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DARS- RECOVERY IN A STRAW PULP MILL

Sven Kaas Hansen,
Managing Director
Fredericia Cellulose A/S

Introduction:

In January 1955 Fredericia Cellulose A/S. Denmark, started a production of pulp from wheat and rye straw. Today Fredericia Cellulose A/S has an annual capacity of approximately 50.000 tons fully bleached straw pulp which is used in high quality printing and writing papers.

Increasing environmental restraints on effluents imposed by the authorities forced Fredericia Cellulose A/S to implement an energy and chemicals recovery system. Among the various recovery processes available, the DARS-process was chosen, and an extensive pilot test programme was carried out in 1985 and 1986.

The erection of the DARS-plant was commenced in October 1987 and at this very moment - in the first months of 1989 - the commissioning is taking place.

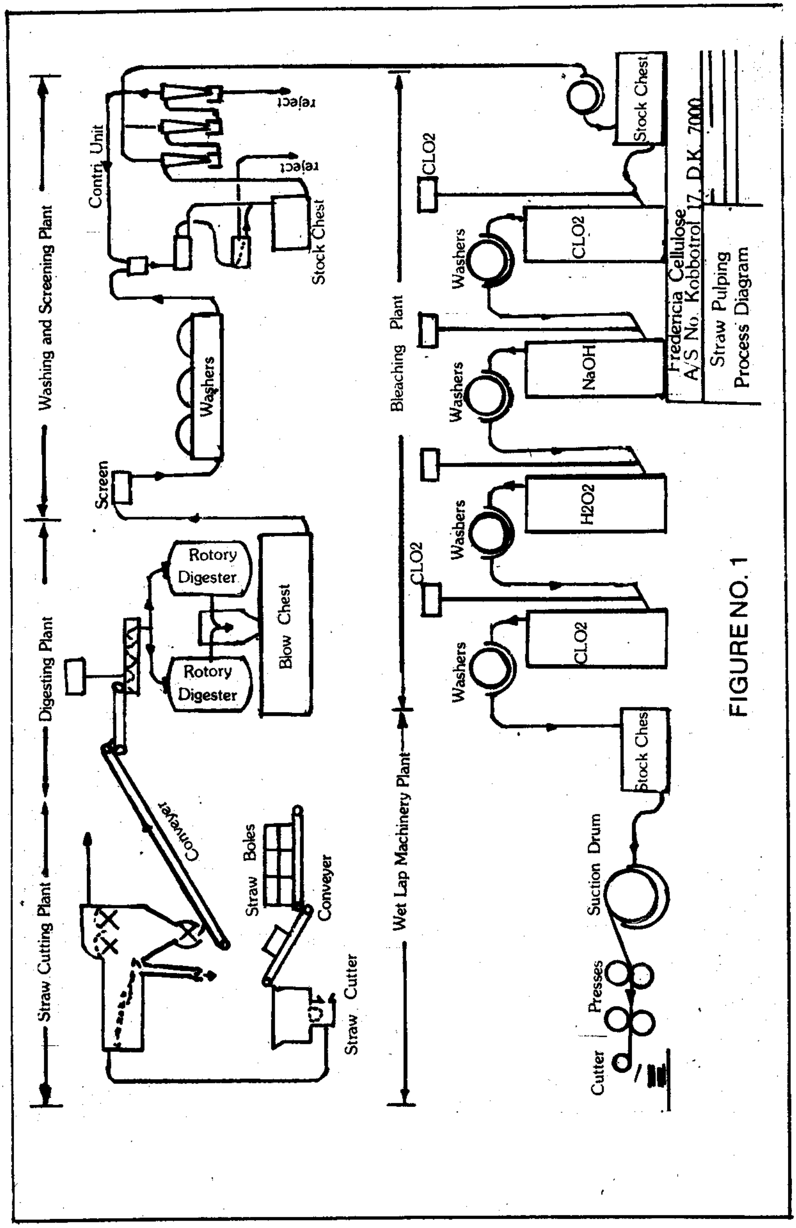
Straw Cutting Plant
Digesting Plant
Washing and Screening Plant
Wet Lap Machinery Plant
Bleaching Plant
Conveyer
Straw Boles
Conveyer
Straw Cutter
Rotory Digester
Rotory Digester
Blow Chest
Screen
Washers
Contri Unit
Stock Chest
reject
reject
CLO2
CLO2
Washers
Washers
Washers
Washers
CLO2
H2O2
NaOH
CLO2
Stock Chest
Stock Ches
Suction Drum
Presses
Cutter
Fredencia Cellulose
A/S No. Kobbotrol 17 D.K. 7000
Straw Pulping
Process Diagram

