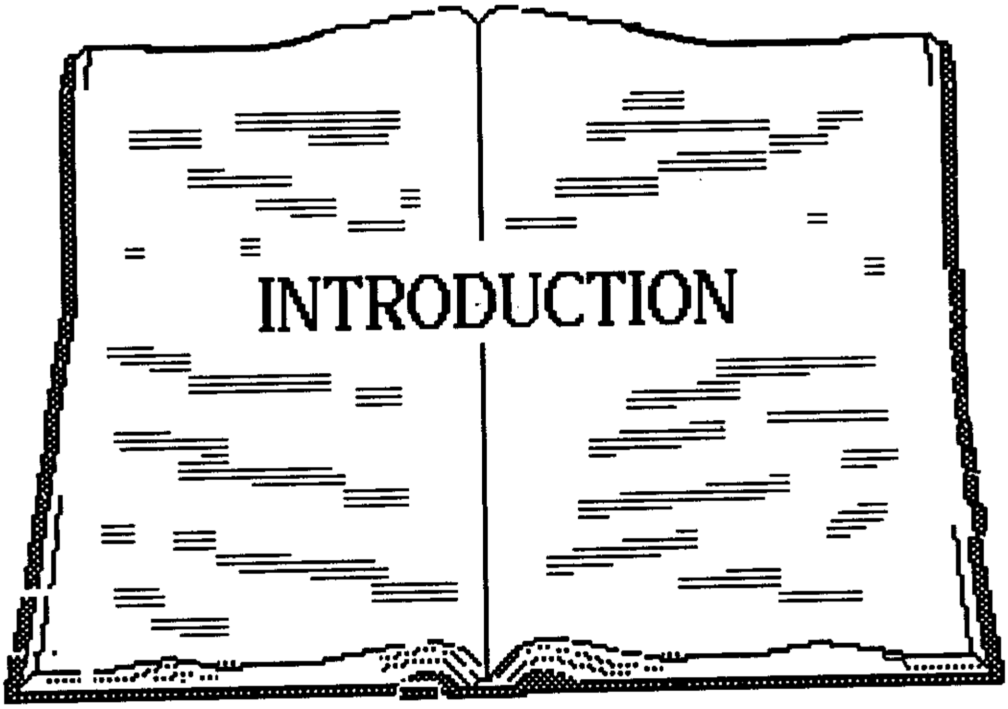

INTRODUCTION

INTRODUCTION

The raw material of wood fibers in Egypt, as well as in many countries of the tropics and subtropics, is of limited supply and the pulp industries is forced to use agricultural residues as alternative sources. In Egypt rice straw and bagasse are used. In other countries additonally, reed and bamboo are used to fill the increasing demand of the paper industry. What all these annually harvested nonwood fiber plants have in common that they contain silica in varying but significant amounts embedded in their plant cells especially epidermis cells.

IBrahim (1988 a) reported that to secure adequate supply of fibers for the everincreasing demand of paper and paperboard, a greater share of nonwood plant fibers is required particulary in those countries that lack sufficient pulpwood supplies.

Althought several species of nonwood plants such as bamboo, reed, sugarcane bagasse, wheat and rice straw have proved to be suitable for making various grades of paper and paperboard of good quality, yet these fibers are still under-utilized because of some economic and technical difficulties. To promote the utilization of nonwood plant fibers in the production of pulp and paper the problem encountered in the processing of these fibers should be solved.One of the most trouble some problems is the inherent high silica content of nonwood plant fibers. This would either cause troubles in the recovery of heat and chemicals from the spent pupling liquor (black liquor) and reduce the effeciency of the recovery plant as in the case of bamboo, reed, bagasse and wheat straw pulp mills or even impede completely the chemical revocery process as in the case of rice straw pulp mills.

Kopfmann and Hudeczek (1988) noted that the harvesting method and the handling of the raw material can either increase or reduce the total silica content of the fiberous material. The silica entering the mill consists of silica from plant cells and silica compounds from the soil that stick to the outer surface of the plants.

Though the handling and cleaning of raw material prior to cooking removes a high percentage of silica on outer surfaces and eliminates part of the organic silica contained in the leaves and knots of rice straw, the remaining silica content can still be high on entering the digester. Cases are known where 18%. SiO_2 was found in cleaned rice straw.

