OCCASION

This publication has been made available to the public on the occasion of the 50th anniversary of the United Nations Industrial Development Organisation.

DISCLAIMER

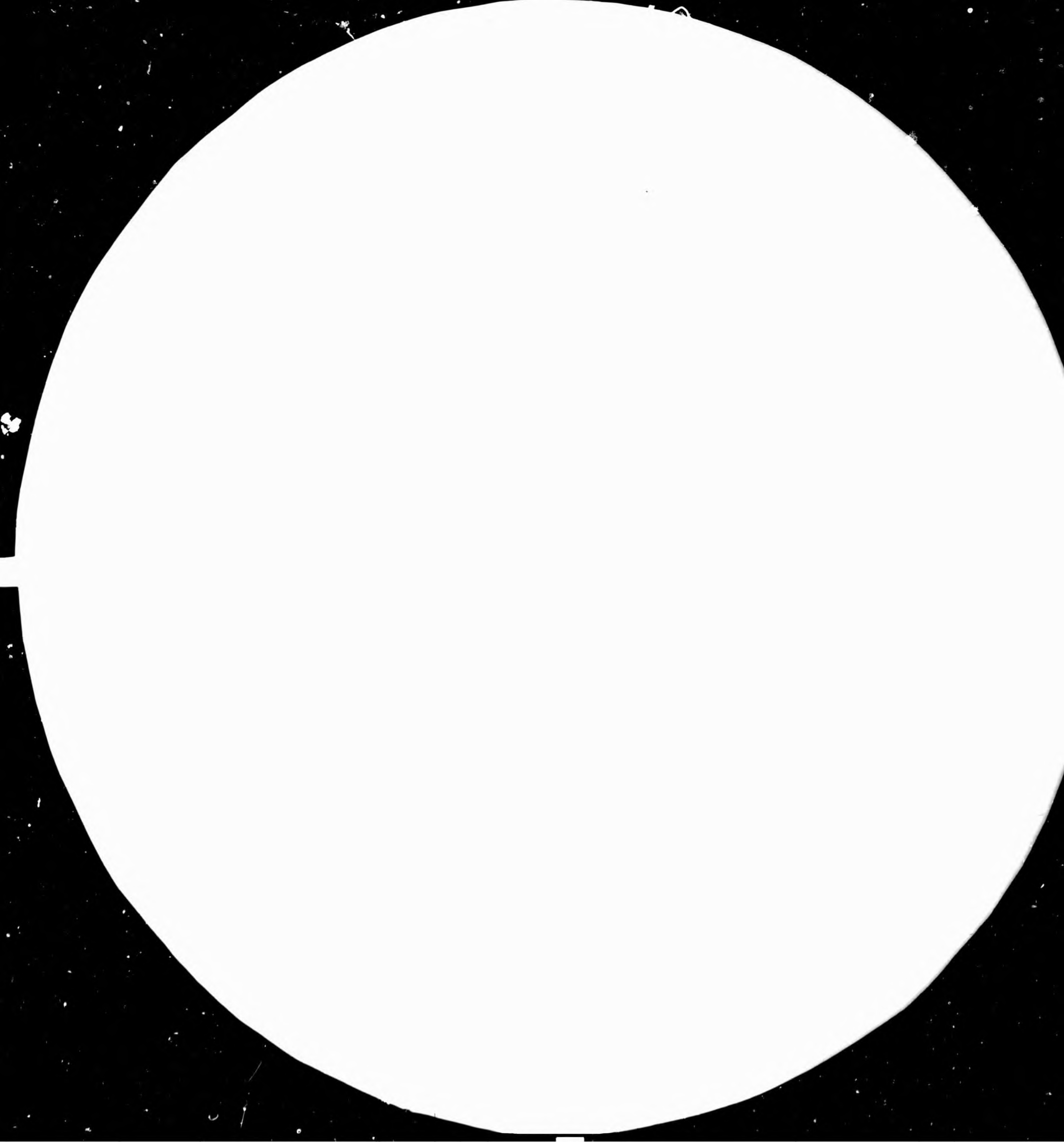
FAIR USE POLICY

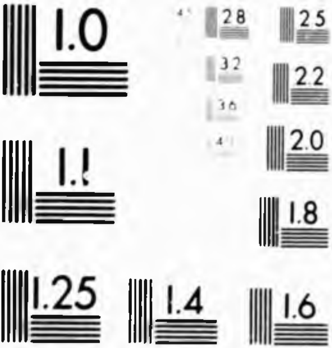
CONTACT

Please contact publications@unido.org for further information concerning UNIDO publications.

