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A STUDY OF HIGH YIELD PULPING
USING HYDROTROPIC SOLVENTS |

Submitted to
the faculty of Western Michigan University
in partial fulfillment of the requirements
for the degree of Bachelor of Science

by
Milton Stibal
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ABSTRACT

A literature survey is presented concerning the use of hydrotropic solvents in producing wood pulps. The strength characteristics of three hydrotropic pulps (54, 77, and 85% yield) are investigated and compared to a commercial NSSC pulp. (70% yield)

The experimental results indicate that the strength characteristics of the hydrotropic pulps increase as the yield decreases, however all pulps were lower in strength characteristics than the NSSC. It appears that the cooking liquor would have to be kept from becoming acid if a higher strength pulp is to be produced.

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LITERATURE SURVEY

A STUDY OF HIGH YIELD PULPS USING HYDROTROPIC SOLVENTS

DEFINITION

According to McKee (1), hydrotropic solutions are those aqueous salt solutions which effect decidedly greater solubility of slightly soluble substances more than does pure water at the same temperature. This phenomenon is the reverse of the common salting-out effect following the addition of many electrolytes to aqueous solutions of numerous solutes. These phenomena of increased solubility were first noted by Newberg in 1916. The salting-in effect (as opposed to salting-out) is shown best by concentrated aqueous solutions of very soluble neutral salts of organic acids, with organic substances as solutes which have a low solubility in water. The phenomenon, however, is not confined to the field of aqueous solutions of organic salts and organic solutes, but is found in the inorganic field as well. It is largely independent of pH and seems to be best explained by the theory of mixed solvents.

CHEMICALS

Some of the chemicals which show hydrotropic properties as far as pulping is concerned are sodium benzenesulfonate, sodium toluenesulfonate, sodium xylenesulfonate, sodium octylsulfonate, sodium ethylbenzenesulfonate, sodium butylbenzenesulfonate, sodium cymenesulfonate, sodium

butylsulfonate, and sodium benzoate. (primarily article 2) The ammonia and calcium salts are also hydrotropic, but not as effective as the sodium salts. (3) It appears that the delignifying power of the sodium benzenesulfonate derivatives increases as the number and size of the alkyl groups attached to the benzene nucleus increases and that the alkylarylsulfonates are better delignifying agents than are the alkylsulfonates. There is very little difference among hydrotropic agents as to the effect on carbohydrates. (2) The dissolution of lignin with hydrotropic solutions appears to take place in two steps. In the first, the lignin is changed by the action of hot water at cooking, and in the second, the lignin so altered is dissolved in the hydrotropic solution. (2,3)

The pulping of coniferous woods with hydrotropic solutions is very unsatisfactory, due to the relatively low solubility of softwood lignin. (1,2,3,4,5,6)

- The most common hydrotropic agent used is sodium xylenesulfonate. There are several reasons for its general use. These are, its relatively low cost, high delignifying power, abundance, and the relative ease of precipitating the lignin from the pulping solution. Lignin can be precipitated from the pulping solution by simply diluting it to ten per cent sodium xylenesulfonate, as opposed to sodium cymenesulfonate, which must be diluted to two per cent.

GENERAL PROCEDURE

In hydrotropic pulping, a solution of from 30 to 50% hydrotropic agent is used. The wood is chipped and is cooked in a digester very similar to the kraft digester. The process is adaptable to continuous pulping. However, in experimental work, both laboratory digesters and bombs are used. The ratio of cooking liquor and wood varies, but, as an example, Lau (7) working with bamboo, used 760 ml. of solution per 100 grams of bamboo.

After the cook, the cooking liquor is drained from the pulp. This same liquor can then be reused five or six times before it has to be sent to the recovery plant. The recovery of the cooking liquor involves diluting the liquor with water and heating until the dissolved lignin precipitates. The heat coagulates the lignin, making filtration possible. After the lignin has been coagulated, it is removed by filtration. The liquor is then sent to a single stage evaporator which brings the filtrate back to the needed concentration.