During the cooking process, alkaline cooking agents partly convert silica into soluble components, while the remainder stays with the pulp. The amount of soluble silica compounds in black liquor depends on the amount of alkali used for cooking. More alkali dissolves more silica. The black liquor from high yield pulp contains a small amount of dissolved silica only, while the SiO_2 contents of black liquor from chemical pulp of lower yield may reach concentrations of up to 15% and more, based on total solids in the black liquor.

Problems With Black Liquor

A deep brown highly alkaline viscous liquid is produced as a result of the pulping of nonwoody fibrous materials. In underdeveloped. countries this black liquor is disposed in water streams or sea which causes serious pollution and is against environment conservation legislations. The black liquor contains the following components :

a - Silica in the form of sodium silicate .

b- Sodium hydroxide .

c- Lignin in the form of sodium ligninate .

d- Hemiclluloses and these are mainly pentozans .

Recovery of Black liquor

As an alternative way of disposing black liquor several trials have been tried for making use of the spent black liquor. These trials can be categorized as follows :

1- trials for making use of silica.

2- trials for making use of sodium hydroxide .

3- trials for making use of lignin .

4- trials for making use of hemicelluloses .

The tried attempts may aim at making use of more than one of the components of black liquor.

A- **Concentration and evaporation :**

One of the early trials of black liquor recovery is its concentration and evaporation to get the soluble matter as solids which facilitates making use of them. ***Saxena (1981)*** reported that the evaporation of black liquor is a bottleneck in many recovery systems. The concentrations of black liquor above about 40% total soilds necessitates the use of a forced circulation concentrator. The design and performance of the concentrator is greatly influenced by the thermal and rheological characteristics and the nature of the constituents of the liquor. The concentraor can be coupled with the existing multiple effect evaporator to increase the capacity and decrease the downtime of the whole evaporator system.

Bharadwaj (1981) described the problems encountered in the evaporation of black liquors which are the formation of black liquor soaps and carbonaceous deposits and scale formation on evaporator tubes. ***Mansour et al. (1992)*** described an indirect gasification process, which can accept feed stock at a wide range of soilds concentration of 35-100% which offers special advantages in recovering chemicals from black liquor derived from nonwood pulping applications. Additional benefits cited for the indirect gasification technology include low pollution, low capital cost, and process flexibility. ***Ibrahim (1988 b)*** noted that silica form hard scales in both the evaporation plant and the recovery boiler leading to a reduction in their effeciency and increased frequency of shutdown for cleaning and overhaul.

B- <u>Desilication of black liquor</u> :

With chemical pulp produced from rice straw, about half the quantity of silica contained in the plant substance is dissolved in balck liquor. This dissolved silica causes problems in practically all stages of the chemical recovery process, even preventing the installation of a chemical recovery system in some cases ***(Kopfmann and Hudeczek, 1988)***.

For a pulp mill that depends on nonwood fiber, silica must be eliminated from black liquor to produce pulp economically and to meet enviroment restrictions. This need is especially valid in pulping rice straw and may also be considered for other nonwood fibers where the purging of excess silica in the lime recycling system has to be minimized . Thus, the interest in a desilication process for in lime operation on a commercial scale has increased considerably within the last decade.

The principle of silica removed has been studied for quite some time, and the findings have been published in various technical papers. During the cooking process, silica is dissolved in a strong alkaline medium, such as NaOH and water. The pH value of this solution is well above pH 11. By lowering the pH value with a suitable acid like carbonic acid, the solubility limit is reached for SiO_2 compounds at slightly above pH 9.

Ibrahim (1988 a) noted that most nonwood plant fibers have high silica content ranging from 1-2% in bamboo and sugarecane bagasse to as high as 8-13% in rice straw compared to less than 0.1% in pulpwood. In alkaline pulping of nonwood plant fibers, the major part of silica dissolved in the cooking liquor as sodium silicate and goes with the spent pulping liquor (black liquor). In the recovery of heat and chemicals from black liquor, the silica causes troubles at the various stages of the recovery system (evaporation - combustion - caustification - lime burning) as follows :

- hard scale are formed in the evaporation and recovery plants
- In caustification, the silicates dissolved in green liquor are precipitated by lime as calcium silicates which interfers with the settling of lime mud.
- In burning of silicious lime glassy materials forms ring scales. High silica contaminated lime mud is unrecoverable and the lime mud becomes a secondary pollution source.