FIGURE NO. 1

The Pulp Plant:

The production process of Fredericia Cellulose A/S is described in figure No.1

Straw is delivered to the mill every day.

When the straw is weighed and the water content is measured the full straw load is placed on a conveyor belt and transported automatically to a chopper.

This system handles large square bales as well as round bales and small bales.

In an air separator the chaff is cleaned of dust and grains.

The chaff is continuously weighed and sodium hydroxide is added in a screw mixer. Digestion takes place in batch digesters at 165°C in approximately 2.5 hours.

The pulp is washed in a 3-step counter-current washing line with drum filters.

It is screened in a 2-step plant with open flat vibrating screens and finally cleaned in a 3-stage hydro cyclone arrangement.

The pulp is bleached in a DEPD bleaching sequence and a brightness of 86% ISO is achieved.

Effluents:

The effluent from the pulping process is divided into two main streams:

1. Black liquor from brown stock washing contains 85-90 % dissolved organic matters from the process.
2. The bleaching effluent contains the remaining 10-15 % of the organic matters and at the same time the bleaching effluent is characterized by containing chlorinated organic compounds which now give rise to environmental scruples.

We will not go into the bleaching effluent in this paper, but it should not be left unmentioned that in 1985 the bleaching sequence of Fredericia Cellulose was changed from a CDE/HD-sequence to the present DEPD-sequence.

Thus, the content of chlorinated organic compounds in the effluent was reduced by 90 %, and after this time an accumulation of such compounds in mussels put out close by the discharge pipe of the mill has not been detectable.

One of the main problems of pulp production in units as small as the straw pulp mill has been to find economical feasible recovery systems for the black liquor.

DARS SCHEMATIC FLOW DIAGRAM

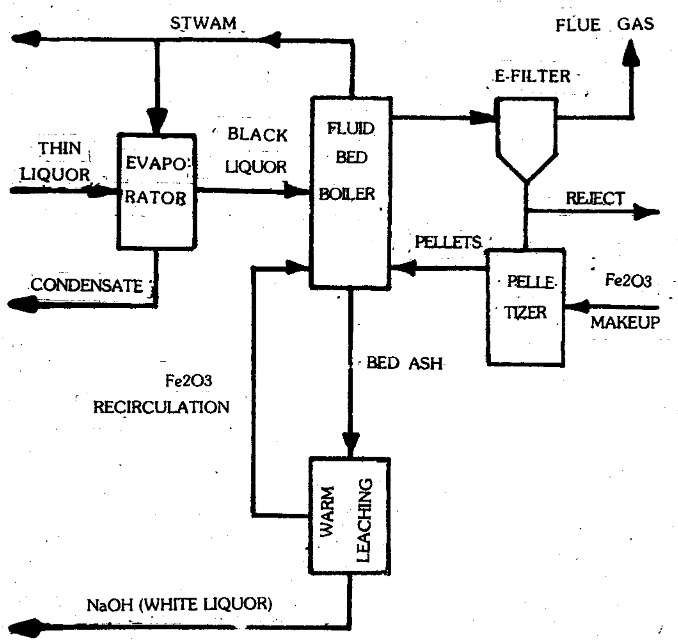

FIGURE NO. 2

Not only on account of pollution has recovery become a necessity. If the production process is to be made competitive, it will also be necessary to regenerate digesting chemicals and energy.

From the very outset in 1955, Fredericia Cellulose A/S has used the monosulphite process, but it became obvious tht if we were to find an economical recovery process, we would first of all have to alter the digestion process and leave out the sulphur compounds.

After quite a number of tests the digestion process was altered into a Soda/AQ process retaining at the same time the high level of quality of the bleached pulp.