The pulp, after cooling, is washed with fresh cooking liquor. The washing continues until only a slight color is given to the washing liquor. Each wash is allowed to stand for 15 minutes at room temperature. After the pulp has been thoroughly washed with the hydrotropic solution, it is washed several times with water to remove any remaining pulping chemicals.

RESULTS OF PREVIOUS EXPERIMENTS

In Lau's (7) work with bamboo, it was found that for a given temperature, the amount of lignin removed in unit time was almost constant during the first few hours of heating, but it then decreased until, after a certain period, the permanganate number tended to become constant. Heating beyond this point would result in an increase in the permanganate number because of decomposition of the pulp. Lau also found that for each 10 C. increase in temperature, the cooking time is reduced by half. At 190 C. and above, both the time needed for cooking and lignin remaining in the pulp are low, but at this temperature the yield is also low. In order to get a pulp (bamboo) with a permanganate number of 11, Lau, using a 50% sodium xylenesulfonate solution had to cook it for approximately six hours at 185 C., and 14 hours at 175 C. After 16 hours at 170 C. the permanganate number was only 12. Upon continued cooking, the permanganate number remained the same. In all of Lau's cooks the alpha cellulose of the pulp was approximately 93%, which indicates that very little degradation occurs below 185 C.

According to Lau's work with bamboo, hydrotropic pulps are intermediate between sulphite and alpha pulp as far as composition is concerned. There is little degradation during pulping and the pulp has a fairly high pentosan content, (5 to 8%).

It was noted by Lau (7) and Fabrycy (5) that adding extra sulfates in the form of sodium sulfate increases the efficiency of the cook. Fabrycy, in his work comparing the effects of hydrotropic agents on various cellulosic materials, used a 33% solution of sodium xylenesulfonate in addition to 4.8% sulfates in the form of sodium sulfate. James and Rosenbock (8) noted that by buffering the pH of the cooking liquor at approximately 7, a much stronger pulp with a higher yield was produced.

As an example of the composition of different hydrotropic pulps, the results of Gromor and Odentsor may be cited (4). These two investigators used a cooking solution of 40% sodium xylenesulfonate with 12-hour cooks at 150 C. The materials being pulped were aspen, birch, pine, spruce, and wheat straw. The hardwoods had a yield of 51.08% and contained 2.75% lignin, 6.5% pentosans, 88% alpha-cellulose, and 0.02% ash. The yield of the softwoods was 66.6% but they retained approximately 50% of their original lignin, thus confirming the relatively low solubility of softwood lignin. Straw had a yield of 48.9%, contained 8.8% lignin, 90.1% alpha-cellulose, and had a copper number of 2.2. The spent liquors contained a relatively low amount of sugars, (11 to 12%) as well as a furfural and volatile acids.

To determine the effect of cooking time, aspen was cooked at 150 C. for periods varying from 0.5 to 6 hours.

The results revealed that during the first two hours 77.2% of the lignin and 21.7% of the reducing substances are solubilized.

ADVANTAGES OF METHOD

In comparing the hydrotropic and kraft processes, McKee (9) points out that the hydrotropic process is superior in several ways. The kraft process gives a yield of five per cent less than the hydrotropic process. The quality of the pulp based on the alpha-cellulose is higher in the hydrotropic pulp. The recovery of kraft liquor requires two step evaporation to high solid content, burning the concentrated liquor, dissolving the ash, causticizing the solution with lime, and then reburning the lime. All this is required after each cook. In the hydrotropic solutions it is only necessary to dilute the solution with water, filter out the lignin, and then concentrate the solution to cooking strength in a single stage evaporator. This needs to be done only after every five or six cooks. According to McKee, ton for ton, the hydrotropic mill would cost two-thirds as much to build as the kraft mill. Lastly, the chemical loss in the hydrotropic process is about 0.5% due to chemicals consumed in the cook, leaks in the system and chemicals not washed out of the pulp.