For more information about UNIDO, please visit us at www.unido.org

UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANIZATION
Vienna International Centre, P.O. Box 300, 1400 Vienna, Austria
Tel: (+43-1) 26026-0 · www.unido.org · unido@unido.org





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
ANSI and ISO TEST CHART No. 2

RESTRICTED

13617

DP/ID/SER.A/511
2 May 1984
ENGLISH

JUTE PRODUCTS RESEARCH

DP/BGD/75/013

BANGLADESH

Technical report: Chemistry of Lignin, with Special Reference to the Jute Fibre and the Photochemical Yellowing upon Exposure to Sunlight*

Prepared for the Government of Bangladesh
by the United Nations Industrial Development Organization,
acting as executing agency for the United Nations Development Programme

Based on the work of K.V. Sarkanen
Consultant in Organic Chemistry

United Nations Industrial Development Organization
Vienna

* This document has been reproduced without formal editing.

V.84-85436

CONTENTS

SUMMARY

This Technical Report is based on the Consultants visit to BJRI in March, 1984. Of two potential approaches for the reduction of photochemical yellowing problems in jute fibers, one based on partial delignification is recommended for immediate study and a work plan for this purpose is set forth for the period April 1 to August 30, 1984. At the end of this period, a detailed Final Report and recommendations for future research will be submitted to UNIDO and BJRI.

1. INTRODUCTION

The purpose of the mission was "to assist the Bangladesh Jute Research Institute (BJRI) with its research program on the chemistry of lignin, with special reference to the jute fiber and the photochemical yellowing which occurs on prolonged exposure to sunlight".

This consultant proposed the mission to be carried out in two parts:

a. A ten day planning trip to Dhaka in March, 1984 and
b. A two month residence in Dhaka in July-August, 1984.

The proposed arrangement was approved by UNIDO, and the consultant arrived to Bangladesh on March 20 after one-day briefing with Dr. H.P. Stout in Edinburgh. This report consists of a detailed proposal for the continuation of the mission.

2. CHEMISTRY OF JUTE AND ITS RELATIONSHIP TO PHOTOCHEMICAL YELLOWING.

As textile fiber, jute has unique characteristics. It deviates from all other cellulosic fibers (cotton, hemp, rayon) by its high content of lignin (13-15 per cent) and hemicellulose (24 per cent). Consequently, in its composition and chemical reactivity jute is more akin to such lignocellulosic biomaterials as wood and straw than it is to other cellulosic fibers. This fact has not been sufficiently recognized in past endeavors in chemical processing (bleaching, sizing, dyeing) of jute where methods established for cotton have been one-sidedly followed.

The photochemical yellowing of jute fibers with accompanying degradation of strength properties is a discoloration problem which jute shares with paper products manufactured from high-yield pulps such as groundwood, thermomechanical pulps (TMP) and high-yield sulphite pulps. Principally, the problem is caused by the photochemical autoxidation of lignin, although polyphenolic extractive components may sometimes be a contributing factor. The process is initiated by the photochemical conversion of phenylpropane units in lignin to the corresponding benzyl radicals (Figure 1). These radicals react with atmospheric oxygen forming hydroperoxyradicals capable of abstracting hydrogen atoms from surrounding molecules. The resulting