Among the different recovery processes we chose as the most interesting process the auto-causticizing system and, after having carried through a large pilot test programme in 1985 and 1986, it was decided to erect a DARS-system.

The erection of the plant was commenced in October 1987 and at the present moment the plant is being commissioned.

The DARS- Process:

The DARS-process for energy and chemicals recovery from soda or soda/AQ spent liquors was invented and patented in 1976 by Toyo Pulp of Japan(1). Later improvements on this process, including combustion of black liquor in a fluidized bed of ferric oxide (hematite) and cold leaching for removal of accumulating non-process elements, were made by the Australian Paper Manufacturers and patented in 1980(2).

The basic chemical reactions in the DARS-process are the same as those in the old Loewing process for manufacture of sodium hydroxide

— $Na_2CO_3 + Fe_2O_3$ ---- $2NaFeO_2 + CO_2$ .... (1)

- $2NaFeO_2 + H_2O$ ---- $2NaOH + Fe_2O_3$ .... (2)

In figure no. 2 a flowsheet of the DARS installation in Fredericia Cellulose is shown.

Black liquor from the soda/AQ pulp, which has been concentrated to 46% D.S. in a 4-effect evaporator, is injected into a fluidized bed of approximately 1 mm ferric oxide particles. The organics combust and the residual sodium carbonate reacts with ferric oxide forming sodium ferrite according to reaction(1).

The flue gases pass through the superheater and the economizer sections and are dedusted in an electric precipitator. The precipitated dust is pelletized with black liquor prior to reinjection into the bed.

The bed product, mainly consisting of a mixture of sodium ferrite, excess ferric oxide, and some unreacted sodium carbonate, is extracted to a second fluidized bed, where it is cooled to 130°C, serving as preheater for the combustion/fluidizing air to the reactor bed.

The sodium ferrite is then hydrolized at 90-100°C in a counter-current column leacher according to reaction(2). Fig. No. 3

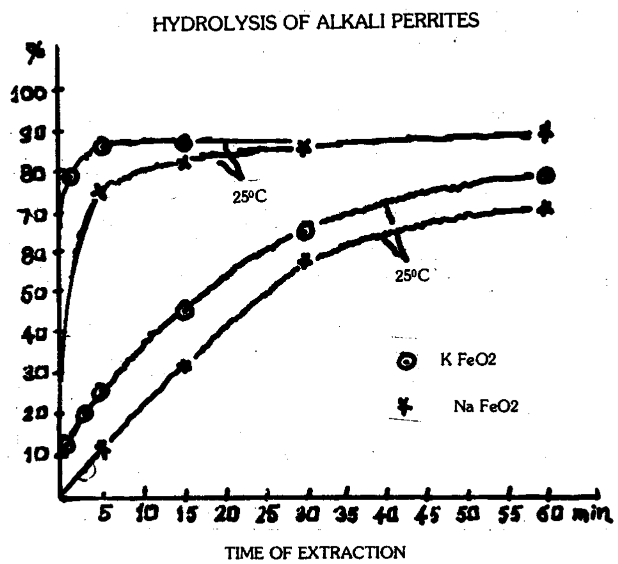

FIG. 3:

The system is capable of producing white liquor of at least 90% causticity and with 120 g NaOH per litre. However, the system is flexible enough to produce higher or lower concentrations, if preferred.

Most of the bed ashes is regenerated to ferric oxide with essentially no change of particle size.

These are extracted from the bottom of the leacher and dewatered to 25% moisture on a vacuum belt before recycling to the reactor bed.

A small proportion of fines is formed during leaching, leaving the column at the top together with the white liquor. The fines are removed in a succeeding polishing filter.

Non-Process Elements (NPE):

Compared to wood, straw has a very high content of inorganics, and this means that the process layout must be designed to handle accumulation of NPE in the black liquor from straw pulping (Table I).

TABLE I

ANALYSIS OF BLACK LIQUOR SOLIDS

C	43.2 %
H	3.94 %
O	34.4 %
N	0.0 %
Na	13.31 %
S	0.42 %
K	3.27 %
Cl	0.61 %
Si	0.85 %
Lower heating value	15.4 MJ/Kg

The most important elements are: Silica, sulphur, chloride and potassium.

