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A STUDY OF HYDROTROPIC PULPING

by

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ABSTRACT

Aspen wood chips and hardwood thermomechanical pulp were cooked with Sodium Xylen Sulfonate solution in various cooking temperature, time length, chemical content and liquor to wood radio.

The process had a very high yield but the products produced a poor strength. Brightness was increased slightly by the treatment. Kappa Number was decreased at the beginning of the cook but increased again as the cook proceeded.

Based on this experimental data, hydrotropic pulp produced from wood chips and thermomechanical pulp was inferior to ordinary chemical pulp (Kraft or Sulfate) both in terms of physical and optical characteristics.

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INTRODUCTION

The phenomenon of hydrotropic was first noted by Neuberg (1) in 1916. The possibility of its application on pulp production was first considered by R.H. McKee and students at about the same time (2). McKee, together with his students, had done a lot of investigation on hydrotropic delignification since then (3, 8). Although some researches in hydrotropic pulping have been done in America (9, 10, 11) most of the development has been carried out abroad (12). The most extensive studies have been carried out by Gromov and his associates in Russia (13).

McKee (5) proposed that a 25 to 30% solution of sodium xylenesulfonate could be used as a pulping solvent due to its effectiveness and relatively low cost (3). Ordinary size chips are cooked in pH of 3.5 for three hours at 315°F. (The temperature and cooking time may vary depending on the wood and the type of pulp desired.) The cooked chips can be washed with either water, dilute hydrotropic solution or water followed by hydroxide solution (14). The pulp can then be processed by the ordinary method.

The most important point of hydrotropic pulping lies in the recovery process. It consists simply of diluting the cooking liquor by adding water, filtering off the precipated lignin, and then evaporating the filtrate to the concentration of the original solution. Since the solubility of lignin in the hydrotropic solution is fairly high (about 350 grams per liter of solution) (3). The cooking liquor can be used five or six times before reprocessing is necessary. Some other modifications of the hydrotropic process that have also been proposed are: semihydrotropic pulping (6), hydrotropic kraft/sulfite pulping (15) and alkaline buffered hydrotropic pulping (14).

McKee compared his new process with the conventional one and claimed that the new process had (5, 6, 13):

- a simplier liquor recovery process
- a higher yield
- a higher alpha-cellulose content in pulp
- lignin which could be recovered in a reactive form
- by-products, such as furfural, which could be recovered
- a rapid pulping rate, thus no need to slowly preheat
- produced no air or water pollution
- lower equipment investment
- lower labor and chemical cost
- pulp which could be bleached easily
- easy chip penetration and washing

Gromov (16) had agreed with McKee on some of the advantages claimed; however, their reports had been challenged by other workers (17). Contractory statements may still be founded regarding the economic problems, the process and the pulp produced (16). A fairly complete account on this was given in a review article by Procter (19). All these problems can only be solved when reliable data over a wide range of process variables are made available. The object of this report is to study some of these variables.

THEORETICAL BACKGROUND

Nature of the Reaction

The hydrotropic pulping is basically a physical solution process in contrast to the chemical reaction phenomenon which is used in all other highly delignified pulping process (18). The hydrotropic phenomenon is (19), essentially, the increase of solubility in a wide range of compounds which are not usually water-soluble, by the addition of some dissolving aromatic acid salts in the solution. For example, in the pulping process, the concentrated solution of sodium xylenesulfonate acts as a solvent for water-insoluble lignin. Since the water-insoluble materials dissolve in hydrotropic solution without actual combination or interaction with the hydrotrope, this reaction may be described as a 'catalytic dissolving action' (12).

Mechanism of the Reaction

Noisillies et.al. (20) suggested that hydrotropic was due to the surface-active properties of the hydrotropic agents. Thus, a hydrotropic agent has a solubilizing action as a result of its ability to form ion-dipole bonds with water and the solvent. (For example, lignin hydrogen-bonds with the electron of aromatic hydrotropic agent.) Noisillies also claimed that the complex formation is apparently not the mechanism of hydrotropic. However, since water prehydrolysis is found to promote subsequent hydrotropic digestion (21, 22), it has been proposed that hydrolysis of lignin by hot water took place before the lignin dissolved. Gromov (22) showed that the presence of acidic or basic hydrolytic reagent would increase the reaction rate of the hydrotropic liquor which might be effective only after some lignin had been broken down.

