times showed some improvement in the K number reduction, but the benefits of oxygen at the first stage of delignification were not fully realized. Activator introduction at later stages of oxygen delignification showed a significant decrease in the overall delignification. The reason for this decrease in efficiency can be attributed to insufficient time for the activated oxidative system to act.

Conclusions

(i) Nitrogen-centered activators coupled with hydrogen peroxide can effectively improve the delignification efficiency of oxygen delignification. Among the group of activators examined, 1,10-phenanthroline was found to be the most effective.

(ii) Injecting the activating system in the middle of the oxygen delignification stage maximizes the benefits.

(iii) The optimal charge of 1,10-phenanthroline was found to be 0.3%. However, this amount of phenanthroline may represent an increase of about 30% in the NOx discharge from the recovery boiler.

(iv) The presence of hydrogen peroxide was confirmed to be essential for activators of this type to operate.

(v) The presence of copper ions improved the efficiency of the activating system, with extensive carbohydrate degradation.

(vi) An injection time of 30 min was found to be the optimal time for the introduction of the activator into the oxygen delignification stage.

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