LIGNIN

Tests on bamboo lignin obtained by the hydrotropic process by Lau (7) and tests on poplar lignin by Dr. Pelipetz showed that they are closely related. Lau's bamboo lignin contained no pentosans or sulfur and had an ash of 0.97%. The lignin was about 70% soluble in methyl and ethyl alcohols. The lignin was fractionally precipitated. The first fraction had a methoxyl content of 14.8% and the second had a 15.4% content. This lignin is relatively reactive and can be used for a base for plastics. (7,9)

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EXPERIMENTAL PART

EXPERIMENTAL DESIGN

The purpose of this investigation is to consider the feasibility of producing a high yield pulp through hydrotropic pulping. It is also intended to test the pulp produced and compare it to a commercially produced pulp.

The experimental work will consist of attempts to produce a pulping operation yielding a 55, 75, and 85% pulp yield. These cooks will be made in experimental bombs using sodium xylenesulfonate as the hydrotropic pulping chemical. This work will be carried out on a hardwood sample.

After cooking, the pulp will be washed both in a fresh pulping solution and water after which it will be mechanically defibered. One portion of the pulp will then be tested chemically for the various constituents of wood. A second portion will be used in making handsheets to determine its strength development characteristics and final physical strength. The results of these tests will then be compared with those of a commercial pulp.

EXPERIMENTAL PROCEDURE

PULPING

A. Pulping Equipment

Two types of pulping equipment were used, bombs and atmospheric cooking equipment. The bombs were constructed from four inch heavy duty iron pipe threaded at both ends. The bombs were approximately a foot long and had an approximate capacity of 1400 ml. Sealing the bombs was accomplished by placing pipe sealing compound on the threads and then placing caps on both ends. These caps were then secured with a pipe wrench. The bombs were heated by partially submerging them in an oil bath.

The atmospheric cooking equipment consisted simply of a wire basket to contain the wood chips so they could be kept completely submerged, a bucket to hold the cooking liquor and a means of heating the bucket and its contents.

B. Pulping Method

Two cooks were made in the bombs (Pulps I & V). The wood chips (Aspen screened $3/8$ to $3/4$ "), approximately 70g per bomb, were placed in the bombs with 750 ml of 40% sodium xylenesulfonate cooking liquor. The liquor was prepared by dissolving 500g of sodium xylenesulfonate in 750 ml of water. The bombs were then sealed and placed in a preheated oil bath. The oil temperature immediately dropped and was then brought slowly back to the cooking temperature.

The one cook (Pulp IV) made at atmospheric pressure was accomplished by submerging approximately 200g of chips, contained in a wire basket, in enough (4500 ml) of the 40% sodium xylenesulfonate cooking liquor to cover them completely. The liquor was then heated to boiling and was maintained at that temperature for the entire cooking period. Water was added so as to maintain a constant volume as it boiled away.

WASHING PULP

After the pulping operation was finished and sufficiently cooled the cooking liquor was drained from the chips. The chips were then placed in a fresh sodium xylenesulfonate solution and allowed to soak at room temperature for uncontrolled lengths of time. This solution was then drained from the chips and a second fresh solution was added. The final washing solution was drained from the chips after several days and then they were ready to be defibered. No attempt was made to save and reuse the chemical.

DEFIBERING AND SCREENING

A. Equipment

The pulp chips were defibered in a Bauer Disk Refiner using coarse and fine plates. The pulps, except I, were screened in a Valley Iron Works Screen.

B. Method

After the chips were washed free of dissolved lignin they were defibered in a Bauer Disk Refiner. The refiner

was set at a load of 3 amperes when running with just enough water passing through it to carry the chips. Pulps No. I and V were sent through the refiner once, using the coarse plate. Pulp IV was sent through the refiner twice using the coarse plate. The pulps were then sent through the refiner using the fine plate. Pulp I was only sent past the fine plate once, pulp IV and pulp V were sent through twice and then screened on the Valley Iron Works Screen. The rejects were then sent back to the refiner until only a small portion of the pulp was rejected.

YIELD DETERMINATION

The yield of the pulp was determined by taking the pulp after defiberizing and screening and pressing it to as high a consistency as possible. This was accomplished by putting the pulp in a muslin bag and squeezing out the water to form crumbs. The pulp was then weighed and an aliquot portion was taken to determine the moisture of the pulp. Once the moisture content of the pulp was known the yield was calculated.

