Project No. RM8

COMPREHENSIVE RESEARCH ON RICE
ANNUAL REPORT

January 1, 1980 - December 31, 1980

PROJECT TITLE: Analysis of Rice Straw as Papermaking and Dissolving Pulp Grades

PROJECT LEADER AND PRINCIPAL UC INVESTIGATORS:

S. H. Zeronian (Project Leader)
D. L. Brink and S. H. Zeronian (Principal Investigators)

LEVEL OF 1980 FUNDING: $11,898

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

1. To establish pulping conditions that can be used to prepare bleachable grade pulps from rice straw using modified soda pulping techniques and to establish the properties of the pulp for papermaking.

   Experiments conducted under the supervision of Dr. D. L. Brink, U.C. Forest Products Laboratory.

2. To prepare and to establish the properties of dissolving-grade or 'chemical' grade celluloses made from rice straw pulp.

   Experiments conducted under the supervision of Dr. S. H. Zeronian, Division of Textiles and Clothing, UC Davis Campus.

SUMMARY OF 1980 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

Objective 1:

A literature review on the pulping and bleaching of rice straw indicated the soda pulping reaction to be the preferred process. Accordingly, four soda and one soda-anthraquinone pulping reactions have been carried out and certain chemical and physical properties of the pulps have been evaluated. Bleachable grade pulp was produced in 47% yield (oven dry straw basis) in 4 minutes at 170°C using 14% sodium hydroxide. This is a remarkably short reaction time.

In preliminary bleaching experiments three of the bleachable grade pulps have so far been evaluated. Twelve experiments have been run using five different bleaching sequences. Best results have been obtained using a conventional CEHEH sequence (C = chlorination, E = alkaline extraction, and H = hypochlorite treatment) yielding, in one case, a pulp of 95% brightness at 26.6% yield. The brightness values using hypochlorite bleaching are unusually high; wood pulps would require the use of more expensive chlorine dioxide to achieve comparable values. Although the experimental program is only a few months old, the initial findings of unusually high pulping rate and high brightness of the resulting bleached pulps using a cheap and easily-handled bleaching agent must be considered as promising with respect to the feasibility of pulping rice straw.

Objective 2:

Procedures are being developed to obtain an ideal cellulose from rice straw to provide a comparison for dissolving grade celluloses prepared from rice straw pulps manufactured by the U.C. Forest Products Laboratory. The properties of the ideal rice straw cellulose are being compared with a commercial dissolving grade cellulose pulp which has been manufactured from wood for the purpose of making acetate rayon fibers. Procedures have been developed for evaluating the quality and usefulness of the dissolving grade pulps we will be making from rice straw.

THe composition of the rice straw has been determined to provide information for the studies. Sugar analyses have given an indication of the types of hemicelluloses in the rice straw. The initial attempts to manufacture a dissolving grade cellulose from rice straw holocellulose have resulted in a product containing a slightly higher hemicellulose content that the commercial dissolving grade pulp indicating that removal of the hemicelluloses will not be a major problem. Ash content of our product is high indicating the need for more intensive extraction treatments.

PUBLICATIONS OR REPORTS: None

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

Results Under Objective 1:

The pulping of rice straw under the sponsorship of the Rice Research Board was initiated in June, 1980. A review of the literature on rice straw pulping and bleaching going back some 30 years was carried out. The literature, although not abundant, gives examples of successful utilization of rice straw in various parts of the world including Eastern Europe, India and Africa and in a variety of end use products. The soda pulping process is clearly preferred over the kraft pulping process (1). The reason for this seems to be principally that rice straw is relatively easy to pulp and the additional delignifying agents present in kraft pulping liquor are not required. Thus, the more complicated kraft processing with its expensive heat and chemical recovery system is usually not justified. The relatively low usage of sodium hydroxide in the soda pulping of rice straw has led in many parts of the world to eliminating any recovery step at all and the spent liquors are simply sewered. This, of course, is not an acceptable option in the U.S. and in our work the question of black liquor recovery is being given full consideration. The literature indicates that two key factors in successful pulping of rice straw concern its relatively high silica content which affects ash content of the pulp (2), knife and tool wear (3), as well as presenting a buildup problem in any black liquor recovery system (3,4). The second factor is the importance of proper initial handling of the rice straw in order to remove dirt, rice grains, and as much of the leaf material as practicable (5). These components consume pulping chemicals and diminish the quality of the pulp. Various wet and dry handling schemes to accomplish this are reported (4,6).

