BACELL’S SOLUCELL - A NEW DISSOLVING PULP FOR HIGH QUALITY REQUIREMENTS

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In 1996 BACELL, a joint venture between KLABIN, the biggest producer of pulp and paper in South America and LENZING, a world wide leading rayon company started the production of dissolving pulp. The design capacity is 115000 t/y prehydrolysis dissolving pulp from eucalyptus.

BACELL has implemented the most modern technology in terms of quality and environmental protection, like vapour phase prehydrolysis and TCF (totally chlorine free) - bleaching with ozone. In the meantime an excellent quality for the viscose fiber production could be established with good specification data like high alpha cellulose content and low kappa number.

The SOLUCELL was intensively tested for its behaviour in the viscose process and showed very positive results in the laboratory, the pilot plant and the mills: the reactivity was high, especially when some surfactant was added, the brightness stable and the fiber properties on a high level.

In 2.1 Cooking

The sulfite process predominates world wide the production of dissolving pulp. Acid sulfite process is mainly used in single stage cooking because of its rapid hydrolysis of hemicellulose and beta-cellulose as well as its good delignification rate.

The first prehydrolysis kraft dissolving pulp mill started production in 1945, processing wood into cord fibres for tires. In 1992 the production of prehydrolysis kraft pulp was 1,1 million tons world wide, of which 40 - 45 percent was based on hardwood. Sulfite technologies are restricted to certain wood species, mainly hardwoods. Prehydrolysis kraft can also use softwood and wood species rich in resins.

In the case of BACELL, the choice of the prehydrolysis kraft process was given by the already existing recovery boiler.

2.1.1 Vapour phase prehydrolysis

Kraft pulps require a lower hemicellulose content to have the same reactivity as sulfite pulps. This is achieved by an acid pre-treatment at high temperature where the hemicellulose is split into oligomer carbohydrates and can be dissolved. So far this prehydrolysis was mostly carried out in an aqueous phase, which was a major disadvantage of the kraft process as it includes the handling and disposal of the prehydrolysate which requires high amounts of energy and evaporation capacity. Scaling and clogging in tubes and valves are frequently caused by resins and the reaction products of hemicellulose and sugar. In some few cases it was even used as source for pentosanes.

A vapour phase prehydrolysis, as it is already exceptionally used in some mills in Brazil and Eastern Europe, should prevent these problems. IVA had optimized the procedure for steam heating of the chips, by providing a uniform injection and distribution of the steam in the digester. This uniformity in combination with a neutralization with hot black and white liquor and followed by a hot displacement leads to the same results as water prehydrolysis, avoiding its high energy consumption, increased evaporation capacity and pollution.

This process enables Bacell to reach a remarkable low pentosane content, quasi tailor made for each client, without the disadvantageous treatment of the hydrolysate.
2.1.2 Process Description (Fig. 1 and 2)

Prehydrolysis and cooking are accomplished periodically in three batch digesters, equipped with a steaming and a liquor circulation system. High pressure tanks for hot white liquor, neutralization liquor, hot and warm black liquor are the basis of the modern Enerbatch technology.

- Chip filling is accomplished by means of low pressure steam in a Svensson chip filling system, which assures a high chip packing degree in the digester.
- For steam heating and prehydrolysis, the digester is heated up with medium pressure steam; hydrolysis of hemicellulose is achieved by organic acids, mainly acetic acid, which are formed during the process and after 40 minutes the major part of the pentosanes are hydrolyzed and dissolved.
- During neutralization and hot displacement the pressurized digester is filled with caustic liquor, consisting of hot black and hot white liquor. This neutralizes the organic acids formed during prehydrolysis and adds the alkali charge required for cooking. Part of the neutralization liquor is displaced to the neutralization liquor tank during the hot displacement.
- The digester is kept at cooking temperature until the desired degree of delignification is reached.
- Cooking is completed by displacing hot cooking liquor with washing filtrate from the washers. In this way the pulp in the digester is cooled down below 100°C and pumped into the blow tank. This cooling is essential to stop degradation reactions suddenly at a certain point.
- The white liquor is heated up by the spent liquor from the previous cook, maintaining the heat energy in the system. With this modern types of displacement cooking, the steam consumption can be reduced to around 40% of the conventional ones.

2.2 Bleaching (Fig. 3)

From the very beginning of the project, there were no doubts, that a new pulp mill must have a TCF-bleaching sequence. On the one hand to gain the advantages on the market, on the other hand to ensure that also the future environmental regulations will be fulfilled.