BEATING

The pulps (hydrotropic and commercial NSSC) were beaten in a ball mill with an approximate capacity of 3500 ml. and 12 pounds of stones. The beating consistency varied from 2 to 3%. The beating cycle started with 12.32

pounds of stone on 3000 ml. of water and 60 to 90 g. of pulp. As the beating was continued, samples were removed for freeness tests and handsheets. Upon removal of these samples, the consistency remained constant but the volume of stock decreased, causing a greater stone weight to stock ratio as the beating continued.

HANDSHEETS

Samples taken from the ball mill were tested for freeness according to TAPPI Standard T-227. (Canadian Standard Freeness) All handsheets for determining the strength characteristics of the pulp were made according to TAPPI Standard T-220. The handsheets were then dried in a relative humidity of 50 per cent before testing.

PHYSICAL TESTING OF HANDSHEETS

All sheets were tested for weight, caliber, burst, tear, fold, and tensile.

A. Weight

The individual sheets weighed on a balance sensitive to 2 mg. were air dry.

B. Thickness

The thickness of the sheets was measured according to TAPPI Standard T-410 with the exception that they were measured individually, as opposed to five at a time. The bulk was then determined by the formula:

$$\text{Bulk} = \frac{(18.06)(\text{thickness in thousandths of an inch})}{(\text{basis weight} \quad \text{pounds-25" x 40"-500)}}$$

C. Bursting Strength

The bursting strength of the sheets was determined according to TAPPI Standard T-403.

D. Folding Endurance

The folding endurance tests were made using an M.I.T. fold tester, according to TAPPI Standard T-423.

E. Tearing Strength

The tearing strength of the sheets was determined using the Elmendorf tearing tester, according to TAPPI Standard T-414. One exception must be noted, that is, several of the tests were made using four sheets instead of five.

F. Tensile Strength

The tensile strength of the sheets was determined according to TAPPI Standard T-404. No stretch measurements were made. The strength test results were then converted from pounds per 15 mm. strip to breaking length in meters. This conversion was calculated by using the formula:

$$\text{Breaking Length} = \frac{(21,500)(\text{tensile-pounds per 15 mm.})}{(\text{basis weight pounds-25" x 40"-500})}$$

All tests were then converted to 50 pounds-25" x 40"-500 to facilitate comparison of the different pulps.

CHEMICAL TEST

The chemical tests were limited to lignin determination of the pulp. This test was carried out according to TAPPI Standard T-222 with the exception that the benzene-alcohol extraction was omitted.

CONCLUSIONS

In hydrotropic pulping, as in most pulping operations, the strength characteristics of a sheet made from the pulp increases as the yield decreases. However, even the lowest yield (54%) hydrotropic pulp does not make a sheet with strength characteristics as high as those of a 70% NSSC pulp.

It was observed that the strength of the pulp increases very rapidly as the first portions of lignin were removed. However, as more lignin was removed the strength increase tended to level off. This may be explained in part by the fact that as the lignin was removed from the chips, the cooking solution became more and more acid. This acid solution caused hydrolysis of the cellulose as well as the further removal of lignin.

It should be noted that the low lignin content degraded cellulose pulp made a sheet with higher strength characteristics than did the high lignin content non-degraded cellulose pulp. From this it would have to be assumed that even degraded cellulose has better paper making qualities than lignin.

From this work, it appears that in order to produce a hydrotropic pulp with favorable strength characteristics, the cooking solution would have to be buffered at approximately the neutral point. This would prevent any acid hydrolysis of the pulp.