Traynard (23) explained that at neutral medium: 'The hydrotropic reactant merely hydrolysis the bond between the lignin and the carbohydrates then dissolves the free lignin which therefore cannot polymerize.'

A more complete mechanism was offered by Gromov (24) who divided the process in three stages;

(a) Solubilization of the lignin in the wood, accompanied by the cleavage of the lignin-carbohydrate bonds (catalyzed by organic acid formed in the process) and also solubilization and hydrolysis of hemicellulose;

(b) Solubilization of the 'liberated' lignin;

(c) Further modification of the solubilized lignin and carbohydrate.

The organic acid forms during the delignification not only catalyze the reaction, it may also favor the hydrolytic degradation of hemicellulose especially at temperatures above 150°C (25).

Since the hydrotropic is essentially a surface-active agent (20), it will be obvious that the initial stages of the delignification are very rapid (8). The much slower process in the later stages of delignification (8, 17) can be explained by the theory proposed by Bailey (26), who stated that there were two kinds of lignin in wood; the 'free' lignin (which could be removed easily) and the other which was chemically combined with cellulose. The latter contributes to the extremely slow reaction at the end of the process. It was also suggested that the resistant lignin might be the result of condensation reaction (11).

Anyway, once the lignin content falls below a certain level, the rate of delignification will be so slow in comparison with the rate of dissolution of holocellulose (8) (or hydrolysis of pentosans and other polysacharides) that the lignin content of the pulp will increase. Gromov (27) proved by graphic method that the rate of lignin extraction was 1.9 times that of carbohydrate extraction.

One more interesting fact is the different rate of pulping between softwood and other materials, such as bamboo (8), bagasse (28) and hardwoods (29). It is proposed (19) that the guaiacyl lignin which would condensate after the hydrolytic cleavage of ary-ether was present in larger amounts in softwood. This may well be the reason of the lower efficiency of hydrotropic pulping of softwood.

Variables of the Reaction

(A) Time - It was first observed by Lau (8) and then by Springer et.al. (13) that the lignin removal in the initial state was very rapid. This rate was almost constant for a period of time, beyond that it would decrease with further heat, until it reaches an equilibrium point where the lignin content becomes constant. Further heating beyond this point would result in an increase of lignin content rather than a further decrease. Similiar results were reported by Kusumoto (15). The equilibrium point will be different for each choice of reaction condition. Generally speaking, a shorter cooking time will reduce the hydrolysis of pentosans and other polysaccharides, increase the pulp yield, improve its mechanical properties and reduce the possibility of degradation (24). However, it had been noted (8) that temperature and pH (13) were important factors too.

(B) Temperature - Increase in temperature will not only decrease minimum lignin content level but the cooking time is also decreased (8, 14). It was proposed that for a given bleachability, an increase of 10 degrees of temperature reduced the cooking time to about one-half (8). However, as temperature becomes higher, the rate of removal of hemicellulose increases and thus the yield is decreased. If alkalies are added to neutralize the organic acid formed during the process, temperature as high as 170°C can be used (29).

(C) pH - During the cooking, some organic acids, such as Acetic acid and Formic acid will be formed (24). Although the lower pH will assist the delignification, it will also degrade the cellulose to a greater extent (11). Thus, it may be desirable to neutralize these acids by adding either sodium sulfate or sodium chloride (22). The results are improved mechanical properties and a somewhat higher pulp yield. Other buffering reagent were also studied (25, 32), but they had the disadvantage of complicating the recovery process.

(D) Concentration of the Chemical - Most researchers used a 30-40% sodium xylenesulfonate solution (13, 14, 33) for their digestion. Since the delignification is dependent on the sodium xylenesulfonate only, a higher concentration may have the advantage of higher solubility of lignin (8). However, there is a certain range within which the concentration can be changed without serious effect on its solventing power. The difference in solventing power between a 50% solution and a 35% solution is small but the latter consumes less chemicals. Also, lower concentration solutiontion needs only be diluted in a lower ratio to lose its hydrotropic properties and precipate the dissolved lignin. Traynard (21) stated that even a 23% solution was powerful enough for the process.

(E) Lignin content in sodium xylenesulfonate solution - Since the lignin saturation point of a 30-40% aqueous sodium xylenesulfonate solution is about 350 gram per litre of solution (3), therotically the solution can be reused more than eight times before the saturation point is reached. However, after it has been used for 5 or 6 times, the solution becomes so viscous that its separation from the pulp is very difficult (8).