Our first aim has been to produce a bleachable grade pulp from rice straw. Given the existing literature background it was appropriate to initiate our laboratory work with an investigation of soda pulping. This will provide the benchmark data with which to evaluate future results with modified and improved processes. Theresults of the initial series of soda pulping reactions of rice straw are shown in Table I. The raw material for these reactions was provided by Mr. George Miller of Cooperative Extension and was given a rough screening to remove dirt and debris. The straw was cut into 3-4-inch lengths and used in 1200 gram charges in a batch digester. The conditions of soda-rice straw reaction No. 1 (SRS 1-0) were selected based on information in the literature and previous experience in soda pulping of wood. The results show virtually complete pulping with less than 1% rejects and low Kappa number (a measure of residual lignin). Subsequent reactions were conducted at shorter reaction times with reaction 4-0 having only a 4 minute at temperature period. Surprisingly, the yields and Kappa number are essentially the same as those from longer reaction times. The H factor values are a measure of the intensity of reaction combining both time and temperature in one expression. Clearly, complete reaction was achieved under even the mildest of the reaction conditions suggesting still further modifications, such as lower temperature or less sodium hydroxide usage, may be possible. One soda-anthraquinone reaction (SAQ-RS 1-0) was also carried out at the 4 minute reaction time. This newly developed modification of the soda process which uses a catalytic amount of anthraquinone in the pulping liquor has been an important breakthrough in the pulping of wood and allows both increased pulping rates and improved pulp yield. With rice straw no additional improvement could be seen as compared with the use of sodium hydroxide alone. All of the pulps shown in Table I meet the initial aim of being of bleachable grade.

Our second aim is to produce bleached pulps suitable for papermaking and for dissolving pulp purposes. Bleaching studies have been conducted on selected pulps prepared by soda pulping, and principally from SRS 4-0. Some 12 different bleaching experiments have been run using different sequences of chlorine, alkaline extraction, sodium hypochlorite and chlorine dioxide treatments. The results of these runs are shown in Table II. All of the sequences shown represent standard commercial practice with different wood pulps. Initially, the chlorine demand of the rice straw pulps was determined to establish the level of chemical application in sequential bleaching. The chlorine demand of 3.25% is relatively low compared with wood pulp. In the initial bleaching experiment--Run No. 1--a pulp of 80% brightness was obtained in 66.5% yield based on pulp (31.3% based on starting straw) with a total chlorine usage of about 5.4%. This compares favorably with literature values for CEH bleaching of rice straw of 7% total chlorine (7).

When hypochlorite was replaced by chlorine dioxide in the third stage (Runs 2-7), no additional improvement was seen in brightness and bleached pulp yields were similar. In fact, lower brightnesses were obtained. In Runs 14 and 15 where hypochlorite was again used, high brightnesses were also experienced. Good results were also achieved with CEH sequences with other rice straw pulps (Runs 10 and 11). The available literature on bleaching also confirms the satisfactory results using only chlorine and hypochlorite (8). The rice straw appears to be relatively easy to bleach. The poorer results with chlorine dioxide is in contrast to the experience with wood pulps which require such a treatment to achieve the highest brightness levels. THe use of hypochlorite would provide advantages both in cost and ease in handling as compared with chlorine dioxide.

Results Under Objective 2:

Considerable time has been devoted to developing methods for characterizing rice straw as many of the available ASTM standard methods are designed primarily for use with wood and wood cellulose and cannot be applied successfully to rice straw. This is due essentially to the structural and compositional differences between trees (which are either gymnosperms or dicotyledons) and rice straw (which, like other annual plants, is a monocotyledon). Holocellulose content is being determined using sodium chlorite and acetic acid, following a procedure developed for use with annual plants (9). This method is a modification of an earlier method (10) designed to produce holocellulose from wood with minimal degradation to the carbohydrate fraction. Alpha-cellulose content of the rice straw is being determined by extracting the holocellulose with alkali (11). Rice straw contains a relatively large amount of protein, compared with wood, and this interferes with lignin determination by traditional methods. An enzymatic prehydrolysis (12) is being used to remove protein, and the lignin content determined following the procedure of Bagby et al. (13). Sugar analysis by gas-liquid chromatography is being used to characterize the rice straw as well as straw pulps. The procedure developed is essentially similar to the procedure proposed by Albersheim (14).

