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Utilization of Fibrous Raw Materials

Part 4

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Purposeful Papermaking Plants: Their Identification and Pulping, Bleaching, and Papermaking Characteristics

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INTRODUCTION

Man first fashioned matted webs from papyrus pith to form paperlike products. Since then, he has searched the plant kingdom for sources of materials on which to record the events of time. Concurrently, fibrous material uses have expanded to serve many of man's needs, and in 1976 the world consumed 154 million metric tons of paper and paperboard products and produced 122 million metric tons of pulp. These statistics are similar to the record amounts reported for 1974 and represent an 11% increase over those for the 1975 recession year.

Historically, nonwood plant materials were not only the first but remained the leading fibrous papermaking raw material until wood was successfully demonstrated during the mid-nineteenth century. Subsequently, the industry has evolved such that 95% of the world's fiber comes from forests. Certain nonwood species continue to be used to good advantage to produce a variety of specialty papers. However, nonwood species are mainly used where desirable trees are scarce. Local fiber deficits are already prevalent in many regions of the world. And now even traditional fiber sources such as Sweden and Finland are importing wood chips. Keays (1) predicts that by the year 2000, there will be a world wood supply shortfall of 200 million cubic meters for conventional practices.

Perhaps the greatest potential for increasing world fiber supply rests with the development of nonwood fibrous plants. Except for bamboo, much of the fibrous nonwood raw materials in world usage accumulates as residue from harvesting and processing of agricultural crops for their primary food and feed components. Among the more prominent fibrous residues are sugarcane bagasse and cereal straws. While the U.S. Department of Agriculture contributed substantially to the pioneering efforts leading to existing industrial technology for these materials, almost no straw pulp is produced in the United States.

STRAW

The disappearance of straw from the U.S. paper industry resulted through a combination of several factors:

1. Development of short-stemmed wheat varieties through genetic improvements decreased the amount of available straw.

2. Acceptance of the combine for harvesting cereal grains and the consequent need for separate collection of straws.

3. Storage and preservation problems.

4. High labor and transportation costs

5. Erosion control practices

6. Competition from wood augmented by improved processing technology with a variety of species.

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Despite similar trends which seem to be developing in other parts of the world, new and expanded use of straws is still evident. Egypt's own expanding straw pulp industry is an excellent example.

Typical chemical characteristics adapted from NRRC data are summarized for a variety of straws in Table 1. While significant chemical differences may exist between varieties, these differences are not reflected by the data and further discussion is beyond the scope of this review. Straw species may have similar chemical compositions; however, the relative amounts of nonfibrous leaf and chaff cellular components, which are present in varying amounts, significantly influence pulp properties. Prominent differences which require special attention during processing are the low lignin and high ash contents in rice straw. As is well recognized, the considerable ash and attendant silica necessitate special attention during subsequent processing and recovery. While cleaning and water washing improve the fiber properties, pulping techniques also influence ash contents of the pulps.

Characteristics of wheat and rice straw pulps are summarized in Table 2. At the Northern Regional Research Center, pressure and mechano-chemical techniques were used to prepare straw pulps, and a twin-vortex pulper was evaluted with wheat straw. The mechano-chemical process reduced the residual ash content of rice straw pulp to less than 5%, whereas the kraft pressure technique produced pulps with ash contents exceeding 10%. Better bleachability was realized with the pressure technique. The twin-vortex pulper at slightly elevated temperature not only decreased the ash content of wheat straw but also provided easy-to-bleach pulps with improved burst and tear resistance (2).

While rice and wheat straw pulps have been bleached commercially by single-stage hypochlorite (H) or two-stage H-H, the more common technique is the three-stage chlorine-alkali extraction-hypochlorite (CEH) sequence to achieve brightness of 75-80%. Somewhat brighter pulps are reported possible by employing a fourth stage of peroxide (P), chlorine dioxide (D), or H. Similar results have been reported for ryegrass straw pulps (3).

SUGARCANE BAGASSE

Bagasse is the major fibrous agricultural residue enjoying world acceptance in paper and board products. United States mills produce more than 200,000 metric tons of bagasse pulp annually for paper and board products. Storage is usually a necessary phase of bagasse utilization, and fiber preservation has been demonstrated with several techniques. Initial attempts to use bagasse were thwarted by the presence of pith. Consequently, successful utilization of bagasse depends upon effective depithing. Basically, three procedures have been used to remove most of the nearly 30% pith from bagasse:

1. Dry depithing at 15 to 20% moisture.

2. Moist depithing at about 50% moisture.

3. Wet depithing at about 90 to 95% moisture.

Chemical composition of bagasse and the separate fiber and pith from widely scattered geographic locations are summarized in Table 3 (4). While the pith fraction has little structural substance, the contents of chemical constituents in the three materials are rather similar. The fiber fractions, of course, have greater cellulose contents and less ash and extractables. Advantages of these compositional changes are further evidenced when comparing pulps prepared from whole bagasse and the fiber fraction (5) (see Table 4).

Delignification of the depithed fiber was more complete and, consequently, less bleaching chemical was consumed to achieve 70% brightness. Furthermore, the fiber provides a freer draining pulp with greater strengths. While these pulps were prepared by batch processes, nonwoods are uniquely suitable for pulping by rapid continuous systems. Any one of several continuous pulping systems should be adaptable.

Bagasse pulps are bleached in commercial facilities by single stage and multiple stages

as described for straw pulps. However, bagasse pulps are generally easier to bleach; therefore, higher levels of brightness can be attained. Peroxide as a final stage reportedly retards pulp reversion during aging (6).

NONRESIDUE FIBROUS PLANTS

The U.S. Department of Agriculture discontinued its program to evaluate agricultural residues as sources of fibrous raw materials during the late 1950's. At that time, the Agricultural Research Service instituted a program to identify potential annually renewable fibrous plants which could be cultivated specifically for papermaking. Following a multidisciplined approach, 506 species were evaluated. Initially, botanists and agronomists collected, identified, and evaluated species, generally from the wild, for their agronomic potential. Subsequently, chemists and engineers determined chemical composition, fiber characteristics, and general appearance and physical characteristics. The more promising species are of the Malvaceae (mallow), Gramineae (grass), and leguminosae (legume) families. Noteworthy individual species were also identified in the Linaceae, Moraceae, and Typhaceae families (7-9). Based on preliminary appraisals, 92 species were examined by laboratory-scale pulping (10,11).

Selected data characterizing certain of these promising species are summarized in Tables 5 and 6. The point values were defined such that a minimum score of 5 was the favorable (7). Since plant scientists were assessing species potential for production in the United States, the score for agronomic potential might be changed for consideration in nontemperate regions of the world. While these species have favorable characteristics which should equate to good papermaking properties, some species (e.g., Ricinus communis with its allergen) may have undiscovered special problems. Many of these species may serve a dual role to provide food or feed and fiber for papermaking. While several of these genera, including Hibiscus, Crotalaria, and sorghum received further attention, we concentrated on one most promising species. Based on chemical and pulping characteristics and on cultural aspects, Hibiscus cannabinus (kenaf) was selected for detailed developmental studies.

KENAF PULPING

Kenaf has been processed by the three principal industrial chemical pulping techniques: neutral sulfite, kraft, and soda (12-15). Characteristics of pulps produced at 15, 18, and 21% applied pulping chemicals are summarized in Table 7. The neutral sulfite technique consumed the least chemical and gave the greatest yields. Pulps from the other processes were equivalent. The maximum applied chemical produced the more readily bleached pulp by a CEH scheme. Low sulfidity in kraft cooking contributes to low bleach consumption and high bulk, while high alkalinity and low sulfidity favor increased strength characteristics, except for the tear factor.

Data for kraft and soda pulping show that, in contrast to the long-recognized superiority of kraft wood pulps over wood soda pulps, strength characteristics of kenaf soda pulps were equal to those of their respective kraft pulps (14). When applied to kenaf, both techniques yield comparably. However, kenaf soda pulps drain slightly better than those of kenaf kraft pulps.

Typical data are summarized in Table 8. Strength characteristics of kenaf pulps are superior at the same freeness level of those of commercial hardwood pulps and, except for resistance to tear, are comparable to softwood pulps.

The preceding kenaf pulping trials were with tumbling or rotary digests equipped with indirect steam heat. However, continuous digesters with short cycle cooking have been demonstrated with a two-tube Pandia Chemipulper (16) and a three-tube Bauer M&D pulper, using respectively kraft and soda chemicals (17).

KENAF PULP BLEACHING

Bleaching during most of our early investigations involved CEH or starting with a first stage chlorine-chlorine dioxide (Cd), a CdEHD procedure selected rather arbitrarily, for comparison purposes, without regard to optimal conditions (12, 16). The objectives of the bleaching tests were to determine chemical consumption and pulp yield at 75% brightness. The four-stage sequence provided bleached pulps at nearly 90% brightness, and an H treatment has brightened kenaf soda pulp to 80% (17). Recently, kenaf whole stem, bark, and core soda pulps cooked to 20 kappa number were treated with various combinations of Cd as a first stage (18). With regard to pulp viscosity, the CdE sequence offers some advantages over CE. However, more study is needed to optimize the bleaching sequence, and research is continuing with other bleaching stages.

KENAF PULPS IN WEB FORMATION

On several occasions, it has been observed that kenaf and wood pulps interact synergistically (19). Subsequently, it was found that pulps prepared from the separated bark and core fractions recombine to give webs with anomalous strength properties exceeding those expected (15). To better understand these characteristics, we examined the mechanical behavior of bark, core, and whole kenaf pulps during web formation on a fourdrinier laboratory papermachine and compared their relative responses to those of a commercial softwood pulp (20). For examination with the scanning electron microscope (SEM), samples were removed from various sections of the web-forming system: (1) at the head box, (2) on the wire, (3) after the couch roll, (4) after the press, (5) after the fourth dryer can, (6) after the final (tenth) dryer, and (7) after the calender stack. To preserve their original configuration, samples were dried by the critical-point drying technique. Bark pulp responds to beating much the same as does a southern pine kraft pulp. Core pulp becomes more flexible during beating and on drying during web formation collapses into a tightly compacted sheet.

The web prepared from bark pulp had very open structures from the headbox through the press, and it was only partially compressed in the dryer. Even after the fourth dryer, fibrils remained projecting from the fibers.

Webs from core pulps remained open structured through the press but coalesced while drying to give tightly compacted, completely collapsed sheets. Calendering produced no visible effects at 500X.

The whole kenaf pulp formed an open web during early formation stages but then began to show the effects of the two components. Bark pulp fibrils in the whole kenaf pulp were less visible following the press than they were when formed separately. After drying, the structure was quite closed but not as tightly as that of the web from all core pulp.

The southern pine pulp webs were open through the press section but formed a relatively closed structure after partial drying. Fibrils remained uncollapsed through the press section but were much less prominent in the sample taken in the dryer section. After drying, all fibrils had compressed into the fibers and into the interfiber spaces. This research is continuing with efforts to further elaborate the papermaking system. Kenaf is a most interesting raw material which offers considerable opportunity to study the papermaking system, and in some areas of the world, including the United States, it is ready for exploitation.

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The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

Table 1

Proximate Chemical Composition of Straws

Component, %	Wheat	Oats	Rye	Barley	Rice
Cellulose					
Crude	48	48	52	47	47
Alpha	33	34	36	34	32
Pentosan	29	28	29	25	24
Lignin	18	18	19	15	13
Ash	8	8	6	6	18
Solubles					
Alcohol-benzene	4	3	4	5	5
Hot water	14	16	12	16	14
1% NaOH	44	46	41	47	50

Table 2

Wheat and Rice Straw Pulps

	Wheat Straw Pulper			Rice Straw Pulper	
Characteristics	Rotary	Twin-vortex	Vortex	Rotary	Vortex
Temperature, °C.	170	118	95	170	98
Time, hr.	2	0.5	0.5	2	1
Chemical, %	12[a]	12[b]	12[a]	14[b]	14[b]
Bleach consumed as Cl_2	6.6	7.9	13.7	1.8	6.8
Screened yield, %	47	53	61	41	37
Ash, %	4.9	2.5	1.9	12.7	4.3
Burst, $g./cm.^2/g./m.^2$	51	58	51	48	55
Tensile, m.	9100	8900	9100	7600	8300
Tear, $g./g./m.^2$	27	42	27	37	27

[a] Kraft.
[b] Soda.

Table 3

Proximate Percent Chemical Composition of Bagasse

Material	Cellulose					Extractives		
	Crude	Alpha	Pentosan	Lignin	Ash	Hot water	Alcohol-benzene	1% NaOH
Whole								
Minimum	50	30	28	18	2	3	3	27
Maximum	57	35	32	22	5	11	11	40
Fiber								
Minimum	56	37	31	19	1	1	2	27
Maximum	63	41	32	22	2	4	4	31
Pith								
Minimum	52	31	31	18	3	2	2	30
Maximum	55	35	33	22	6	5	3	36

Table 4

Characteristics of Bagasse Kraft Pulps

Source and Component	Screened Pulp, %				Bleaching, 70%		Freeness SR, ml	Strength at 500 ml		
	Yield	Ash	Lignin	Pentosan	Consumed %	Yield %		Burst $gm/cm^2/gm^2$	Breaking Length, m	Tear, g/gm^2
Florida										
Whole	42	2	6	32	27	34	750	54	9470	43
Fiber	56	1	3	32	9	51	810	57	8800	45
Hawaii										
Whole	48	3	5	26	19	38	810	40	5870	44
Fiber	52	2	3	32	3	49	850	48	7950	51
Louisiana										
Whole	52	2	4	32	9	49	800	44	7900	35
Fiber	60	2	3	33	5	57	820	52	8990	37

Table 5

Characteristics of Annual Plant Sources for Papermaking

Family and plant species	Point value[a]	Soluble 1% NaOH	Cellulose Crude	Cellulose Alpha	Density, g/cc	Fiber length, mm Bast	Fiber length, mm Woody
Monocotyledoneae							
Gramineae							
Guadua amplexifolia	9	30	61	43	0.6	1.4	---
Gynerium sagittatum	5	30	58	38	0.48	1.04	---
Lygeum spartum	8	42	49	34	0.60	1.54	---
Phyllostachys bambusoides	5	26	56	36	0.88	1.45	---
Sinarundinaria murielae	5	29	61	36	0.73	1.13	---
Sorghum almum	6	41	55	36	0.28	1.46	---
Sorghum bicolor	8	44	52	32	0.25	0.93	---
Stipa tenacissima	6	33	60	48	0.84	1.08	---
Dicotyledoneae							
Asclepiadaceae							
Asclepias syriaca	8	42	43	29	0.50	2-20	0.45
Asclepias incarnata	8	39	44	30	0.41	4-18	0.31
Euphorbiaceae							
Ricinus communis	6	33	50	34	0.33	5-13	0.72
Leguminosae							
Crotalaria juncea	5	30	55	38	0.32	3.80	0.60
Crotalaria intermedia	7	32	55	38	0.46	2.27	0.59
Crotalaria mucronata	6	30	55	38	0.39	3.02	0.62
Sesbania exaltata	7	29	51	34	0.32	1.94	0.52
Sesbania sonorae	6	28	54	36	0.33	2.35	0.55
Sesbania vesicaria	7	27	50	33	0.44	1.73	0.60
Malvaceae							
Abutilon americanum	8	32	46	29	0.94	1.18	0.57
Abutilon theophrosti	9	44	43	28	0.32	1.30	0.57
Althea rosea	7	37	48	30	0.32	1.93	0.71
Hibiscus cannabinus	5	31	54	35	0.26	2.60	0.60
Hibiscus sabdariffa	6	38	49	32	0.28	2.27	0.68
Moraceae							
Cannabis sativa	6	30	56	38	0.33	2.4-20	0.57

(Continued)

Table 5-Continued

Family and plant species	Point value[a]	Soluble 1% NaOH	Cellulose Crude	Cellulose Alpha	Density, g/cc	Fiber length, mm Bast	Fiber length, mm Woody
Polygonaceae							
Rumex crispus	9	44	47	31	0.53	1.09	
Thymelaeaceae							
Gnidia oppositifolia	7	30	52	35	0.55	3.27	0.42
Urticaceae							
Boehmeria nivea	6	33	54	38	0.21	5-36	0.55

[a]Minimum score of 5 is most favorable (7).

Table 6

Characteristics of Kraft Pulps

Material	Kraft chemical %	Screened pulp Yield %	Screened pulp Freeness ml, SR	$KMnO_4$ number	Strength at 600 ml, SR[a] Burst $g/cm^2/gm^2$	Breaking length m	Tear g/gm^2
Monocotyledoneae							
Gramineae							
Guadua amplexifolia	15	49	895	30.1	53	----	118 (690)
Gynerium sagittatum	15	50	875	35.9	86	----	129 (685)
Lygeum spartum	15	48	840	14.4	59	8700	123
Phyllostachys bambusoides	15	50	900	48.5	92	----	114 (700)
Sinarundinaria murielae	15	43	905	32.1	46	----	68 (650)
Sorghum almum	15	50	795	26.8	47	8000	65
Sorghum bicolor	15	49	800	50	45	7700	50
Stipa tenacissima	15	44	890	10.5	51	7230	120
Dicotyledoneae							
Asclepiadaceae							
Asclepias syriaca	15	47	570	51.5	18	----	62 (465)
Asclepias incarnata	15	57	675	62.1	22	----	78 (540)
Euphorbiaceae							
Ricinus communis	15	52	725	67.4	37	----	54 (560)
Leguminosae							
Crotalaria juncea	21	52	810	14.2	49	9150	86
Crotalaria intermedia	15	53	785	55.9	30	----	64 (630)
Crotalaria mucronata	15	58	840	44.1	46	----	49 (670)
Sesbania exaltata	21	54	815	18.2	59	9500	56

(Continued)

Table 6-Continued
(Dicotyledoneae)

Material	Kraft chemical %	Screened pulp Yield %	Screened pulp Freeness ml, SR	KMnO number	Strength at 600 ml, SR[a] Burst $g/cm^2/gm^2$	Strength at 600 ml, SR[a] Breaking length m	Strength at 600 ml, SR[a] Tear g/gm^2
Sesbania sonorae	15	59	820	60.3	37	----	49 (625)
Sesbania vesicaria	15	55	810	62.4	34	----	43 (660)
Malvaceae							
Abutilon theophrosti	15	57	760	60.8	42	----	56
Althea rosea	25	41	680	30	36	7200	54
Hibiscus cannabinus	21	46	795	25.0	67	11,100	96
Hibiscus sabdariffa	15	53	770	64.3	48	----	59
Moraceae							
Cannabis sativa	21	50	675	16.6	59	11,100	95

[a] Parenthetic values are SR freeness values at which strengths were determined and are exceptions to the 600 ml.

Table 7

Characteristics of Kenaf Pulps[a] at Three Levels of Neutral Sulfite, Kraft, and Soda Chemicals

Chemical, %	Characteristic: Screened Yield, %	Chemical consumed, %	Initial freeness, ml, SR	Strength at 600 ml, SR: Burst factor, gcm^2/gsm	Breaking length, m	Tear factor, g/gsm
Neutral sulfite						
15	57	77	700	42	7700	74
18	58	72	735	50	8300	80
21	59	73	735	47	8350	77
Kraft						
15	51	94	720	46	7500	70
18	48	90	740	58	9500	74
21	45	85	730	60	9800	85
Soda						
15	52	95	710	41	7400	73
18	46	92	750	54	9000	81
21	45	85	735	56	8700	93

[a] Two hours at 170° C.

Table 8

Pulp Characteristics of Frost-Killed Field-Dried Georgia Kenaf, Everglades 71

Characteristics	Soda, AA %[a]		Sulfate, AA %	
	16.3	19.0	16.3[b]	16.4
Yield				
Crude, %	62	52	55	55
Minus 8-cut, %	60	50	53	54
Cellulose				
Crude, %	87	94	91	90
Alpha, %	68	70	71	72
Pentosan, %	19	19	20	20
Lignin, %	4.9	1.6	2.5	0.9
Chemical consumed basis applied, %	88	78	88	85
Initial freeness SR, ml	790	765	705	740
Kappa number	45.4	20.5	27.3	24.2
Bleach consumed as Cl_2, %	10.2	5.8	6.5	7.0
Yield bleached, %[d]	53	49	48	48
Burst, $g/cm^2/gsm$[e]	54	63	50	53
Tear factor, g/gsm[e]	102	102	93	97
Breaking length, m[e]	9600	10,200	10,300	11,030

[a] AA = active alkali.

[b] Sulfidity = 10%.

[c] Sulfidity = 34%.

[d] Basis digester charge; 75% brightness; CEH sequence.

[e] At 500 ml SR freeness.

Problems of the Paper Packaging Industry in Egypt

Dr. Abdelfattah M. Ghoneim
Mills Manager
Moharrem Press
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The main factors affecting this industry are the usual factors affecting all other industries: raw materials, machines, and trained labor. I shall concentrate here on the problems of raw materials and the chemical treatments demanded in the paper packaging industry.

Corrugating Paper

The manufacture of corrugated boxes is a very important branch of this industry. Its first problem is that local liner and corrugating medium are not up to specifications.

Local liner is made of waste paper mixed with some virgin kraft pulp and some unbleached bagasse or rice straw pulps. Strength properties are very poor, and basis weight and caliper fluctuate in each reel.

Local corrugating medium is made of lime-cooked rice straw mixed with some third-grade waste paper. It has a very weak flat crush, and other strength properties also are low. In addition to its heterogeneity in basis weight and caliper, the paper is abrasive because of the presence of particles of dust and sand originally present in the used waste paper.

Problems with paper have to be solved in the paper mills. In our corrugated board industry, we have a problem to be solved: the production of wet-rigid corrugated cases required for the export of agricultural products. These cases ought to withstand the wetness and humidity of storage in wet conditions without collapsing. The corrugating medium should be impregnated with wax or resin which would increase its rigidity (flat crush) under humid conditions. The adhesive also should be mixed with a thermoset resin to make it water resistant.

We have tried to use a wet-strength fluting medium specially manufactured in a local paper mill. We also have considered impregnating the fluting medium (in-line) on the corrugator with a wax blend, and we have purchased the equipment for this prupose. Other proposals made to us are curtain-coating the finished board and dipping (or cascading) the board in hot-melt blends. Howevever, we need help in solving this problem in the most suitable and economic way, as it deals with an important matter, the export of agricultural products.

Treated Papers

Our second product is gummed, coated, and chemically treated papers.

Gummed paper is manufactured by coating paper with animal glue, gum arabic, or dextrin on special gum-coating machines. Heat-sealing paper is manufactured on the same machines using polyvinyledine chloride (50% emulsion). Our problem here is that the viscosity of this emulsion is lower than is needed, and we must add something to raise the viscosity. We have tried adding polyvinyl acetate, but it causes frothing and sedimentation on the coating cyclinder. Addition of casein glue has given a better result but at a much higher cost.

In this case also, local 60 gm./m.^{2} white paper has been quite unsatisfactory, either

in homogeneity of weight and caliper or in sheet formation and strength properties.

We impregnate paper on the same gumming machines with an imported chemical (Quilon) which is a chromium complex stearate. The impregnated paper becomes water repellent and is used to wrap exported goods, especially yarn, that must be protected against humidity. Our problem here was with local paper which sometimes had bad sheet formation and contained pinholes that spoiled the required effect of waterproofing. We also have impregnated kraft paper with local phenolformaldehyde resins to make electric-resistant paper. We have used imported kraft paper with locally produced resins, but the results from tests at Alexandria University are not yet satisfactory.

Printing

We intend to coat paper with china-clay for printing purposes. We do not have any experience in this field, and we need much help in getting proper formulations. A good part of our packaging paper industry deals with printing. Here also paper is the first problem. Local paper often lacks the following characteristics:

- Smoothness
- Flatness
- Whiteness
- Homogeneity of basis weight and caliper
- Dimensional stability
- Pick resistance to offset inks

The last property is very important in the case of locally coated papers.