Although the level of organic materials in the solution can be controlled by adding fresh solution for each cooking, it has been found that the accumulation of lignin and other organic materials in the solution did not have any effect on the power of the solution or the properties of the pulp (8).

(F) Liquor to wood ratio - The liquor to wood ratios that are used by researchers range from 20:1 (34) to 6:1 (13). Although it is possible that the higher liquor to wood ratio may increase the rate of delignification, no study has been done on its effect on the quality of pulp produced.

EXPERIMENTAL DESIGN

The hydrotropic reagent used was Sodium Xylene Sulfonate solution. The original reagent was a purchased product with a concentration of 41.9%. Since moisture content in the chips set a limit on the maximum cooking liquor concentration that could be prepared, liquor with 30% or less solid was used in this project.

Part I:

The chips used were Aspen. The average size was about 1 1/2 inches long, 3/4 inches wide and 1/4 inch thick. Moisture content of the air-dried chips was determined by taking random samples from the whole batch. Wood chips with an equivalent oven-dried weight of 100 grams were put into a steel bomb of about one foot long and two inches in diameter. The prepared liquor was then poured into the bomb which was then sealed. A set of six bombs was then submerged into an oil bath which had been pre-heated to a certain temperature. (This temperature was controlled in such a way that it had a range of ± 5°C.) During the digestion, the bombs were rotated continuously to achieve an uniform digestion.

After digestion, the bomb was cooled, opened and the solution was drained while the pulp was still warm in order to prevent reprecipitation of the lignin from the liquor. The pulp was then washed with a 15% solution of Sdoium Xylen Sulfonate solution for 15 minutes, it was screened out and washed once with a 5% sodium xylen sulfonate solution and then twice with water. The chips were then air-dried for several days and samples were taken for yield and Kappa Number determination. The chips were disintegrated in a defibrator and then refined in a small Valley Beater to a freeness (Canadian Standard Freeness) of 300. Handsheets of 2.5 gm/Noble & Wood were prepared in a Noble and Wood Handsheet Maker.

Part II:

In the final stage of the experiment, it was decided that thermomechanical pulp would be used as an alternative wood source. A bag of thermomechanical pulp was obtained from Bauer Company of Springfield, Ohio.

The thermomechanical pulp was of hardwood origin. No chemical was added during the pulping and cleaning process at the Bauer Company. The light brown pulp had the form of cotton bundle. Handsheets were prepared from the untreated pulp as a control sample.

Cooking process in this part was about the same as in Part I. The only exception was a different washing procedure.

Since disintergration was not needed in this case, the pulp was not refined in the Bauer refiner.

Test in handsheets was performed according to the following method:

(a) Tensile strength: Tensile strength of the handsheets was tested by using the Instron Tensile Tester. In all cases, a strip of 25 mm width was used. No attempt was made to measure stretch and strain.

(b) Fold: Fold test was done by using the MIT fold endurance tester in accordance with TAPPI Standard Method T 511.

(c) Tear: Tearing force was tested according to TAPPI Standard Method T 414 ts-65. Four piles of samples was used in each case. The result was calculated according to the formula:

$$\text{Avg. tearing force} = \frac{16 \times \text{Avg. Scale Reading}}{\text{No. of piles}}$$

(d) Brightness: TAPPI Standard Method T 646 was used in testing the brightness of the paper by using a GE Brightness tester.

(e) Kappa Number: Kappa number was test according to TAPPI Standard Method T 236 m-60. A sample of approximately 0.5 gm was used in each run.

PRESENTATION AND DISCUSSION OF DATA

Yield

Generally speaking, the yield of the cooking process was rather high. With the exception of 6-30-175-2* (please see footnote), all the rest had yield higher than 85%. The presence of yield greater than 100% in both 6-30-150-1 and 6-30-150-3 might be caused by improper washing.

Tensile, Fold and Tear

Mechanical properties of these pulps were generally poor. Tensile strength ranges from 4 to 5 kg.; Fold ranges from 1 to 3 and tear from 13.5 to 28.0 gram. Properties of the pulp obtained from different process had differences so small that comparisons of data were difficult. However, increase in cooking time, (6-30-150-3 vs. 6-30-150-2), did increase the tensile strengths and folds of the paper. Increase in temperature, (6-30-175-2 vs. 6-30-150-2) gave similar effects. Since 6-30-150-1 had a freeness much higher than other pulps, it was not included in the discussion of mechanical properties.