The chemical composition of our rice straw (obtained from Mr. George Miller, Cooperative Extension, UC Davis) is given in Table III which also summarizes the chemical composition of rice straw as determined by a number of researchers both in the U.S. and elsewhere. The agreement between our data and those of others is reasonable.

Table IV gives data on the non-glucose carbohydrate composition of a high quality dissolving grade acetate (RA) pulp obtained from wood. We will be comparing the properties of our rice straw dissolving grade pulps with those of the RA pulp. The non-glucose carbohydrate composition of the rice straw itself is also given in this table as well as the celluloses we have prepared from rice straw. Considerable attention has been paid to developing techniques for analyzing accurately the carbohydrate composition of the acetate pulps. The objective in the preparation of a high quality acetate pulp from any cellulose source is complete removal of the hemicelluloses as well as other impurities. However, some hemicelluloses will remain and the type of residual hemicellulose can influence the quality of the pulp. The presence of hemicelluloses is indicated by the presence of sugars other than glucose in the pulp and thus can be determined from the carbohydrate analysis. It will be noted that the RA pulp still contains small amounts of non-glucose sugars indicating that this commercial pulp still retains hemicellulosic material. Rice straw or rice straw holocellulose contains a large amount of xylose, lesser amounts of arabinose, galactose and mannose; and trace amounts of rhamnose and fucose.

The properties of the cellulose that can be extracted from rice straw are not known. Thus, we are preparing as pure a cellulose as possible from rice straw (i.e., an ideal cellulose) by a laboratory procedure which involves alkaline extraction of rice straw holocellulose and comparing its properties with those of other celluloses (i.e. wood cellulose or cotton cellulose). The properties being measured include carbohydrate composition, ash, molecular weight, and level-off degree of polymerization (LODP). Cellulose acetate will be made from these samples and such properties as haze and color measured. The properties of dissolving grade cellulose from rice straw pulped at the U.C. Forest Products Laboratory will then be compared with those of the ideal cellulose.

The carbohydrate analysis (Table IV) indicates that the product of our first attempt for preparing an ideal cellulose (straw α-cellulose, Table IV) contains a higher quantity of xylose than the commercial RA pulp. This is confirmed by our carbohydrate analyses of the respective LODP products. LODP samples are made by boiling celluloses in dilute hydrochloric acid. Xylans are associated with acetate color and haze and thus may be detrimental to the quality of any acetate pulp produced. It appears possible therefore that more intensive or additional extractive treatments may be required to reduce the xylose content further. The ash content of our straw α-cellulose is too high (9.3%) for use as a dissolving grade acetate pulp (Table V). The inorganic material is held tenaciously by the α-cellulose since the ash content of the α-cellulose LODP, which is crystalline in nature, is also relatively high (6.5%). As the hemicellulose content is reduced by more intensive or additional extraction treatments it is possible that the ash content of the samples will fall. Alternate methods of reducing ash content will also be considered.

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Table I. Rice Straw Pulping Conditions and Results

Reaction Number	SRS 1-0	SRS 2-0	SRS 3-0	SRS 4-0	SAQRS 1-0
Reaction Conditions					
Temperature, °C	170	170	170	170	170
Time to temp., min.	30	17	20	15	22
Time at temp., min.	30	15	7.5	4	4
NaOH usage, %[a]	14	14	14	14	14
Liquor-to-straw ratio	6.25:1	6.5:1	6.5:1	7.5:1	7.5:1
Straw charge, g. O.D.	1200	1200	1200	1200	1200
Anthraquinone usage, %[a]	--	--	--	--	0.05
Results					
Yield, %[a]					
Accepts	46.8	47.4	45.2	47.6	47.1
Rejects	0.6	1.2	1.0	0.9	1.1
Total	47.4	48.6	46.2	48.5	48.2
Kappa No.	10.9	11.4	10.9	11.2	11.0
Residual NaOH, %	--	--	--	--	0.93
H factor	558	245	170	116	101