During the reaction in the bed, the silica entering the system with black liquor forms soluble as well as insoluble compounds.

As sodium ferrite does not undergo hydrolysis at low temperatures, the soluble salts in the bed ashes can be removed in a cold-wash stage prior to hot leaching.

The accumulation of insoluble silica compounds in the ferric oxide loop is controlled by a continuous purge of the finest dust fraction from the electrofilter. An arrangement has been made with a nearby cement plant for the delivery of fresh make-up ferric oxide in exchange for the purged material.

Silica in black liquor can cause excessive evaporator scalings. The plant is equipped with a 4-effect evaporator extended with a common duplex effect. Thus, any effect can be taken out of operation for cleaning, while maintaining full production. Pilot tests have shown that silica scalings can be effectively removed by a rinsing sequence starting with diluted nitric acid followed by a 50 % NaOH solution.

Sulphur is oxidized during combustion and leaves the reactor with the bed ashes as alkali sulphates. Sulphates are known to cause agglomeration in a fluidized bed. The level of sulphate is controlled by the cold-wash stage, where alkali sulphates are easily dissolved.

The fluidized Bed Boiler.

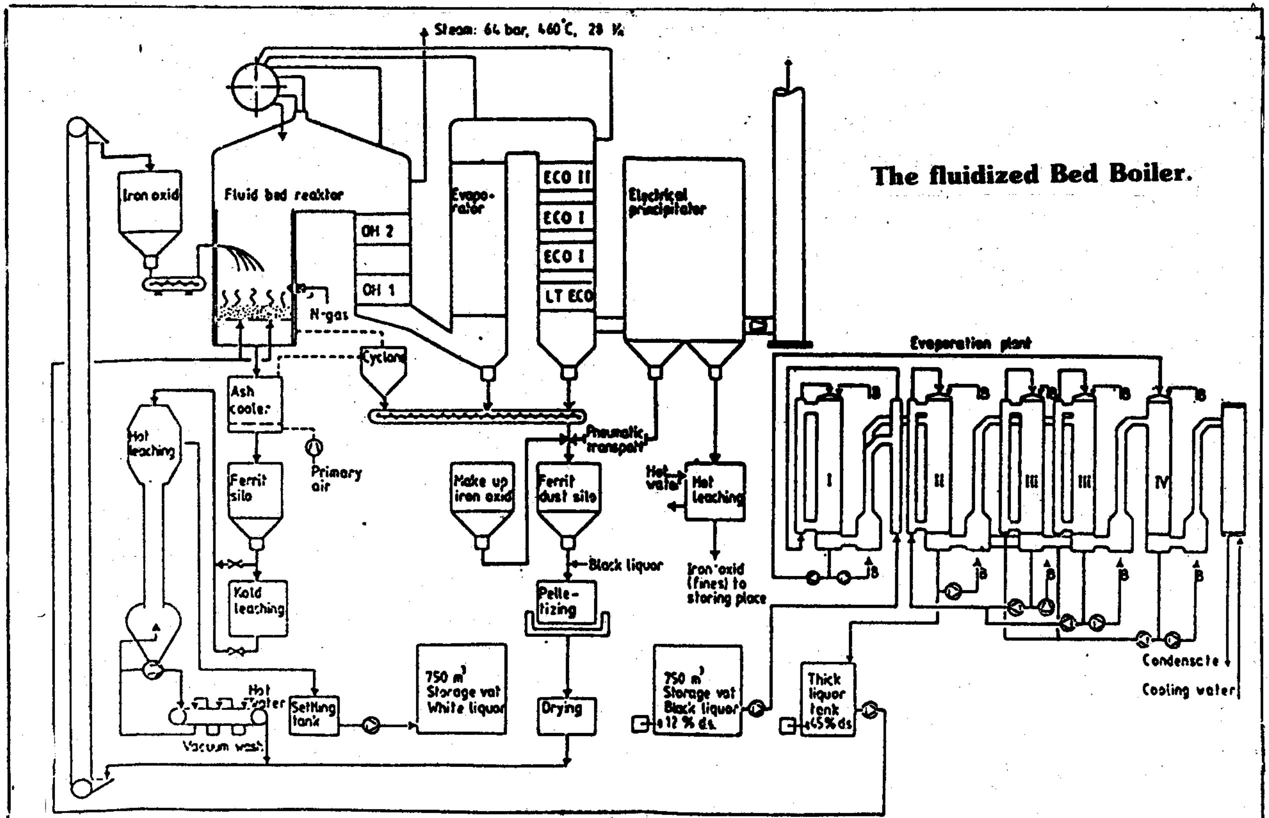

FIG 4.

The same reflections apply to the Alkali chlorides that leave with the bed material. But the main part of chlorides are vapourized at the prevailing bed temperature and leaves the reactor with the flue gases. Upon cooling, the chlorides condense on the surface of the dust particles. In this way the finest dust with the highest specific surface has an increased content of chlorides relative to the coarse dust fractions. In the electrofilter the fine particles are precipitated in the last section of the filter. The solid loop purge is, therefore, most effectively introduced in this place.

Our laboratory experiments have shown that potassium will causticize in the same way as sodium does.

Thus, the content of potassium in black liquor will provide a valuable contribution to the chemicals recovery balance.

The recovery furnace is a natural circulation wall tube boiler, comprising a superheater section, an evaporator section and a high and low pressure economizer section.

Steam at a rate of 28 t/h is produced at 6400 kPa, 460^{0}C, with a flue gas outlet temperature of 120^{0}C.

The fluidized bed has been designed for a residence time of 1.6 h at 100% load. The bed material is extracted from the bottom of the bed through two vertical pipes to the fluidized bed cooler.