* Nomenclature: In the text and in the figure, the following nomenclature was used to designate the various process. For example: 6-30-150-1 means that - liquor to wood ratio 6:1,
solid content in liquor 30%
cooking temperature 150°C,
cooking time 1 hour.

DATA FOR PART I

Cooking Condition	Yield	Basis Weight (gm)	Caliper (.001 in.)	Tensile (kg/25 mm)	Fold	Tear (gm)	Bright-ness	Kappa No.	pH	
									Initial	End
6-30-150-1	107.6	2.47	13.5	0.25	0	20	24.4	102	8.4	4.1
6-30-150-2	91.9	2.53	9.0	4.0	2	16	17.6	120	8.2	4.8
6-30-150-3	102.5	2.56	7.5	5.1	2.8	18.4	16.9	135	8.8	3.5
6-20-150-2	89.6	2.52	8.1	4.1	1	13.5	16.9	144	9.0	4.5
6-30-175-2	60.4	2.47	7.0	4.8	3	28.0	18.5	119	9.3	3.7
8-30-150-2	87.6	2.44	7.8	4.8	2.5	17.3	18.3	123	9.1	4.3

Brightness

As the highest brightness (in 6-30-150-1), was 24.4, increase in cooking time, liquor to wood ratio, cooking temperature and lowering of chemical concentration all seemed to have lowered it a certain extent.

Kappa Number

Since no bleaching was performed on the pulp, Kappa Number test was run instead. The resulting Kappa Number ranges from 102 to 144. Increase in cooking time and temperature increase the Kappa Number. It is possible that holocellulose was dissolved at the end of the cook. But the rate of lignin extraction was so low that holocellulose dissolve faster than the removal of lignin, thus increases the proportion of lignin in the pulp.

pH

As one would expect, pH of the liquor decreased during the pulping process, (from 8 or 9 to 3 or 4). This was the result of the formation of organic acid such as acetic acid or formic acid. An attempt was made to use sulfuric acid to neutralize the cooking liquor at the beginning of cooking, but the result was completely burned cook. Thus in other cookings, the liquor was used as it was and no pH control was made.

Refining

The 6-30-150-3 pulp was proved to be the easiest to refine. With the exception of 6-30-150-1 all the other samples took 30 to 90 minutes to refine to 300 CSF. The freeness of 6-30-150-1 stayed as high as 700 even after 2 1/2 hours of refining. Hence handsheets were prepared from the pulp with 700 freeness and no more refining was attempted. Longer cooking time would shorten the refining period while increase in temperature, chemical content and liquor to wood ratio all seemed to lengthen it.

Precipitation of Lignin

Since the most important aspect of the hydrotropic pulping is the recycling of cooking chemicals by precipitation of lignin from the cooking liquor, the efficiency of lignin precipitation was tested. Using a sample of a 30% solution, it was found that lignin started to precipitate when the liquor was diluted in a ratio of 1:3 (original:final). However, as the dilution factor was increased to 1:5, the efficiency of precipitation would increase slightly. (Lignin precipitated in 1:3 dilution was 0.0093 gm/c.c of original liquor, while in 1:5 dilution, it is 0.0165 gm/c.c). On the other hand, increasing the dilution factor meant more water to be evaporated, and thus more energy consumed, when the liquor was concentrated again for reuse. The economical factor must be considered if dilution was carried out in industrial process.

Part II

As a control, handsheets were prepared from the untreated thermomechanical pulp. After two cooks were performed, it was apparent that the treatment did not significantly improve the properties of the pulp. Subsequently, two more cooks were performed in order to determine the effect of washing and different chemicals.

In pulp 120-30-150-1 (I) regular sodium xylene sulfonate was used. In pulp 120-30-150-(II), the reagent used was of the same chemical nature, but it is a product from a different company. In pulp (III), the chemical and cooking condition were the same as in I except that after the regular washing, the pulp was washed twice with water at 50°C in order to remove the chemicals that might have precipitated on the surface of the fiber.

Yield

As in part I, the yield in each case was high. It ranges from the 81% in 12-30-150-1 (III) to 90% as in (II). Since a considerable amount of fines was lost during the washing of the pulp, the actual yield should be somewhat higher than indicated.