[a]Percentage based on oven dry straw

Table II. Rice Straw Bleaching Conditions and Results

Pulp	Bleach Run No.	Bleach Sequence[a]	Residual Chlorine, %[b] C	H	H	D	D	Bleached Pulp Yield, %[b]	Bleached Pulp Brightness, %[c]
SRS 4-0	1	$C_{3.26}\ E_2\ H_{2.17}$	0.40	0.9				66.5	80
	2	$C_3\ E_2\ D_{0.55}$	0.24			--		68.2	--
	3	$C_3\ E_2\ D_{1.1}$	0.17			--		70.1	76
	4	$C_3\ E_2\ D_{1.65}$	0.24			0.1		67.0	71
	5	$C_3\ E_2\ D_{2.2}$	0.24			0.1		65.7	70
	7	$C_3\ E_2\ D_{1.1}\ E_1\ D_{0.55}$	0.17			--	0.02	66.0	71
	14	$C_{3.3}\ E_2\ H_{1.7}\ E_1\ H_{0.5}$	0.10	0.5	0.29			59.2	85
	15	$C_{3.4}\ E_2\ H_{1.7}\ E_1\ H_{0.5}$	0.29	--	0.06			56.5	95
SRS 3-0	10	$C_3\ E_2\ H_{2.17}$	0.29	0.7				73.1	80
SAQRS 1-0	11	$C_{2.9}\ E_2\ H_{1.93}$	0.30	0.6				74.4	82
	12	$C_3\ E_2\ D_{1.1}$	0.10			--		69.6	86
	13	$C_3\ E_2\ H_{1.43}\ E_1\ H_{0.5}$	0.10	0.5	0.29			58.7	89

[a]C = chlorination, E = sodium hydroxide extraction, H = sodium hypochlorite treatment, D = chlorine dioxide treatment. Subscripts indicate the application of the active chemical as a percentage of the starting dry pulp weight.

[b]Based on oven dry starting pulp weight.

[c]Relative to magnesium carbonate block.

TABLE III

Rice Straw Composition[1]

	Davis Data			American Rice[2]			American, Egyptian and Indian Rice Combined[2]		
	Average	Range	No. of Samples	Average	Range	No. Values Reported	Average	Range	No. Values Reported
Moisture	8.7	8.6- 8.8	4	8.8	8.7- 8.8	2			
Ash	15.9	15.8-16.0	3	16.9	14.9-18.8	5	16.8	13.5-20	15
Lignin	9.7	9.5- 9.8	2	12.1	10.6-13.1	5	14.5	10.6-25.5	15
Alc-benz extractives	4.4	4.3- 4.4	3	4.7	3.9- 5.9	5	4.3	1.7- 6.0	14
Holocellulose	66.0	65.1-67.5	3	58.8	---	1	66.5	58.8-77.8	3
α-cellulose	33.5	33.5-33.6	2	30.4	25.3-36.2	4	30.5	25 -40.7	11
Hot water extractives	15.4	13.4-18.3	4	13.8	11.8-15.5	5	13.7	5.3-19.6	11

[1]Based on oven dry weight of straw.

[2]A total of 6 investigations reporting composition of American rice straw were found; 6 for Egyptian rice straw, and 4 for Indian rice straw.

TABLE IV.

Sugar Analysis by Gas Chromatography[1]

	Rice Straw	Straw Holocellulose	Straw α-cellulose	Commercial RA Pulp	Straw α-cellulose LODP[2]	Commercial Pulp LODP[2]
Rhamnose	.03	.05	.02	-	.04	.02
Fucose	.05	.05	-	-	-	-
Arabinose	2.62	3.38	.06	.04	.10	.04
Xylose	14.26	17.83	1.21	.42	1.06	.44
Mannose	.31	.18	.07	.24	.06	.20
Galactose	.96	.78	.02	-	.01	-

[1]All values given in percent of oven-dry material.

[2]LODP = Level of degree of polymerization product.

TABLE V

Ash Contents of Samples

Sample	Ash[1] %
Commercial dissolving grade pulp	.10
Rice straw	15.9
Rice straw holocellulose	15.3
Straw α-cellulose	9.3
Straw α-cellulose LODP[2]	6.5

[1]Based on oven dry weight of sample.

[2]See Footnote 2, Table IV.