APPENDIX

TABLE I

Cooking Time, Temperature, and Conditions

Pulp	Type	Yield	Max. Temp.	Time to Max. Temp.	Time at Max. Temp.	Orig. pH	Final pH
I	Bomb	77.8%	150 C	.5 hr.	.75 hr.	9.1	5.4
IV	Atm.*	85.1%	100 C	---	6 hr.	9.1	7.4
V	Bomb	54.0%	170 C	1.5 hr.	4.5 hr.	9.1	5.0

* Cook At Atmospheric Pressure

TABLE II

Lignin Determination (Based On Weight Of Wood)

Pulp	Yield (A)	Lignin Remaining	Lignin Removed (B)	Non-Lignin Material Removed (100-A-B)
I	77.8%	12.6%	10.8%	11.4%
IV	85.1%	15.5%	7.9%	7.0%
V	54.0%	3.9%	19.5%	26.5%

ASPEN CONTAINS 23.4% LIGNIN

TABLE III

Physical Test Results Of Pulp I

	Freeness		
	750	516	137
Weight (g/sheet)	1.20	1.30	1.29
Thickness (1/1000 of in.)	7.3	4.8	3.2
Bulk (cc/g)	3.09	1.88	1.26
Density (g/cc)	.324	.532	.794
M.I.T. Fold	0	4	24
Tear (5 sheets)	2.5	7.8	6.4
Mullen (#/in. sq.)	1.75	13.10	19.80
Tensile (#/15 mm.)	.48	8.70	9.45

TABLE IV

Physical Test Results of Pulp IV

	Freeness			
	580	430	303	165
Weight (g/sheet)	1.29	1.30	1.29	1.28
Thickness (1/1000 of in.)	8.0	6.7	5.4	4.6
Bulk (cc/g)	3.15	2.62	2.13	1.83
Density (g/cc)	.318	.382	.469	.547
M.I.T. Fold	0	0	0	0
Tear (5 sheets)	4.4	4.2	3.6	3.3
Mullen (#/in. sq.)	1.20	1.55	2.75	3.80
Tensile (#/15 mm.)	1.52	2.44	3.69	4.38

TABLE V

Physical Test Results of Pulp V

	Freeness		
	434	325	183
Weight (g/sheet)	1.32	1.34	1.34
Thickness (1/1000 of in.)	3.6	3.5	3.4
Bulk (cc/g)	1.39	1.33	1.29
Density (g/cc)	.719	.752	.775
M.I.T. Fold	15	17	30
Tear (5 sheets)	12.0	10.8	9.8
Mullen (#/ in. sq.)	18.85	22.65	25.75
Tensile (#/15 mm.)	9.93	10.05	12.50

TABLE VI

Physical Test Results of 70% Yield NSSC Pulp

Freeness

	463	365	186
Weight (g/sheet)	1.35	1.34	1.35
Thickness (1/1000 of in.)	3.8	3.3	3.1
Bulk (cc/g)	1.02	.89	.83
Density (g/cc)	.985	1.14	1.21
M.I.T. Fold	45	349	1097
Tear (5 sheets)	15.0	13.4	11.7
Mullen (#/in. sq.)	34.95	50.4	56.5
Tensile (#/15 mm.)	14.5	15.5	20.6

TABLE VII

Physical Test Results Corrected to 50#-25"x40"-500 Basis Weight
Taken From Figures II, III, and IV

		Freeness			
<u>Pulp I</u> (77.8% Yield)	500	400	300	200	
Breaking Length (meters)	4040	4160	4250	4360	
Burst (#/in. sq.)	14.2	16.2	18.2	20.2	
Tear (g/sheet)	26.5	25.4	24.2	23.0	
 <u>Pulp IV</u> (85.1% Yield)					
Breaking Length (meters)	880	1240	1720	2010	
Burst (#/in. sq.)	1.2	1.5	3.0	4.0	
Tear (g/sheet)	15.0	13.7	12.6	11.7	
 <u>Pulp V</u> (54.0% Yield)					
Breaking Length (meters)	--	4620	5000	5520	
Burst (#/in. sq.)	--	21.4	24.5	26.7	
Tear (g/sheet)	--	39.0	35.6	33.5	
 <u>NSSC Pulp</u> (70% Yield)					
Breaking Length (meters)	--	6780	7750	8540	
Burst (#/in. sq.)	--	48.4	56.2	58.7	
Tear (g/sheet)	--	43.8	41.3	39.8	