Another problem of printing is the local high-gloss varnish, which sublimates during printing and condenses on all machines and air conditioning ducts. We had to stop using it and to try to use an all-over lacquer which permits gluing.

For printing playing cards or any nonabsorbent coated paper, we have to reduce printing machine speed and to put a sheet of paper between each two prints. This increases cost and labour. It has been suggested that we use UV or IR inks with their installations. We have no experience in this field, however, and we would appreciate guidance.

We also need a plastic lacquer to coat printed playing cards that both waterproofs and gives a waxy coating that allows easy slipping of the playing cards. What we have now is a lacquer that fulfills either one of these properties but not both.

Cellulose Fine Structure and Reactivity

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To review the status of this subject is really an unnecessary task before this audience, for Dr. Fahmy, Dr. Hebeish, and the rest of their groups have been so active in this field that I can add little to their contributions. But perhaps there is merit in viewing a familiar scene from a different vantage point. I hope so.

Let us first consider the meaning of our terms. The chemical structure of cellulose is well-established today; fine structure deals with the arrangement of these molecules.

Cellulose occurs in nature as fibers--very long, tough, threadlike bodies. Freed of encrusting materials, fibers can be separated into the component fibrils or microfibrils, which are also long, tough, threadlike bodies on a microscopic or submicroscopic scale. By suitable chemical treatments, the microfibrils can be separated into individual long, tough, threadlike molecules.

I speak of "cellulose" as a single entity, an organic compound with individual molecules. Only a few decades ago, the word was used as roughly synonymous to "crude fiber" or to "pulp," but increased knowledge has made it possible and desirable to differentiate between fiber components. Today, cellulose is well known as an organic polymer with certain chemical and physical characteristics.

It is briefly a β-1,4-glucan, meaning that a long chain of glucose molecules are joined regularly, the first carbon of one glucose unit by a β- linkage to the fourth carbon of the next (Figure 1).

The most reactive part of the cellulose molecule is the hydroxyl group. It may be considered a small magnet with a positive and negative pole. Two cellulose chains lined up parallel to each other behave like two strings of small magnets. The hydrogens of the hydroxyl groups can form hydrogen bonds to oxygen atoms in the neighboring chains. Such hydrogen bonds are weaker than the main covalent bonds along the chain, but there are many of them and they contribute considerably to the strength and toughness of the fiber. Most of the chains in the cellulose microfibril are so regularly aligned that they give an x-ray diffraction diagram like small crystals. The molecules responsible for this crystal lattice are locked in place by hydrogen bonds.

In Sarko's representation (1) of hydrogen bonding between alternate chains in this so-called "crystalline" portion of cellulose, to which representation Blackwell (2) also agrees, the black circles represent oxygen atoms and the dotted lines hydrogen bonds (Figure 2). The molecules are stiffened by the intramolecular bonds O(3)-O(5') and O(2')-O(6) and are held to each other by O(3)-O(6) bonds. Such a series of similarly spaced molecules forms a molecular sheet. The available hydrogens are all used up in this structure, so the sheets are held to neighboring sheets by weaker forces, probably Van der Waals'. This scheme differs considerably from that of Liang and Marchessault (3), where the sheets are hydrogen-bonded to each other (Figure 3). Also, Liang and Marchessault propose antiparallel molecules in adjacent sheets; that is, molecules in one sheet run in the opposite direction to those in the next. Sarko's model has parallel sheets of molecules.

However that may turn out to be, this regular arrangement of chains is so dense that even water molecules do not penetrate it (4), and it extends essentially throughout the microfibril. Besides the cellulosic microfibrils, however, there are other carbohydrates, the hemicelluloses, in the fiber; and there is an interpenetrating system, between and to

some extent within the fibers of something quite different chemically, that is, lignin. If cellulose is to serve as a chemical raw material, that is, as a dissolving pulp, these other materials must be removed. In fact, most of the lignin has to be removed for most papermaking, if only to facilitate defibering.

Methods to Remove Lignin

The methods of delignification depend on the ultimate use of the fiber and on the raw material. The cotton fiber is almost pure cellulose, and in making chemical cotton from linters an alkaline pressure cook and a mild bleach removes the slight wax and pectin content. Wood and straw contain both hemicelluloses and lignin; straw contains more hemicelluloses and less lignin. Since lignin is an entirely different type of polymer from cellulose, it can be removed chemically without much damage to the cellulose by either the kraft or the sulfite process. Straw can be pulped by a milder chlorination process, and other fibers respond to modifications of these processes. The production of a dissolving pulp requires a subsequent alkaline treatment and, for kraft dissolving pulps, a prehydrolysis stage for hemicelluloses as well.

Affinity for Water

If we accept the "crystallinity" of cellulose and the imperviousness of the crystallite to water, we must explain the marked affinity of the fiber for water. Highly dried cellulose will compete for water with such strong dehydrating agents as sulfuric acid. The adsorption isotherm of water and cellulose (5) is familiar to most of you (Figure 4). The simplest way of explaining the adsorption of water is that cellulose does not consist of perfect crystals; there are a number of ways of visualizing the imperfections. The original proposal [see Hermans' review (6)] of alternating ordered and disordered regions (the fringed micelle theory) has been modified by Hearle (7) to the fringed fibril theory and by Frey-Wyssling and Mühlethaler (8) to a single defective crystal. Less similar models are Frey-Wyssling's earlier proposal (9) of a crystalline core with a paracrystalline cortex, Ruck's "cable" model (10), Tonnesen and Ellefsen's folded chain (11), and Manley's helical folded chain (12). Scallan (13) has developed a quantitative model for the fringed micelle, which I should like to discuss.

Scallan's calculations are based on the hypothesis that the accessibility of cellulose to acid hydrolysis and to water is different. Figure 5 is a qualitative model of the fringed micelle structure. In the fringed fibril model the crystallites are more nearly perfect and are interconnected by an occasional molecule crossing over. The defective crystal model contains only very small disordered regions as defects. If we subject the model structure to acid hydrolysis, all of the glycosidic linkages in the disordered region are available but not those in the crystalline region. Water sorption or deuteration, on the other hand, takes place on all the hydroxyls in the noncrystalline phase, but also on those hydroxyls which project from the surface of the crystallites (Figure 6).

Sizes of Molecules and Crystallites

Figure 7 indicates the cross section of a crystallite. Although represented here as square, it is probably rectangular. The same principle of calculation will apply to rectangles, but the value for accessible hydroxyls will be slightly higher. The calculation of the width of the molecule can be done on the basis of the relationship:

$$f = {}^{2n-1}/_{n^2}$$

where f = the percentage of projecting hydroxyls, 44% in the figure, and n = number of molecules per side. The actual value of f for a given type of cellulose may be obtained from the equation:

$$R_D = R_A + f(1-R_A)$$

where R_D and R_A represent the fraction of the whole sample accessible to deuteration and to acid, respectively. Since we know the distance between molecules from x-ray data (5.7 Å is the average of spacings 101 and 101) we can thus calculate the width of the micelle.

The length of the crystallite may be estimated from the leveling-off DP. A very brief description of this phenomenon will suffice here. When cellulose reacts with dilute acid, the DP drops rapidly at first, then much more slowly. Under some conditions, it stays almost constant. The most common interpretation of this is that the rapid reaction is chain scission in the regions of low order and that the leveling-off DP corresponds to the crystallite length.

Figure 8 is a scale drawing of some common types of cellulose micelles, and Figure 9 presents the parameters for these types. These slides illuminate an important point. The crystallite width of native cellulose is about the same as that of the elementary microfibril as seen under the electron microscope. In other words, the microfibril is essentially one long chain of crystallites; this is the real unit of cellulose. The portion joining the crystallites endwise, which is accessible to almost all reagents, is the very small disordered region (Figure 9). This is so small relatively that the defective crystal and the fringed micelle the ry are practically equivalent.

Effects of Liquids

Water, as we have seen, is adsorbed on cellulose but does not penetrate the microfibril. Other liquids behave differently, and this has an important bearing on swelling, solubility and reactivity.

When bone-dry cotton (essentially pure cellulose) is immersed in water, the fiber width is increased about 20% (14). The x-ray diagram is not changed. This is called intercrystalline or interfibrillar swelling. The water is adsorbed by H-bonding with accessible hydroxyls, mostly on the fibrillar surface. This water separates the fibrils and increases the fiber width. Many liquids, such as the aliphatic alcohols, exhibit a lower intercrystalline swelling than water, and some nonpolar liquids, such as benzene, are essentially nonswelling.

Intracrystalline or intrafibrillar swelling is more striking. The liquid penetrates into the microfibril itself, and the increase in fiber width is much greater and may even result in solution. Let's first look at some intrafibrillar swelling that does not cause solution. Some nonaqueous liquids that are more polar than water swell cellulose more than water does, such as dimethyl sulfoxide; so do some amines. The case of ammonia and the amines has had special attention by the x-ray scientists, who have found that new amine-cellulose complexes have produced a new internal arrangement in the crystallite, but the swelling agent most studied has been aqueous sodium hydroxide. The literature review by Warwicker, et al., is excellent (15). About 1850, Mercer showed the effect of strong (15-20%) caustic on cotton and used it commercially to produce mercerized cotton (16). Warwicker is one of many who have measured this swelling (Figure 10). Several points are worth noting. Swelling is greater at lower temperatures. As far as alkali concentration is concerned, there is a maximum at room temperature at about 16% NaOH, There is still, after all these years, some argument about the interpretation of all the phenomena. The hydrogen bonds between the sheets of molecular chains on the 002 crystallographic planes are broken, and the free hydroxyl groups either react with the alkali to form an alcoholate, as Benoyelle (17) proposes, or with the hydrate water of the sodium ion, according to Chédin (18). At all events, the hydrated sodium ions enter the structure, and the very large hydrated ions push the crystal laminae apart to produce the observed change in dimensions. However, the laminae are not separated into individual molecules, as would be necessary to produce solution.

There are liquids, however, which go further and result in solution, which may be considered as infinite swelling. Before we take these up, though, a simplistic comparison of solution processes for small molecules and for macromolecules may be helpful.

Figure 11 shows the steps involved in swelling and dissolving a polymer such as cellulose. These are essentially those involved in dissolving a small molecule such as sugar. First, the solvent must reach the solute (diffusion). Then any bonds holding the solute molecules together, e.g, hydrogen bonds, must be broken by some component of the solvent. Then the solute molecules must be solvated. In the case of cellulose, the free hydroxyls

are solvated, not necessarily all by the same component of the solvent. Since the number of bonds per molecule of sugar is three or four orders of magnitude less than with cellulose, the rates are different. Also, the hydrogen bonds in cellulose are not equivalent as to ease of scission. Moreover, H-bond breaking and forming are equilibrium reactions, and the molecules must be separated to prevent recombination. This is one thing solvation does. For some solvents, the stages shown in parentheses may occur with cellulose (not usual with sugar). Completely solvated molecules are readily separated; this is solution. But in a chain of 1,000 or more units, some may be solvated with enough mobility to permit the entrance of more solvent (swelling), and yet the presence of some unsolvated or unbroken bonds holds parts of the chain to other chains. This results in a swollen gel, which might be called "partial solution." It does not occur with small molecules, but swelling is a characteristic stage in polymer solution and is the final stage of interaction in some cases.

Such limited swelling occurs with mercerizing liquors, with ammonia or the aliphatic amines, and with true solvent mixtures at concentrations outside the range in which cellulose is dissolved. The interaction of cellulose with sodium hydroxide stops at the stage of the swollen gel. But there are organic hydroxides of comparable basicity to sodium hydroxide with extremely large cations, such as trimethylbenzyl ammonium hydroxide, which actually dissolve cellulose. It is believed that these form bulky complexes with cellulose which prevent reaggregation of cellulose molecules and form a true solution.

The molecular species in cellulose solutions are rarely unchanged cellulose. They may be ionized forms or protonated forms or complexes of one sort or another. Alternatively, it may be a chemical derivative of cellulose that dissolves, either an unstable one such as cellulose xanthate or a stable one such as cellulose acetate. Even omitting the stable derivatives, there are still a good many solvents for cellulose. Figure 12 tabulates aqueous solvents. Figure 13 tabulates some nonaqueous solvents.

Cellulose Reactions

Much that has been said of solution applies equally to reaction; they are similar interactions. In fact, we have already noted that the molecular species dissolved in a cellulose solution is frequently a cellulose derivative or a complex, albeit commonly an unstable one.

Reactions may be conveniently divided into homogeneous reactions (in which there is a single phase, usually a solution for both the cellulose and the reagent) and heterogeneous reactions (usually with the cellulose in a solid phase and the reagent in either a gaseous or a liquid phase). Homogeneous reaction is similar to other solution reactions. The attack on the cellulose is random; any molecule or any hydroxyl along the molecule is equally available. Heterogeneous reaction is different; the cellulose still retains the fiber form or, at least, some form of structure. The stages we discussed in connection with swelling have corresponding stages here; reaction may be initiated at any stage of the swelling process. If a uniform and fairly complete reaction is desired, homogeneous reaction is preferable; if this is impossible, a highly swollen state can be used with a swelling liquid that does not interfere with the penetration and reaction of the reagent. If only a partial reaction is desired, as is often the case, swelling may or may not be advisable. These considerations will be important in many of the individual cases which we shall be discussing shortly.

Since the course of the reaction is so greatly influenced by reaction conditions, let us consider separately three types of reaction media: aqueous, alkali-swollen, and nonaqueous. There are important industrial processes of each type, and I shall not attempt to discuss them all -- life is too short -- but I shall cover some of the more important ones.

One of the most important reactions of cellulose that takes place in aqueous solutions is cross-linking. It does not really belong in a discussion of dissolving pulps, but rather with our neighboring discussion on cotton. I hope I'll be pardoned if I draw on work done by my former colleagues at the Southern Regional Laboratories in New Orleans.

Cotton (or rayon) can be cross-linked by a number of compounds, in fact, by almost any compound or mixture which can develop two sites in the same structure, which are reactive to the hydroxyl group. Perhaps the simplest such compound is formaldehyde, which reacts in

aqueous solution as if it were dihydroxymethane. Indeed, there is evidence that this species may exist in formaldehyde solutions. For my purposes today, formaldehyde is the only cross-linking agent which I shall discuss, for an excellent piece of work done almost 20 years ago by Reeves, Perkins, and Chance (19) on this subject very clearly brings out the importance of fine structure on the cross-linking of cellulose. Figure 14 points out the processes which occur in cross-linking unswollen cotton and waterswollen cotton. Actually in these experiments the cross-linking was carried out with formaldehyde and acetic acid in various concentrations ranging from anhydrous acetic acid (not quite nonswelling, but much more so than water) to pure water. Fibers cross-linked in the swollen state have poor dry wrinkle recovery, low wet density, and unrestricted swelling in contrast to those cross-linked in the nonswollen state. Reeve's explanation of this can be followed on the slide. In nature cellulose molecules are held together by H-bonds. (Incidentally, the same argument applies also to microfibrils or to diurnal layers in cotton.) In conditioned cotton, some of these bonds are broken; in wet cotton, more of them, opening up the internal structure. Cross-linking of any given length can span much more of the dry than the wet fiber as shown at the bottom. In fact, cross-linking of the wet fiber has essentially only replaced H-bonds by chemical cross-links, as can be seen by comparing the original dry cotton with that cross-linked in the swollen state.

This difference in reaction caused by changes in the fine structure occurs in many other reactions, but it is so clearly indicated by Reeves's explanation that I have discussed cross-linking first.

Reactions Related to Pulp and Paper

For many reactions, most etherifications and the xanthation reaction, pulp is first swollen, most commonly with caustic soda. In this case, small differences in fine structure are eliminated by the swelling action of the alkali. Still, we can find something of interest here as well. Take methylcellulose, for instance. Ordinary methylcellulose, manufactured by the action of methyl chloride on alkali cellulose, has the solubilities shown in Figure 15. However, Traube and his coworkers (20, 21, 22) methylated the addition compound, sodium cupricellulose, and found the resulting methylcellulose water soluble at DS as low as 0.8. This was attributed to more uniform distribution of substitution. This result, corroborated by Timell (23), indicates that the molecules are more readily available. This evidence was carried a step further by Bock (24), who methylated solutions of cellulose in aqueous trimethylbenzylammonium hydroxide and similar bases. In this case, water-soluble ethers were produced at DS 0.6 or 0.7.

Cellulose xanthate is a more interesting case than methylcellulose, though the fine structure of the original pulp is of less interest. Fahmy and Roffael (25) have shown that of the various differences between pulps, only the retention values for water and for alkali correlate with differences in filterability.

On the other hand, the fine structure of the rayon itself is very important. Many of the various types of viscose rayon differ in the fine structure of the fiber. The basic principles of processing and structure were well expressed almost 20 years ago by Sisson (26) and most of his ideas are valid today.

If the cellulose xanthate solution is passed into a simple bath of sulfuric acid and sodium, ammonium, or magnesium sulfate, two main processes occur: coagulation (salting-out) by the salt and regeneration of cellulose by the acid. If stretching is introduced between these two steps, high orientation and large, highly ordered crystalline areas result. If, however, regeneration is retarded in some way until the coagulum is less swollen, the crystallites formed are smaller and less perfect. This latter is the so-called skin structure as distinguished from the other, core structure. Since the less ordered, accessible regions of the skin have a different affinity for dyes and, of course, other large molecules (resins, for instance) they are easily distinguished microscopically.

There are two major ways of producing such retardation of regeneration. One of these is by the addition to the xanthate solution of certain organic compounds which serve as retardants (amines, polyoxyalkylene derivatives, quaternary bases). The other method is the addition of a zinc salt to the spinning bath. In this case, the solution is converted

to an outer layer of zinc xanthate on the filament surface. This material is tough and can be stretched more than a regenerated structure, giving higher orientation, while zinc cross-links probably promote nucleation, but hinder growth, which accounts for the many small crystallites.

Types of Rayons

Most rayon producers make a number of types of rayon, and there are many companies. Thirteen companies manufactured 96 types in the United States in 1969, and one company alone produced 23 (27). Many of these differ considerably from each other in their properties, but not always because of differences in fine structure. There are also many types containing additives, fibers containing flame retardants or other additives, or grafted fibers to attain various effects (28). The complete story of grafting, however, is too long and involved to cover here.

Many rayon types differ predominantly in fine structure, however. There are, for instance, those crimped rayons (26) which consist of two components, skin and core, in an unbalanced structure such that the differences in swelling and shrinkage of the two components produces the crimp.

Probably the most important special types of rayon with different fine structure are the high tenacity yarns originally developed for tire cord (29). Here the crystallites are smaller and more numerous than in regular rayon (30) and the so-called "all-skin" fibers, when fully processed, have a uniform, dense structure and a circular or kidney-shaped cross section. The fibers are spun from a dilute viscose solution of high DP into a bath high in zinc and relatively low in acid at low speed at a temperature of 50°-60° C.

Other types of rayon to be mentioned are the high wet-modulus rayons which, like cotton fibers, resist deformation in the wet state (30). The HWM rayon processes reduce or eliminate aging, so that the cellulose, both at the start and in the finished fiber, has a much higher DP. The resultant fibers have higher density, crystallinity, and orientation, with both longer and thicker crystallites than regular rayon. These highly oriented fibers have a distinct fibrillar structure.

There are two types of HWM rayons, the "polynosics" and the modified HWM types. The latter uses organic modifiers in the viscose, as already discussed. The polynosics are spun from low-alkali viscose into dilute acid-sodium salt baths at low temperature under conditions favoring high crystallinity and orientation. The polynosics have even higher wet modulus than the modified types.

A third type of fiber with high wet-modulus uses a different type of organic modifier, formaldehyde (31). The action of formaldehyde is different from that of the other modifiers, however. Whether it is added to the viscose or to the spinning bath, it reacts with cellulose xanthate to form the S-hydroxymethyl derivative. Further reaction evidently occurs also, as there is some cross-linking by methylene groups in the finished fiber. This type of rayon is no longer commercially available in the U.S.A.

Cellulose Derivatives

Finally, let us look at derivatives formed in nonaqueous systems. The most important of these is cellulose acetate. This has been an important commercial product since the early 1920's, and we know more about its manufacture than about that of most other cellulose products. The fine structure of the pulp is of great importance; at least, one aspect of it is.

Cellulose acetate may be prepared either from cotton linters pulps or from dissolving pulps, usually from wood. In either case, it is necessary to have rapid and complete reactivity. Whether dissolving pulps are made by the sulfite process or by the prehydrolyzed draft process, a final alkaline extraction is necessary to remove all the hemicelluloses. To reach the requisite high alpha content, 95-96%, the 3-4% caustic used for viscose pulps is usually not satisfactory. Increased concentrations remove the hemicelluloses but lower the yield by degradation. The yield can be kept high by the use of mercerizing strength caustic (17.5%) at lower temperatures, but the swollen pulp hornifies on drying and becomes

unreactive because of the hydrogen bonding. Using 8% caustic at 30° C. is satisfactory if done in the absence of air. However, one must be careful not to over-dry, for this, too, may reduce reactivity because of hornification, i.e., hydrogen bonding, which reduces reactivity (32). Even cotton linters, which has much milder purification procedures, is generally dried at 60°-80° C. if it is to be used for acetylation, so as not to impair reactivity, for even less swollen pulp than alkali-cooked pulp may undergo some hornification (33).

To ensure uniform reactivity, pulps are activated before acetylation by steeping in acetic acid. The concentration, time, and temperature conditions and the addition of acid catalyst or not will depend on the pulp and the process.

But before discussing the usual commercial acetylation, let us say a very little on the acetylation of pulps for paper. Bletzinger (34) and Aiken (35) showed at very low degrees of such fibrous acetylation (up to about 0.3) there is actually an increase in moisture content and in papermaking properties. This was later corroborated by Herdle and Griggs (36). All these investigators found that at higher DS moisture content begins to drop off. Above DS of about 1.0 paper is too low in strength to be of value. These data are explained by an initial loosening of structure overbalancing the blocking of the hydroxyls, while in the later stages the hydrophobic nature of the acetate groups is the controlling factor. Fahmy (37) advanced our knowledge of this considerably when he showed partial deacetylation of such pulps in the higher ranges down to a final DS of about 1.0 gave higher strengths than pulps acetylated directly to these values. This was attributed, I believe correctly, to a more uniform substitution so attained. At very low DS this effect was not observable.

The usual solution process of preparing cellulose acetate is so well known that we can omit any lengthy discussion of this, but the role played by fine structure can be beautifully illustrated by looking briefly at cellulose triacetate. As you know, it can be prepared by the solution process if, instead of hydrolyzing the "dope," we add magnesia to neutralize the acid and continue acetylation. But it can also be prepared by acetylation in the presence of a nonsolvent. The two products differ, however. Cellulose triacetate (DS 2.9) prepared homogeneously by the solution process is soluble in chlorinated hydrocarbons and some acid solvents (acetic acid, cresol and some others). At DS 3.0, completely acetylated, it is soluble only in acid solvents (38). Heterogeneously fibers (fully acetylated cotton, for instance) are only partly soluble in these solvents over the range DS 2.7-3.0, perhaps because a very few of the original hydrogen bonds remain unbroken. This is confirmed by looking at the results of Buras on fully acetylated cotton (39). Under conditions leading to so-called complete acetylation in the presence of a nonsolvent, a DS of 2.7-3.0 was obtained with the lint fiber, but the constraints on swelling produced on the fine structure of the cotton during processing were such that yarns reached only 2.4-2.7 and fabrics 2.7-3.0.

I wish we knew more about some of the nonaqueous reactions of cellulose. It is particularly interesting to find that research at ITT Rayonier has shown that fibers spun from DMSO solutions of cellulose have high-wet modulus fully comparable to the HWM fibers produced from zinc cellulose xanthate. This work has been presented before the American Chemical Society and TAPPI, but not yet published. The solutions used were with the DMSO-N_2O_4 (40-41) and the DMSO-formaldehyde solvents (42) recently developed.