Caliper

Since high bulk is a property of thermomechanical pulp, the caliper of these handsheets are expected to be higher than that of the handsheets made from wood chips. However, caliper is not sensitive to the different treatments used in this experiment.

Tensile, Fold and Tear

The physical strength of the pulp is rather poor. It was unable to perform any fold test in the samples, since the strips broke down as soon as the spring was released. Thus a zero fold was recorded. This result is also reflected in the tensile data; all the samples had a tensile strength of less than 1 kg/25 mm strip. The hydrotropic solution treatment did not improve the strength of the pulp. It was thought that washing the pulp with hot water might help to wash away part of the lignin and hence increase the strength of the pulp. However, this process did not work very well in this case. As for tear, the treated thermomechanical pulp had a slightly lower tear. It might be accounted for as the

DATA FOR PART II

Cooking Condition	Yield	Basis Weight	Caliper (.001 in.)	Tensile (kg/25 mm)	Fold	Tear	Brightness	Kappa No.	pH	
									Initial	End
Control	-	2.53	9.2	0.5	0	23	18.5	115	-	-
12-30-150-1										
I*	88.4	2.49	12.4	0.4	0	16	19.2	108	9.1	5.4
II	90.5	2.51	11.7	0.42	0	16	21.9	103	8.2	6.7
III	80.9	2.53	12.0	0.46	0	15	17.4	106	9.0	5.2
12-30-130-5	90.1	2.52	10.4	0.54	0	18	20.4	113	9.1	6.6

*I Regular chemical, regular washing

II SXS (different chemical), regular washing

III Regular chemical, extra washing

sodium xylene sulfonate removed part of the lignin that coated the surface of the fiber, thereby increased the fiber bonding and decreased the tear.

Brightness

Of all the tested properties of the pulp, brightness was the only characteristics that was improved by the hydrotropic solution treatment. This should be an expected result since the darker lignin was removed in the process. However, in contrast to what was expected, extra washing did not improve brightness, but it decreased instead. It might be concluded that extra washing might have washed the excess chemical away, but the precipitated lignin stayed intact and decreased the brightness.

Kappa Number

Kapaa Number was slightly decreased by the treatment as expected. The Kappa Number changed from 115 to 105, indicating that there was a 10% lignin removal in the first hour of cooking. However, the difference between the controlled sample and the pulp cooked for 15 minutes was not big enough for any conclusions to be drawn.

pH

pH of the cooking liquors dropped about three to four point during cooking. The resulting liquor was not as acidic as it was in Part I. It was possible that since part of the organic acid in the pulp was removed during the thermomechanical pulping, there was not enough of it left to really change the pH of the liquor. For some unknown reasons, liquor prepared from the SXS (chemical produced by another company) had a pH closer to the neutral point both before and after the cook.

Refining

It was observed that during refining, the pulp was completely disintergrated to fine partical rather than the usual fibrillar form. However, if the weight on the blade of the Valley Beater was reduced to 2500 gm, (rather than 5500 gm according to the TAPPI Standard,) it was possible to retain a small portion of fibers. Thus refining in this part was performed by using a 2500 gm weight on the blades.

SUGGESTION FOR FURTHER STUDY

Although the result of this project seemed to be in contradiction to results obtained from researches, it had been predicted by Matthews (15). He claimed that the mechanical properties would be greatly improved if a short second stage cooking (Kraft or Sulfite) was performed. It might be feasible for future researches to investigate this possibility.

Kusumoto (17) had also performed similar experiments with Aspen, the results from which were equally unsatisfactory. Using other wood species may bring better results.

CONCLUSIONS

The pulp obtained by cooking Aspen wood chips with Sodium Xylen Sulfonate solution under various conditions gave high yield but poor mechanical and optical properties. Pulping thermomechanical pulp with hydrotropic solution turned out to be an unsatisfactory process. It yielded a pulp that had a physical strength that was lower than that of the untreated pulp. The only improvement was the slight increase in brightness.

The pulp obtained in both parts was very brittle, suggesting that hemicellulose had been removed from the fiber. It might not be feasible to use this pulp that had a fairly high lignin content as a source of bleached pulp. Lignin could be precipitated out of the used liquor if the liquor was diluted to a solution of 10% solid. The precipitation efficiency could be increased if the liquor was diluted more.

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