4-1970

A Study of the Feasibility of Using a Pulping Aid with Polysulfide Kraft Cooks

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A STUDY ON THE FEASIBILITY OF USING A PULPING AID WITH POLYSULFIDE KRAFT COCKS

by

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A Thesis submitted to the
Faculty of the Department of Paper Technology
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

April 1970

ACKNOWLEDGEMENT

To my fellow students and friends, who have helped me so many times in so many ways, I could never begin to thank them. To the late Drs. Truman A. Pascoe and Robert A. Diehm, I will never forget them for the examples they set. To Dr. Stephen I. Kukolich for his guidance and suggestions, I will be eternally grateful.

ABSTRACT

The purpose of this paper was to determine the feasibility of using a pulping aid with a polysulfide kraft cook. Since any change in an operation such as pulping must yield a product such that the quality is better or not appreciably reduced and at the same time must be economically acceptible, the feasibility was based on these factors. Tests were made on a standard kraft cook, a polysulfide cook, a cook using the pulping aid alone and a cook using the pulping aid with the polysulfides. From the work conducted, there were no significant changes in the physical and optical tests performed while at the same time, a slight increase in the yield over the standard kraft cook was noted.

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Introduction

"In any pulping process, there is a constant challange to (a) improve the pulp quality, (b) increase the yield, and (c) reduce the operating costs" [1] It seems today seems today that there are very few major breakthroughs in any well established process. The manufacture of paper is no exception. What's more, the types of pulp and paper mills are many and none of them produce their product exactly the same. Each has its own little "tricks" is uses to get a better product at lower cost. There are two ideas that appear to have potential for many pulp mills. The first of these is the use of sulfer or polysulfides to increase the yield in the kraft cooking process. The second is the use of pulping aids, such as wetting agents and surfactants to aid in the penetration of cooking liquors into the wood, thus increasing the pulping efficiency. The use of pulping aids can be used in all types of pulping, not just kraft.

1. Diehm, R. A., Larson, H. L., and Meinstein, S. p364

Historical Background - Polysulfides

The fact that increasd concentrations of sulfur and polysulfides in kraft cooking liquors have resulted in higher yield has been known for more than twenty years. Most of the research in this area has been done in Scandinavia, with work also being done in Japan, Canada, and the United States. As expected, the results of this work varies with the species. Work therefore has been done on several species; Southern pine (1), Silver pine (2), Loblolly pine, other softwoods and Red Oak (3), and others (4,5). The general conclusion that has been reached indicate an increase in yield without any appreciable loss in strength. This strength loss was most noted in tear but this loss was not critical. There were some reports on the bleachability of the pulp but these reports were mixed.

According to Sanyer (3)and Barker (6), the polysulfides were obtained by adding elemental sulfur to the cooking liquor. There was no evidence that there was any colloidal sulfur in the system (7). The sulfur was connected to sulfide molecules. A normal sulfide molecule has the form, S^{-2}. A polysulfide molecule has the form S_n^{-2} where n=2,3,4.... In the cooking liquor the value of "n" is not a constant figure, for each molecule may have a different value for "n".

The major reason for not having a vast acceptance of the use of polysulfides and excess sulfur, is the high chemical loss. Effective recovery systems have not been worked out and the cost of operation with these losses and the affect they would have on the enviorment would be to severe.

The theory that has been proposed concerning the increase in the yield concerns the protection of the wood carbohydrates, probably through the oxidation of their reducing end groups by the polysulfides and decreased peeling-off degradation in alkali (3). By this mechanism then, the pulping liquors attack the lignins and have a reduced affect on the cellulose. It follows then that an increase in the yield should be attained because of the longer cellulose chains.

Historical Background - Pulping Aids

The application of surfactants as a pulping aid is another idea that could have wide acceptance in the paper industry. Work on the approach does not span the time that polysulfides do, but unlike them, it can be applied to just about every type of pulping.

It was shown by Brown (8) that the penetration of cooking liquors into wood cubes with the use of surfactants can be greatly increased. The relative amounts of these increases is related to the dryness of the wood. For example, a 50% increase in penetration may be realized with a very dry wood cube, but greenwood of the same species might show only a 2-3% increase. From this, he concluded that a more efficient pulping operation with less rejects was a possibility. He also concluded that the pulp would increase in strength and brightness and there would be an improvement in the washing of the pulp.