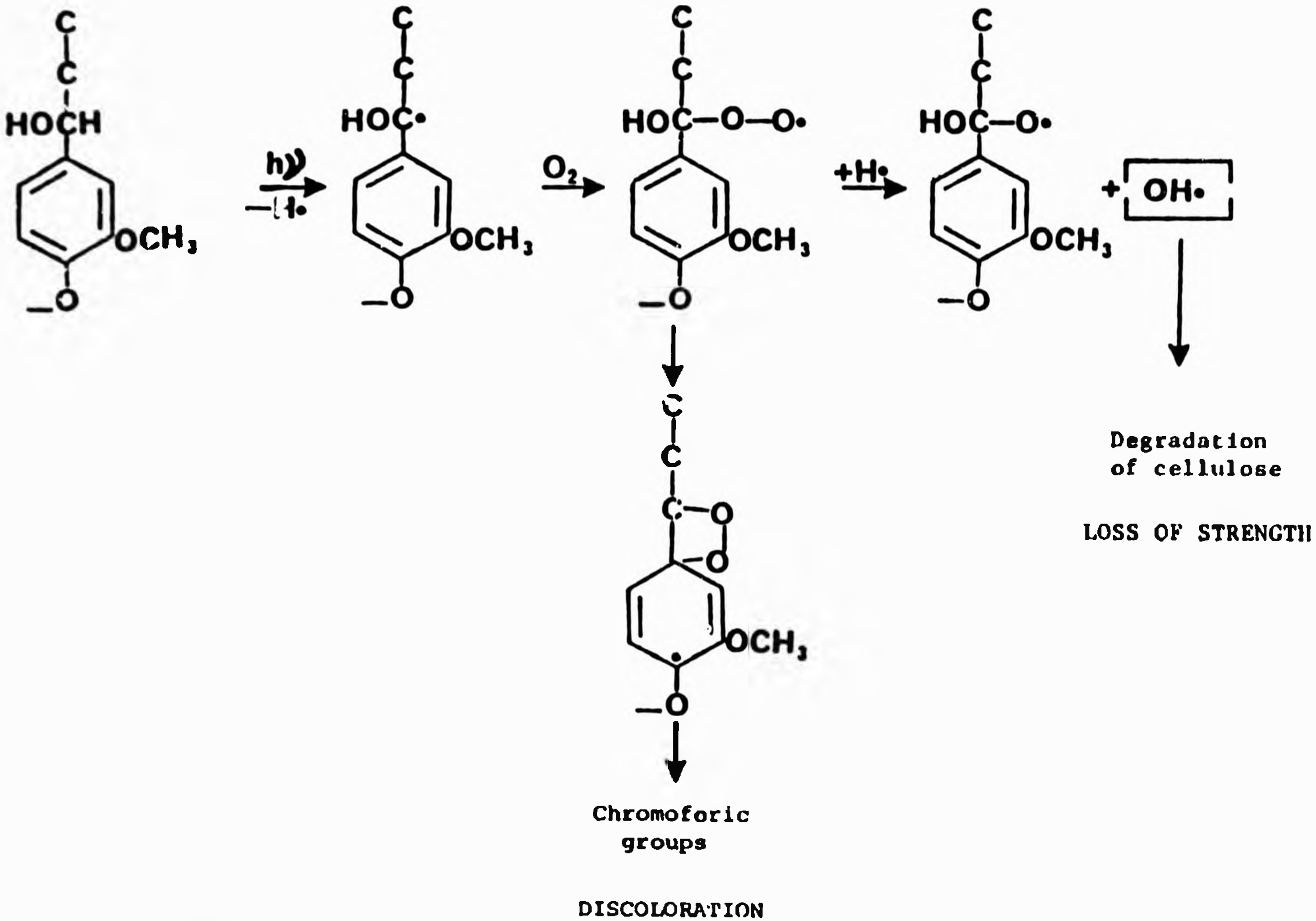


Figure 1. Tentative mechanism for the photochemical yellowing and strength degradation of jute fiber.

hydroperoxides generate colored chromophoric groups probably *via* intermediate dioxetane structures causing the yellow discoloration. They may also decompose with the generation of hydroxyl radicals. These, in turn, may either accelerate the yellowing process or, alternatively, attack the cellulose component causing its degradation. The latter phenomanon is analagous to the photochemical tendering of cotton fibers by certain anthraquinone dyes. The degradation of cellulose and other polysaccharides can also generate chromophoric groups and thus contribute to the discoloration of the fiber.

There are two ways to reduce the yellowing of jute fibers:

i. To incorporate inorganic or organic components in the fibers that may either quench the photon-excited aromatic groups in lignin or to scavenge intermediate radicals in the chain process. It is difficult to predict, *a priori*, how succesful protection of the fibers could achieved by this method.

ii. Controlled removal of the lignin component and/or its conversion to a photochemically more resistant form. An existing project at the Institute by Mr. Nurul Amin is already pursuing this avenue. Partial removal of lignin also reduces the intrinsic coarseness of the jute fiber. On the negative side, losses in dry - and particularly, in wet strength are unavoidable.

It is obvious that both of the approaches mentioned should be pursued. The first approach would have specific application for jute based yarns for carpets as pointed out by Dr. Bhuiyan, while the second alternative has interest for the improvement of textile yarns. However, moving ahead on a too wide front during the initial stages may not be advisable. It is therefore proposed that initial work be concentrated on the delignification area.

