Papermaking Potential of Zostera and Cladophora, Two Marine Weeds

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Abstract

An oxygen pulping method converted Zostera and Cladophora to usable pulps. A usable Cladophora pulp was also made in over 70 percent yield by a simple alkali treatment. The pulps could be bleached fairly easily with hypochlorite and/or chlorine dioxide. Pulp strength was low, and the only promising use found was as an additive to newsprint or corrugating medium and board.

Introduction

Large masses of marine weeds in the coastal waters of New York State sometimes constitute a serious problem. Excessive growth of such weeds may hinder navigation of fishing and pleasure boats, as is the case with Zostera (eelgrass) along the south shore of Long Island. In addition, the decomposition of large masses of dead plants on the shore creates a considerable odor and nuisance problem, clogging water intakes and piling up on the beaches; this is especially serious in the Lake Ontario area, where the culprit is the alga Cladophora.

One scheme proposed to overcome these problems involves harvesting and converting the plants to useful products. Since both plants are fibrous, with substantial cellulose content, one potential product is paper. Although feasibility of manufacturing paper from these materials depends largely on such factors as harvesting, storage, and marketing, the first order of business should be to determine 1) what type of fiber or paper can be made from the materials, and 2) what process is most suitable. This study provides preliminary answers.

The literature contains numerous references to papermaking based on grasses (IPC Bibliography 1970), and the use of straw and reeds for this purpose has been known for a long time (Rydholm 1965). But literature on the use of marine weeds like Zostera and Cladophora is scarce. Thus, Burkholder (1968) gives undocumented references to patents for the manufacture of "high-grade paper" from eelgrass. Kitzevetter (1936) claims that Zostera is suitable for making cardboard, and Rozenberger (1932) states that an acid-alkaline method gave a low-grade, high-cost paper from Cladophora fracta. A recent French patent (1967) claims the production of cellulose from algae by an acid-alkali treatment.

The most successful processes were those involving alkaline (soda) cooking (Aronovsky 1943 and Ernst 1959), although various sulfite processes (Aronovsky 1954 and Lathrop 1949) and chlorine-based processes (Hinricks 1957) have also been used. The soda process and the sulfite process were chosen for preliminary study because they offered the best hope for developing a procedure that would involve a minimum of air and water pollution.

Conclusions

Papermaking pulps can be made from both Zostera and Cladophora. Compared to conventional pulps, these pulps are low-quality, and it is questionable whether they could be used independently as a raw material for paper. However, our experiments showed that they do have a beneficial effect when added to groundwood in amounts up to 20 percent. This indicates that bleached Zostera and Cladophora pulps could be used as additives to pulp stocks of lower grades of paper such as newsprint, while unbleached pulps could be added to corrugating medium and fiber and particle boards.

Results and Discussion

PULPING

Phase I of this study was a general screening of the most promising pulping methods for yielding a material to be used as paper stock or as an additive to paper furnishes. We found that conventional methods used for pulping of grasses (NaOH, Na_2CO_3, Na_2SO_3) produce an inferior product. Using an oxygen-alkali method led to substantial improvement. Although the physical properties of these pulps were to some degree comparable to those of grass and straw pulps, yields and color of the pulps were unacceptable.

The aim of Phase II was to increase the yields of pulp and to determine if further simplification of the proposed technology was possible. In both instances, we obtained positive results.

Zostera. Table 1 gives selected results of pulping Zostera. The yield of the pulp prepared with NaOH in the presence of O_2 was about 29 percent (batch E14), and the strength properties were comparable to those of groundwood. However, the brightness of the pulp was low. In the cooks using water and O_2 the yield improved, but properties deteriorated.

TABLE 1 Properties of Zostera Pulps Obtained by Oxygen Pulping

Batch Number	EG 4	E 14	EG 10	E 13
Chemical	NaOH, 10%	NaOH, 10%	Water	Water
Temp., °C	150	150	150	150
O_2, psi	140	140	140	140
Time, hr	2	1	2	1
Yield, %	26.3	29.1	29.7	31.6
Canadian Standard Freeness (CSF), ml	354	310	415	415
Burst Factor	16.0	16.0	17.0	11.4
Breaking Length, m	3730	3830	3760	3105
Tear Factor	87	78	43	71
Brightness, %	--	23	21	--

Cladophora. With Cladophora, we explored two pulping systems, both resulting in acceptable pulps. The first system consisted of soaking the wet plant at ambient temperature in a 5 percent solution of caustic soda; the second involved passing the plant through a disc refiner and washing it (similar processing of

Zostera gives a worthless pulp). Table 2 gives the results. After bleaching with chlorine dioxide, both pulps show relatively high brightness. The yield in the first case was 72 percent (batch C 15), as opposed to 22 percent by the technique used in Phase I (batch C 5). The strength properties were about the same, but the brightness of pulp C 15 was much lower than that of pulp C 5. However, the latter can be bleached to 58 percent brightness with only 10 percent loss in yield. The disc-refined Cladophora pulp (C 18) was obtained in almost 90 percent yield and had by far the best strength properties. It was also easy to bleach.