In 1960, work was done by Diehm and others (9) in the use of surfactants in cold caustic pulping of aspen wood. For their studies, sodium xylene sulfonate (SXS) was used. They first proceeded to verify the work of Brown. This they did. The next step was to compare cold caustic pulping of aspen wood with and without the use of SXS. The following conclusions on their studies were reached;

1) A softer pulp was produced, requiring less energy at the expellors.
2) There was an increase in yield.

3) Bursting and folding endurance developed as beating time was prolonged.
4) The pulps were slightly stronger then those made without the use of SXS.
5) The quality of the pulp was not diminished.
6) The pulp was bleachable.
7) Caustic liquor with SXS can be recycled because the SXS is not consumed.
8) The SXS pulps defiber faster.
9) The somewhat improved strength characteristics combonEd with the increased yield would tend to indicate a better fiber penitration, with less damage to the fibers.

In mill operations at Menasha's Otsego, Michigan mill, the use of a surfactant has been used. (10) This NSSC mill arrived at some of the same conclusions that were reached above. The surfactant was used in the impregnation step of the cooking cycle. The liquor penetration into the chip was improved and because of the lower internal resistance a more uniform distribution of the chemicals throughout the chip. Because of this,, There was a reduction in the number of uncooked centers thus improving the refining of the pulp and subsequent better paper quality and runnability. The actual cooking chemical was reduced in some cases.

The pulping aid used at the Otsego mill was Busperse-47 a product of Buchman Laboratories, Inc. Busperse-47 is composed of dimethyl amides of unsaturated, long chained fatty acids. It is unaffected by high temperatures and pressures or strong cooking liquors such that are present in a pulping process. It is resistant to hydrolysis and is non aqueous and non ionic.

In literature from the Laboratories, (11) the affects on several different kinds of pulp; bleached and unbleached NSSC, Bleached chemimechanical, sodium bisulfite and unbleached hardwood kraft, were mentioned. Of particular importance was the selection on kraft. Using a batch process, there was a two per cent increase in the yield and a reduction in the alkali consumption. Because of this, there was an overall saving of about $70 per day.

The mechanism that is belived working here is as follows. " the hydrophilic-lipophilic balance of Busperse-47 is such that in wood pulping systems the product is preferentially absorbed at resinified or lignified surfaces and had a relatively low affinity for the hydrophilic surfaces of cellulose. The penetration property of Busperse-47 is assumed to be related to these factors. As the cooking chemicals containing Busperse-47 react with the lignin and other materials that bind the fibers together, the adsorbed Busperse-47 disperses the eroded solids and thus exposes new surfaces for reaction. This results in a faster, more efficient softening of the interfiber bonding agents and a more rapid opening of the clogged capillary pores."[2]

While this interpertation is not exactly correct, a combination of the two methods would yield the combined affect of a microscopic chemical attack, with the polysulfides and a macroscopic physical attack the pulping aid.

2. Unpublished work form Buchman Laboratories page 3

Laboratory Work

Pulping

For this study, wood chips of Red Oak were used, These chips were of uniform size as they were all retained on a 3/8 inch screen. The chips were clean and contained very little bark. Actual measurment show less then .2% bark by weight. Samples of the chips were dried for 36 hours to obtain moisture content as all measurments are based on ovendry basis.

The cooking liquor was made up of a standard kraft cook. The contents of the liquor was;

Na_2S . . . . 9 actual grams/liter

NaOH . . . . 38 actual grams/liter

$NaCO_3$ . . . . 11 actual grams/liter

This resulted in a sulfidity of 30%.

The other liquors were composed of the formulation above, to which was added:

a) 1% (on O.D. fiber) of elemental sulfur

b) .5% (on O.D. fiber) of Busperse-47

c) 1% elemental sulfur and .5% Busperse-47

The liquor was added in a 4:1 liquor to wood ratio. The chips were cooked in the oil bath "bomb" digester because with it, uniform cooking time and temperature could be maintained. The time was four hours and the temperature was 175°C. Samples of about 100 grams of oven dry wood was used.