3. ORIENTING EXPERIMENTS CARRIED OUT AT THE UNIVERSITY OF WASHINGTON.

Before undertaking the mission at BJRI the consultant performed some exploratory laboratory on jute delignification together with Mr. Hossein Resalati, a graduate student from Iran. The purpose of these experiments was to determine, whether or not near-quantitative delignification is possible without destroying the integrity of the native fiber bundle structure. A brief synopsis of the results obtained is presented in the following.

Over 90 per cent delignification of jute yarn is possible by such conventional pulping processes as kraft delignification (Na_2S plus NaOH), alkaline sulfite ($Na_2\ SO_3$ plus NaOH) and semialkaline sulfite ($Na_2\ SO_3$ plus $Na_2\ CO_3$). In all these processes, reasonable reaction rates are obtained in the temparature range 140 to 170°C. Anthraquinone addition (0.1% of fiber) accelerates the rate of delignification in all these processes. The wet, delignified yarns retain their integrity, but have low wet strength and low resistance to rubbing when wet. However, upon drying, the yarns regain their strength to a substantial degree. The yarns obtained using alkaline sulfite methods were lighter in color and could be further bleached by chlorine dioxide solutions.

The prelimenary results obtained suggested strongly that alkaline delignification processes in common use in wood pulping industry show promise in the modification of jute fibers in such a manner that their photochemical yellowing tendency is reduced. The chemical cost in this type of delignification is only a fraction of that associated with chlorite delignification, the only process explored in earlier studies. Experience in wood pulping also suggests that the degradation of cellulose in jute fibers will be less in alkaline as compared with chlorite delignification. A particularly interesting potential of alkaline delignification exists in the upgrading of jute cuttings for application in textile fibers and this avenue definitely deserves to be explored.

Over-all, it is the opinion of this consultant that the initial results in the alkaline delignification of jute fiber are promising enough to merit setting up a cooperative research program between the BJRI and the University of Washington. The details of this proposal program are outlined in the secciors that follow.

4. PERSONNEL AND EQUIPMENT

Work at the University of Washington will be carried out by the consultant in collaboration with Mr. Hossein Resalati, a Ph.D. candidate from Iran. Mr. Resalati has expressed interest to shift his Ph.D. topic from bagasse delignification to jute fiber delignification. The work will be carried out in small scale using thermostated rocking autoclaves and M & K digestors with forced liquor circulation.

The following arrangement is proposed for the project at the BJRI. The individual in charge of the laboratory experiments will be Mr. Mohammed Ali under the supervision of Dr. Rahman. Professor A. Jabbar Mian from the Dhaka University has kindly agreed to participate in the direction of the project. Since Mr. Ali will probably be carrying out research for his Ph.D. work in a foreign university during the autumn 1984, it will be important to make arrangements for the continuation of the delignification project during his absence. Mr. Nurul Amin has collected a substantial amount of data on chlorite-delignified samples and their modification with urea- and melamin formaldehyde resins. Comparative studies on fabric samples delignified by the alkaline sulfite method would be of great interest.

The high temperature dyeing apparatus available at Dyeing and Finishing Department is outstandingly fitting for the conduct of the delignification experiments. Separate equipment is available for the treatment of small (100g) and large (25 kg) smaples. The equipment allows a maximum working temperature of 150°C under pressure with efficient liquor circulation, and loose fiber, yarns and fabrics can be delignified with equal ease. The only drawback of this equipment is the fact that delignifications at 150 to 170°C are outside of its range. However, Dr. Bhuiyan has pointed out that a high-pressure rotating pulping autoclave has been ordered from Germany. Thus, high temperature delignifications will be feasible to perform in this autoclave once it has been installed.

Critical to the success of the working plan are measurements of photochemical discoloration and strength retention. Adequate apparatus is in operation in the Physics Department but is currently hopelessly overloaded with light fastnewss samples from the Dyeing Department. A duplicate apparatus stands idle because of need for repair. It is proposed that the duplicate instrument be transferred immediately to the Chemistry Department, promptly repaired and assigned for use in the delignification studies.

It is rewarding to note that all equipment necessary for the conduct of the delignification project is available at the Institute. Work on this project can therefore be started without delay.

5. WORKING PLAN

The following schedule is envisaged for the implementation of the research project:

First Period, April 1 to June 30, 1984. Parallel work will be carried out at BJRI and the University of Washington using small (~100g) samples of loose fiber, jute cuttings, yarn and woven fabrics. The purpose of this phase is to define the optimal conditions for delignification (chemical charge, reaction temperatures and times). After the return of this consultant to Dhaka in early July, the combined results will be used to design experimentation on a large scale (25 kg).