Burst vs. Lignin Content of Hydrotropic Pulp Figure

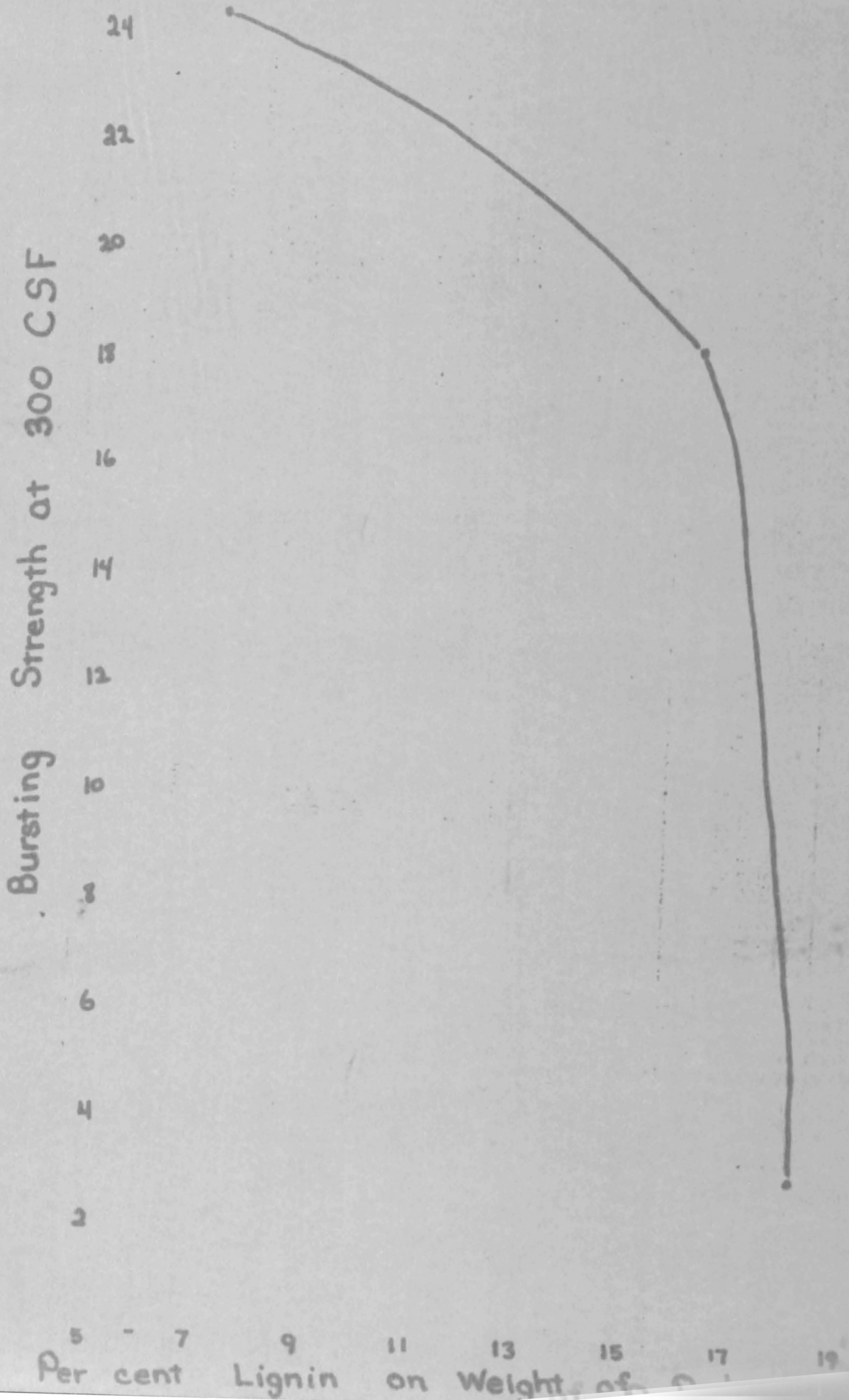
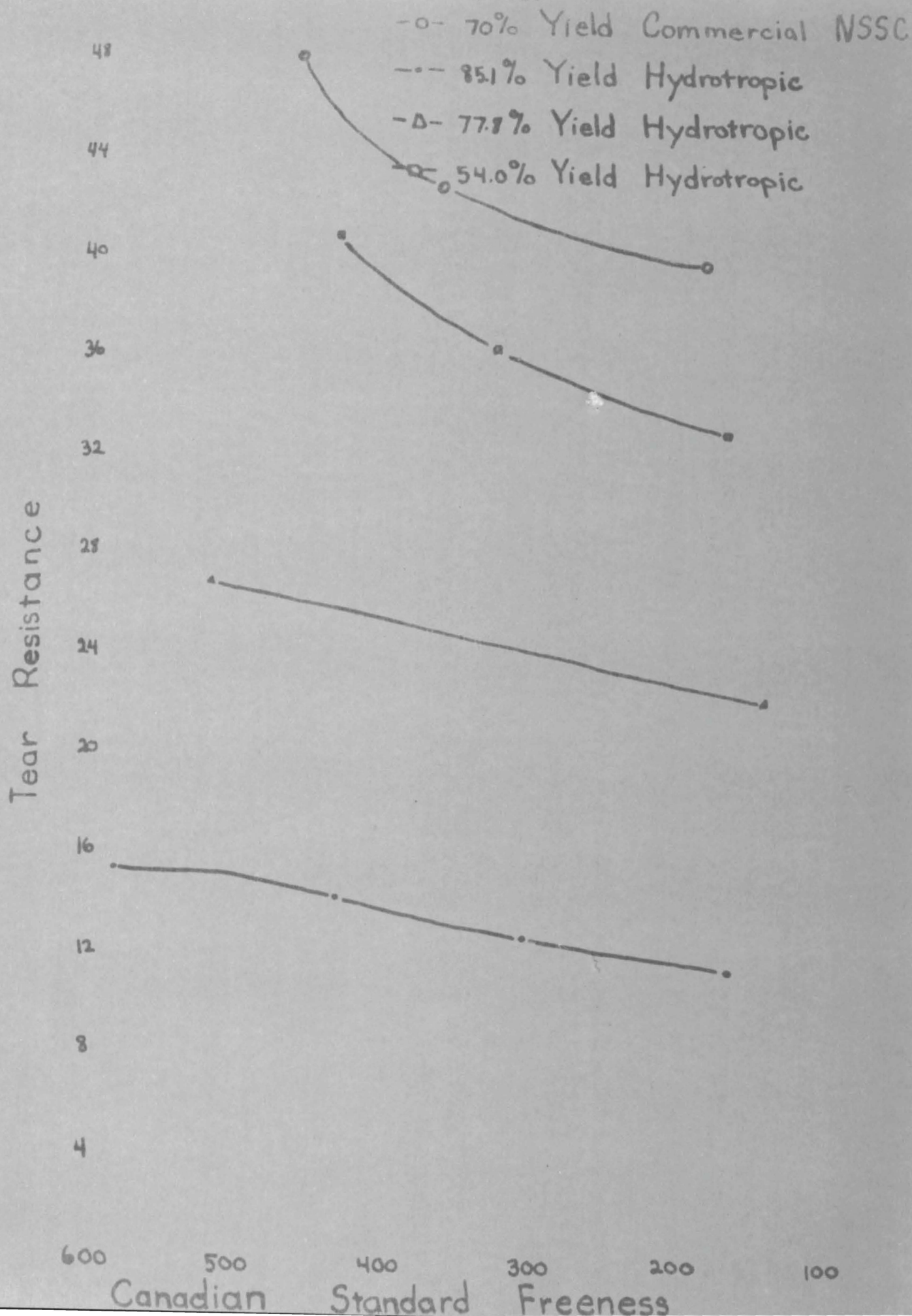