Correct bed height is maintained by regulating the extraction rate according to the measured pressure drop across the bed.

The fluidizing/combustion air is preheated by cooling the bed ashes to 130^{0}C and passes two dedusting cyclones before entering the air-box under the reactor bed.

The bed bottom fluidizing air distribution for both reactor and cooler bed is made of grate elements with drilled holes, mounted on water-cooled tubes for the reactor bed and air-cooled tubes for the cooler bed.

Based on experiences from the pilot tests it is essential to assure good distribution of black liquor in the bed. Local reducing conditions and local incorrect ferric/carbonate ratios can lead to unacceptable agglomeration reactions in the bed.

In order to overcome the said problems, the firing system is designed with 28 blak liquor lances and 11 gas lances for heating up, evenly distributed over the bed bottom area and inserted from below through the airbox.

A special pressure air-driven ejector system has been developed to enable replacement of a blocked lance during operation, without risking fall-out of hot bed material.

Designing Capacity.

The DARS-plant in Fredericia Cellulose A/S has the following design data:

Operation Time	: 8.000 h/Yearr
Pulp Production	: 6,25 TADT/h
Fired Strong Liquor 46% DS	: 15 t/h
COD Consumption	: 60.000 t/Year
NaOH Production At 100 %	: 12.000 t/Year
Net Energy Production, Oil Equivalence	: 8.000 t/Year
Combustion Temperature	: 950 ^{0}C

With the present price and currency situation in Denmark, the following economical data can be given:

Recovery of NaOH	4.1 mio. US $
Recovery of Energy	1.2 mio. US $
Operating Costs	+ 0.9 mio. US $
Operating Cost Savings	4.4 mio. US $
Total Investment	21.0 mio US $

Final Remarks

When the energy and chemicals recovery plant has been put into continuous operation, time will show whether our anticipations from the DARS-system are fulfilled, but we expect that the system will prove to be economically and technically feasible for small pulp mills with a production based on annual plants.

Fredericia Cellulose A/S and Burmeister % Wain Energi A/S established a jointly owned company, DarCell A/S, and having acquired a licence agreement with Amcor Limited, DarCell A/S is now able to offer an integrated system comprising pulp mill based on annual plants together with a DARS-sytem.

References:

1. NAGANO et. al. (Dec. 20, 1986) U.S. Patent 4,000,264
2. COVEY, G.H. AND ALGAR, W.H. (Sept. 23, 1980 U.S. Patent 4,224,209