TABLE 2 Properties of Cladophora Pulps Obtained by Oxygen Pulping

Batch Number	C 5	C 15	C 18
Chemical	NaOH, 5%	NaOH, 5%	--
Temp., °C	150	--	Disc Refining
O_2, psi	140	--	--
Yield, %	22.1	72	90
CSF, ml	410	485	425
Burst Factor	9.9	8.1	16.3
Breaking Length, m	1640	2120	3980
Tear Factor	70	66	54.2
Brightness, %	45.1	26.3	14.5

MARINE WEED PULPS AS ADDITIVES

Zostera pulp (Table 1, E 14), bleached with 3 percent ClO_2, and Cladophora pulp (Table 2, C 15), bleached with hypochlorite and chlorine dioxide, were refined to a Canadian Standard Freeness of 90 ml and mixed with a groundwood pulp in the proportions 20:80. Table 3 shows the strength properties of the mixed pulp sheets as well as those of the pure components.

The results indicate that Zostera pulp added to a groundwood pulp in an amount up to 20 percent reduces the breaking length of the groundwood but improves the tear factor slightly. Adding

Cladophora fibers, on the other hand, leaves the breaking length of the composite virtually unchanged while the tear factor shows a substantial increase. Thus, both pulps can be used as an additive in high groundwood content paper furnishes, although Cladophora has a slight advantage.

TABLE 3 Composition of Groundwood and Marine Weed Pulps and Their Properties

Groundwood, %	100	--	80	--	80
Zostera Pulp, %	--	100	20	--	--
Cladophora Pulp, %	--	--	--	100	20
. . . .	. . .	. . .	. . .	. . .	. . .
CSF, ml	70	--	90	--	90
Burst Factor	14	12	12	13	14
Breaking Length, m	2980	2480	2560	2800	3010
Tear Factor	33	59	40	63	46
Brightness, %	59	41	54	58	54

EFFECTS OF THE STAGE OF MATURITY OF THE PLANTS ON PULPING RESULTS

Zostera and Cladophora were sampled at various stages of maturation, in July, at the end of August, and at the beginning of October, and were pulped by most of the methods listed above. There was practically no difference in strength properties or pulp brightness of the different samples. We also compared never-dried and dried Zostera to study response to pulping. The stems of the wet material seemed slightly easier to fiberize than those of the dried plant.

CHARACTERIZATION OF EFFLUENTS

The spent liquors were alkaline after pulping with alkali and oxygen, and could be reused after makeup for additional pulping. The liquor characteristics from the oxygen-alkali one-hour cooks (5% NaOH, 140 psi O_2) are shown in Table 4.

TABLE 4 Liquor Characteristics from Oxygen-Alkali Cooks

	Zostera	Cladophora
TOC (Total Organic Carbon)	1500 mg/l	5000 mg/l
BOD_5 (Biological Oxygen Demand)	2400 mg/l	1500 mg/l
Solids in Spent Liquor	0.718 g/100 ml	0.564 g/100 ml

CHEMICAL ANALYSIS

We performed a detailed chemical analysis of Cladophora and Zostera, according to Cronshaw et al (1958) and Jermyn and Isherwood (1956). Their methods were modified to account for the mineral components which affect the results. In this way, more reliable values of α-cellulose content, hemicelluloses, proteins (proteins and lignin in Zostera), and ash were obtained (see Table 5).

TABLE 5 Chemical Analysis of Zostera and Cladophora Plants

	Zostera		Cladophora	
Ash, %	18.5		17.7	
Pentosans, % (TAPPI Standard T223os71)	9.8		11.6	
Proteins, % (TAPPI Standard T418su72)	8.8		17.3	
Sequential Analysis	Method 1*	Method 2**	Method 1	Method 2
Alcohol-Benzene Extractives, %	2.71	2.71	9.43	9.43
Hot Water Extractives, %	21.49	21.49	14.29	14.29
Alkali-Soluble Hemicelluloses, %	5.02	6.79	4.71	6.07
Chlorite-Soluble Lignin and/or Protein, %	9.94	30.14	21.36	15.87
Residue after Steps 1-4, Ash-Free α-Cellulose, %	52.58	33.10	41.47	46.61

* Cronshaw et al ** Jermyn/Isherwood

The great discrepancy in values for α-cellulose and lignin/proteins obtained by the two methods is because the Jermyn/Isherwood method was devised for cell walls of the ripening pear--an entirely different biological material. Cronshaw et al modified the method to suit marine algae. They did not, however, account for the mineral components carried through all steps of the analysis. When this is corrected for, the results are more acceptable.