I thank you all for the privilege of discussing these matters with you and for your attention. This talk has been an informal review of the fine structure of cellulose, with examples of its influence on reactivity in various media. For a more formal review of the effect of both gross and fine structure on various cellulose reactions, Segal's paper (43) can be highly recommended.

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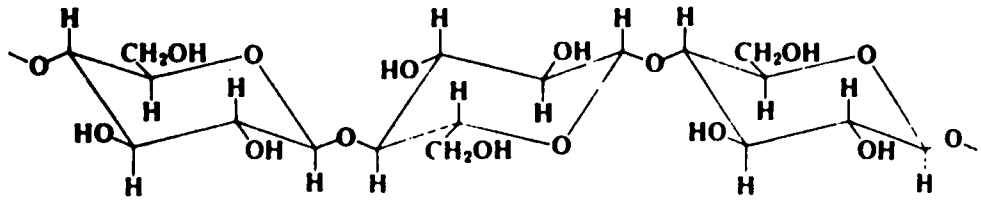

Figure 1. Cellulose

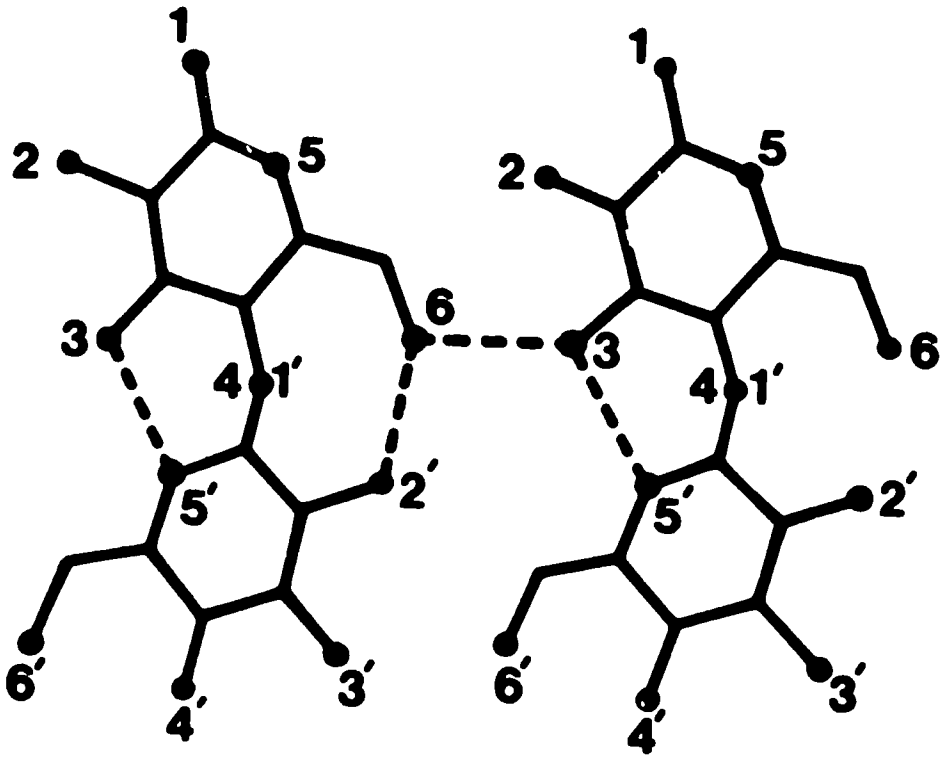

Figure 2. Hydrogen bonds (dotted) between adjacent cellulose chains (002 plane).

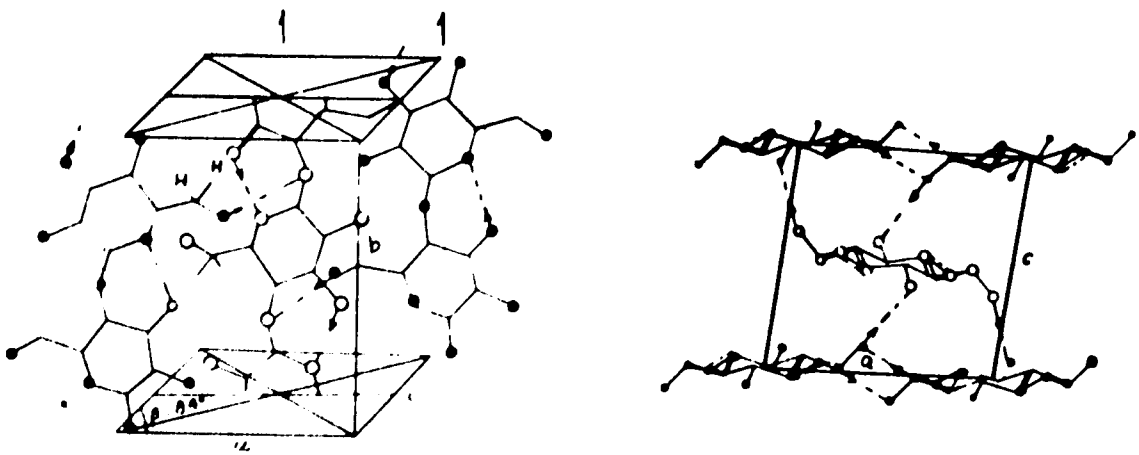

Figure 3. Cellulose unit cell: (left) arrangement of CH_2OH groups in cellobiose unit; (right) hydrogen bonds in cellulose I unit cell.

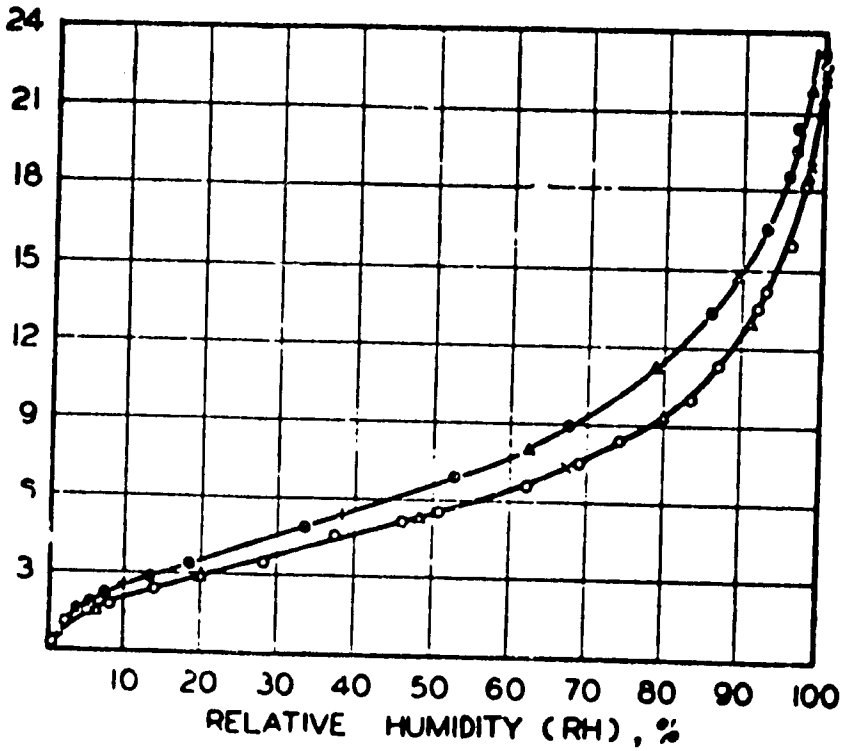

Figure 4. Sorption isotherms of cellulose

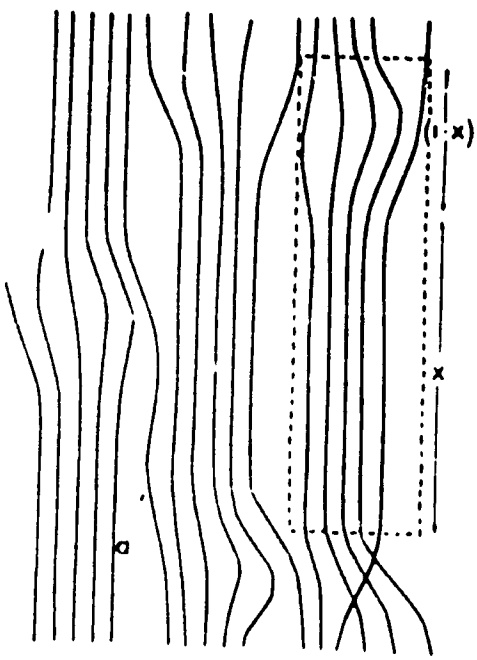

Figure 5. Cellulose fine structure

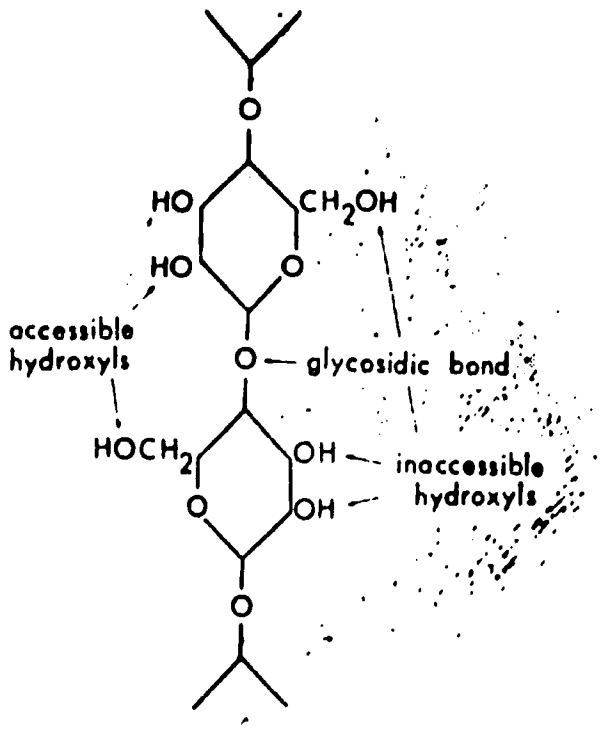

Figure 6. Crystallite surface.

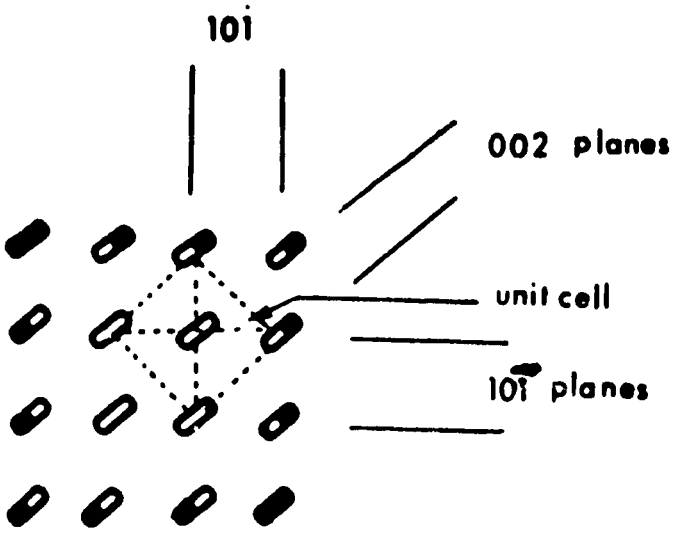

Figure 7. Cross section of crystallite

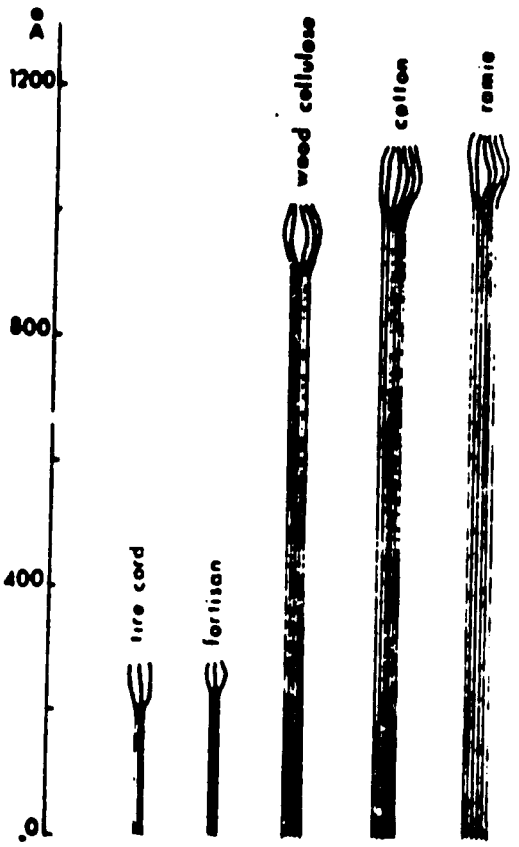

Figure 8. Cellulose crystallites

VARIOUS PARAMETERS OF THE FRINGED MICELLE

Cellulose	Crystallinity %	n	Crystallite Width, A	Crystallite Length, A°
Viscose Rayon	64	2.9	16	180
Wood	89	4.7	27	927
Cotton	89	5.4	31	1015
Ramie	89	5.8	33	1045

Figure 9. Some Typical Celluloses

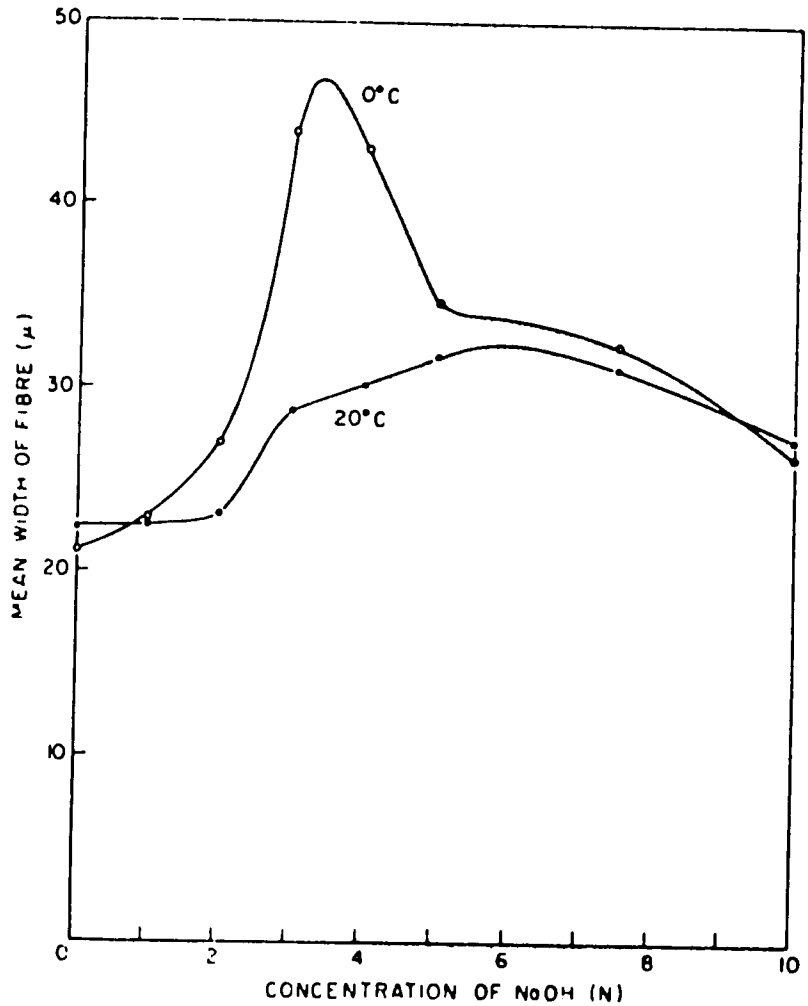

Figure 10. Mercerization

STAGES OF SWELLING OF CELLULOSE

Adapted from Faserforsch. Textiltech. 24, 113 (1973)

Diffusion

Hydrogen Bond Breaking

Solvation
(or Complex Formation and Solvation)

[Hdyrolysis or Degradation]

[Diffusion out of Fragments]

Separation of Solvated Portions

Figure 11. Swelling and Solution

AQUEOUS SOLVENTS FOR CELLULOSE

1. Acids

   a. Sulfuric
   b. Phosphoric
   c. Hydrochloric

2. Salts

   a. Zinc Chloride

3. Alkalies

   a. Quaternary Ammonium Hydroxides

4. Complexes

   a. Cuprammonium Hydroxide
   b. Cupriethylenediamine Hydroxide
   c. Cadmium-Ethylenediamine Hydroxide
   d. Iron-Sodium Tartrate

Figure 12. Aqueous Cellulose Solvents

NONAQUEOUS SOLVENTS FOR CELLULOSE

1. Single Compounds

   a. Amine Oxides
   b. Quaternary Salts
   c. Bis(bihydroxypropyl) disulfide
   d. Hydrazine

2. Solutions (other than the preceding)

   a. Amines in Polar Solvents
   b. Sulfur Dioxide and Amines in Polar Solvents
   c. Nitrogen Oxides or Nitrosyl Chloride in Organic Solvents
   d. Polyphenols in Pyridine
   e. Chloral in Pyridine
   f. Formaldehyde in DMSO

Figure 13. Nonaqueous Cellulose Solvents

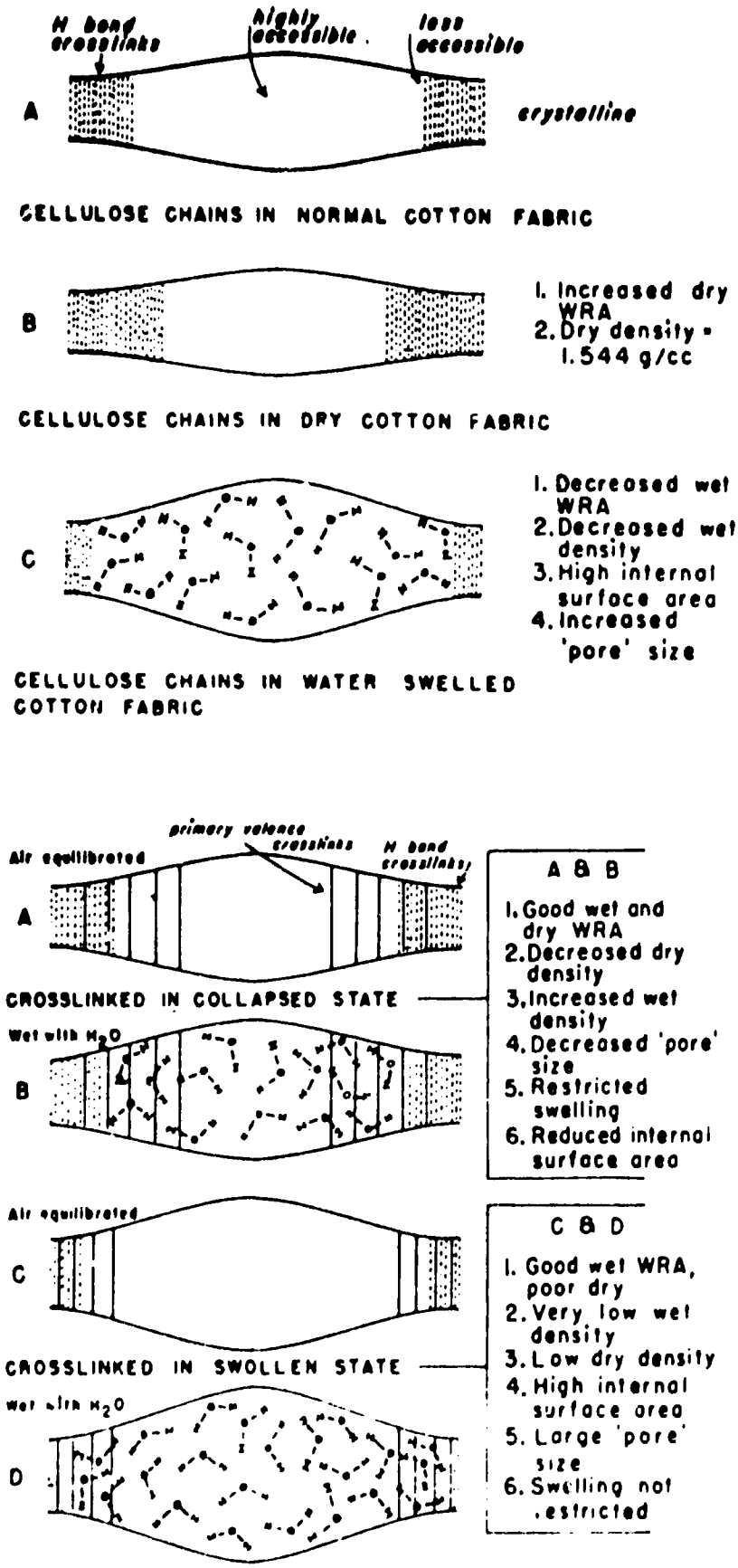

Figure 14. Model for dry and wet cross-linking of cotton. Dotted lines represent hydrogen bonds; transverse lines (lower figure) represent covalent linkages.

SOLUBILITY OF METHYLCELLULOSE

DS	Solvent
0.1 - 0.6	Dilute Alkali
1.3 - 2.6	Cold Water
2.6 - 2.8	Organic Solvents

Figure 15. Methylcellulose Solubility

Recovery of Rice Straw Black Liquor

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In the preparation of chemical and semichemical pulps from either wood or nonwood plant fibers, considerable quantities of cooking chemicals (200 to 500 kg. per ton of pulp) are used. The waste or black liquor resulting from the pulping process contains about 95 to 98% of th total chemicals charged to the digester, while about 2 to 5% of the chemicals are lost with the pulp from the washing system. In addition, about half the weight of the fibrous raw material dissolves in the waste or black liquor during the cook. However, the composition of the black liquor varies considerably in different mills and depends on the type of fibrous raw material, the cooking chemicals, and the method and conditions of cooking. The organic substances removed from the fibrous raw material during the cook, as well as the inorganic chemicals charged, are present mainly in the form of salts. The content of solids is around 20% for kraft black liquor and 14% for sulfite waste liquor from wood. However, the solids content varies with the type and the moisture content of the wood used, the amount of liquor charged to the cook, and the pulp yield and may be as low as 17% for kraft and 12% for sulfite waste liquor.

It is of vital economic importance to recover the cooking chemicals for preparation of new cooking liquor. Also, the heat economy requires that part or all of the organic substance dissolved during the cook should be burned to generate heat. The combustion of the organic substance is also necessary for combating stream pollution caused by effluents of pulp mills, especially when they are located in mid-country or near important fishing districts. Another alternative for the combustion of the organic substances is the conversion of these substances to valuable by-products such as alcohols, organic acids, vanillin and, other lignin derivatives.

IMPORTANCE OF RECOVERY OF RICE STRAW BLACK LIQUOR TO RAKTA CO.

Rakta Pulp Mill, Alexandria, is producing about 24,000 tons/year bleached rice straw soda pulp. In 1979, the production capacity will be doubled to about 50,000 tons/year. The total amount of rice straw used will be approximately 160,000 tons/year. The caustic soda required for cooking the straw will reach approximately 16,000 tons/year.

The black liquor resulting from cooking the straw will amount to 800,000 tons/year with a total solids content of approximately 9%. This means that the black liquor would contain 72,000 tons of solids, including about 15,200 tons of alkali in the form of free caustic soda and sodium salts of organic and inorganic acids.