At the end of the cooking cycle, the digesters were removed form the oil bath were allowed to cool overnight. The following day, the cylinders were opened and the chips removed. The chips were broken up and then washed. The washing was done using a Buchner funnel until the filtrate was clear. The entire sample was placed in a oven for 36 hours. The sample was weighed and the yield was determined from this data.

Papermaking

Samples of each kind of pulp was taken and hand sheets were made on the equiptment form Noble and Wood. The sheets were then placed in the humidity room for 36 hours to condition the sheets.

Testing

The handsheets were tested for mullen, tensile, tear and brightness. All tests were run according to the methods prescribed by TAPPI except the tensile which was conducted on the Instron.

Discussion

The evaluation of the various was based on the physical tests that were performed. As mentioned the tests conducted consisted of mullen, tensile, tear and brightness. The discussion of each test follows.

Mullen

In general the test of mullen or burst, is a good indication of the bonding in the sheets. The data obtained for the four types of pulp are;

Standard Kraft Cook(SKC)	8.6 psi
SKC plus 1% elemental sulfur	8.8 psi
SKC plus .5% Busperse-47	8.7 psi
SKC plus sulfur and Busperse	8.9 psi

The differences in the results are within experimental error and threr fore it is assumed that there is no differences in the bonding of the pulp.

Tear

Most affecting the test of tear is the fiber length of the fibers. The longer the fibers, the greater the the tear. The bonding in the sheets is also responsible for a good quantity of the tear strength. The tests conducted on the handsheets show very little difference and consequently it is assumed that there is very little difference in the pulp and any test difference is due to experimental error.

Standard Kraft Cook	75.8 grams
SKC plus 1% elemental sulfur	75.6 grams
SKC plus .5% Busperse-47	75.0 grams
SKC plus sulfur and Busperse	76.2 grams

Brightness

No difference in the brightness was noted. No tests on the bleachability were conducted.

Standard Kraft Cook	26.5
SKC plus 1% elemental sulfur	26.7
SKC plus .5% Busperse-47	27.7
SKC plus sulfur and Busperse	27.0

Tensile

The greatest difference in the physical and optical tests were noted in the tensile tests on the handsheets. More than any other test, the tensile is dependent on the weakest section of the sample. Like a chain, it will break at the weakest section. Since the handsheets were made from the pulp without any refining or screening, the number of shives and uncooked portions was considerable. As the handsheet was formed these imperfections in the pulp became part of handsheet. These represent areas of poor bonding. The tensile test picked up the differences in the quantity of the number of shives and uncooked portions. Where two uncooked portions were in bonding contact with each other, a very weak portion of the hand sheet was produced. The greated the number of shives, the greater the chances of two uncooked bundles being together. The efficiency of the cook was thus based on this factor. A 10% increase in tensile was noted in the cook with elemental sulfur and the pulping aid. A slightly less increase was noted with the pulping aid alone. With just the elemental sulfur, the increase was not large enough to formulate any conclusions.

Standard Kraft Cook	3.46
SKC plus elemental sulfur	3.52
SKC plus Busperse-47	3.62
SKC plus sulfur and Busperse	3.81

Yield

Yield determinations were conducted on the pulps produced.

Standard Kraft Cook	42.0%
SKC plus 1% elemental sulfer	42.8%
SKC plus .5% Busperse-47	42.6%
SKC plus sulfur and Busperse	43.1%

Using the b sis of the standard kraft cook, the increase in the yield with the polysulfide cook was expected as reported earlier. The increase with the pulping aid was not expected and the increase is assumed to be with in the experimental error of the experiment. Of course of most importance is the combination of the elemental sulfur and the pulping aid. The largest was noted in this pulp over the standard kraft cook. From this data, it is belived that the combination of the two additions work well together and donot interfer with each other. If they did, the increase in yield would not be as large and prpbably would be less than any of the two method alone.

Conclusions

The following conclusions were reached on the study that was conducted.

1) The pulp that was produced was equivalent to or better then the physical tests that were conducted on the standard kraft cook.

2) There was a slight increase in the yield.

3) From the tensile tests on the hand sheets, the efficiency of the cooking was increased with the use of the pulping aid and the elemental sulfur.

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