FINAL REPORT

LOW ODOR, HIGH YIELD KRAFT PULPING

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From

W.T. McKean, University of Washington

L. L. Edwards, University of Idaho

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ABSTRACT

In laboratory cooks pure oxygen was profiled into the circulation line of a batch digester during two periods of the cooking cycle: The first injection occurred during the heating steps for the purpose of in-situ generation of polysulfide. This chip treatment was studied to explore stabilization against alkaline induced carbohydrate peeling and to increase pulp yield. Under optimum conditions small amounts of polysulfide(1.3 g/l) were produced with yield increases of about 0.5%. These increases fell below earlier reports suggesting that unknown differences in liquor composition may influence the relative amounts of polysulfide and thiosulfate generated during the oxidation. Consequently, further studies are required to understand the factors that influence the ratios of those two sulfur species.

The second oxygen injection occurred at the end of kraft pulping, before pressure release from the digester. At that time in the cooking cycle, all odorous sulfur compounds are contained in the digester at their highest concentrations. So an effective oxidation may result in conversion of all species to non-volatile form and may provide the basis for low or zero odor kraft mill operations. Kraft cooks of Douglas fir chips to low(28 to 29) and high(95 to 96) kappa with and without introduction of oxygen at the completion of the cook were carried out in 10 liter, laboratory, circulating batch digester. The results indicate that all of the hydrogen sulfide, methyl mercaptan and dimethyl disulfide species were converted to nonvolatile compounds by the IDO treatment in from 4 to 7 minutes. Dimethyl sulfide was reduced in concentration by about 50% under the same conditions. Furthermore, the results indicate that the oxidized sulfur compounds were not susceptible to reversion to the odor-causing, reduced forms. At the optimum temperature(125° C), approximately 2% oxygen(on OD pulp) was required for all TRS destruction(except ≈ ½ of the DMS). Finally IDO had no significant impact on pulp yield, physical properties or bleachability.

Oxidation reaction time depends on oxygen pressure. As an example, 10 minutes at 125° C and 40 psig oxygen pressure would result in full destruction of hydrogen sulfide, methyl mercaptan and dimethyl disulfide. Complete oxidation of the sulfide, MM and DMDS in the main extraction line of a continuous digester should be achievable by including a 0.25 m^3 oxidation segment for each MT/hr of liquor flow between the digester and the first flash tank and adding 5.2 lb O_2/ton of liquor.

Profiling of oxygen into the early periods of digester heating cycles can produce small yield increases, but further work if required to understand the chemical basis as a basis for attempting to reach higher yields. Profiling oxygen into the circulation lines of continuous digesters appears to provide a feasible approach to lower cost, low odor kraft mill operations. Odor control in batch digester systems appears more difficult since the low liquor circulation rates at the end of the cook will create difficulties in efficiently contacting the oxygen with the full digester liquor charge.

TABLE OF CONTENTS

INTRODUCTION 3

OBJECTIVES 3

ODOR CONTROL BY IN-DIGESTER BLACK LIQUOR OXIDATION(IDO) 3

- Background 4
- Approach 5
- Summary 6

YIELD INCREASE BY OXYGEN PROFILING IN THE BEGINNING OF THE KRAFT COOK 6

- Background 6
- Approach 7
- Summary 8

LITERATURE CITED 8

APPENDICES 9

INTRODUCTION

Development of low odor, high yield kraft pulping technologies continues to be a priority of the forest products industry. Sodium sulfide which is an essential component in the kraft pulping process results in generation of several reduced sulfur compounds(TRS). Release of the digester contents at the end of pulping results in atmospheric emissions of TRS substances from numerous points in the fiber line. The major emission points can be controlled by add-on collection and combustion systems. But, the numerous low concentration sources remain untreated, so the presence of these odorous compounds can sometimes still be detected in the vicinity of kraft mills.

Since all odorous sulfur species are contained in the digester, their complete destruction before the digester pressure release could eliminate the need for collection and treatment of the multiple fiber line emission points. So this technology could permit near-odor free operations. Early work demonstrated that oxidation of the black liquor above about 130° C would dramatically reduce the amount of volatile, odorous TRS compounds. This project determined optimum in digester oxidation(IDO) conditions for odor control, for negligible liquor reversion at minimum impact on pulp properties and the impact on black liquor heating values and mill operations and costs.