The value of alkali present in the black liquor, calculated on the basis of L.E. 115/ton of sodium hydroxide, would be 15,200 x 115 = L.E. 1,748,000. The value of heat that could be generated from the liquor dry solids, calculated on the basis of L.E. 7.5/ton of mazut with a calorific value of 10,000 Kcal./kg. compared with 2,820 Kcal./kg. for black liquor dry solids, would be

$$\frac{72,800 \times 2,820 \times 7.5}{10,000} = \text{L.E. } 152,280$$

The total value of heat and chemicals of the black liquor per year would be 1,748,000 + 152,280 = L.E. 1,900,280.

It is evident that the recovery of rice straw black liquor for heat and chemicals

would be very profitable to Rakta Co., as it will save most of the cooking chemical (caustic soda) together with a part of fuel oil. In addition, recovery of black liquor will reduce the stream pollution in Abu Qir Gulf, Alexandria, where the effluents of the mill are disposed.

STUDIES ON RECOVERY OF HEAT AND CHEMICALS FROM RICE STRAW BLACK LIQUOR

The Silica Problem

Rice straw black liquor is still not recovered for heat and chemicals because of its high content of silica (10-14 g./l.) which causes troubles in the recovery process. These troubles prevent the normal operation of a standard recovery plant (evaporator-recovery boiler-causticizer) as explained below (2).

In the evaporator, silica reduces the evaporating capacity by forming scales of sodium silicate and other insoluble silicate compounds (calcium, aluminium, etc.) on the evaporator tubes. Therefore, operation must be stopped from time to time to remove the scale. Removal of the scale is not easy, either physically or chemically.

In the recovery boiler, silicate compounds, together with other chemicals, gradually form beehive deposits on the walls of the boiler and between boiler tubes, causing a drop in boiler function. When there is a remarkable accumulation of silica in the causticizer, sedimentation speed of lime sludge during the causticization of green liquor is reduced, which makes the separation of alkali liquor difficult.

Past Studies and Methods of Desilication

As already mentioned, silica trouble is the significant problem in the use of rice straw black liquor for recovery of heat and chemicals in a standard recovery plant. It is logical, therefore, to remove the silica from the black liquor before it enters the recovery plant. In this connection, several methods for desilicating the black liquor have been developed. They are the calcium oxide method, the carbon dioxide method, and the magnesium sulfate method.

Silica can be precipitated as calcium silicate by means of calcium oxide. The temperature, the quantity, and the conditions of calcium oxide addition and the concentration of the black liquor are very important factors. Precipitation of silica from aged weak liquors meets with considerable difficulties (1) because a part of the silica occurs in slimy form which impedes, if not prevents, filtration.

Silica may also be precipitated by reducing the pH of the liquor. There are several ways to reduce pH, such as by introducing carbon dioxide or carbon dioxide-containing gas mixtures, e.g., flue gases (1-8). The application of carbon dioxide-containing gas mixtures preferred to pure carbon dioxide to prevent local over-acidification and resulting increased precipitation of lignin (1).

pH can be reduced by addition of sodium hydrogen carbonate (7,8), magnesium chloride, or sulfuric acid (4). However, use of sulfuric acid and its salts is prohibitive in processes using sulfur-free black liquors. Desilication is very poor when using magnesium sulfate (2) and recovery of chemicals is not possible using the salts of hydrochloric acid.

The precipitation of silica occurs within a range of pH 10.2 to 9.1. Coprecipitation of lignin occurs. Its part of the total precipitated quantity, however, ranges within tolerable limits. Coprecipitation of lignin increases linearly in this pH range with decreasing pH value. At a pH smaller than 9, lignin precipitation intensifies. On the other hand, the silica content in the treated black liquor depends on the pH value.

None of these methods has been applied on a commercial scale in pulp mills using rice straw.

Recent Studies on Desilication of Rice Straw Black Liquor at Rakta Mill

The object of this study has been to determine which of the different desilication methods is most suitable for removing silica from rice straw black liquor in order to enable trouble-free evaporation, combustion, and caustification of the liquor. Desilication was to be effected by precipitation with sodium bicarbonate, with calcium oxide, or by acidification with a carbon dioxide-containing gas mixture. Parallely, the sedimentation behavior as well as the filterability of the separated silica was to be examined.

The black liquor used in this investigation showed the following analysis:

pH	10.8
Density, g./ml.	1.047
Dry solids, %	8.68
SiO_2 content, g./l.	9.74
Calorific value of dry solids, Kcal./kg. DS	2,820

Desilication with Sodium Bicarbonate. Precipitation of silica in black liquor was done by the addition of a 10% aqueous solution of sodium bicarbonate to the black liquor to reach a pH of 9.5 and mixing the mixture for 30 min. followed by agitation for another 10 min. and then filtering. The addition ratio of sodium bicarbonate to silica was 0.59:1.

Desilication with Calcium Oxide. Silica was precipitated by the addition of quicklime containing approximately 60-70% active CaO at a $CAO:SiO_2$ ratio of 1.2-2.4:1. The mixture was boiled for different periods of time ranging from 5 to 60 min. The mixture was subsequently filtered through filter paper with the following results ($CaO:SiO_2$ Ratio 2:1):

Retention period, min.	5	15	30	60
Filtration period, min.	3.35	2.15	1.30	1.33
pH	11.8	12.5	12.4	12.3
SiO_2 in filtrate, g./l.	2.0	0.4	0.2	
Amount of precipitate, g.	68	73	73	
Analysis of precipitate				
SiO_2%	11.5		14.3	
CaO, %	52.0		45.0	
Na_2O, %	2.7		3.0	
Org. C, %	6.3		7.3	
CO_2, %	3.9		8.2	

Desilication with Carbon Dioxide. Flue gas from an oil-fired boiler was used for precipitation of the silica at a temperature of 50° to 55° C. The gas was introduced in the black liquor through a glass tube with an opening diameter of 2 mm. at an introduction speed of 3.57 l. flue gas/min. The reaction took 250 min. to a pH of 9.5. It was observed that the pH decreased continuously without any significant formation of foam during the precipitation of silica. At the end of the reaction period, the precipitate was filtered.

Test Results. The results should be summarized as follows:

1. No complete silica precipitation was obtained with any of the three precipitating agents (i.e., sodium bicarbonate, quicklime, and flue gas) when the black liquor contained approximately 4% dry solids).

2. Nearly complete precipitation was reached when the black liquor contained approximately 8% dry solids. After filtration of the precipitates, an average desilication of 95% was found, corresponding to a residual silica in the liquor of 0.3-0.7 g.SiO_2/l.

3. The precipitation with sodium bicarbonate solution, flue gas, and quicklime in a black liquor concentrated to 20-33% dry solids content resulted in suspensions which caused great difficulties on filtration. The filter was completely clogged in a short period, so that filtration could not be completed.

4. Filtration was tried by three different means; namely, paper filter on a 15 cm. filtering flask, a pressure filter type Niagara, and a laboratory centrifuge. The following table provides a brief outline on the separability of the precipitate as a function of the filter equipment used:

Precipitating Agent	DS in the Black Liquor	Separability of the Precipitate		
		Paper Filter	Centrifuge	Niagara F.
$NaHCO_3$ Solution	Approx. 10%	-	+	-
	" 30%	-	+	?
Flue gas	Approx. 10%	+	+	?
	" 22%	-	+	-
Quicklime	Approx. 10%	+	+	+
	" 30%	?	?	?

+ good separability.
- No/poor separability
? No result

The table shows that the precipitates obtained in the individual test can easily be separated from the mother liquor on a paper filter only in the tests in which silica was precipitated with flue gas or in which calcium silicate was precipitated with quicklime from undiluted black liquor.

The filtration properties of a suspension are greatly influenced also by the precipitation conditions as for example type and composition of the precipitating agent such as flue gas or quicklime, speed of precipitation and retention time of the precipitate after its precipitation.

5. Washing the precipitate with fresh water often resulted in a wash water containing higher silica content than that of the filtrate.

6. The amount of flue gas required for silica precipitation was between 50 and 100 l. flue gas l. black liquor. The introduction period for the flue gas was approximately 7 hr., but it is possible to shorten the reaction time by finer distribution of the flue gas.

7. In the precipitation of silica by quicklime, the retention time of the precipitate after precipitation had a considerable influence on the filtration speed. A retention time of approximately 30 min. resulted in a minimum filtration period.

CONCLUSION

The significant problem in the recovery of rice straw black liquor for heat and chemicals is its high content of silica which causes troubles in the recovery process. Past and recent investigations have shown that it is possible to achieve a desilication of up to 95% by using quicklime, flue gas, or sodium bicarbonate as precipitating agents. However, difficulties have been encountered in separation of the precipitate from the mother liquor. In this respect, further investigations would be necessary to overcome such difficulties. Moreover, the larger amounts of silica or calcium silicate sludge which would be obtained after desilication have to be examined for further utilization.

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Background and Activities of the Cellulose and Paper Laboratory

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The Cellulose and Paper Laboratory was established in 1954 as one of the laboratories of the National Research Centre. Work in the laboratory began with a staff consisting of a research supervisor, two research scholars, and two technical assistants. The main function of the laboratory at that time was to carry out research for awarding M.Sc. and Ph.D. degrees in collaboration with the university. Research programs, however, were planned so as to tackle--as far as possible--problems of the existing local industry and to help industrialization of indigenous fibrous raw materials. To the present, 12 Ph.D. and 25 M.Sc. degrees have been awarded as a result of reserach supervised and carried out in the laboratory. Most of the chemists who received their postgraduate degrees in the Cellulose and Paper Laboratory constitute mainly the present staff of the laboratory. This staff is now made up of 15 Ph.D.'s, four M.Sc.'s, and two technical assistants.

Since its establishment, the laboratory has carried out research covering a wide range within the field of chemistry and technology of cellulose, fibers, pulp, paper, board, cellulose derivatives, films, semipermeable membranes, grafting copolymerization, lignin, wood-plastic composites, and other related products. In this respect, the most varied fibrous raw materials were considered, especially those abundant locally such as straws, reeds, sugarcane bagasse, flax, cotton stalks, Eucalyptus wood, cotton staple fibers, cotton linters, etc. Work started with producing paper pulp and dissolving pulp from straws, reeds, and bagasse. These raw materials contain less cellulose and more inorganic matter than wood and usually possess lower fibrous content of small average length. Accordingly, more problems are encountered when using these agricultural residues for producing pulp.

The work carried out here enabled considerable improvements to be made in the quality of pulp obtained from these residues, not only for fine papermaking but also for dissolving purposes. Some work was done in collaboration with industry for producing writing and printing paper from rice straw. Also, work on bagasse for producing paper pulp was planned so as to provide necessary information for setting up a bagasse pulp industry in Egypt. Other raw materials such as cotton stalks were thoroughly investigated. Debarking of cotton stalks, which is rather difficult because of the thin and branched nature of the stalks, necessitated the use of whole stalks. This in turn called for several adjustments of pulping and bleaching methods and conditions to get bright and speckless pulp.

Papermaking Experiments

Beside fine paper, other paper types were also produced on a laboratory scale from indigenous raw materials such as kraft pulp from the long fiber fraction of bagasse and wheat straw. Newsprint also has been one of the topics studied in this laboratory. For wood, mechanical pulping has established itself as an economic process for newsprint production. It delivers high-yield pulp which can run easily at high speeds on paper machines, and the paper so produced possesses good printability. Agricultural residues, however, cannot be defiberized mechanically by the grinders used for grinding wood. Hence, a great number of methods have been suggested by several authors for producing newsprint from agricultural residues, especially from bagasse. These methods range from mechanochemical to semichemical and chemical methods and require blending bagasse pulp with mechanical or chemical wood pulp in different ratios. Thus, hundreds of different ways and means could be used for production of newsprint from bagasse. In this laboratory we have modified some methods and suggested one blend for producing newsprint on a laboratory scale from bagasse. However, the work needs further laboratory experiments, and pilot plant work also is necessary.

The choice of the most suitable method for producing newsprint from bagasse for a specific country is still not easy or simple. The pulp and paper expert group convening in Vienna in 1971 adopted a resolution that further work, especially on the pilot plant scale, is necessary. The sugar company in Egypt is the main organization interested in setting up a newsprint mill in Egypt from bagasse. A representative of the company will give a lecture on this subject. In connection with newsprint it is worth mentioning that promising results were obtained in this laboratory regarding newsprint making from undebarked cotton stalks.

Recovery of Chemicals

With the development of a pulp industry in Egypt, recovery of chemicals from black liquor gained more importance. At present, only one mill, the bagasse pulp mill, is recovering chemicals from black liquor. A detailed review of this process and the problems encountered with it in practice will be presented to you by the production manager of the mill.

Factories using rice straw have no recovery system because of difficulties arising from the presence of high amounts of silica in the black liquor. Desilication of the black liquor of rice straw pulping has been investigated in this laboratory. The isolated silica was used successfully as a filler in papermaking and, with less success, as a pigment for paper coating. Simultaneously, extensive work has been carried out on the recovery of chemicals from rice straw black liquor by straw pulp and paper companies. The work, however, needs to be supplemented by pilot plant scale experiments. The chairman of the board of directors of each company will present a lecture on the experience gained in this field.

Experiments on Hardboard, Particle Board, and Paper Coating

Activities of the Cellulose and Paper Laboratory were further extended to include making hardboard and particle board. It was possible to improve the quality of boards obtained from rice straw, flax, bagasse, and cotton stalks. The chairman of one of the board companies will present a lecture on this subject.

Additives in papermaking as well as chemical modification of paper pulp have been extensively investigated in the Cellulose and Paper Laboratory and still represent one of the current research subjects in the laboratory. A huge number of research articles from other laboratories have been published on this subject. Nevertheless, it is not clear from the literature whether addition or chemical modification is preferable for a certain specific purpose. In our study we found that, in general, physically adding cellulose derivatives or polymers to pulp during papermaking is more suitable than chemically modifying cellulose pulp or grafting copolymerization except for few cases where grafting imparts new properties to paper. Hemicellulose has been successfully used in this laboratory as an additive in papermaking. It was found that some hemicellulose types and fractions act as binders which raise paper strength considerably. Modification of paper surface by coating has been tackled only to a small extent in this laboratory. Problems of packaging paper and coating in local industries will be discussed by the Director of Moharram Press in his lecture.

Preparation of Dissolving Pulp

Extensive research work has been carried out in this laboratory on dissolving pulp. Special attention has been given to indigenous raw materials. Such materials--namely, agricultural residues--suffer from many defects compared to wood, which is the traditional source of dissolving pulp. By a combination of several mechanical and chemical treating steps, pulps of high purity could be obtained from agricultural residues.

Since chemical purity is not the only factor affecting cellulose reactivity and hence dissolution, experiments were extended to prepare the cellulose derivatives and the end

product. For instance, pulps were xanthated and dissolved to viscose. Viscose filter clogging constant was estimated for different samples and correlated to such pulp parameters as crystallinity index, polymolecularity, and fiber swellability in water or alkali solutions. In this connection, the mechanism of the xanthation reaction was thoroughly studied. It was found that, in general, one or two pulp physical parameter besides pulp chemical criteria could reveal pulp suitability for viscose preparation, especially regarding filter clogging which should be as low as possible.

Experiments were further extended to the preparation of rayon filaments from the obtained viscose. In this respect, it is worthwhile to mention that a research team, including representatives from the National Research Centre and five pulp, paper, and rayon factories, was set up in 1970 to investigate utilization of bagasse for producing viscose rayon on a laboratory scale (50 kg. bagasse charge and 1 kg. charge pulp for viscose). The experiments ended successfully in 1972. However, further piloting on a larger scale is necessary for an ultimate evaluation of bagasse as a raw material for viscose rayon and for furnishing solid information for feasibility studies. The production manager of Esco Rayon and Cotton Company will give a talk about this project and its results.

Other cellulose derivatives have been prepared from agricultural residues, such as acetate, nitrate, and carboxymethyl cellulose. Films and semipermeable membranes have been prepared from some derivatives and their permeabilities correlated to some parameters of the original pulp.

Last but not least, an extensive research program was dedicated to fine structure of cellulose fibers especially in the native, never-dried state. The result of this work on cell wall water has thrown more light on cellulose reactivity.

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Value Recovery from Pulping Wastes

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Before we review the American experience in recovering value from pulping wastes and attempt to gain some insights which may have application to Egypt, it may be well to recall the differences between our two countries. The United States is so rich in fiber from forest resources that agricultural residues and annual crops contribute a minor fraction of the pulp produced. Water, the second most important ingredient in pulping and bleaching, is also available in large supply. Labor is extremely expensive, and costs of production can be minimized by large capital investment, heavy equipment, and large mills. It may be that in virtually all these respects and others, the situation in Egypt differs from that of the United States. The transfer of technology is, therefore, a risky business, and the knowledge of foreign "experts" should be applied only by those who understand the restraints and possibilities of the local situation. With that caveat, we begin.

My experience with wood chemistry and the chemistry of pulping processes covers three decades, and it may be of interest to review briefly the attitudes and the successes and failures of wood chemists and paper technologists over that period. In the summer of 1948, the first Lignin Round Table was held at the Institute of Paper Chemistry in Appleton, Wisconsin. At that time, there was little agreement among wood chemists of the nature of lignin, but there was a genuine enthusiasm that if more were learned regarding its structure, real economic benefits would accrue from by-product utilization. In marked contrast to the general sentiment of the conference was a statement of one attendee whose remarks I still remember: "If you want to make money from lignin, keep it in the pulp."

Since that time, an enormous amount of research effort has been expended on lignin. We now understand that it is a three-dimensional or lamellar network polymer[1,2] degraded in the pulping process to multibranched fragments of wide molecular weight distributions. We understand that linkages between monomeric units are diverse, some with carbon-to-carbon bonds, some degradable carbon-oxygen-carbon bonds. The main dimeric structural elements are known.[1] The behavior of lignin with solvents has been clarified.[3] The important reactions in pulping are known in detail.[4] The biosynthesis of lignin has been investigated, and our knowledge of it is consistent with the biosynthesis of a variety of natural phenolic materials and also consistent with our conclusions regarding lignin structure.[5] Nevertheless, the problem of lignin as an underutilized raw material remains.

It is perfectly clear that one can derive from lignin a few fine chemicals such as vanillin and dimethylsulfoxide and, indeed, a substantial number of bulk polymeric commodities, which require special capital investments and completely different marketing organizations than the usual paper products, and still have almost all of the original waste to dispose of.

The history of hemicellulose research and application is similar. In 1947-48, very little was known of the structure of noncellulosic polysaccharides in plant fibers. Since then, refinement of separation methods, including chromatography, development of polymer methodology, and application of instrumental methods to structure analysis, has led to a detailed knowledge of the structure of the major components of the mature cell wall[6] and even developing primary cell wall.[7] Yet a recent article in Tappi, which reviews the recovery of carbohydrate degradation

products from alkaline pulping liquor, emphasizes the difficulty of finding economical recovery processes and new markets for the products and concludes that the ideal objective would be the development of new ways of avoiding carbohydrate losses during delignification.[8]

It is important to recognize that attractive technologies can often be developed without a complete underpinning of fundamental knowledge. Indeed, that has been the case with much of polymer technology. Cellulose and cellulose derivatives were used as plastics, films, coatings, regenerated fibers, and explosives before the structure of cellulose was known.[9] The reason for the poor utilization of fiber components is not due to a lack of knowledge of their structure and properties but is due to the difficulty of separating, isolating, and processing them as reasonably useful commodities without undue cost.

If one compares the relatively modest successes in by-product utilization with the changes and improvements in paper technology over the past 30 years, one must be impressed with the technological approach. The direction proposed by the paper technologist at the First Lignin Round Table has been followed. The technologist has used a very few general methods to allow him to use a higher proportion of the fiber in paper. First, he has developed a variety of semichemical, chemimechanical and mechanical methods of obtaining useful fiber from raw materials. Secondly, he has recognized that no single fiber is able to provide the wide variety of properties needed in even one type of paper, much less the infinite variety of papers that are useful in today's society. He therefore blends fibers, not only those obtained by different pulping methods but also those from different plant sources. It is well recognized that if a particular fiber does not add strength to a sheet, it may add bulk or opacity or some other useful property.

Potential Sources of Fibers

Therefore, it seems appropriate to look first to potential fiber sources if one wishes to minimize waste. I note that current Egyptian fiber sources are largely agricultural residues, and all are short fibered.[10a] One might ask whether Egypt can afford to base all of its paper production on this limited resource as the country moves into a more highly developed state. Is it realistic to consider the establishment of other plant sources which might provide long fibers to blend with high yield chemimechanical pulp from agricultural wastes? What possibility is there of growing leucaena,[11] or eucalyptus, or bamboo for pulp in Egypt and if there is, what advantages could accrue by their use in blends? Which would be preferred? Could a higher percentage of fines be used if longer fibered material were available for blends?

There is, at the present time, considerable interest in the growth of various plant crops on the arid lands of southwestern United States and Mexico. The ones of interest will be harvested for their extractive content. They include Euphorbia as a source of hydrocarbons,[12] guayule for rubber, and jojoba for wax and an industrial oil which can replace whale oil.[13] The economics of some of these developments might be better if their fibers could be used as well. Is this development of significance to Egypt?

I am aware of one major company in the United States that has even made an exploratory evaluation of the farming of algae in lagoons (estimated growth rates 50 to 200 tons per acre) in the subtropics as a source of fiber, so I would urge those responsible for the development of local paper industries not to ignore the question of new fiber sources. Egypt will need them, and if the fiber is not grown here it will have to be imported. This question is of significance beyond that of minimizing waste but is certainly pertinent to value recovery from waste.

Methodologies for Recovering Values

Value can be recovered from wastes in at least four forms: as organic chemicals

or products, inorganic pulping reagents, energy, and pure process water. The methods that can be applied successfully depend on whether the process is high or low yield and its detailed chemistry. One may discuss present methodologies or those that have reasonable probability of application in the next five years or longer range exploratory approaches that are still untested and, therefore, highly speculative. I hope we can consider some of each.

Fortunately, a definitive statement on the utilization of organic chemicals from wood by F. W. Herrick and H. L. Hergert of ITT Rayonier has just appeared.[14] Their emphasis is on products and processes which have been developed at least to a pilot plant stage, and their paper includes a review of the present state of the problem with 206 references (which I shall not repeat) and also includes reasonable prospects for the near future.

As a result of the recent increase in the price of oil worldwide, there has been a great resurgence in interest in alternative sources of chemicals and energy. Herrick and Hergert have not been impressed by the present excitement. They point out that even if oil prices were to double, wastes would still be a poor choice as a raw material for most organic synthetics and polymer production even on a price per pound basis. The same point has been elaborated by P. Becher,[15] who emphasized the enormous weight losses that are suffered on converting the highly oxygenated carbohydrates to typical basic feed stocks such as ethylene, butadiene, butanol, acrylonitrile, etc. These conclusions appear valid whether one considers wood pyrolysis, pulping, or hydrogenolysis as a mode of approach to chemicals. Many of the statements of Herrick and Hergert are pertinent to the utilization of agricultural residue pulping wastes as well and are worth summarizing.

Extractives are more available from woody species than from most grasses, and much effort has been expended in their isolation and commercialization. The most notable success has, of course, been the traditional naval stores industry producing turpentine and rosin from a limited number of pine species. The older manual collection of oleoresin from living trees has been largely superceded by recovery of "sulfate turpentine" by steam distillation and tall oil by skimming of kraft pulping liquors. The yield of these materials can now be greatly enhanced by treatment of the pines with "Paraquat" herbicide. This treatment results in a greater sensitivity of the trees to insect attack, and probably the biosynthetic energy of the plant is diverted away from fiber production. However, the increased yields of these materials in so-called "light wood" is seven to eight times that of normal wood and so dramatic that the method will undoubtedly be continued.[16] It has, in fact, sparked other experiments in chemical treatments to enhance production of other desired plant products.[13] The resin acids, fatty acids, and terpenes of the oleoresin have all been successfully commercialized, but I believe the nonsaponifiable steroids have found little utilization in the United States.