Fig. I LIGNIN CONTENT OF Hydrotropic Pulp vs Burst

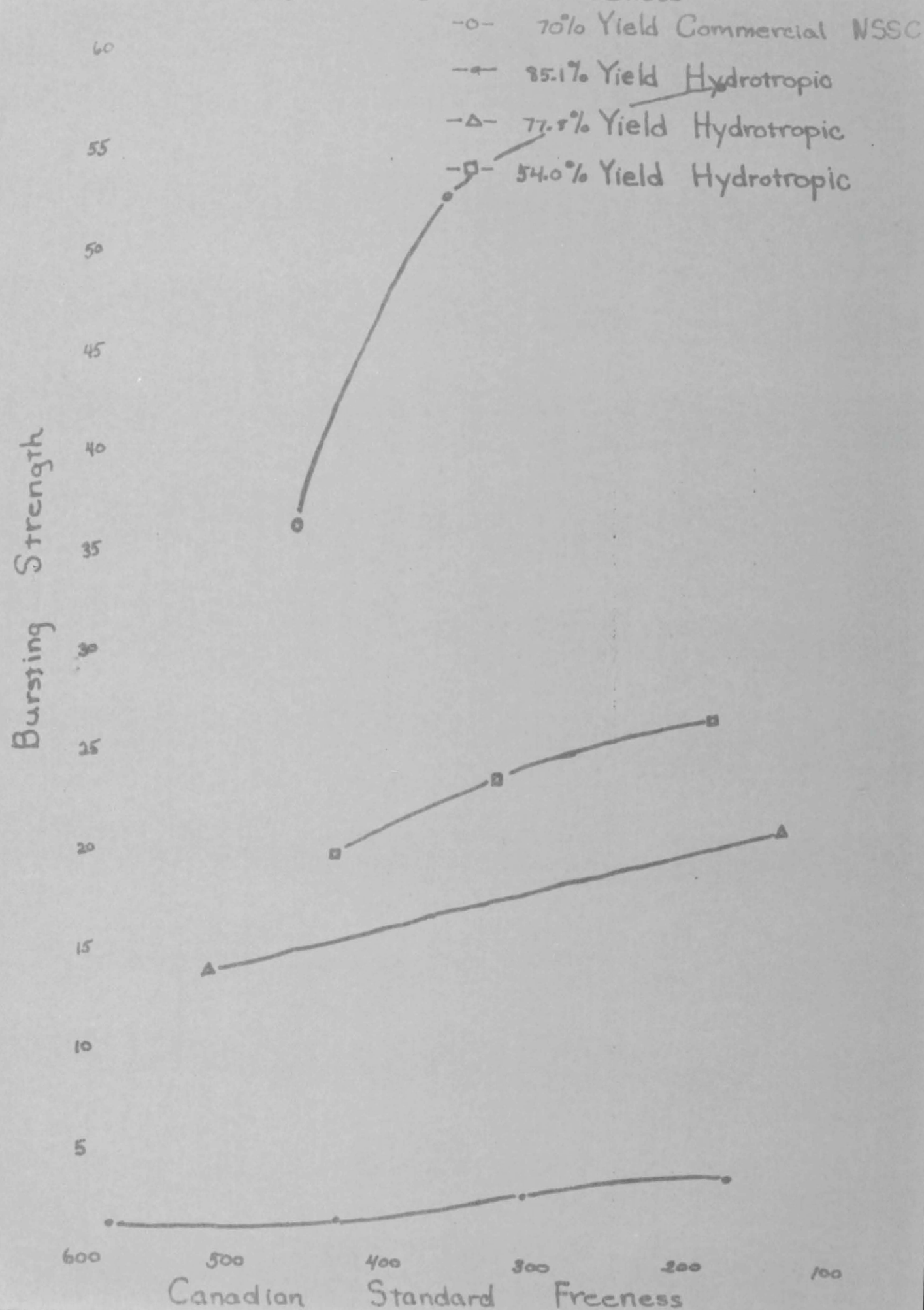
Tear Resistance vs. Freeness



TEAR RESISTANCE VS. FREEDOM

Fig. II

Bursting Strength vs. Freeness



Breaking Length vs. Freeness