To minimize the silica problem in the chemical recovery, most pulp mills based on nonwood plant fibers are operating their recovery plants with high available alkali in black liquor. This is to reduce the viscosity of black liquor on the one hand and to minimize silica scaling (by preventing the hydrolysis of Na_2SiO_3) on the other hand. However, Na_2SiO_3 goes through evaporation and combustion into the green liquor and SiO_2 is then removed by caustification as $CaSiO_3$ with the lime mud. Though this is a simple way to deal with the SiO_2 problem in case SiO_2 in weak black liquor is in the order of 2-6 gm/L, but it is not possible to recover the lime because of high SiO_2 content of the lime mud. Moreover, this method is not operative for higher SiO_2 - containing black liquor like that of rice straw.

Therefore it becomes clear that desilication of black liquor a head of the recovery plant would be the best solution for silica problem in all respects.

Li (1988) descirbed a desilication process for black liquor from rice straw pulping that does not require chemicals or the passage of flue gas into the black liquor. An alkaline sodium sulfite cooking process is used . The pH value after digestion should be kept between 10 and 11, and the silica should be allowed to precipitate naturally. The black liquor should be kept at 80 ^{o}C and remain at this temperature for 4-8 hours in a cone bottomed tank to encourage the precipitation of hydrosilicic acid.

Ibrahim (1988 b) reported on a reliable and effecient desilication system to solve silica-related problems in the recovery of heat and chemicals from black liquor from the pulping of nonwood fibers such as reed, bamboo, rice straw and wheat straw. In this system, the black liquor is treated with flue gas without the use of any additional chemicals : it is also possible to recover lime from the resulting lime mud. A new method of treating silica sludge separated from black liquor is also described that reduces chemical losses caused by desilication and makes it possible to recover silica in the form of a white powder suitable for use as a filler in pmkg. ***Kopfmann and Hudeczek (1988)*** described the development, made by them, of a desilication process at RAKTA mill at Alexandria, Egypt, a rice straw and bagasse-based pulp mill. In this process, black liquor is acidified to a pH of 9.7-10.0 in a stream flow reactor by continuously mixing the liquor with power boiler flue gas containing carbon dioxide at a constant pressure drop. After acidification, the black liquor is stirred gently for 45-65 min in the presence of excess carbon dioxide to allow the silica to precipitate. The silica sludge is separated immediatly from the black liquor in a two - step centrifugation process that features a separator followed by a decanter. Incineration of the silica sludge yeilds a high - brightness silica granulate that can be used in pmkg and other processes.

El- Ebiary (1983) reported that Egypt's General Company for paper Industry "RAKTA" established in 1960 , is probably the world's largest rice straw pulp mill, producing 45.000 o.d tpy of bleached straw pulp. Problems of chemical recovery, owing to the high silica and fines content of the black liquor, have been researched in cooperation black liquor, and making better use of the black liquor for its calorific value.

D- Delignification :

Singh (1990) reported some trials for making use of the lignin produced in the pulping process as dye dispersants, adsorbent / desorbents, micronutrients for agricultural application, asphalt emulsions, cement dispersents, polymer application, and oil well field chemicals.

El-Taraboulsi and Nassar (1979) reported on trials to make use of lignin. The soda black liquor was desilicated by precipitation of 90% of its silica content during a one - week storage period. A lignin - carbohydrate product, was precipitaed from the clear liquor by addition of 5% sulphuric acid followed by a mild acid hydrolysis of most of the carbohydrates, giving a lignin product of 86% purity. This product was converted into lignin acetic acid, cyanoethyl lignin, lignin propionic acid and lignin amine. These products were tested as paper sizing agents, drilling fluid additives and flocculating aids. The sizing effect of the different lignin derivatives (from highest to lowest) is : lignin propionic acid, cyanoethyl lignin, lignin acetic acid, unmodified lignin . The sizing effect of lignin propionic acid approaches or exceeds the sizing effect of rosin; however, because of the color it imparts to pulp stock, its use is limited to unbleached pulp. As drilling fluid additives, the lignin derivatives ranked (from best to worst) : lignin amine, lignin acetic acid, cyanoethyl lignin, alkali lignin. As a flocculating aid, lignin amine hydrochloride acted much faster than an alum standard.