Practical methods for the isolation of a number of pure lignans and flavanoids from sulfite liquor or bark extracts have been devised. However, in most cases sufficient markets have not been uncovered to warrant continued production. More complex polymeric product mixtures have, in specific cases, been more successfully commercialized. This success may reflect the ability of the pulp and paper industry to market bulk commodities better than high priced chemical specialties. However, it probably also is related to the character of the natural products themselves.

Recovery of Chemicals from Wood Wastes

Among the commodities that have been derived from wood wastes are the following: vegetable tannins from quebracho, chestnut, wattle, and hemlock bark. However, the market for vegetable tannins has decreased in the last two decades with the development of a variety of synthetic tanning agents for leather and the partial displacement of leather by plastics in footwear. Tannins and polyphenolics from bark--often sulfonated--are used also as oil well drilling mud additives and dispersants, phenolic adhesive components and fillers, carriers for agricultural micronutrients, and chemical grouting agents.

One of the major growth areas for polymers is in water-soluble and water-swellable products. This is evidenced in the growth of carboxymethyl cellulose and the interest in the starch-based "super slurpers" and various cellulose graft copolymers. One might expect a market for larch gum, an arabinogalactan that can be extracted from American larch in yields up to 16% and averaging 10%. The extraction is advantageous, for the extracted wood consumes less chemical in pulping and is preferred for use in board products. The gum is on the market[17] but so far apparently has not developed a major use.

More directly pertinent to utilization of annual plant residues is the work on recovery of value from cell wall components. Losses of hemicelluloses occur in both alkaline and acid pulping processes. Acid processes include the prehydrolysis of various species, including southern pine prior to kraft pulping for chemical pulp, and also the acid sulfite pulping of northern conifers. Depending on the acidity and duration of treatment, the polysaccharides may be degraded to monomeric or remain as polymeric products. Prehydrolysis of hardwoods or annual plants, of course, produces a pentose-rich fraction, while the soft woods provide mannose-rich products.

An explosive steam defibrization of hardwood chips for fiber board, termed the Masonite process, produces an aqueous extract of the same type, which is concentrated to a molasses-like consistency (65% solids) and is sold successfully as a cattle feed additive. Practical methods are also available to isolate xylose or mannose from the appropriate liquors, using fermentation of hexoses to ethanol and methanol extraction for the former and crystallization of a bisulfite adduct for the latter.

A number of products are derivable from the hemicellulose fraction. Xylitol from xylose and mannitol from mannose are available by hydrogenation. The recent discovery that xylitol reduces dental caries has led to its commercialization in Finland and its incorporation in American chewing gum. It is doubtful that even American chewing habits can provide a suitable outlet for the available xylose. Unfortunately, the use of mixtures of wood-derived polyols for industrial purposes finds severe competition from the purer products derived from glucose.

Furfural is derived from acid treatment of pentose sugars. In the United States, these sugars usually come from corn cobs, grain hulls, or sugarcane bagasse. The entire U.S. production is about 175 million pounds per year. Recent two-stage process studies on sugarcane bagasse, using sulfuric acid as a catalyst, have been carried out and have led to the formation of furfural from pentoses and levulinic acid from hexoses. Both products have also been derived from hardwood residues, but a commercial process for production of levulinic acid developed by Crown Zellerbach was closed because of an unsatisfactory market situation.

It is also possible to extract high yields of pentosans deacetylated but undegraded from small particle size hardwood sawdust or straw with hot alkali at less than pulping temperatures.[18-20] The extraction occurs rapidly, and the percent solubilized is a function of temperature, alkali concentration, and species. A variety of species have been tested, and around 75% to 90% can be removed from a number of hardwoods, sugarcane bagasse, and wheat straw with a single extraction of 12% sodium hydroxide at 80°. At lower temperatures and high alkali concentrations, the more highly swollen cellulose restrained within the lignin matrix forms a lattice which effectively prevents pentosan extraction. Lower alkali concentrations extract proportionately less. The extraction could presumably be carried out in a countercurrent continuous process and the residue pulped at higher temperatures with less carbohydrate decomposition and lower alkali demand. The pentosan could be used as paper additive perhaps for glassine or grease proof stock. Other markets for these low molecular weight polymers may be hard to find.

Presumably in the short times used for alkali pulping of annual plants, grasses, and bagasse, a substantial proportion of the hemicelluloses may still be in polymeric form. However, under the more drastic conditions characteristic of kraft or soda cooking on either hardwoods or conifers the polysaccharides are fragmented to produce reducing end groups which allow the polysaccharides to degrade via the well-known stepwise "peeling reaction." The end products are the iso and meta saccharinic

acids and a variety of smaller hydroxyacids. Acetic and formic acids are also formed These reactions are, of course, the main alkali consumers. Although, as Herrick and Hergert emphasize, the quantities of sugar and hydroxy acids formed are enormous and a number of uses are known for closely related products such as gluconic, tartaric, and lactic acids, no practical commercial recovery and separation processes are known.

In summary, the isolation and purification of pure sugars or simple carbohydrate derivatives from pulping liquors are generally expensive and the potential market therefore limited. Probably the only likely bulk chemical commodities are those such as furfural or levulinic acid that are volatile and can be stripped off the liquors. These are probably most accessible from prehydrolysis liquors. Since a substantial quantity of hemicelluloses will be destroyed in the pulping process anyway, prehydrolysis or preextraction might perhaps be applied more generally even for paper pulps.

Two methods of recovering acetic acid from pulping liquors are described by Herrick and Hergert. The Sunoco Products process is notable in that it recovers the acid from a neutral sulfite semichemical pulping liquor. The liquor is concentrated to 40% dry solids and acidified with sulfuric acid. Acetic and formic acids are readily extracted by 2-butanone from the solution at high salt concentration, and the acetic acid is further refined to 99.5% purity. The sodium sulfate is used in making up kraft liquor alkali.

Acetic acid is also being recovered from spent sulfite liquor evaporation condensates by adsorption on activated carbon. It is desorbed as ethyl acetate. This process is being demonstrated at Flambeau Paper Co., Park Falls, Wisconsin.

Utilization of Lignin

There is little new to report in the chemical utilization of lignin. The oxidative degradation of sugar-free lignosulfonates to produce vanillin and closely related compounds has a long history. The preparation of dimethyl sulfide by alkaline reaction of kraft black liquor with sulfur and its oxidation to dimethyl sulfoxide was pioneered by Crown Zellerbach in 1961 and continues to operate successfully. Pyrolysis with lye or lime to give catechol and 4-alkylcatechols has also been developed but not widely used. Hydrogenolysis has been investigated. At temperatures less than 250° C., 4-alkylguaiacols and related products are formed. From about 250° to 350° C., the aromatics are hydrogenated to cyclohexane derivatives. At temperatures above about 350° C., pyrolysis, dehydrogenation, and rearrangements occur with the formation of phenol and simple alkyl-substituted phenols.[21] These products are probably the most marketable in quantity, but an extensive investigation of the Noguchi process, the most promising of these methods, by Crown Zellerbach failed to produce an economic process. In all cases, most of the lignin appears as higher boiling products, and optimum yields of monomeric phenols are usually around 20 to 25%. Alkali lignins usually give lower yields of phenols with 4-ethyl side chains rather than propyl.

Now and for the foreseeable future, the bulk of lignin from chemical pulping processes will be utilized as fuel. As the least oxygenated (and hydrogenated) of wood wastes, it has the highest heat value and is, therefore, the most useful as fuel. At the present time, almost all kraft liquor containing both lignin and carbohydrate degradation products is burned and inorganic chemicals and energy recovered. Spent sulfite liquor solids produced in the United States amount to 6,840,000 tons. About 313,000 tons, or around 5%, are sold as marketable products. Herrick and Hergert list principal uses for spent sulfite liquor in order of decreasing size (Table 1). It will be noted that the most important is as a fuel, and all but one are uses for relatively crude polymeric mixtures. In some cases the sugars are first removed by fermentation and the residual lignosulfonates sold. However, for animal feed the desired components are the wood sugars. Although Herrick and Hergert estimate that these markets may grow to 1,000,000 tonnes by 1980 and indeed that in theory animal feeding could absorb the entire output, it is obvious that the major

portion will be burned. That portion which is sold will be used in market-oriented formulations for specific materials outlets, only rarely pure chemicals.

Although the search for chemical products from carbohydrate wastes has had only limited success, it seems clear that these materials have a higher market potential than lignin and a lower heat value to recover. Prehydrolysis permits the isolation of a reasonably pure carbohydrate fraction which in any case would be largely lost in the pulping process. Alternatively, preextraction of undegraded hemicelluloses is possible from grasses and hardwood sawdust. In addition to conversion to furfural and levulinic acid, a much larger potential market is as an animal feed additive. There is no reason why this market cannot also absorb some solid wastes as well. During the Second World War, markets for Swedish pulp were cut off, and local pastures could not support the desired beef and dairy cattle population. The Swedish solution was to enhance the digestibility of cellulose by a severe degradative sulfite cook and feed the pulp to cattle. It would appear that various inexpensive treatments could also enhance the digestibility of fines and pith and help provide animal fodder in Egypt, where agricultural land is limited. These might include the use of white rots to enhance digestibility[14] or ammonia treatments to enhance accessibility.[22]

The Role of Microorganisms

The potential of microbiology to increase the value of carbohydrate wastes has hardly been tapped. Hexoses in sulfite and prehydrolysis liquors have been fermented to ethanol in order to allow recovery of pure lignosulfonates in the one and to improve the recovery of xylose or furfural from the other. Pentoses, hexoses, and other monomeric carbohydrate materials are converted by Torula yeast to cellular material containing 50% protein which is sold as an animal feed additive. In Finland the fibrous fungus Paecilomyces varioti is grown for similar uses, since it is more readily separated from liquors by filtration (the Pekkilo process). A Czechoslovakian publication discusses the use of Mycelium sterilium fungus, grown similarly, as a poultry feed.[23] The treatment of wood wastes by white rot fungi to convert lignocellulosic material into protein-rich microorganisms that can be used as fodder is also under investigation.[24] However, the selection of microorganisms for efficiency, processability, and nutritional value has scarcely begun.

None of these organisms can utilize the saccharinic acids formed in alkali cooks, but they are utilized by activated sludge bacteria. The sludge biomass has a protein content, color and taste similar to the yeasts and presumably could also become an approved feed additive. If sodium hydroxide oxygen pulping becomes more common, similar organisms may be needed for the utilization of these pulping liquors. It is significant that the Chemistry Department of the Swedish Forest Products Laboratory has, at present, an outstanding program in microbiology.[24-27]

Other products can be made by fermentation. Acetic acid, butanol, and acetone come immediately to mind. At the present time, these products usually are derived from petroleum, but fermentation might be feasible at some time. Antibiotics are produced by fermentation in 1-5% sugar solutions, usually corn steep liquors or distiller solubles in the United States. It is conceivable that some valuable antibiotic producers prefer pentoses! In Japan, Jujo Paper Company[28] and Sanyo-Kokusaku Pulp Company[29] produce ribonucleic acid from Torula yeast. This has a market in food or pharmaceuticals.

It has been pointed out by Wells[30] that the development of extracellular, microbial polysaccharides as commerical products is rapidly expanding as new plants are coming on stream. This new plateau of production will first be absorbed into existing industries. At the present, applications of these products in food, pharmaceutical, and medical fields are being developed for their properties as viscosity extenders, foam stabilizers, and emulsifying agents. Large predicted polymer requirements in tertiary oil recovery will require very large amounts of product. However, improved high productivity fermentation systems and improved separation

methods will be required for this use to become commercially viable.

investigation are the following:[31]

- Dextran is produced from sucrose by various Leuconostoc species, and a relatively linear one from NRRL strain B512 is used as a blood volume expander and for other pharmaceutical and industrial purposes. When cross-linked, it is a useful chromatographic substrate.

- Xanthan gum is produced aerobically in various culture media containing glucose, including cottage cheese whey, by the bacterium Xanthomonas campestris. It has interesting rheological properties and interacts synergistically to form gels with (1-4)-β-glycans and even with locust bean gum, a galactomannan. It is the first biosynthetic polysaccharide to find widespread use in the food industry.

Both polysaccharides are being tested for tertiary oil recovery processes. The production of a number of other microbial extracellular polysaccharides is being developed for a variety of purposes. These include alginates; levans; "Zanflo," a heteropolysaccharide produced by Erwinia tahitica; "PS7" made by an Azobacter species; "Curdlan," a (1,3)-β-D-glucan gel former; and Pullulan which forms water-soluble biodegradable films with high impermeability to oxygen. The bacterial synthesis of cellulose is also well-known.

It is quite apparent that microbiological research should be an important part of any long-range waste recovery research program. Microorganisms can be a rich source of high value products: enzymes, coenzymes, sterols, nucleotides, metabolic intermediates, and water-soluble and insoluble polysaccharides, and the paper industry has a vast culture medium going to waste.

Bagasse as a Raw Material

In the production of paper fiber from bagasse, one of the most important wastes must be pith. I note that your laboratory has been successful in also making dissolving pulp from bagasse fiber. Since the chemical components of the pith must be very similar to those of bagasse fiber, there is some possibility that the pith might be used for this purpose instead. Undoubtedly there would be serious problems of process modification to be solved, but the successful achievement of the objective would be worth considerable effort.

The most generally recovered values from spent liquors are those of energy and inorganic chemicals. The sulfite mills have for some time been converting from calcium to sodium, magnesium, or ammonium bases in order to facilitate concentration for combustion without excessive scale formation. Depending on the system and the choice of base, either sulfur dioxide or both base and sulfur dioxide are recovered for reuse. Neutral or acid sulfite liquors are sometimes concentrated and added to kraft recovery systems.

Non-wood plant fiber pulping is usually by soda or kraft process. In the pulping of woods, the technology of recovery for these processes is highly developed, but application of the same methods to non-wood plant fiber pulping has resulted in great difficulties. These were reviewed at conferences in Memphis in 1972[32] and in Atlanta in 1973[33] sponsored by the Non-Wood Plant Fibers Committee of TAPPI. Papers on the recovery problems encountered when pulping bagasse, bamboo, and wheat straw were presented. The recovery problems of all three classes of plant fibers were similar and appeared to be caused primarily by the high silica content and the high proportion of short fibers, vessel segments, and, in the case of bagasse, residual pith. The origin of the troubles was, nevertheless, not always clearly defined or rigorously identified. (I wish to thank Marvin Bagby for calling my attention to these papers).

The difficulties are most obvious in pulp washing, evaporation of liquors, and combustion. The experience of an Argentinian mill[34] pulping depithed bagasse was typical. The depithed bagasse was stored three to eight months in wet storage. Analysis of the fiber was 22.7%, 1% alkali soluble, 30.1% pentosan, 21% lignin, and 1.3% ash, of which was 0.7% silica. The fiber was cooked in Pandia continuous digesters with sodium hydroxide (about 1.75N containing about 2% of the base as Na_2S) at a liquor to total solids ratio of 2.86. The bagasse consistency was 38% at the screw feeder. The amount of alkali was about 10% by weight of bagasse. The cook was at 170° C. for 10 to 15 minutes. The residual pulp contained only 2% lignin. Ninety-two tonnes of solids dissolved per 100 tonnes of bone-dry pulp produced. This must mean that virtually all (90%) of the lignin and pentosans were removed, with nearly all of the cellulose retained. Pulp washing on three rotary vacuum filters with 40 mesh screens was inefficient and resulted in high dilution caused by poor drainage characteristics of the pulp. The resultant liquors amounted to 14 cu. m. per tonne of pulp. I believe this is perhaps 50 to 60% more liquor than is required for washing wood pulp. Presumably the poor drainage results from the physical characteristics of the pulp, retention of vessel segments, pith, and short fibers. However, much of this material passes through the 40 mesh screen and must be removed on an 80 mesh screen before evaporation.

If any other factor is responsible, it is difficult to relate it to any fiber component. There is no evidence, of which I am aware, that either hemicellulose or lignin from these species has any special physical properties or molecular size to cause problems. Any contribution the silica might make to viscosity at this dilution should be minimal. If, however, microbial action occurs during storage and polysaccharides are generated, these gel formers could cause serious difficulties. Dextran formation has blocked the pipes in sugar refineries when production has been stopped for a few days, so pipes are now routinely drained when a shutdown occurs. It might, therefore, be of interest to determine whether microbial polysaccharides are present, if it is not already known. It would be of interest also to know whether unstored or prehydrolyzed bagasse pulp has as difficult drainage problems. If not, probably the source of the difficulty is in foreign or hydrolyzeable polysaccharides as well as fiber structure. The poor drainage characteristics of the bagasse pulp are an extremely serious problem in this mill, for not only is excessive energy required to concentrate the liquors but also 8.4% of the alkali is lost in the washing stages. Over 3% additional is lost in evaporation and recovery boilers and 3.7% in recausticization. These latter losses are more typical of wood pulping. The most realistic solution proposed to this problem was to use especially designed washers with high surface area and low specific load factor.[35]

The evaporators in the bagasse mill required frequent cleaning because of clogging of the first components by organic material, calcium carbonate next, and in the last components aluminum silicate. The liquors were concentrated only to 40% to avoid silica scale and transferred to a cascade evaporator to concentrate to 62% solids. The high viscosity of the bagasse liquors required an oversized cascade drive, and in an Indian mill pulping bamboo[36] the high viscosity of concentrated liquors required special firing nozzles to maintain steady operation of the recovery boilers without excessive supplementary fuel.

The main difficulties in the evaporation and combustion of liquors appear to derive from their high silica content and can reasonably well be predicted from the ash content of the fibrous raw material (Table 2). Typically, 65 to 70% of the ash is SiO_2, which dissolves as complex silicates in the alkaline pulping liquors. Two methods of dealing with the problem were proposed. The first under development at an Indian mill pulping bamboo[36] was to concentrate the black liquors to 30% solids and add slaked lime at a ratio of 1.8:1 lime:silica at 90° C. and filter off the calcium silicate formed. The second method, suggested by D. K. Misra, is used in Greece.[35] This consists of adding additional alkali to the brown stock wash waters before evaporation. When free alkali is present at a concentration of 8-10 g./l. in bagasse liquors and 12 g./l. in waters from wheat straw pulping, silica and lignin precipitation is retarded and the viscosity of the hot concentrated liquors is minimized. Scale formation and necessary shutdowns for cleaning are reduced and more even boiling is possible in the recovery boilers, although supplementary fuel

is still required.

Silica also interferes with the recausticization process in a number of ways. It causes slow settling of the lime slurry and causes glass formation and other problems in the lime kiln. Continuous buildup of silicate in the lime can only be avoided by discarding part of the lime. In the Argentinian bagasse mill, 17% limestone make up was required, of which 8% was considered "normal" loss and 9% caused by silica. This, of course, results in a sludge disposal problem.

The most innovative proposal fo. soda black liquor recovery was the use of a wet combustion method which permits the direct combustion of the liquors at as low as 8-11% solids content.[37] A somewhat simpler plant design is possible if pith is added to give 16% solids content. The principles of the process are not recent, for they date at least back to a Norwegian patent of 1912 and were described by Zimmerman in 1958. Rydholm in his 1965 text "Pulping Processes"[10b] refers to the Cederquist and the Zimmerman-Hammermill-Borregaard processes for wet combustion of acid and neutral sulfite liquors. No chemical recovery is indicated in these references, however. J. E. Morgan[37] reported in Atlanta on wet combustion of eucalyptus soda pulping liquors and proposed the process as a method of improving chemical and thermal efficiency and overcoming the silica problem in non-wood plant fiber mills (Figure 1 and Tables 3 4, 5, and 6).

The process is based on the oxidation of dissolved or suspended organic solids in water by molecular oxygen at elevated temperatures and pressures. For the desired 95-98% oxidation, temperatures at 300° to 320° C. and pressures of 2,500 to 3,000 p.s.i.g. are needed. The oxidized liquor leaving the reactor consists of concentrated sodium carbonate and some bicarbonate (180 g./l. as NaOH) at 100° C. and a small amount of salts of short-chain aliphatic acids that do not build up in the soda circuit. The recovered liquor is practically colorless and contains no carbon particles. Inorganic fiber impurities including silica, magnesia, calcium, and alumina settle in the dregs and can be readily washed and separated. The soda is recovered to the extent of 99%, and its solution can be diluted with other waste streams prior to causticization with lime. This process offers a 20% increase in thermal efficiency of the bagasse recovery operation. Energy recovery from the reactor exhaust vapor is in the form of saturated process steam and electric power, and their proportions can be varied over wide limits. These claims are based on seven years of operating experience on eucalyptus and laboratory experiments on non-wood fiber pulping liquors.

A French patent describes a similar wet combustion process using pure oxygen rather than air. This can operate at lower temperatures (180° to 300° C.) at least in the presence of iron or copper oxide as catalyst.[38]

Treatment of Bleaching Liquors

We will return to the question of liquor causticization later. Next I should like to comment briefly on the treatment of bleaching liquors. In my opinion, the most innovative proposal in this field is that of Rapson and Reeve[39,40] which they call, with some exaggeration, "an effluent-free kraft mill." Their method includes washing pulp in a completely countercurrent manner from the last stage of the bleach plant through the unbleached pulp washer and sending the combined washings into the evaporator (Figure 2). They envision bleaching with chlorine and chlorine dioxide alternating with alkaline extractions. Their proposal includes some modifications of the bleaching sequence, of the proportions of chlorine and chlorine dioxide, and of the bleach chemical production. However, their main proposal is to causticize the liquor prepared from the smelt in the usual manner and to concentrate it to 20-40% alkali. At this concentration, sodium chloride and carbonate precipitate, leaving sodium hydroxide and sulfide in solution for pulping. Pure sodium chloride can be prepared by leaching out the carbonate and can be reused for bleach. Various liquor condensates from evaporators are cleaned up and returned for washing the bleached pulp and other purposes. A pilot plant has been set up with Canadian Government support, and the process is being investigated.

It would appear that this process would be of even greater interest in non-wood fiber pulping. The use of sodium hydroxide in place of kraft liquor avoids complications introduced by sodium sulfate, thiosulfates, etc. To the extent that oxygen bleaching can replace chlorine and chlorine dioxide, the concept of a nearly closed system becomes even easier to apply. It appears that a combination of the effluent-free mill and wet combustion recovery plant would also be compatible. Rapson and Reeve estimate heat savings by retention of the heat in effluents that are now discharged. Furthermore, the organic matter from the bleach plant, now normally discarded in effluents, would be burned in the furnace to increase the heat recovered per tonne of pulp by 5 to 10%. Finally, of course, a process which uses little water should be of great interest in Egypt.

New Bleaching Procedures

There are a number of different bleaching procedures under investigation that also should limit water usage. They are variations on high consistency bleaching--consistencies of 20 to 40% in which no free water is present--and medium consistency bleaching at 10-15% solids. We became aware of this field around 1960-67 when we were investigating the reaction of ozone on wood and cellulose.[41-43] We soon found that ozone is not a specific reagent for the oxidation of double bonds but also can act as a Lewis acid to enhance hydrolysis of glycosidic linkages and as a free radical initiator for oxidation chains with molecular oxygen.[44] As such, it is sensitive to heavy metal catalysis, as was later found--to their sorrow--by the research group at the Pulp and Paper Research Institute of Canada, which is attempting to commercialize the ozonization of mechanical pulp to enhance its bonding in paper (the Paprizone process).[45] However, the most dramatic effects we noted were due to transport processes. The rates and selectivity of bleaching were greatly enhanced under conditions where no free water was present and the consistency was around 40 to 50%. Similar observations were made on the ozone pulping of wood samples. We were able to demonstrate that the rate-determining step in these processes was the transport of chemical across the immobilized water phase clinging to the solid surfaces or associated with even very small clumps of fibers. Simple stirring of pulp suspensions did not move this water layer, and reaction rates were much lower in slurries than in the gas phase. In addition, over oxidation occurred at surfaces before homogeneous attack could take place in slurries.