MORPHOLOGY

The dimension of fibers (length, diameter, cell wall thickness, lumen width) were determined for Cladophora and Zostera after maceration with hydrogen peroxide and glacial acetic acid. We studied the structure of their cell walls under the electron microscope. Besides fibers, the plants contain other morphological elements (e.g., epidermis, parenchymatous cells) which should also be studied. Table 6 gives data on cell dimensions. The fiber dimensions of the two plants are comparable to those of grasses or hardwoods, a range suitable for papermaking.

TABLE 6 Morphological Measurements of "Fibers" of Zostera and Cladophora Plants and Pulps

	Z Plant	Z Pulp	C Plant	C Pulp
Length, mm		1.9(0.7)		1.5(0.8)
Diameter, μm	7.8(3.0)*	4.3(1.7)	157.9(16.6)	6.6(3.7)
Cell Wall Thickness, μm		1.8(0.6)		2.6(1.0)
Lumen Diameter, μm		0.8(0.7)		1.4(2.0)

* Numbers in brackets refer to standard deviations.

Zostera. The pulp fibers originate from the stem of the plant. The leaves yield mostly parenchymatous platelets on pulping. The liberated fibers have many parenchymatous and epidermic cells attached (see Figure 1). The latter come from the thin epidermis covering the stem.

Cladophora. Microscopic study showed that the plant retains most if its original structure (see Figure 2), even through pulping, except that the globules filled with chlorophyll are removed from the internal cytoplasmic strands, leaving behind the translucent, gelatinous envelopes. Very short, thin fibrils are detached from the parent fiber during pulping (see Figure 3).

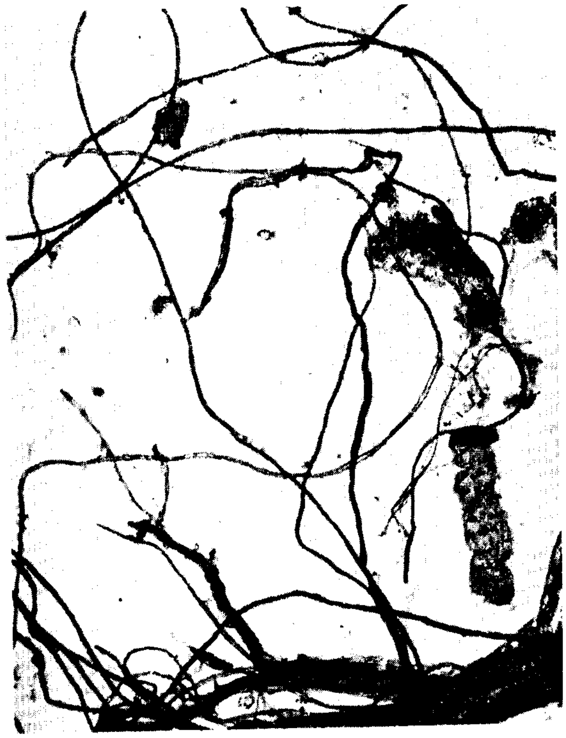

FIGURE 1 Zostera Pulp
E 5 (80X)

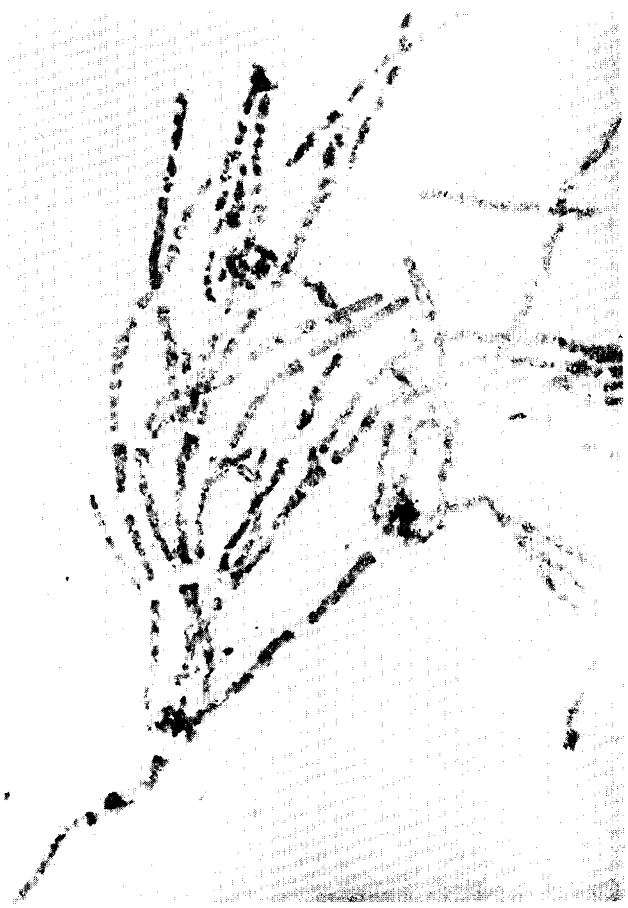

FIGURE 2 Cladophora--Whole Plant (16X). Taken with red filter.

FIGURE 3 Cladophora Pulp
C18 (80X)

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