Makino (1972) described a process for manufacturing organosilicone synthetic resin from alkali pulp black liquor. Black liquor from straw pulping is concentrated, acid is added to adjust the pH to 8-10 to convert silicates into silicic acid. To the clear black liquor aquous solution of ammonia is added, heating affects condenstation polymerization under conditions sufficiently alkaline to avoid the precipitation of any alkaline lignin salt and to produce organosilicones. The resins and oils thus produced are useful as insulators and heat resistant materials .

Bioconversion of Wastes Into Valuable Substances

Biological processes are commonly used to clean different waste waters. Conventional processes, activated sludge, biofilters, etc., use random mixtures of microorganisms to consume the organic waste material, which is partly converted into biological sludge owing to the undefined nature of this sludge eventual uses of it are limited to low-qualified ones : manure, soil conditioner, etc. For cleaning specific wastes, particularly those containing high concentrations of sugars, e.g whey, spent sulphite liquor , etc. yeasts have been used in more or less pure culture to give feed and food products. The preferred yeasts of species *Candida* and *Saccharomyces* have, however no ability to produce the enzymes needed to utilize starch. In the Symba process as described by ***Skogman (1976),*** this is made possible by the symbiotic culture of two yeasts, *Endomycopsis fibuliger* and *Candida utilis,* on the starch waste.

Endomycopsis produces the amylases which are needed to break down the strach to sugars. *Candida utilis,* being a fast-growing organism steals, the sugar as soon as it is formed, thereby growing and producing a product which consists mainly of *Candida utilis.* The extremely high amylase productivity of *Endomycopsis* strain used limits the need of this yeast to less than 4% by weight in the finished product.

Skogman (1976) concluded that by such symbiotic culture most of the carbohydrates and many other substances as organic acids, proteins, amino acids etc, are utilized in one step, avoiding a costly presteps of hydrolysis, BOD of the waste water is thereby can be reduced by 90%.

Another example of bioconversion of nutrients in wastes into proteins is the production of yeasts from whey. ***Forage and Righelato (1978)*** described several attempts for the bioconversion of whey organic matter into yeast protein. Liquid whey contains 6-8% solids, 80% of which is lactose and 15% protein. The growth of several microorganisms on the waste has been investigated and a number of plants making microbial protein have been built in the United States, Eastern Europe and Australia, ***(Muller, 1969; Martin, 1970 ; Lodder, 1970 and Wasserman, 1958, 1961).*** Fermentation are of two types, either batch e.g the wheat process ***(Powell, et al., 1964)*** or continuous such as those developed by the Societe des Alcools du Vxin , ***SAV (1963) and Naditch, et al., (1960).*** In the first process *kluyveromyces fragilis*,where two strains *Torula cremoris* and *kluyveromyces lactis* are used in the second.

A third example is that described by ***Forage and Righelato (1978)*** for the production of yeast from sulphite waste liquor. About 10^8 m^3 of spent sulphite liquors are produced annually by wood pulping mills. The liquor contains the degreadation products of pentozans, lignin and other non-cellulosic components of wood. It has a carbohydrate content of 2-4%, 1-2% volatile acids and 4-5% lignin sulphonates (***Peppler, et al., 1970)*** With a BOD of 25,000-50,000 mg/L. It can be a serious cause of pollution and in most mills, evaporation and burning or water purification to reduce BOD is required prior to discharge. Because it is produced all year round in large quantities it makes a good substrate for SCP production. In some cases alcoholic fermentation is practised followed by aerobic SCP production on the spent wash. About half the BOD is removed by the growth of yeast so subsequent evaporation or water treatment is still necessary. The orgnism used in almost all SCP plants is *Candida utilis*, which can use a wide range of sugars and organic acids as carbon sources. The process differs substantially from the procedure for continuous production of feed yeast from mollasses only in the preparation of the feed stock. Sulphur dioxide is removed by aeration or by steam-stripping of the liquor at pH 1.5-3.0. The acidity is then adjusted to pH 5-6 prior fermentation . The liquor contains few viable organisms and in many cases no further sterilization is practised.

The dried yeast is not reported to have different nutritional properties from that derived from other carbohydrate sources and ***Naess (1975)*** reports that lignosulphonates which are probably carried over into the yeast have no effect on the feed value. Yeast plants using sulphite waste liquor have been reported to be operating in Switzerland, Germany, USSR, Czechoslovakia, USA and Japan. the total quantity of yeast produced from sulphite liquor is now about 50, 000 tones/annum.