Early work also demonstrated that IDO applied during impregnation, heating and in the early period of cooking may produce increased yields relative to conventional kraft pulping. This project explored optimum conditions for improved yield, bleachability and for minimum impact on mill operations and costs. Thus, the total scope of the project demonstrated the potential for oxygen profiling in the early and late periods of kraft pulping to produce higher yield and low kraft odor.

OBJECTIVES

OBJECTIVE 1:

Demonstrate the feasibility for irreversible oxidation of all odorous kraft sulfur compounds to non-odorous species before pressure relief to atmospheric conditions(IDO). Optimize the oxidation to obtain zero odor with minimum oxygen consumption and impact on liquor heating value and on pulp properties and bleachability.

OBJECTIVE 2:

Increase yield by optimized oxygen injection during the early periods of kraft pulping. Maximize pulp yield while retaining pulp properties and bleachability.

The following discussion of results is divided into two parts associated with OBJECTIVES 1 and 2.

I. Odor Control by In-Digester Black Liquor Oxidation(IDO)

1.0 Background

Unavoidable generation of odorous sulfur compounds associated with the kraft process has been well documented(Sarkanen, et. al. 1970). In kraft digesters the sulfide added with white liquor exists as a pH and temperature-dependent mixture of sulfide($S^=$) and hydrosulfide(HS^-) anions. These strong nucleophiles react with lignin methoxyl groups to produce methyl mercaptan(MM) and dimethyl sulfide(DMS) in a two-step reaction sequence(McKean, Hrutfiord, Sarkanen 1965). Consequently, MM and DMS accumulate to maximum concentrations in the digester at the end of the cook. Dimethyl disulfide(DMDS) forms solely by oxidation of MM. Generally, the digester is devoid of oxygen, so conversion of MM to DMDS during pulping will be limited by the presence of trace amounts of oxygen or of small amounts of wood-derived oxidizing agents. Total DMDS concentration will slowly increase during pulping, but will be limited by simultaneous hydrolysis reactions(Bentvelzen, McKean, Gratzl 1976).

The concentrations of $S^=$ (and HS^-) decline during pulping(McKean, Gratzl 1974) as a result of consumption during lignin degradation reactions. However, these species are partially regenerated by alkaline-induced splitting of sulfide from the lignin(Rydholm 1965) toward the end of the cook. With sufficient residual alkali, sulfide behavior approaches that of a catalyst and the sum total of sulfide and hydrosulfide consumed during pulping declines by only 10 to 20%.

The pH-dependent hydrolysis of these two species is shown below:

$$S^= + H_2O \overset{pK\approx 13}{\Leftrightarrow} HS^- + OH^- \qquad (1)$$

$$HS^- + H_2O \overset{pK\approx 7}{\Leftrightarrow} H_2O + OH^- \qquad (2)$$

Normal kraft digester pH values fall in the range of 11 to 14, resulting in distribution between the $S^=$ and HS^- forms over all kraft digester conditions. However, hydrogen sulfide(H_2S) can be formed from the hydrosulfide ions when the pH falls below about 8. Since these pH levels may be approached in pulp washing, black liquor oxidation and in the recovery furnace area, the potential exists for some H_2S formation and emission from those processes by air or steam stripping of the volatile gas. Consequently, black liquor oxidation systems(BLO) have been developed to prevent emissions by converting residual sulfide in the black liquor to nonvolatile sodium thiosulfate and sodium sulfate. In these systems, air or oxygen is added to a sparged tank reactor operating at 60 to 90° C and at atmospheric pressure. In well designed units nearly all the $S^=$ becomes oxidized with liquor retention times of 1.5 to 2.5 hours. Partial MM and DMDS oxidation occurs while DMS resists oxidation under these conditions. In early BLO systems some $S^=$ would reform(reversion) after the oxidation. Modern systems operate with sufficiently severe oxidation to minimize reversion.