At about the same time, J. S. Hart, N. Liebergott, and F. H. Yorston at the Pulp and Paper Research Institute of Canada were investigating gas phase high consistency bleaching using commercial bleaching chemicals. They also found greatly enhanced reaction rates and improved specificity.[46] This work has now developed into the "Papribleach process."[47] A new gaseous reagent, chlorine monoxide, has also been announced.[48] A recent paper has shown that the sequence CgEDgEDg produced bleached pulps with properties that match or surpass those of bleached pulps obtained by the conventional CEDED slurry process.[47] In the Papribleach process, alkaline extractions may be done with either gaseous ammonia or by rapid press extraction with caustic soda.[49] Laboratory work on gas phase high consistency bleaching of Southern pine kraft pulp showed lower costs for steam and chemicals, showed that a 2-minute press extraction was equivalent to a 1-hour extraction at 10% consistency and that a decrease in wash water to about 1,000 U.S. gallons/ton of bleached pulp and a 16-38% reduction in pollution load of bleaching effluents was to be expected.

The use of high consistency bleaching has been known for a long time. The conventional explanation for its faster rate has been that in a given charge of chemicals per tonne of pulp, the concentration of chemicals (in g./l.) will increase and the rate of reaction will also increase with decrease in water content, i.e., with increase in consistency.[10c] This is a completely inadequate explanation and inconsistent with a number of observations. The more important factor is the fact that the rate of transport across the liquid envelope is rate-determining.

Rapson proposed an alternative method in medium consistency bleaching which he called "dynamic bleaching" and which was again based on the recognition that the

rate of diffusion of bleaching chemicals across an immobilized liquid layer is the rate-determining step.[50] In his process, the bleaching chemicals are moved continuously through the pulp. By passing the bleaching solution through a layer of pulp, displacing the liquid already present in the pulp layer, the bleach is in constant motion relative to the pulp fibers. The rate of mass transfer to the fiber wall is greatly increased. Bleaching, washing, and extraction solutions can be passed through the pulp in sequence with little mixing. He has given an example of a kraft pulp undergoing five stage bleaching to an 89.5 brightness in 19 minutes as opposed to several hours in a conventional bleach plant.

Another method of limiting the use of water and decreasing the use of energy that is being taken very seriously in the paper industry is the dry forming of a paper sheet. It is significant that for a number of years, "Paprican," a publication of the Pulp and Paper Research Institute of Canada, has listed research areas in "Novel Methods of Paper Forming," "Fundamentals of Air Jet Impingement on Curved Surfaces," and most recently "Gas Phase Papermaking," all with I. J. Pye as supervisor. Web formation with other fibrous materials by air placement is well known, and attempts at paper formation by the method are not new but are continuing. The main problems involved are even formation of the sheet and fiber bonding. The latter can presumably be accomplished with resin additives, so even formation is clearly the limiting problem. It is obvious that the first applications will be in paperboard where formation is least critical. It is my understanding that a dry-forming paperboard production plant is now operating in England.[51] Although not directly related to the title of this paper, this topic appears of sufficient significance to warrant mention in passing.

The Use of Electrolytic Processes

Returning to the recovery of values in pulping wastes, I should like to comment briefly on the possibility of using electrolytic processes for various purposes. In a recent publication, the use of electricity from the Aswan dam to produce hydrogen for ammonia synthesis was described. This is not, I believe, economic in the United States and suggests that electricity may be applicable here in processes that would not be attempted in the United States. Nevertheless, Herrick and Hergert emphasize that one of the most pressing needs of the pulp and paper industry is for separating or purifying processes, and they suggest that ultrafiltration or electrodialysis may provide suitable routes for recovering sugar or sugar derivatives while purifying lignin fractions. This is by no means impossible. Goring demonstrated the separation of lignosulfonic acids from salts and sugars and the concentration of the lignin fraction by a process of electrodecantation.[52] In this process, the sulfite liquor is electrolyzed within a semipermeable membrane. The small ions pass through the membrane and the lignosulfonates collect at the membrane surface and form a solution of high density which settles to the bottom of the container and can be withdrawn. Various refinements of similar systems have been suggested for separation of the three classes of components on a commercial scale.

Electrolysis may also be a feasible alternative in Egypt to causticization with lime of recovered soda solution. Presumably sodium hydroxide and hydrogen would be generated at the cathode and oxygen, carbon dioxide, and silica sludge at the anode. Hydrogen could be used for chemical purposes or fuel and oxygen utilized in bleaching or for other purposes.

A considerably cheaper process has recently been disclosed by Allied Chemical Corporation. This process utilizes electrodialysis with a bipolar membrane and a cation selective membrane.[53,54] In some applications, an anion selective membrane may be used as well. Batteries of these electrodialysis cells are set up and in the presence of a salt split water into hydroxide and hydrogen ions, without the generation of molecular hydrogen and oxygen (Figure 3). It has been developed as a method of recovering sulfur dioxide absorbed from power plant stack gases in solutions of sodium hydroxide and sodium sulfite. The developers claim lower costs than a limestone throw-away disposal process and another regenerative "Davy Powergas" process. The theoretical power requirement for generating a ton of sodium

hydroxide is 500 kilowatt-hours. Presumably electrodialysis of sodium carbonate would produce sodium hydroxide and carbon dioxide and silica sludge but no hydrogen or oxygen. Capital investment is reported to be less than for electrolysis and energy consumption substantially lower. In view of the difficulties of lime regeneration caused by silica contamination, perhaps the application of this process should be considered.

In closing, it should be emphasized that most of the processes described in this paper are most useful for recovering value from liquors containing substantial quantities of organic wastes. Nevertheless, the initial point that was made deserves reemphasis. Any method which permits the replacement of a low yield chemical pulp by a higher yield product is probably of maximum benefit. Sometimes this can be done by rather simple modifications of current practice. For example, recently a two stage process for the pulping of hardwood chips was described that produced a pulp in 80% yield that was free of fiber bundles.[55] The process consisted of impregnating mixed hardwood chips with aqueous sodium sulfite solution containing 7% of the wood weight as chemical. The impregnated chips were heated and defiberized at 160° to 170° C. in an Asplund-type digester producing coarse pulp in about 90% yield. A subsequent treatment with 0.6% sodium hydroxide and compression to 25% consistency followed by one pass through a Bauer double disk refiner under compressive stress yielded in 80% overall yield a pulp free of fiber bundles that could be blended with the sulfate pulp to produce saturating paper, printing paper, and several kinds of converting paper. The pulp provided bulk, opacity, absorbency, and dimensional stability greater than kraft pulp. This kind of simple, well-chosen process modification can also make a very significant contribution to minimizing waste from pulping processes.

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Table 1

Uses for Crude Spent Sulfite Liquor (Concentrated)

1. Fuel for heat and power generation, with inorganic chemical recovery.

2. Manufacture of dispersants and oil well drilling mud additives.

3. Additive in animal feeds at 4% by weight.

4. Soil stabilization, binder; dust abatement.

5. Extender for phenolic and urea resin adhesives for plywood and particleboard.

6. Binder for coal, ores, and dry minerals.

7. Mineral treatment, processing, and refining.

8. Raw material for vanillin production.

Table 2

Fibrous Raw Material Analysis

Fiber Source	Ash, %	Essential Chemical Constituents		
		Lignin, %	Pentosan, %	Cross+Bevan Cellulose, %
Wheat straw	6-7	16-17	27-28	52-54
Rice straw	14-20	12-14	23-25	46-49
Esparto	6-8	17-19	27-32	50-54
Sugarcane (rind fibres)	2	19-21	30-32	59-62
Reeds	3-6	18-22	28-32	52-58
Bamboo	1-2	24-29	16-18	60-63
Leaves	0.6-12	7-10	17-24	70-80
Deciduous wood	1	23-30	19-26	54-61
Coniferous wood	1	26-34	7-14	53-62

Table 3

Operating Data for 100 B.D. Tons Day
Bagasse Recovery Plant

Pressure 3000 P.S.I.G.
Temperature 608° F.

Input	No Pith	With Pith
Black liquor solids (lb./hr.)	11,000	11,000
Water with black liquor (lb./hr.)	88,200	88,200
Pith solids (lb./hr.)	---	2,100
Water with pith (lb./hr.)	---	2,100
Air flow (lb./min.)	786	980
Air compressor power (hp.)	5,420	6,800
Hp. Pump Power (hp.)	400	430
Output		
Net process steam at 800 P.S.I.G. (Saturated) (lb./hr.)	30,000	38,000
Generated electric power (hp.)	5,420	6,800
Soda in oxidized liquor (as lb. equivalent NaOH/hr.)	4,200	4,200
Water with oxidized liquor (lb./hr.)	20,000	20,000

Table 4

Silica Content of Various
Pulp Mill Liquor Samples

Liquor Type	Oxidation Treatment	Black Liquor, Si/Na x 10^3	Oxidized Liquor, Si/Na x 10^3	Si Removed, %
Abaca	Lab.	8.54	2.75	68
Bagasse	Lab.	86.54	9.6	89
Bagasse with pith	Lab.	222.45	10.11	95
Synthetic I	Lab.	63.69	7.67	88
Eucalyptus	Plant	4.00	1.3	68
Synthetic II	Lab.	6.93	0.43	94

Table 5

Settling Time for Oxidized Bagasse Liquor Solids

Settling Time, Hours	Oxidized Liquor Settled Solids, %
0.00	0.4
0.25	1.1
0.50	1.3
1.00	1.4
2.00	1.4
4.00	1.4
24.00	1.4

Table 6

Laboratory Oxidation of Bagasse Black Liquor

(1 Hour at 608° F.)

	Bagasse		Bagasse Plus Pith	
	Black Liquor	Oxidized Liquor	Black Liquor	Oxidized Liquor
C.O.D. g./l.	63.4	6.4	80.9	5.4
% C.O.D. reduction	---	90.0	---	93.3
Total solids g./l.	70.0	27.3	79.7	29.9
Ash g./l.	28.7	23.2	34.1	26.0
pH	12.2	9.0	11.1	9.0
Volatile acids as acetic acid g./l.	6.1	3.8	5.7	1.7

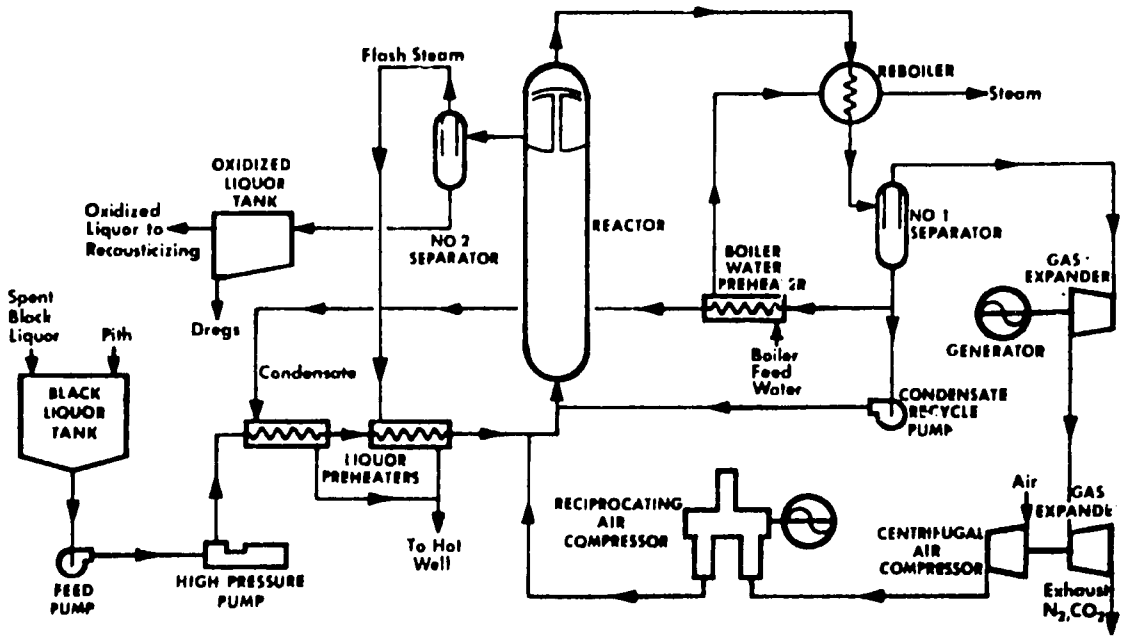

Figure 1

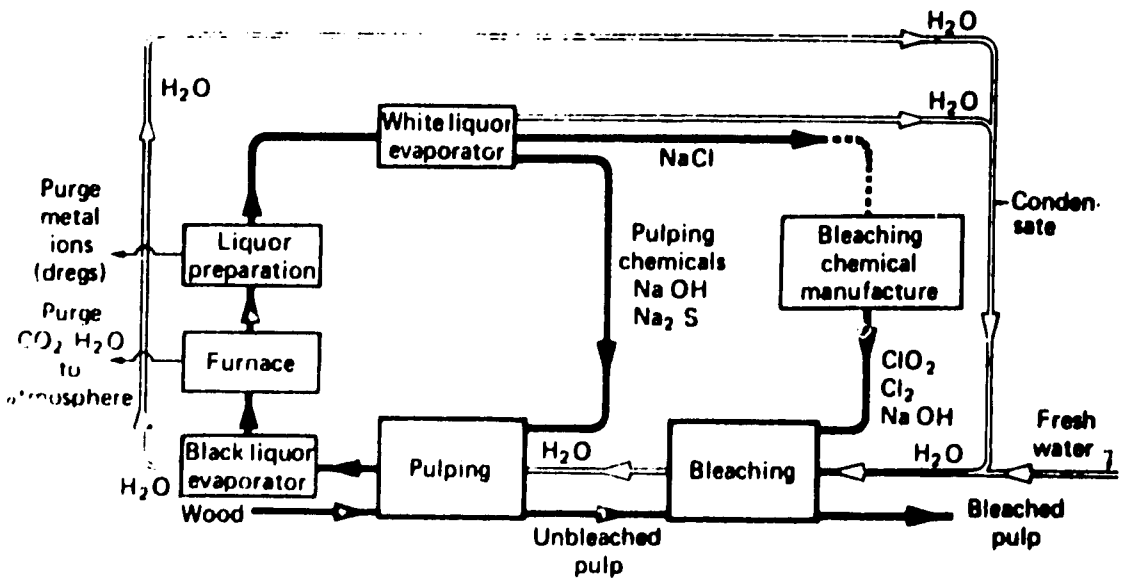

Figure 2

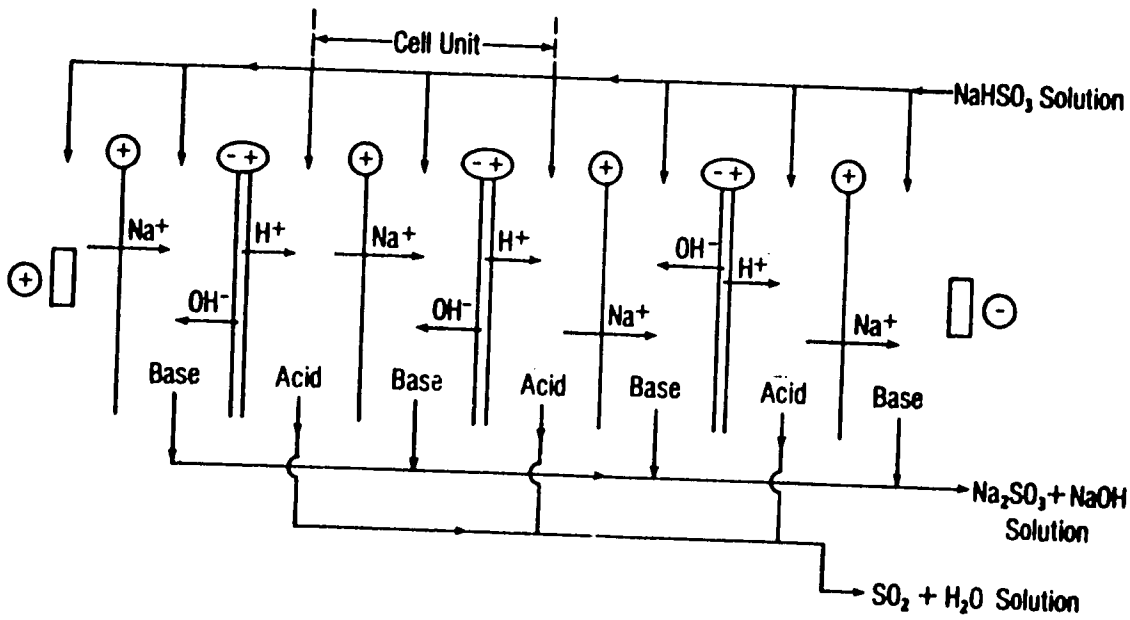
Cell Unit
NaHSO3 Solution
Na+
H+
OH-
Base
Acid
Na2SO3+NaOH Solution
SO2 + H2O Solution

Figure 3

The Silica Problem in Black Liquor from Rice Straw Cooking

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This essay deals with the desilicification of black liquor from rice straw cooking to facilitate its use during the soda recovery process. If the silica content of the black liquor is more than 5 g./l., it will tend to deposit and form scales on the inner walls of the evaporiser pipes. In this case, frequent chemical and mechanical cleaning of the evaporiser is necessary, resulting in loss of time, decrease in efficiency, and an increase in cost.

Studies on desilicification of black liquor were based on the following:

1. By treating black liquor with CO_2 gas or flue gases. Silica precipitates below pH 9 and above pH 6.5, and the precipitate is easily filterable.

2. By treating black liquor with $Ca(OH)_2$. The sludge of SiO_2 and $Ca(OH)_2$ precipitates. This sludge is bulky, contains an appreciable quantity of black liquor, and is not easily filterable.

3. By addition of NaOH to black liquor. NaOH is added to increase the NaOH: SiO_2 ratio, in order to keep SiO_2 in a soluble state during evaporation. The added NaOH will be regained during the recovery process.

4. By storing or aging the black liquor for a few days. The SiO_2 in time is separated and precipitated on the bottom of the container.

5. By treating black liquor with slightly acidic chemicals, such as $NaHCO_3$, $MgCl_2$, $MgSO_4$, etc. The SiO_2 can be precipitated and separated.

All studies made on desilicification can be summarized as follows:

Treatment with CO_2

Schwable, L. Kuna, and L. Graber. Silica in solution can be precipitated by acidic reagents such as CO_2. The silica practically begins to separate after all the free alkali is changed to carbonate about pH 9. The efficiency of desilicification by CO_2 is independent of the initial concentration, while it depends on the silica which remains soluble after CO_2 treatment and on the initial $Na_2O:CO_2$ ratio in the black liquor.

The trials of desilicification were done by CO_2 in the pilot plant until 1 gram SiO_2 per litre remained in the soluble state. The efficiency was calculated as follows: (1) The initial concentration of SiO_2 was 30 gm./l. and after treatment with CO_2 it dropped down 1 gm./l. The efficiency of desilicification = 29/30 = 96.67%. (2) The initial concentration of SiO_2 was 10 gm./l. and after treatment with CO_2 it dropped 1 gm./l. The efficiency of desilicification = 9/10 = 90%.

Schwable and the others treated the warm black liquor with a flow of air containing 10% CO_2. The trials showed that the precipitation of silica depends on the absorbed quantity of CO_2 and that a concentration of SiO_2 of 0.2 -0.4 gm./L could be reached after treatment with CO_2.

Sekina in Rakta Pulp and Paper Mill. Sekina and Aime from the technical department of Rakta Pulp and Paper in Alexandria made a trial to separate silica from black liquor at room temperature (28° C.) by treatment with CO_2 generated from Kipp's Apparatus. The results were as follows:

ANALYSIS OF INITIAL BLACK LIQUOR

Dry content after total evaporation	69.93 gm./l.
Mineral ash after ignition	18.03 gm./
Loss on ignition ("mainly organic matter")	51.90 gm./l.
SiO_2	3.33 gm./l.
Free alkali	2.48 gm./l.
pH	10.7

The black liquor was then treated with CO_2 for 90 minutes at 28° C. SiO_2 was precipitated in a colloidal state which was very difficult to filter. The filtrate was found to have the following composition:

Dry content after total evaporation	67.48 gm./l.
Mineral ash after ignition	15.83 gm./l.
Loss on ignition ("mainly organic matter")	51.65 gm./l.
SiO_2	2.13 gm./l.
Free alkali	Nil
pH	6.5

From these results it was found that the precipitate was mainly SiO_2 bound with a small amount of organic matter and that only 36% of the total silica was removed.

The precipitate obtained after filtration from 100 ml. of black liquor was 2.45 gm. It was found that the precipitate had the following composition:

Total mineral weight of precipitate	2.45 gm.
Ash after ignition	2.20 gm.
SiO_2 in ash	1.20 gm.
Organic matter	0.25 gm.
Nonsilicious ash	1.00 gm.

Treatment with $Ca(OH)_2$

B. N. E. Guen. From black liquor containing 7 to 10 gm./l. SiO_2, 90% of the SiO can be separated in 5 to 10 minutes by treatment with $Ca(OH)_2$. The effect of lime is especially selective when the sedimentation is done with fresh black liquor. The result of the separation of SiO_2 from black liquor after treatment with 55 gm. CaO per liter of black liquor for 10 minutes at 80° C. was as follows:

	Black Liquor Before Treatment	Black Liquor After Treatment
Dry content, gm./l.	136.23	131.62
Loss on ignition of dry content, %	54.65	54.00
Mineral ash of dry content, %	45.35	46.00
Ca O gm./l.	---	1.28
Na_2 O gm./l.	18.6	23.25

Dr. Lengyel from The Pulp and Paper Research Institute, Budapest, treated the black liquor at boiling temperature with 200 gm. CaO per liter of black liquor. The SiO_2 decreased from 9.34 gm./l. to 0.66 gm./l. but only 50 to 80% of the treated black liquor could be obtained because of the voluminous sludge and the difficulty in washing it. The sludge therefore bound to it about half of the black liquor's volume.

Storing or Aging of Black Liquor

Sekina and Aimé noticed during working on rice straw black liquor at Rakta Pulp and Paper in Alexandria in November 1963 that a light brown precipitate settled following a few days of storage in a closed container. Analyzing this precipitate, it was found to be mostly SiO_2. It was found also that the pH was decreased by aging. Initially, the pH was 10.7; during the third and fourth days of storage it was 10.0; on the fifth day it was 9.5; and on the 15th day, it was 6.7. This decrease in pH is an indication that certain reactions occurred, neutralizing the free alkali and extending into the acidic range. One explanation can be that the black liquor is liable to decompose with time because of the activity of carbohydrates, which evolve CO_2 gas that is responsible for the decrease in pH and the precipitation of SiO_2. Alternatively, the container may not have been well closed, and CO_2 from the surrounding air reached with the black liquor. In any event, the SiO_2 which settled upon storage in the container proved to be easy to be filtered.

The analysis of black liquor after storage for different times was:

Storage, Days	pH	Total Ppt., gm./l.	Total Ash, gm./l.	SiO_2 Removed gm./l.	SiO_2 Remaining gm./l.
0	10.7	0.0	0.0	0.0	3.33
2	10.3	2.086	1.28	1.045	2.29
3	10.0	4.035	3.002	2.476	0.86
4	10.0	4.368	3.389	2.468	0.87
5	9.5	4.766	3.497	2.57	0.76

Seventy-four percent of the total silica content in black liquor could be removed after three days of storage.

Experimental Work in The Pulp and Paper Research Institute, Budapest

In March 1965, Drs. Lengyel and Sekina performed laboratory experiments on black liquor treated with $Ca(OH)_2$ in different amounts (200%, 400%, and 600% of CaO in proportion to SiO_2 content). The black liquor was freshly prepared from a rice straw cook in the pilot plant of the institute. The fresh black liquor was divided into two portions. The first portion was kept in a big bottle well sealed with paraffin oil and the second portion was kept in an ordinary reagent bottle without sealing.