Shiyuan et al (1987) reported on a trial of fermenting pentose-containing spent-sulphite liquor into ethanol . Ethanolic fermentation of spent sulphite liquor with ordinary baker's yeast is incomplete because this yeast cannot ferment the pentose sugars in the liquor. By using the yeast *Candida shehatae* for fermentation, pentoses as well as hexoses were fermented nearly completely, alcohol yields were raised by 33% and sugars removal increased by 46%. This yeast is well suited to industrial operations wherever hexoses and pentoses are both to be fermented to ethanol.

An interesting trial was carried out by ***Hussein et al., (1992)*** for the bioconversion of hemicelluloses of rice hulls black liquor into SCP. Several isolates of fungi and actinomycetes that can consume hemicelluloses of rice hulls black liquor were isolated from 10 soil samples. The highest bioconversion rate of black liquor hemicelluloses into biomass and SCP was achieved by *Aspergillus terreus* followed by *Paecilomyces simplicissia* then *Actinopolyspora* sp.

The RAKTA waste water problem

Public health hazard caused by industrial waste is pollution with toxic materials, these substances include acids, alkalies and specific organic and inorganic metal salts. Danger to health comes not only from direct use of polluted water but also from fish that have lived in the polluted stream since many poisining substances are absorbed by fish. With mild pollution fish may acquire a bad flavour, wherease with more severe contamination the fish get sickened or killed. When pollution develops, fish may leave the polluted areas. Fish and all aquatic animals or plants require the presence of an appreciable concentration of dissolved oxygen. In polluted waters, organic wastes under the influence of bacterial action deplete the dissolved oxygen by consuming it in biochemical oxidation reaction. Discharged into water organic wastes may cause turbidity or colour changes which seriously affect the replenishment of dissolved oxygen by diminishing light penetration into water and retard photosynthesis.

Almost fourty kilometres to the east of Alexandria the biggest, in the middle east, paper pulping and paper milling RAKTA company was established in 1964. The industrial waste water from RAKTA is considered one of the most serious pollution sources in Alexandria. Waste waters from this factory is discharged without any treatment into Abu-kier drain which in its turn discharges into Abu-kier bay .

Ibrahim (1982) informed that the RAKTA paper company in Alexandria, Egypt, Produces ca 50,000 t/yr of bleached rice straw soda pulp from ca 150,000 t/yr of rice straw and 15,000 t/yr of caustic soda. Although ca. 800,000 t/yr of black liquor with a total solids content of ca 9% are generated during the pulping process, the smooth recovery of chemicals (free NaOH and Na salts of organic and inorganic acid) and of heat is rendered impossible by the high silica content.

Unfortunately only two studies ***(Salib, 1986 and Elewah, 1987)*** were carried out on the waste waters of RAKTA. ***Salib (1986)*** divided the waste water of RAKTA into two types :

(a) pulp-mill water wastes of which the most dangerous is the black-liquor resulting from the alkali treatment of rice straw in digestors under pressure together with the first and second wash waters of the resulting pulp. This black liquor is distinguished by high alkali concentration (2494 mg/L NaOH), high lignin content and hemicelluloses. Salib (1986) reported that dissolved oxygen in these waters was zero because of the high organic matter. BOD and COD were 3829 mg/L and 10452 mg/L respectively.

(b) paper-mill waste water and these contain fine fibers, BOD was 873 mg/L and COD was 1128 mg/L.

The stated figures indicate highly polluted waste waters if directly discharged into the sea which is sorrowfully what is practiced. ***Elewah (1987)*** reported that alkaline pulping wastes, mainly that of RAKTA, causes serious bad effects on fish and other aquatic life and on the recreational uses of the Abu-kier bay. Such unresponsible discharge of RAKTA waste waters is against the Egyptian water pollution control low No. 93/1962 which limits COD discharage value to 60 mg/L and BOD to 40 mg/L. As stated before only two studies have been carried on the depollution of RAKTA waste waters. The first study ***(Salib, 1986)*** dealt with the chemical methods of depollution and suggested the following measures:

(1) Plain sedimentation of the final waste waters which could remove 42-57% COD, this process is considered as the first stage of treatment to remove the settleable solids and floating matters.

(2) Coagulation proccess using lime 2g/L which proved to be more effecient and economic than aluminium suflate or ferric chloride. This treatment reduced COD by 54-80% and removed colour by 51-99%.