The quantities of MM, DMS and DMDS in the digester vary with wood species, sulfidity, pulping time and temperature. Release of the digester contents at the end of the cook results in pH or stripping dependent atmospheric emissions of the odorous substances from numerous points in the fiber line. Despite major improvements in odor control, the presence of these odorous substances can still be detected in the vicinity of kraft mills. Fiber line emissions containing the sulfur compounds range from low volume, high concentration from the digester area and from some black liquor oxidation systems to numerous high volume, low concentration streams. "Add-on" collection and combustion processes control emissions from many of the low volume sources. These add-on systems, while costly, reduce the "circle" of detection around the mills. Because of leaks, the hard to treat, low concentration sources and the high sensitivity of many people to traces of sulfur compounds, cost effectiveness of these processes are approaching a limit. So a truly sulfur odor free kraft mill may require modified approaches.

In-digester black liquor oxidation(IDO) may provide a basis for more complete odor control for the whole fiber line and associated recovery steps. Virtually all of the substances associated with kraft odor are contained in the digester before blowing to atmospheric pressure and will rapidly oxidize at elevated temperatures. For example, the $S^{=}$, MM and DMDS were totally converted to non volatile species when oxidation was done at 120 to 170° C in the digester before release of the digester contents to atmospheric pressure(Kringstad, 1972; McKean, 1974). Furthermore, no reversion of oxidized species occurred during subsequent storage and liquor evaporation(McKean, 1974; Bentvelzen, 1976; Vance, 1977). Oxidation just prior or during the digester blow required about 1.9% O_2 on wood which amounts to about 25% more than used in weak or strong BLO. So the higher temperature IDO probably consumed some oxygen by oxidation of black liquor organic substances. This is in contrast to the high consumption reported after liquor pH adjustment and oxygen injection 30 to 45 minutes before the digester blow(Fones, 1960). These studies suggest that IDO time and temperature could be optimized to minimize oxygen consumption while achieving high oxidation efficiency of the TRS substances. But the best range of oxidation conditions requires further study to evaluate the cost effectiveness of IDO.

2.0 Approach

The present study was conducted in laboratory batch circulation digesters equipped to oxidize the circulating liquor by oxygen injection into the circulation line and to periodically collect small samples of circulating liquor for chemical analysis. The experimental design included:

1. Determine total reduced sulfur compounds(Σ MM, DMS, DMDS, $S^{=}$, HS^{-} = TRS), sodium thiosulfate, sodium sulfate content and organic/inorganic ratio and heating value of black liquor from laboratory cooks for linerboard and bleachable grade pulps;

2. At the end of the cook, but before the digester blow, inject oxygen(IDO) into the digester over a range of conditions and determine TRS oxidation efficiency and changes in the liquor heating value.

3. Test stability of IDO liquors in terms of reformation of TRS substances.

4. Measure strength and bleachability of pulps with and without IDO.

3.0 Summary

Detailed results of a laboratory investigation of in-digester black liquor oxidation (ID) for the oxidation of TRS compounds from kraft pulping are given in an M.S. thesis authored by Wilson and contained in Appendix I. Kraft cooks of Douglas fir chips to low(28 to 29) and high(95 to 96) kappa with and without introduction of oxygen at the completion of the cook were carried out in 10 liter, laboratory, circulating batch digester. The results indicate that all of the hydrogen sulfide, methyl mercaptan and dimethyl disulfide species were converted to nonvolatile compounds by the IDO treatment in from 4 to 7 minutes. Dimethyl sulfide was reduced in concentration by about 50% under the same conditions. Furthermore, the results indicate that the oxidized sulfur compounds were not susceptible to reversion to the odor-causing, reduced forms. At the optimum temperature(125° C), approximately 2% oxygen(on OD pulp) was required for all TRS destruction(except ≈ ½ of the DMS). Finally IDO had no significant impact on pulp yield, physical properties or bleachability.