The fresh liquor analyzed as follows:

Specific gravity at 20° C.	1.05
Dry content	98.80 gm./l.
Loss on ignition of dry content	62.37 gm./l.
Mineral ash of dry content	36.43 gm./l.
SiO_2	7.3 gm./l.
Total alkali as Na_2O	20.25 gm./l.
Free alkali as NaOH	1.75 gm./l.

After analysis, the black liquor was treated with $Ca(OH)_2$ and 12 days allowed to pass. Three samples of 50 ml. each of black liquor were taken from the paraffin-oil-sealed bottle and treated with different amounts of commercial CaO (200%, 400%, and 600% calculated as 100% pure CaO) at 20° C. for 10 minutes. Every sample of CaO was mixed with 50 ml. of water and then added to the 50 ml. of black liquor to make the diluted concentration about the same as the diluted black liquor coming from the washing section at Takta. The treated portions were mixed for 10 minutes and then filtered. The filtrates were analyzed with the following results:

	Dry Content gm./l.	SiO_2, gm./l.	CaO, gm./l.
Fresh black liquor	98.8	7.8	---
Original black liquor, 12 days old	89.7	1.8	0.008
Original black liquor treated with 200% CaO	81.1	0.5	1.176
Original black liquor treated with 400% CaO	79.6	0.45	2.00
Original black liquor treated with 600% CaO	81.3	0.52	4.224

It was shown from the analysis that the SiO_2 after 12 days of black liquor storage under a paraffin oil seal was decreased from 7.3 gm./l. to 1.8 gm./l. in spite of no contact with air.

After 45 days of storage under paraffin oil, the black liquor was analyzed. At the same time a sample of black liquor kept in a normal bottle without sealing was also tested. The results were as follows:

	Dry Content gm./l.	SiO_2 gm./l.
Fresh black liquor	98.8	7.3
Black liquor sealed with paraffin oil	87.7	0.63
Black liquor unsealed	88.0	0.36

It is clearly shown that SiO_2 decreases in black liquor under storage, whether sealed by paraffin oil or not.

Three portions of black liquor after 45 days of storage under paraffin were taken and treated with 200%, 400%, and 600% CaO at 50° C. for 10 minutes. Analysis of the treated black liquor was as follows:

	Dry Content gm./l.	SiO_2 gm./l.	CaO gm./l.
Original after 45 days	87.7	0.63	0.008
Black liquor treated with 200% CaO	88.1	0.16	1.67
Black liquor treated with 400% CaO	84.4	0.07	1.94
Black liquor treated with 600% CaO	86.6	0.024	2.4

From the analysis it was found that silica decreased from 0.63, 0.07, and 0.024 gm./l. by treatment with different amounts of CaO at 50° C.

Paper Technology

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Papermaking fibers produced by pulp mills are not suitable as such for the manufactu of paper. Stock preparation covers operations such as repulping and blending of different types, addition of various chemicals and fillers, and mechanical treatment necessary to make fibers suitable for forming into paper sheet. Different methods and technologies ar applied to produce different paper grades. Different types of paper are given in Appendi 1.

Technology in the following areas are lacking:

Fillers and Loading

Inorganic natural or synthetic pigments are incorporated into paper or board as fil ers to fill air space between cellulose fibers in order to get improved texture and feel, high print quality, control of strike-through, and opacity. The most commonly used fill ers are clays, calcium carbonates, sulfates, silicates, and high strength pigments (e.g., ZnS and TiO_2).

To be learned is the technology of addition of fillers, filler retention, filler dis tribution, and filler properties (e.g., refractive index, oil absorbancy, opacity, scatter ing coefficient, printing opacity, brightness, and structure of particles, such as specifi gravity, dimensions of dispersed particles, and abrasiveness.

Internal Sizing

Paper and boards are sized for satisfactory performance upon contact with various liquids. Writing papers must be sized so that inks do not strike too deeply into or through the paper. The rate of water penetration into bag and other wrapping papers must be slowed down. The internal sizing process incorporates resins or synthetic sizes or paraffin emulsion into the furnish.

Techniques to be learned include:

- Measurements of pore sizes by the bubbles point tester.
- Bonded fiber areas.
- Determination of intrafibre penetration (Valley size or KBB tester).
- Manufacture of rosin size.
- Rosin dispersions.
- Emulsification of rosin size
- Sizing variables due to pulps.
- Technology of rosin application.
- Retention of rosins.
- Distribution of size.
- Synthetic sizes.
- Wax emulsions.

Surface Sizing or Surface Treatment

Surface treatment is a broad term for the addition of dry- or wet-strength additives with or without pigments, glue, starch, or CMC upon the surfaces of an already formed web or board. The techniques to be learned include application at wet end and press section and size press.

Wet-end Adhesives for Dry Strength

Wet-end adhesives are synthetic chemicals, such as polyacrylamides, or natural bonding materials, such as gums or starches, for distribution throughout the fiber suspensions prior to the forming of webs. Adhesives improve hydroexpansivity of the paper and remove linting caused by loose fibers on the surface of papers which cause defective printing. The technology to be learned includes preparation of the adhesives, properties of the adhesives, tests of the adhesives, application to the fibers, and retention.

Wet-end Adhesives for Wet Strength

Most paper or boards lose strength upon the increase in water taken from the surrounding air (high relative humidity) or by soaking in water. Therefore, the pulps are treated with wet-strength resins such as melamine-formaldehyde. The technology to be learned is preparation, properties of these adhesives, application to the fibers, and retention.

Coatings

A pigment coating in which an aqueous mixture of pigments and adhesive is applied to the surface of the paper is used primarily to make printing papers for magazines and coating.

Technologies to be studied include:

- Coating machines.
- Coating adhesives.
- Coating pigments.
- Properties of coating mixtures and flow properties of thereof.
- Evaluation of coated papers.
- Synthetic polymeric pigments, e.g., polystyrene (plastic coating pigments).
- Hot melt coating.

APPENDIX I

I. Printing grades

Banknote, record, and document
Blotting, filter, laminating and absorbent
Book, bristol, dover, drawing, tabulated cards
Newsprint, rotogravure, catalog, offset
Duplicating paper
Envelopes, chart, map, airmails, etc.

II. Industrial grades

Bag, wrapping, kraft liner
Cigarette tissue
Construction paper and board
Food packaging, cups and container stocks, bread wrap, greaseproof paper, glassine paper
Gumming and label
Electrical insulating paper
Paperboard
Light weight sanitary tissues
Waterleaf

Soda-Oxygen Pulping of Bagasse and Rice Straw

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The interest of the pulp industry in nonsulfur pulping arises from the need to minimize environmental pollution. One of the problems of soda-oxygen pulping of wood is the difficulty of penetration of oxygen into regular size chips (1). Thus, when wood was cooked in chip form, only the surface of the chips was cooked, with the center remaining uncooked. The basic problem is the contact between oxygen and lignin (2).

Precooking of the chips in alkali before the oxygen cook with or without a fiberizing step between the two stages has been developed (3,4). Recently, thermomechanical fibers of spruce, pine, and hardwoods were used instead of wood chips in oxygen-alkali pulping (5).

In contrast to wood, the open structure of bagasse and rice straw allows easy diffusion and penetration of chemicals. Bagasse and rice straw are the two main fibrous raw materials for pulp and paper production in Egypt. The loose structure of these raw materials makes it possible to accomplish oxygen pulping in one step without fiberization (6).

Soda-oxygen pulping has some attractive features:

1. Soda-oxygen pulping gives higher yields and lower lignin contents than soda pulping.

2. One of the characteristics of soda-oxygen pulps is that they beat considerably faster than kraft pulps (7). This easier beatability of the soda-oxygen pulps is quite evident with the higher yield pulps. It was found that the oxygen pulps required one third of the beating energy of conventional kraft pulps.

3. A second feature of soda-oxygen pulps is that at any given freeness, these pulps form a denser sheet than kraft pulps of the same kappa number when unbleached (7).

4. Fully-bleached pulp cannot be produced unless chlorine chemicals are applied. However, when the soda-oxygen pulp is bleached with chlorine chemicals, the chemical consumption is less than that in the bleaching of a sulfate pulp with equivalent kappa number.

Soda-Oxygen Pulping of Bagasse

Pulping bagasse with soda-oxygen resulted in an increase in pulp yield from 6 to 10% over that obtained from soda pulps prepared under the same pulping conditions. Thus, with 15% alkali at 5 kg./cm.^{2} oxygen pressure, the yield was 67% compared to 62% in case of soda pulping.

The lignin content decreased considerably with increasing oxygen pressure. The degree of reduction in lignin content depends on oxygen pressure. Thus, on using 5 kg./cm.^{2} pressure, the lignin content of the produced pulp was decreased by about 22%. Applying 10 kg./cm.^{2} oxygen pressure resulted in a reduction of lignin content by about 40%. Because of the lower lignin content, pulps prepared in this manner will require less bleaching; thus, a production cost savings could be realized.

Strength properties of the oxygen pulps were a function of oxygen pressure. Optimum strength properties were obtained at 5 kg./cm.^{2}. Soda-oxygen pulping resulted in a 9 to 11% increase in breaking length and 22 to 36% increase in burst strength compared to soda pulping, whereas the tear factor was improved slightly. Increasing oxygen pressure above 5 kg./cm.^{2} resulted in a decrease in strength properties.

Soda-Oxygen Pulping of Rice Straw

Soda-oxygen pulping of rice straw showed the same trend as that observed for bagasse, i.e., higher pulp yields than those obtained with the soda process. At 100°C., an increase in oxygen pressure from 0 to 10 kg./cm.^{2} was accompanied by a 6 to 8% increase in pulp yield. The increase in pulp yield at 120°C. amounted to 4 to 7%.

A significant decrease in lignin content was achieved by the soda-oxygen pulping of rice straw. At 5 kg./cm.^{2} oxygen pressure, about a 25% reduction in lignin content can be achieved. At 100° C., increasing the oxygen pressure to 10 kg./cm.^{2} resulted in about a 45% reduction in lignin content.

Soda-oxygen pulping at 5 kg./cm.^{2} oxygen pressure gave pulps with greater strength properties than those of the corresponding soda pulps. The increase in strength properties was more pronounced at 100° C. than at 120° C. and amounted to 11 to 13% in breaking length and 16 to 17% in burst strength. In addition, a considerable improvement in tear was obtained. Once again, increasing the oxygen pressure from 5 to 10 kg./cm.^{2} had a detrimental effect on strength properties at all test conditions.

Oxygen Bleaching

The use of an oxygen stage can replace the chlorine and extraction stages in the conventional CEH and DEH bleaching sequences. By partially replacing the chlorination stage by an oxygen/alkali stage, BOD and color of effluent water from the mill can be reduced considerably (8).

Oxygen-alkali bleaching has been applied to birch sulfite dissolving pulp (9). This pulp was bleached by an oxygen-hypochlorite treatment. No inhibitor such as magnesium compounds was used, as the aim was to reduce viscosity.

A worldwide drive to reduce water pollution from pulp bleaching plants has resulted in mill-scale application of oxygen-alkali delignification in South Africa, Sweden, France, the United States, and Japan (8). The waste liquor from washing of the oxygen pulp is recirculated and used in brown stock washing. Thus, most of the organic matter dissolved during the oxygen-alkali stage goes into the mill's chemical recovery system.

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Recent Research on Cellulose-Polymer Composites and Lignin

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In this article, recent research activities will be reviewed involving wood-like cellulose-polymer composites, finishing of paper (paper-polymer composites), and lignin structure and uses.

WOOD-LIKE CELLULOSE-POLYMER COMPOSITES

Wood-plastic composites could have a promising potential for industrial and engineering uses, and since the mid-1950's, extensive research and development work has been carried out on the subject of making wood-plastic combinations.

The first series of experiments was performed in this laboratory with bagasse pretreated with a methanol-benzene mixture, water, dilute alkali, and acid in the hope of resolving some of the polymerization difficulties encountered in preparing ligno-cellulose-polymer grafts. Results of polymerization reactions have been reported in nine reserach articles describing the processes and the factors affecting the graft polymerization. Four of these articles were based on work done in the Institute of Macromolecular Chemistry in Darmstadt during my stay in West Germany on a Humboldt fellowship. The rest of the articles were based on work in my laboratory here at NRC.

The processes followed in graft polymerization are a modified ceric ion process developed by us in Darmstadt and the sodium bisulfite-soda lime glass process initiated in my lab in Egypt. The most recent process is development of the second process to use clay and kaolin instead of the sodium bisulfite-soda lime glass system.

The prepared ligno-cellulose-polymer composites were pressed under controlled temperature and pressure to obtain wood-like composites. The latter are denser than the natural wood, and their specific gravities usually fall below 0.85-1.15. The compression strength reached 1.8 ton/cm.^{2} and the deformation 7%. Wood-like composites also resist decay and attack by fungi even when soaked in water for more than 40 days.

The second series of experiments was carried out to determine the influence of polymer loading and the type of ligno-cellulose on the wood-like composite properties. Variation of the pressure and temperature during the molding of the wood-like composites and their influence on the latter properties were also considered. Results showed the achievement of wood-like composites of compression strengths exceeding 20 ton/cm.^{2}. The induced changes in the electrical resistance by gamma radiation was measured for some wood-like cellulose-polymer composites. Increasing the percentage of the polymer in the composite samples resulted in an increase of the activation energy. The resistance changes to a lower value by gamma irradiation. This may let such composites be used as gamma dosometer in the megarad range.

PAPER-POLYMER COMPOSITES

Research currently under way in this lab on paper-polymer composites was preceded by studies of the properties of paper prepared from chemically modified fibers. Increased strength and decreasing opacity were achieved for paper prepared from carboxymethylated pulps because of increased interfibrillar bonding. Partial transformation of sodium carboxymethyl cellulose to the free acid form resulted in a considerable increase of the paper

strength and opacity. Pulp acetylation resulted in decreased strength properties. These were regained through carboxymethylation of the acetylated fibers, and a tremendous increase in tensile strength was achieved that was higher than for paper formed only from carboxymethylated pulps of the same degree of substitution (D.S.). However, the opacity was reduced considerably, as well as the tear resistance. For such paper, the fiber bonding was ascribed to an electrostatic attraction between the positively charged acetyl groups and negatively charged carboxymethyl ones.

Research on paper-polymer composites implied addition of polymer and modified starch (oxidized and grafted with polyacrylonitrile) while beating the pulp stock during the process of papermaking. The results showed that the sizability increased much more by addition of polyacrylonitrile grafted starch than by oxidized starch and polyvinyl alcohol. Modification of the polyacrylonitrile grafted starch leads to still more improvement of the sizability. The fold endurance and tensile strength also were improved.

Filling of paper with modified china clay and koalin was another aim for the present research on paper finishing. Encouraging results have been obtained by grafting both substances with vinyledene chloride and methylmethacrylate by a process initiated in this lab. Also, an emulsion from such mixture was obtained which will find its use in the coating of paper.

LIGNIN STRUCTURE AND USES

In previous work, alkali lignins isolated under mild conditions from cotton stalks and bagasse are actually low molecular weight aromatic compounds, the so-called alkali hemilignins. Woody cotton stalks and nonwoody bagasse contain lignin and hemilignin but in different ratios. Alkali hemilignins isolated from both types of plant have the same skeletal structure. The latter consists mainly of condensed and uncondensed guaiacyl units and, if already present in the plant, of p-hydroxyphenylpropane units. However, the difference between bagasse and cotton stalks hemilignins lies mainly in the type of linkages (beta-aryl ether linkages and alpha-vinyl linkages of the phenyl coumaran type).

Recent research in my lab includes studies on the structure of some organosolve lignins. Inspection of IR spectra of organosolve lignins isolated from woody cotton stalks by using different acidified organic solvents and two different means of extraction (separately and successively) revealed differences in the structure of the isolated lignins that were due to differences in the manner of extraction and the solvents used. In general, all organosolve lignins showed polymeric association of hydroxyl groups, C=N and stretching vibration of C-H of the saturated hydrocarbons. Free hydroxyl groups were only present in some of the isolated lignins. In the carbonyl region, it was possible to note specific frequencies for the stretching vibrations of different types of carbonyl functions; two quinonoid carbonyls in two rings, two quinonoid carbonyls in the same ring or aliphatic ketone in conjugation with C=C, saturated aliphatic aldehyde, aryl ketone or α-β unsaturated aldehyde, and aryl aldehyde or saturated open chain ketone. The ratios of the intensity of carbonyl bands to the band at 1515 cm^{-1} due to C-H stretching vibration in the benzene ring are in general higher for lignins isolated by successive extraction than those isolated by separate one. Also, for the lignins isolated by the former manner of extraction, the intensity ratios of some of the carbonyl bands increased with the order of the solvent used for extraction. Most organosolve lignins showed vicinal trisubstituted aromatic structure and some showed the presence of 1,3,5-trisubstituted aromatics. Few possessed para substituted (or to a lesser extent unsymmetrically trisubstituted aromatic structure), o-disubstituted, m-disubstituted, or hexa-substituted aromatic structure. However, all the isolated organosolve lignins except one showed the presence of 1:2, 1:4, or 1:2:4 aromatics. Organosolve lignins consisted of one or more of the following units: condensed guaiacyl, uncondensed guaiacyl, and syrangyl and showed absence of conjugation with the aromatic ring.

As regards the uses of lignin, it was possible to prepare dyes suitable for nylon and wool from alkali lignin. This was registered as an Egyptian patent. Study of the effect of substituted groups of alkali lignin dyes on the light fastness of the dyed nylon and wool revealed that the greatest light fastness was for the nonsubstituted lignin dye. Substituted lignin dyes with electron repelling or attracting groups showed lower light fastness.

Investigation for the methoxy content and absorption range for the hydroxyl-valence-stretching vibration for the prepared lignin dyes indicated their probable participation in influencing the light fastness on the dyed nylon. Increased methoxy content induced decreased light fastness. Intermolecular hydrogen bonding improves light fastness, while the intramolecular one adversely affects it. For the dyed wool, because of the presence of the acidic substituent sulfanilic acid group, the lignin dye containing it possessed the highest light fastness. For other substituted lignin dyes, the dyeability appears to be a product of the value of σ- (Hammett constant) of the substituent and the methoxy content present in the dye.

The research work was further extended to trace the influence of the different types of lignin on the effectiveness of the prepared dyes. Thiolignin, hydrochloric acid treated lignin, and nitrobenzene oxidized lignin were used for the dye preparations. The light fastness of the dyed nylon decreased because of the presence of sulfur, halogen, or acid group in the prepared dyes, while because of the last named the dyed wool showed increased light fastness. Again, intermolecular and intramolecular hydrogen bonding play a role for those prepared dyes.

Successful trials have been carried out to dye mixed cotton and polyester textiles with the prepared lignin dyes through adjusting the pH of the dyeing bath with buffer solution. Studies to determine the proper conditions of time and pH were carried out to achieve the greatest dyeability for such textile.

Another type of lignin dye could also be prepared through nitration of lignin. The nitrolignin fraction dye was separated and used to dye wool and nylon with a yellow color.

An important use for lignin is through finding the biological activities of lignin derivatives. Some investigators prepared lignin derivatives which found use as growth stimulators for plants and increased the percentage of vitamin C. In this lab, lignin carbamate, nitrolignin, and chlorolignin were prepared and are now under investigation.

The Hardboard Industry in Egypt

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Although the first true hardboard to be produced with a considerably high density can be traced back to the 1920's, it was not until 1968 that the first plant was established in Egypt (at Farascour)--to make hardboard from agricultural residues (namely, rice straw).

The main steps of production applied at the Farascour plant start with raw materials preparation and continue through pulp preparation, addition of resin, sheet formation, hot pressing, and conditioning.

Preparation of Raw Material (Chopping)

The raw material (rice straw) is delivered to the plant usually in the form of compressed bales. After removal of the binding wire, bales are split by hand before the material is fed to the cutters. The cutoff chaff is then cleaned, and the powderized chaff as well as metallic foreign substances are eliminated by means of dedusting units and magnetic separators.

Preparation of Pulp

The process used to prepare pulp at the Farascour plant is the Asplund process in which special equiment called the defibrator is used. This unit is designed for continuous introduction of the raw material into a steam chamber (preheater), continuous refining by attrition discs in the presence of steam, and continuous discharge of defibrated fibers.

Additives

The primary self-bending in the board sheet is caused by the surface tension forces created by evaporation of water from the structure in the wet-felting process. The plastic properties of lignin and the hemicelluloses remaining in the pulp are not sufficient to give boards made from rice straw pulp favorable mechanical and physical properties. Therefore, a bonding agent is added during the manufacturing process. This phenolformaldehyde resin (1.5% based on dry pulp) is precipitated among the fibers by adding dilute sulfuric acid to a pH of 4.5.

Sheet Formation

After the pulp is prepared with resin, it is felted for shaping the board. The method used is the wet-felting process, in which the mat is formed from a low-consistency pulp suspension (2%). The pulp is delivered by means of a pump to the head box of the endless wire machine (Fourdrinier machine), where the water is separated first by gravity, then by the application of vacuum, and finally by pressure produced by rollers. The pressed wet sheet (moisture content 65%) is trimmed to size and then sprayed with paraffin wax by a paraffin machine before it is conveyed to the hot press.

Hot Pressing

Pressing the fiber mat is carried out in a multilayer (20 layers) hydraulic press heated by hot water (185-195° C.) and the maximum pressure applied is 50 kg./cm.^{2}. In the press, water is squeezed out, the sheets are compressed to the required thickness, and the resin is cured.

Conditioning and Trimming

For the finished product to have the proper moisture balance, it is conditioned in a special device (conditioning chambers) in which it is subjected to a relative humidity of 80 to 85% at 50° C. up to 8 hours. After humidification, boards are trimmed to the required size (360 x 122 cm.) using logitudinal and cross trim saws.

Production of Hardboard

The production of hardboard at the Faraskour factory in Egypt began in 1968 and has grown steadily since start-up:

Year	Production	Year	Production
1968/69	87,980	1974	317,352
1969/70	223,236	1975	368,725
1970/71	280,671	1976	339,055
1971/72	490,864*	1977	182,538**
1973	298,346		

Research

To improve the quality of the produced hardboard, the main raw material (rice straw) has been blended with other agricultural residues such as cotton stalks, linseed, sugarcane bagasse, barley straw and reeds. The effect of this blending has been studied with the following results.

Cotton Stalk Pulp. It was found that blending of cotton stalk pulp with rice straw pulp leads to the improvement of the bending strength of the produced hardboard in absence of resin and also with 1.5% and 3% resin (phenolformaldehyde resin). As for resistance to water, it was found that water absorption of the produced hardboard was slightly raised using no resin and blending cotton stalk pulp with rice straw pulp, while water absorption was slightly decreased when using 1.5% or 3% resin.

When using cotton stalk pulp, the percentage of resin required was reduced to 0.5% (instead of 1.5% in the case of rice straw pulp), and at the same time the bending strength was raised. This is due to the high percentage of lignin in the cotton stalk (23%) compared to that of the rice straw (only 9%).

From an economical point of view, blending cotton stalk with rice straw is preferable because of the consumption of the synthetic resin is reduced to about 30%.

Other Agr cultural Residues. It was found experimentally that the addition of other agricultural residues (linseed, barley straw, sugarcane bagasse, and reeds) to rice straw improves the phsyical and mechanical properties of the produced hardboard remarkably.

When linseed is added, both the bending strength and the water absorption is improved whether resin is used or not. The same behavior is noticed when sugarcane bagasse and reeds are blended with rice straw pulp. In these cases, the percentage of water absorption is remarkably lower when linseed pulp is blended with rice straw pulp.