Second Period, July 1 to August 30.

Larger scale delignifications will carried out using loose fiber and cuttings in order to produce sufficient material for carding, spinning and weaving in order to determine what advantages can be gained in these operations from the hopefully reduced coarseness of the delignified fibers. It should be noted that this phase of the project would require assistance by a large group of the Institute personnel, and it is hoped that such assistance can be implemented. By the end of this period, a careful and objective evaluation of the results obtained is in order and it would appear desirable to invite representatives of the jute industry and Dr. Siddequallah to participate in this evaluation. The scope and direction of the continuation of the project should be based on the outcome of the evaluation. For example, it will possible to determine the relative promise of delignifation as a means of upgrading the quality of jute cuttings in comparison with improving regular jute fibers for textile applications.

6. PROGRAMS AT BJRI and UNIVERSITY OF WASHINGTON

Due to the shortness of time for the preparation of this report, only a few salient points of the plan for the first period will be indicated here:

i. The principal delignification work will be carried out at BJRI and the University of Washington on sulfite-hydroxide and sulfite-carbonate systems with and without anthraquinone. Comparative studies will be performed using sodium- and ammonium bases. University of Washington will concentrate on the higher temperature range (150 - 170°C). The important point in these studies will be the determination of the degree of delignification corresponding to the fiber liberation point.

ii. At the University of Washington, the consultant has developed a convenient method for the determination of lignin in jute fibers, based on the use of permanganate. This method will be communicated to the researchers at the BJRI.

iii. Researchers in both locations will maintain exchange of information by monthly correspondence.

7. GENERAL REMARKS ABOUT THE ACTIVITIES OF THE BJRI

This consultant was very favorably impressed by the competence of the personnel, the quality of the equipment and the flexibility of administration at the BJRI. A few comments are included for further improvement of the research activities:

a. Library needs more general books and periodicals in the field of lignocellulosic materials including wood. Recommended items are listed in Annex 1.

b. Traineeships. UNIDO traineeships of three months duration are extremely valuable for the scientists at the Institute. This consultant had the opportunity of getting aquainted with two gifted scientists, Mr. Nurul Amin and Mr. Mohammed Ali. The approval of both traineeships is strongly recommended. It would seem very likely that the facilities and lecture programs at the University of Washington would be appropriate for the traineeships of both scientists. Furthermore, such instruments as refined optical and scanning electron microscopes, ultracentrifuge and light-scattering equipment which are not available in Bangladesh but are indispensable for their Ph.D thesis work, can be extended to their use at the University of Washington.

8. CONCLUSIONS

It appears clear from the above discussion that opportunities to improve the properties of jute fibers and -cuttings, particularly for textile applications, exist in chemical treatments that cause modification and/or partial removal of the lignin component. The reason why this approach has hardly at all been applied in jute research to-date is due to the fact that chemical processes developed for an essentially lignin-free fiber, cotton, have served, so far, as an one-sided model for jute technology. The potential of novel chemical treatments exists in three areas:

a. Reduction of photochemical discoloration and weakening of jute fibers.

b. Upgrading of jute cuttings.

c. Reduction of the coarseness of regular jute fibers.

In view of the importance of the three problem areas mentioned, it appears desirable that chemical modification of jute fibers becomes a continuing research and development activity at BJRI. For the planning of such activity, this report sets forth a work plan for the period April 1 to August 30, 1984, with well-defined goals and an evaluative process at the end of the period. After the completion of this project, a Final Report containing conclusions and recommended future action will be submitted to UNIDO and BJRI in early September.

ANNEX 1

BASIC LITERATURE RECOMMENDED FOR AQUISITION BY THE LIBRARY OF BJRI

E. Sjöström: Wood Chemistry, Fundamentals and Applications (Academic Press, 1981).

K.V. Sarkanen and C.H. Ludwig (Eds): Lignins, (Wiley-Interscience, 1971).

N.M. Bikales and L. Segal (Eds.): Cellulose and Cellulose Derivatives, Volumes IV and V (Wiley-Interscience, 1971).

S. Rydholm: Pulping Processes (Interscience, 1965).

For review of abstracts of recent published papers, the following periodical is recommended:

Bulletin of the Institute of Paper Chemistry, Appleton, Wisconsin.