The second study carried out by ***Elewah (1987)*** suggests the following recommendation for the treatment of RAKTA waste waters before being discharged:

1- Storage of concentrated black liquor which results in a very effective lowering of the BOD and COD. Open lagoones are suggested for this process. In principle ***Elewah (1987)*** agrees by this process with that suggested by ***Salib (1986)*** which he defined as plain sedimentation.

2 - Application of a counter current washing system for the unbleached pulp to decrease the amount of black liquor from 25,000 cubic m/day to 3700 cubic m/day. this enables the increase of the concentration of black liquor from 1% to 7-8%. This could enable economic recovery for heat and chemicals.

3 - Biological treatment of the black liquor using marine micro-organisms to an acceptable BOD discharge level (40 mg/L). ***Elewah (1987)*** was the first to suggest such biological treatment and she reported that her suggested system produces hygenic biomass of high protein content, to pay back a substantial amount of the running costs of the system and she suggests the use of such biomass as fertilizer or at the best as animal feed.

It is clear that ***Elewah (1987)*** was the first to deal with the bioconversion of the organic matter contained in the RAKTA waste waters into biomass and to suggest certain uses for this biomass.

UTILISATION OF BLACK LIQUOR SPENT IN PULP INDUSTRY AS A NATIONAL PROJECT FUNDED BY THE ACADEMY OF SCIENCE AND TECHNOLOGY

In february, 1989 the Academy of science and technology cliamed about its issue about the second five year program of national projects. One of these projects was "The utilization of black liquor spent in pulp industry" . This was the project No. 14 of the projects of industry reserach council.

Several groups of researchers applied for this project and it was decided by the Academy to accept the proposal applied by the research group supervized by ***Prof. Dr. Assem Mahmoud Hussein*** Head of the Botany Department, Benha Faculty of Science, Benha Branch, Zagazig Univeristy

The proposal applied by this group in collaboration with ***Dr. Hassan Ibrahim*** the Head of the directory council of the RAKTA company is summerized in the given block diagram.

According to this scheme black liquor is produced as a result of the NaOH treatment of rice straw. Lots of 200 liter was obtained from the RAKTA company every month.

جمهوريه مصر العربيه
اكاديميه البحث العلمي والتكنولوجيا
المجالس النوعيه
مجلس بحوث الصناعه
برنامج الصناعات الكيماويه
اعلان ١٨/٢/١٩٨٩
مشروع رقم ١٤

استغلال السائل الاسود المتخلف من تصنيع العجائن السليولوزيه

الهدف: الاستفاده من مكونات السائل الاسود مثل الكيماويات واللجنين وغيرهما وتقليل تلوث البيئه بهذه المواد .

المده: ثلاث سنوات من تاريخ التعاقد والتمويل .

اسم المتقدم: أ.د عاصم محمود حسين رئيس قسم النبات كليه علوم بنها
أ.د حسن ابراهيم رئيس مجلس اداره الشركه العامه لصناعه الورق (راكتا)

جهة البحث الرئيسيه: قسم النبات كلية علوم بنها .

جهة البحث المشاركه: الشركه العامه لصناعه الورق - راكتا .

تاريخ التقدم: مارس ١٩٨٩ .

اجمالي التمويل: ٢٥٠ الف جنيه منها ٥٠ ألف عمله حره

شامله مساهمه الشركه العامه لصناعة الورق بمساعدات عينيه مقدارها ٥٠ الف جنيه . كما يساهم قسم النبات بمساعدات عينيه مقدارها ٥٠ الف جنيه .

المتقدمون

الباحث الرئيسي	الباحث الرئيسي المناوب
أ.د عاصم محمود حسين	أ.د حسن ابراهيم
رئيس قسم النبات كليه علوم بنها	رئيس مجلس اداره الشركه العامه لصناعة الورق (راكتا)

أكاديمية البحث العلمي والتكنولوجيا
شعبة بحوث الصناعات الكيماوية

السيد الاستاذ الدكتور / عاصم محمود حسين
رئيس قسم النبات ـ كلية علـــوم بنهـــا

تحية طيبة وبعد ..