* 18 months
** 6 months

Bagasse: A Fibrous Raw Material for Pulp and Paper in the Arab Republic of Egypt

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Bagasse consists of the remnants of sugarcane stalks from which the juices containing sugar have been extracted by crushing. For decades, bagasse was used exclusively as fuel in the sugar mills. Small and older mills need all of their bagasse for the generation of process steam. Larger and more modern mills have a surplus of bagasse.

As a source of fiber for the production of pulp and paper, bagasse is one of the newer developments. Major installations came into operation after World War II.

Bagasse is discharged continuously from a sugar mill during crushing. A pulp mill is not faced with harvesting problems, but it must provide storage to assure a supply of fiber during the many months when the sugar mill is shut down. Costwise, it is very advantageous to locate the pulp mill next to the sugar mill. In this way, transportation costs are avoided.

Sugar cane is grown in Upper Egypt in the Nile Valley from about 400 km. south of Cairo to Aswan. It is used to make sugar and edible syrup for domestic consumption and for export. In 1967, about 176,500 feddans (about 183,000 acres) were planted with cane, and 5,385,360 tons of cane were harvested that year.

There are plans to increase both the area of plantations to about 230,000 feddans (nearly 240,000 acres) by 1980 and the yield of cane per feddan by extending the existing drainage and irrigation systems and by increased use of fertilizers and new varieties of cane. Presently, three main varieties of sugarcane, all developed in Egypt, are being planted and grown. They are No. 310, No. 413 and No. 509.

Sugar mills operate only during the sugarcane harvesting season, and in Egypt, the crushing season runs 120 to 140 days.

Bagasse would be available in large quantities to the Egyptian pulp and paper industry. The present sugarcane production if completely converted into pulp would yield more than 200,000 tons/year of bleached pulp. The cultivation of sugarcane has increased steadily over the years, and the government is planning further increases. As an incentive, the price of sugarcane has been increased stepwise from L.E. 2.6/ton in 1971 to L.E. 7.5/ton in 1976 (from $3.72 to $10.73 at current exchange rates). At the prevailing price, it is expected that more farmers will plant sugarcane in preference to other less profitable crops.

There are seven sugar mills, including the new one at Deshna, and mills and their bagasse outputs are listed in Table 1. Of the seven sugar mills, only one, Edfu, has a relatively small bagasse pulp mill attached to it. The actual output of this mill at present is about 40 tons/day. The availability of bagasse from the Edfu sugar mill would be sufficient for a pulp mill using 140 tons of bagasse pulp per day.

EDFU PULP MILL

The Edfu pulp mill belongs to the Societe des Sucreries et de Distillerie. It was constructed between 1963 and 1965 next to the Edfu sugar mill which has a capacity of about 1,000,000 tons of sugarcane per year. It is located on the west bank of the Nile near Edfu. The mill was designed to produce 60 tons/day of unbleached bagasse pulp. Most

of the chemical recovery section was designed for future expansion to 120 tons/day. In reality, the design capacity is not reached on a continuous production basis. Output is actually 40 tons/day because of several difficulties that will be mentioned in the course of this description.

During the sugar milling season from January to June each year, 450 to 500 tons/day of fresh bagasse are diverted from the boiler feed conveyor in the sugar mill to the moist depithing station of the pulp mill. A drag conveyor feeds the whole bagasse into Horkel depithers. The accepted bagasse is pressed into bales by semiautomatic balers and transported by narrow-gauge railroad to the bagasse storage yard. There was a direct connection for feeding fresh bagasse directly to wet depithing and the pulp mill, but this mode of operation is not used. A number of difficulties are encountered when fresh bagasse is processed in the pulp mill:

- Inadequate pith removal.
- A 30% increase in cooking chemical consumption.
- Nonuniform cooking.
- Difficulties on the wet lap machine.
- Higher black liquor viscosity.

After storage, bagasse is transported to the mill again by narrow gauge railway and fed into the bale slushing pulper by means of an inclined apron conveyor. The bagasse is continuously slushed at 2-3% consistency and pumped to three Horkel depithers. A magnetic drum separates tramp iron, and a drag conveyor with a perforated bottom raises consistency to 10 to 12% before the feed to the Horkels. Pith separated at this stage is supposed to be pressed to 40% dryness before being fed to a pith boiler for burning, but this system still is not in use because of difficulties encountered in pressing the pith to an acceptable dryness for burning in the boiler.

Wet depither bagasse leaves the Horkels with about 20% solids content and is fed via a set of belt conveyors to an intermediate storage slab from which it can be bulldozed into a live bottom bin.

A two-tube Pandia 42" x 24" digester is fed by a screw feeder through an inclined conveyor between bin and Pandia. The digester can produce up to 2.3 tons/hour of bone dry pulp, which limits the theoretical production to around 55 tons/day. About 12% active alkali as Na_2O is used in cooking to a permanganate 9. Cooking time is 9-10 minutes at 6 kg. pressure.

The digester is followed by a blowtank with a blow heat recovery system. Washing is performed on 3 vacuum filters arranged for countercurrent liquor flow. Washing is followed by a screening system with selectifiers and centricleaners. After thickening, the pulp is wet lapped on wet lap machines.

The original installations consisted of a two-stage flash dryer with two stages of presses and a head and bailing system behind. This system is not in use as a result of serious difficulties caused by the formation of small pulp nodes known as fish eyes.

Evaporation is by a four-effect five-body multiple effect evaporator. In practice, this evaporator cannot reach the specified capacity. This is attributed to scaling. In all probability, the design did not take the lower values of heat transfer of the viscous black liquor into consideration or the black liquor strength. It is lower than expected. The bodies are simply too small.

The recovery boiler is designed for doubling the pulp production. The causticizing plant is designed for double the present capacity, and lime is produced in small stationary kiln.

The quality of Edfu pulp is within parameters specified for bagasse pulp, and it has very good drainage properties because of the extensive depithing carried out before cooking.

MODERN TECHNOLOGY OF BAGASSE UTILIZATION IN PULP AND PAPER MILLS IN SOUTH AMERICA

In a short visit to South American bagasse pulp and paper mills, we have found modern technology adopted in bagasse utilization to be as follows.

Bagasse Storage

There are new trends for wet bulk storage. Many installations exist, but for each project a study should be adopted, taking in consideration environmental conditions to select the most suitable one. In the most recent installation, the concrete bases of bagasse piles were covered with asphalt to protect the concrete from being corroded by the acidity of bagasse in storage. Field losses are not known, but benefits of this storage systems are:

1. Reduction of labor and bailing costs.
2. Less storage area.
3. Help in reducing water solubles in bagasse.
4. No wet depithing is required.
5. Reduced fire hazards.

Pulping

Three processes are adopted for pulping bagasse in South American mills:

Full Chemical Cook. Bagasse receives a full chemical cook in a continuous horizontal digester. Pulp produced is used to make fine paper and board of good quality. Yield of bleached pulp is 50% on fully depithed bagasse fed to the digester, KnO, 10-12 bleached to 85° GE brightness through a three-stage CEN. Chlorine consumption is 5.5%. About 85% of the pulp is used to make fine paper on a machine running 400 to 500 m./min.

The Cusi Process. This process includes depithing as well as pulping. About 20% to the bagasse is eliminated as pith. The pulping phase of the process involves fractionation of depithed bagasse into two fiber fractions, designated fibers A and B. This fractionation is achieved by a mild soda cook (20-25 mintues at 180° C., with a chemical charge of caustic soda of 6-8% on the weight of the feed). The two fractions are separated by screening. The A fiber amounts to 15 to 18% of the weight of depithed bagasse passing through the screens. The retained material is B fiber. The A fiber is mixed with kraft waste and is used in the manufacture of corrugating medium. The B fiber is pulped or refined to provide the desired product.

For pulping, fiber B is impregnated with an excess of dilute caustic soda. This liquor is pressed in rotary presses to provide a fiber consistency of about 35%, so that the net chemical pickup by B fiber is about 10% of its weight of caustic soda. The cook is carried out in the vapor phase at about 160° C. for 10 to 12 minutes in a continuous digester. The pulp after washing could be used for such paper products as wrapping and linerboard in the unbleached state. Alternatively, the pulp could be bleached in a three-stage sequence to a brightness level of 75-80° GE with a bleach consumption of 8% as available chlorine.

Yield of unbleached pulp from B fiber is about 55%. The overall utilization of bagasse as expressed by the yield of A fiber and of unbleached pulp from B fiber amounts to about 50 to 52% of the whole bagasse to the depither.

If a semichemical pulp is desired, the B fiber is refined. Such a pulp has been used experimentally in the furnish for newsprint and several other types of paper products. Today, with improvements in depithing and less severe cooking conditions, it is possible to recombine the two pulp fractions to obtain a good grade of bagasse pulp. However, on the basis of results obtained with today's depithing and cooking techniques using single-stage cooks (as in all other processes), the Cusi process has no particular advantage for the production of bagasse pulp. The two-stage cook and fractional intermediate screening add costs and complications and result in a dilute black liquor, which means higher costs for chemical recovery.

Pedaco Process. The first stage of this pulping process incorporates the impregnation of depithed bagasse with hot black liquor for a short period at atmospheric pressure. This liquor is expelled in the screw feeder to the continuous digester and with it about 12% of the weight of depithed bagasse processed. Caustic soda, the cooking liquor, plus steam are added to the fiber as it enters the digester. Pulping is carried out in a vapor-phase cook for about 20 minutes. For the various grades of pulp, the digester conditions are shown in Table 2, the only variable being the chemical stage.

Paper Manufacturing. Bagasse pulp is used in the furnish for all kinds of paper:

- Bond paper; 85 to 100%; machine speed of 400 to 500 m./min.
- Tissue paper; 60 to 87%; 700 to 1,000 m./min.
- Boards; 60 to 100%.
- Kraft for cement sacks; 60 to 85%; 90 g./m. cluepack unit installed on paper machine.
- Corrugating medium; 85 to 90%.

Recovery of Bagasse Black Liquor. Only a few mills in South America have installations for recovery of bagasse black liquor. Other mills dispose their liquor and have pollution problems. For difficulties encountered in recovery of bagasse black liquor, especially scaling caused by silica, higher viscosities that lower heat transfer in evaporators and create problems for pumping, one of the mills in Mexico has installed the Coupeland system to replace the conventional recovery boiler. The system differs in using the fluidized bed for combustion of black liquor at lower solid content, thus avoiding problems encountered in scaling during evaporation and allows combustion of black liquor at 37% solids. Black liquor comes out of the evaporators at 22% solids, and a cascade evaporator further concentrates it to 37%.

The ratio of costs to install the Coupeland system with costs to install a recovery boiler is 1:1, but heat generated from the black liquor is just enough to heat the air necessary for combustion of the black liquor in the fluidized bed.

However, the plant still has many problems, as that was the first installation in bagasse mills. Problems of black liquor evaporation were minimized, but chemical losses were high, with a recovery efficiency of 55% compared to 88% reported for the conventional recovery system in that mill when it was used.

A mill that installed a lime kiln to recover lime for causticizing dumped 50% lime mud and had a makeup of 50% fresh limestone to compensate for silice buildup in the system.

Black liquor generated from high-yield bagasse pulping has not been proved to be adaptable through the conventional recovery system.

PROBLEMS IN BAGASSE UTILIZATION

The history of progressive development of various bagasse pulping processes and their extensive and rapidly expanding application in a large number of industrial units indicate conclusively that few technical problems remain to be solved for the conversion of bagasse into a valuable product; namely, pulp. Once the pulp is produced, the subsequent conversion into finished paper products follows the standard papermaking practice.

The tremendous spurt in development activities in all the developing countries and the consequent increase in the demand for paper products of all types coupled with the fact that resources of conventional raw materials such as wood are extremely limited and ever dwindling have made it imperative that alternative cheap sources of raw materials be immediately tapped. It has now been universally recognized that bagasse is the material of choice to fill this urgent need.

However, there are still problems facing the utilization of bagasse, mainly in the pulping and recovery of bagasse black liquor, that must be solved to attain successful utilization of bagasse in the pulp and paper industry. Some of these problems are:

Cane Milling

A large portion of the cells, both fiber and nonfiber, are severely damaged by the cane crushing process in the extraction of juice. The effect on the nonfiber cells is probably not too serious from a papermaking standpoint. Approximately 40% of the fibers are fiber fragments resulting from prior damage, almost certainly suffered during crushing. An even greater percentage may suffer incipient damage to the point where they break under drastic defibering action, either during cooking or blowing of pressure cooks, but this cannot be determined visually.

In general, the unbroken fibers average 10% longer than all fibers, or about 25% longer than the broken fibers. It would be expected that crushing would tend to selectively break the longer, thinner and more desirable fibers for papermaking, and there are some indications from the fibers that this is occurring. The predicted average length and length-to-width ratio of bagasse fibers would be 25% greater if fiber damage could be avoided. The term "useful fibers in bagasse" should replace the pith fiber content, as broken fibers in bagasse are lost during depithing operations and are of no use from the papermaking point of view.

It is difficult to categorize crushing mills used in the sugar industry, but those equipped with and without shredders and those equipped with the diffusion system for extraction of juice yield completely different fibers in their adaptability to pulping and depithing conditions. The type of crushing mill has a serious effect on the percentage of pulp yields from bagasse and consequently affects to a large extent the production costs for the conversion of bagasse to pulp. The effect of cane crushing on bagasse fibers and pulp quality remains a fertile field for research. If the present effect is as great as implied, development of alternate juice extraction procedures to avoid the damage would considerably improve the quality of pulp now obtainable from bagasse.

Fresh Bagasse

It is a well-known fact that the erection of bagasse paper plants adjacent to sugar mills reduces the costs of transportation of bagasse to the paper mill. Moreover, such a location gives an opportunity to feed fresh bagasse to the pulp mill during the crushing season and thus avoid costs of bailing and storage losses. At Edfu processing fresh bagasse during the crushing season was not successful and led to low production levels because of difficulties in depithing, high chemical consumption in cooking, poor pulp drainage on brown stock washers because of improper depithing, and a more-vicious black liquor. Viscosity for black liquor generated from pulping of fresh bagasse is reported to be 15 cps. at 8.5% solids compared to 4 cps. for the same black liquor concentration generated from pulping of stored bagasse.

This is a problem that should be solved. Extensive research work should be done on the extraction of the water-soluble sugar and salts in fresh bagasse before depithing or pulping. Savings in costs in a bagasse mill using fresh bagasse are considerable. It is also important for newsprint production from bagasse, as the color of fresh bagasse is lighter than stored bagasse and pulp generated from it has a brightness of 60° GE, which could be used for production of newsprint without any bleaching.

Recovery

Chemical recovery in bagasse pulp mills is now becoming a necessity because of the ever-increasing size of the mills being constructed. A mill under 100 tons per day could not justify the capital investment for chemical recovery. Also, we are on the verge of entering a new era in bagasse pulping where complexes are being considered in the 300 MT/day range to produce bleached market pulp from bagasse. Recovery then becomes an integral part of the design of these mills.

The function of the chemical recovery section is to take weak black liquor from the brown stock washers and convert the reusable portion into white liquor for cooking more pulp. Heat recovery consists of burning the portion of the bagasse removed from the pulp to assist in the chemical reaction and also to produce steam in sufficient quantities to support the process and supply the steam for digestion. The overall operation is generally called a recovery cycle.

While kraft mills are almost always built with recovery cycles, as the recovery boiler is required to convert the makeup salt cake (sodium sulfate) into a useable form, pulp mills using bagasse or other agricultural residues seldom have this feature. One reason is that most of these mills are built as cheaply as possible to decrease the capital cost. Another reason is that most of these mills are small or have a low chemical or fuel cost. A recovery cycle for a small mill has a very high cost per ton of capacity, because a recovery boiler for a 15 ton/day mill would still cost close to $500,000. The differences from a wood pulp recovery cycle, aside from the difference in makeup chemicals between the kraft and soda processes, are few but very critical. The weak black liquor from the brown stock washer in the case of a bagasse mill has a lower solids content than that from a wood pulp mill. This difference is caused by the contained moisture in the bagasse being much greater than is the case in a wood pulp mill and the fact that steam is injected directly into the bagasse in the digester rather than indirectly heating the cooking liquor, as is done in normal wood pulp cooking. Slow drainage of bagasse pulp compared to wood pulp is also a considerable factor in low-solids content bagasse black liquor. Because bagasse contains a high percentage of silica in the pith and fiber, the various liquors (black, green, and white) transport the silica, which has detrimental effect on the equipment. Black liquor is evaporated to a lower solids content in the multiple-effect evaporator, as the viscosity of the liquor is high.

Aside from the decreased operating cost of a mill with a recovery cycle, a major benefit is that pulping chemicals are not discharged in the effluent. With recovery of at least 80% of the pulping chemicals in the recovery operation, less than 20% of the pulping chemicals discharged into the effluent. This makes the problem of effluent treatment of a mill of this nature much less difficult than if recovery were not used.

Because of these considerations of economics and ecology, a heat and chemical recovery system must be used for a large bleached pulp mill.

Problems in Recovery

High silica content and high viscosity of the black liquor from pulping of bagasse would appear to be major problems in operating recovery processes. The concentration of silica can vary widely depending on the region in which cane is grown, growing conditions, type of cane, harvesting methods, and other factors. Silica in black liquor causes fouling of the liquor side of evaporator tubes, slag for matron in the recovery boiler, and smelt buildup on the walls of the furnace. It hinders settling of the mud in the recausticizing station and generally increases the chemical losses in the circuit.

Evaporation cannot be carried out to achieve the desired concentration because of the viscous characteristics of the black liquor. Transfer of a liquor from one effect to next becomes increasingly difficult as the viscosity increases rapidly with increasing concentration. An attempt to lower the viscosity by raising the temperature would disturb the process temperature gradient. If the high temperature at the final effect is still maintained, the result will be charring of the organic substances, which provides the necessary necessary base for the formation of scale. The performance of the evaporators will drop rapidly, and eventually they will be inoperative.

In addition to the viscosity problem, the presence of silica in high proportions in the black liquor hastens the process of rapid scale formation. The performance of the evaporating system would be highly unpredictable. Many mills are obliged to drain (bleed) black liquor to the sewer to maintain pulp production at the expense of high chemical loss and polluting the environment.

Similarly, recovery furnace operation becomes extremely unstable because of wide fluctuations of liquor concentrations and firing rates. Liquor of low concentration sprayed to the furnace requires the use of huge quantities of auxiliary fuel to support combustion. On many occasions, this situation cannot continue long, and unburned black liquor solids continue to accumulate in the furnace. Finally, liquor firing has to be suspended and melting the hearth becomes necessary.

Although the damaging effect of the viscosity ends at this point, the presence of silica in the black liquor continues its harm all the way to the end of the recovery cycle. In green liquor, silica appears mostly in the form of sodium silicate. Its presence greatly retards the settling property of the lime mud in the recausticizing stage, which affects the white liquor and clarification and causes high chemical losses through the lume mud. Reburning the lime mud for the regeneration of quick lime is difficult because of the presence of silica. Furthermore, silica builds up accumulatively in the system unless a sizable portion of the lime mud is thrown out and makeup limestone quantity is increased to compensate for this loss.

This sort of operation can hardly achieve any economic success, aside from the totally unsatisfactory lime kiln operation. To reduce viscosity problems, it has been found beneficial to maintain a free alkali level in black liquor from 4 to 6 gm/ht as Na_2O. Doing so, however, could not help at high black liquor concentrations, i.e., more than 60% solids content.

The installation of a Coupeland system does readily help in reducing the problems caused by viscosity and scaling, as it needs black liquor at low solids content (22%) from the outlet of the evaporators and 37% after cascade. For the present installation at a bagasse mill at Mexico, there are still many difficulties in operation of the fluidized bed reactor, and further work is being done to make the operation successful. In another Canadian mill where the Coupeland reactor is used in conjunction with a recovery boiler, they still have trouble in running the Coupeland reactor, although it is a wood pulp mill and the black liquor generated is the same as any wood black liquor. They have to shut down for two weeks after a run of four weeks to clean heavy scaling on the walls of the Coupeland reactor. At the Edfu pulp mill, all the problems of recovery of bagasse black liquor do exist, as it was the first installation to recover bagasse kraft black liquor, and it is still the only one in the whole world. Extensive work should be done in the field, as the recovery of chemicals is of vital importance with respect to costs and pollution problems.

THE PRODUCTION OF NEWSPRINT FROM BAGASSE

Newsprint has historically been produced from wood fibers, mainly soft woods. The main component is mechanical groundwood (75 to 85%), while the remainder (15 to 52%) is long-fiber softwood chemical pulp.

Recently, disc refiners are being used more frequently to produce the groundwood rather than conventional stone grinders after being treated by a thermal process. These produce a stronger pulp and therefore enable a reduction in the percentage of the more expensive chemical pulp.

Most tropical countries do not have adequate resources of softwood forests and are therefore compelled to import their total newsprint and magazine paper requirements. Today, most of the world newsprint demand is met by Canada, Scandinavia, Chile, and the U.S.S.R. with smaller amounts coming from a few other sources.

During recent years, a great deal of investigation and experimental work has taken place on the use of sugarcane bagasse for the production of newsprint. Two bagasse newsprint mills are presently under construction, one in Peru and one in Mexico. The former, with a capacity of 350 tons/day, may start up early next year, while the latter will not be in operation before late 1978 or early 1979. These are presently the only two newsprint mills in the world scheduled to operate on bagasse.

Both mills will use the Cusi process for production of newsprint from bagasse.

Capacity is to be improved by using a china clay as a load, and various amounts of softwood have been blended with bagasse pulp in trial runs on a pilot plant scale. Chemicals will not be recovered in the Peruvian plant, while in the Mexican plant a Coupeland system will be installed to recover chemicals.

To what extent should depithing be undertaken for bagasse to be used for newsprint, how to improve opacity, and the recovery of chemicals are still questions requiring extensive research work.

FUTURE UTILIZATION OF BAGASSE

Bagasse could be used in A.R.E. for the production of many kinds of paper that are imported, and to fill the gap in the market that exists for others.

Writing & Printing

The estimated consumption for 1976 was 96,280 tons, of which 47,600 tons were imported. The deficit by 1985 will be 100,000 tons. Bagasse could be used to increase the production of writing and printing papers.

Newsprint and Magazine Paper

There is presently no newsprint made in Egypt, and consumption equals imports. Projected consumption in 1980 will be 60,000 tons, and in 1982 it will be 75,000 tons. It is evident that the potential for the development of a very substantial newsprint production industry exists in Egypt, assuming it can be justified technically and economically.

Table 1

Bagasse Output of Egypt Sugar Mills*

Sugar Mill**	Sugarcane Crushed Tons	Bagasse Percent of Cane	Bagasse Moist Tons	Moisture Content, %	Bagasse O.D. Tons	Residual Sugar in Bagasse, %
Abo Qurgas	547,000	33	180,500	54	83,000	4.6
Nag Hammadi	1,364,000	35.3	484,300	54.6	220,300	5.3
Dishna	Started in 1977					
Qus	741,000	34.3	254,500	52.6	120,600	5.4
Arment	88,800	30.8	271,500	50.8	133,500	6.1
Edfu	760,000	33.2	252,500	51.1	123,400	5.1
Komombo	1,090,000	34.9	380,700	52.4	181,200	5.2
Total	5,383,000		1,824,000		862,000	

* Figures based on 1976 harvest. Some values are estimated.

** An eighth mill, El Balyana, is in the planning stage.

Table 2

Digester Conditions for Pedaco Pulping Process

Pulp Grade	Bleachable Pulp	Linerboard Wrapping	Corrugating Medium
Permanganate number	23	28	34
Yield, %	50	65	70
Caustic soda charge (on depithed bagasse), %	11	7	5
Digester conditions			
- Temperature, °F.	347	347	347
- Pressure, p.s.i.	125	125	125
- Retention time, min.	20	20	20