Incorporation of the odor control reaction kinetics, determined above, into a GEMS model of a kraft pulp mill allowed prediction of mill level results. Of course, the oxidation reaction time depends on oxygen pressure. As an example, 10 minutes at 125° C and 40 psig oxygen pressure would result in full destruction of hydrogen sulfide, methyl mercaptan and dimethyl disulfide. Complete oxidation of the sulfide, MM and DMDS in the main extraction line of a continuous digester should be achievable by including a 0.25 m^3 oxidation segment for each MT/hr of liquor flow between the digest and the first flash tank and adding 5.2 lb O_2/ton of liquor. More complete details of the model development and predictions under a range of operating conditions are given in an M.S. thesis authored by Fox and contained in Appendix II.

II. Yield Increase by Oxygen Profiling in the beginning of the Kraft Cook

1.0 Background

The major components in wood are cellulose, hemicellulose and lignin with proportions that depend on wood species. During kraft pulping the major objective is lignin removal to an extent which depends on the pulp product. Sulfide anion, which is an integral part of kraft pulping liquor, contributes to those reactions which result in degradation of the lignin macromolecule during pulping. Ideally we would retain all of the cellulose and most of the hemicellulose with removal of about 90% of the lignin. In kraft pulping

some cellulose and considerable hemicellulose is degraded and dissolved along with the lignin. Consequently, yield loss is an inevitable result of the pulping reactions. Since the lignin must be removed, attempts to increase kraft pulp yield normally focus on stabilizing the cellulose and hemicellulose portion of the wood against degradation by the alkali present during the pulping reactions. Loss of the carbohydrates involves hydroxide induced modification of the reducing sugar present at one end of each polysaccaride polymer. The resulting peeling reactions ,which are described in more detail in the M.S. thesis by Witworrasakul located in Appendix C, convert the reducing sugars to soluble form and result in yield losses. In normal kraft pulping these reactions result in dissolution of 5 to 10 % of the wood cellulose and up to 50% of the hemicellulose. Efforts to increase yield usually involve disruption of the hydroxide induce peeling.

Addition of polysulfide to normal kraft liquors represents one approach to increasing the pulp yield. Polysulfide oxidizes the reducing end-group to a more alkali stable form. Thus, oxidized cellulose and hemicellulose suffer less degradation which consequent yield increase. An extended discussion of the chemistry is given in Appendix C. Several technologies are available to generate polysulfide in kraft liquor. They involve considerable capital investment. So the premise of this project was to attempt low cost, polysulfide generation directly in the digester and in the presence of the wood chips during heating steps. It was hoped that the small amount of polysulfide generated during the oxidation directly in contact with the chips would result in the stabilization described in Appendix C.

The objective of this work focussed on oxidation of the black liquor/white liquor blends typically present during digester heating.

2.0 Approach

Kraft cooks were made in a 10 liter laboratory batch digester at normal conditions. Replicate cooks were made with addition of oxygen to the digester circulation line during heating steps. Samples of the circulating liquors were assayed for polysulfide and for active alkali. Pulp were compared for the two systems to measure the effects of the oxidation step in terms of yield, pulp chemical composition and pulp properties. Pulping conditions were adjusted in a systematic pattern to seek optimum conditions for yield increases.

3.0 Summary

The oxygen pressure, reaction temperature and proportion of black liquor/white liquor influence the quantity of polysulfide and thiosulfate generated during the oxidation. Of course, the appearance of thiosulfate means that the liquor had been over-oxidized and the polysulfide was below expected levels. The optimum conditions for the oxidation were about 40 psig oxygen pressure, 60 to 80° C and about 25 minutes oxidation time. These conditions resulted in generation of polysulfide in the pulping liquor of about 1.3 g/l as S_o. However, even under the best conditions, sulfidity was considerably below the expected values since significant amounts of thiosulfate were formed during the

oxidation. In addition, the best yield increases amounts to about 0.5%. These results are different from earlier reported experiments. Consequently, it appears that some unknown, active catalysts may have been present in earlier work which were not present in the current study. These differences suggest the need for further study to identify catalysts and to better understand the underlying chemistry.

The experimental results described in Appendix C were incorporated in a GEMS model of an operating kraft mill to understand the overall mill impact on production rates. Excessive loss in sulfidity resulting from the oxidation step would require increased pulping time and cause a drop in production rate. So the IDO approach to yield increase does not appear attractive until improvements can be made in the oxidation selectivity can be made to favor polysulfide formation over the generation of thiosulfate.

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