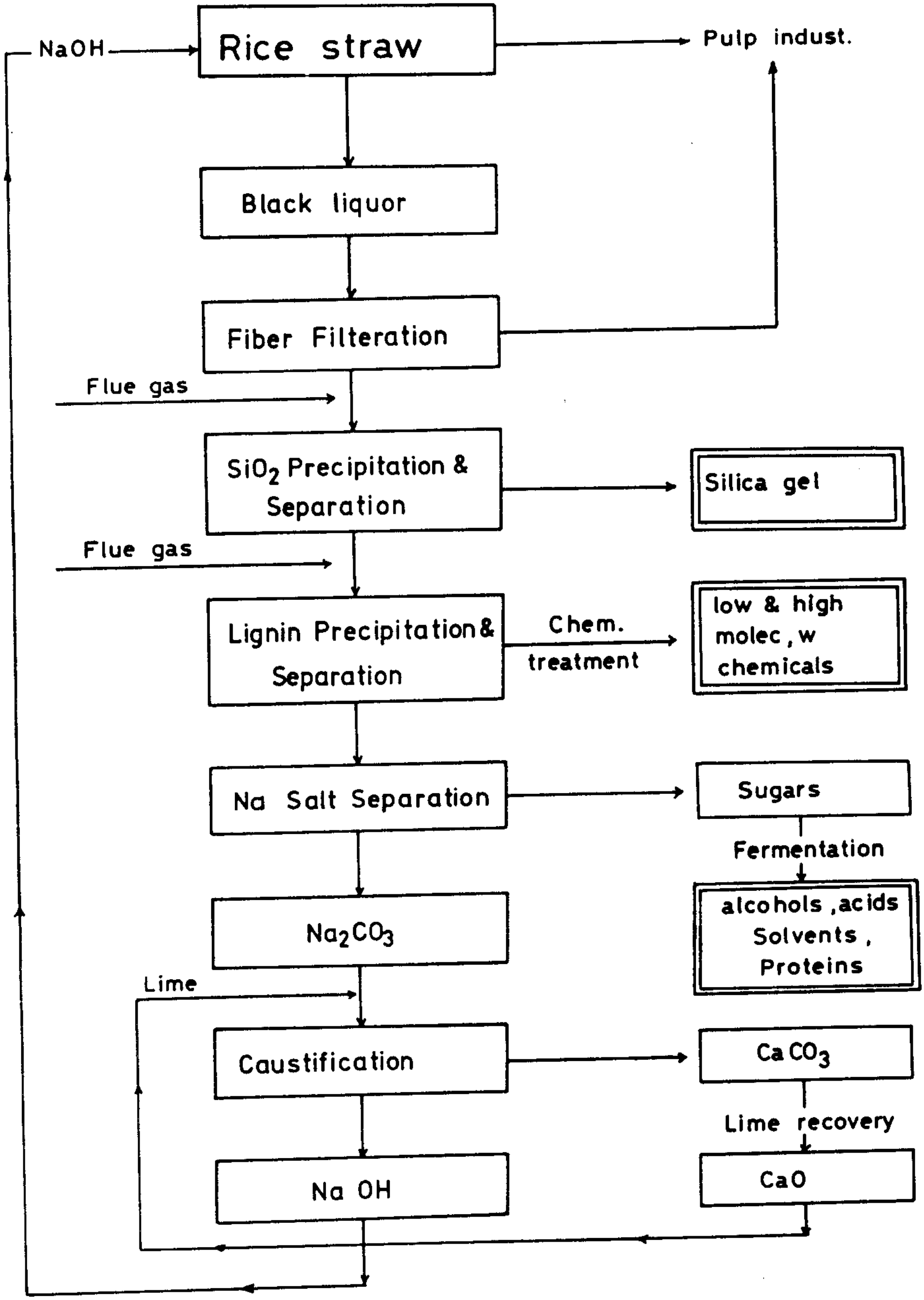
يسرنا افادتكم بان شعبة بحوث الصناعات الكيماويه المنبثقة عن مجلس بحوث الصناعات اعتمدت توصية لجنة الفحص والاختيار لمشروع استغلال السائل الاســـود الناتج من تصنيع العجائن السليلوزيه بالموافقه على العرض المقدم من سيادتكـــم للقيام بتنفيذ المشروع .

برجـــــاء الاحاطه والعلـــــم ...

وتفضلوا بقبول فائق الاحترام ،،

مقرر شعبة بحوث
الصناعات الكيماويـــــة
(دكتور مصطفى عبد المطلب شعبان)

تحريرا فى / ٩ / ١٩٨٩



Block diagram illustrating the work plan.

The work was directed towards achieving the following :

1- Desilication of black liquor
2- Delignification of black liquor
3- Bioconversion of black liquor hemicelluloses into single cell proteins