The only realistic alternative, producing ECF-pulp by using chlorine dioxide instead of ozone, requires more or less the same operating, but higher investment costs.

After an intensive evaluation, the bleaching sequence 00-A-ZQ-P was established, using only oxygen based chemicals as oxygen (O), ozone (Z) and hydrogen peroxide (P) besides sulfuric acid (A) and EDTA (Q) for metal removal.

### Bleaching Conditions

<table>
<thead>
<tr>
<th>O</th>
<th>A</th>
<th>Z</th>
<th>Q</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>185</td>
<td>130</td>
<td>60</td>
<td>55</td>
</tr>
<tr>
<td>Consumption (%)</td>
<td>14</td>
<td>19</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>pH</td>
<td>11</td>
<td>6.5</td>
<td>2.2</td>
<td>2.2</td>
</tr>
</tbody>
</table>

**Bleaching Sequence:**

- **0:** Oxygen delignification
- **A:** Addition of sulfuric acid
- **Z:** Ozone bleaching
- **Q:** EDTA addition
- **P:** Hydrogen peroxide bleaching

#### 2.2.1 Development

LENZING has installed its ozone bleach plant in 1992, being the first installation worldwide at that time. Based on the excellent experience concerning pulp quality and operations with sulfite pulp, our aim was to transfer this technology to prehydrolysis kraft pulp.

The basic work was done in LENZING's research department, in cooperation with KVAERNER Pulping and RIOCELL.

#### 2.2.2 Process description

- Facing the very low lignin content of high quality dissolving pulp, it is evident that the oxygen delignification stage has to be extremely efficient. Therefore a two stage version without intermediate washing was chosen. The benefit of an intermediate washing was not big enough to justify an additional installation. The conditions in this reaction are rather drastic with temperatures up to 125°C, an oxygen pressure of 0.7 MPa and an alkali charge of approximately 25 kg/bdmt. So we can gain a delignification rate of more than 70% at a reasonable viscosity loss of around 25%. It is well established that trace levels of transition metals have a profound negative impact on ozone and peroxide bleaching as well as on the rayon process. The presence of transition metals, particularly Co, Fe, Mn and Cu ions result in both, excessive ozone and hydrogen peroxide consumption by self decay and in degradation of carbohydrates, apparently caused by free radical reactions. To use ozone and hydrogen peroxide effectively in the subsequent bleaching stages, transition metals must be removed or at least deactivated.

A major part of our eucalyptus is growing on the typical red, iron containing soil you can find in Bahia. So the logs have a relatively high content on iron and the risk to contaminate the process and the pulp was imminent.

A very efficient log washing at the wood yard diminishes the entry of soil to the system substantially. Decide then, there was implemented a separator, open washing stage between O and Z, where the pulp is treated with sulfuric acid at a pH around 2.5.
The ozone stage was also designed as a ZO-stage, where the ozone reaction is followed by a chelation with EDTA.

- The final bleaching of BACELL corresponds to the concept realized in Lenzing, as the basic engineering was done by LENZING TECHNIK.

- Ozone is very effective in reducing the lignin content to very low levels, which is an essential issue for dissolving pulps.

- The ozone bleaching is carried out as a Medium Consistency stage with two MC-mixers. Oxygen as basic material for ozone is produced on site in a PSA-plant, the off gas of the ozone bleaching is used for the delignification and white liquor oxidation.

- The final stage is an alkaline peroxide stage to adjust the brightness target. The reaction conditions of this peroxide stage can be rather moderate because of the high incoming brightness and the excellent activation by the preceding ozone stage. For that reason the viscosity loss can be kept rather low.

2.3 Drying Machine

The existing drying machine was modernized, using many parts of the existing drying section.

The wet end of the machine was completely rebuilt. The TETRAFORMER is a new development, combining the sheet formation properties of a Fourdrinier machine with the low energy consumption of a double wire press. After some trials on the Bolton pilot plant of BELOIT, this prototype was installed at BACELL for the first time.

3. Operations

The mill started operations in January 1996 and in March the first lot of prime grade dissolving pulp left the production line. Already after a short period, the quality for viscose fiber grade pulp could be stabilized on a high level and the feedback of our customers is a very positive one.

In the meantime there were made several tests to establish special grades for filaments, acetate and others in tight cooperation with clients.

The actual capacity of the mill was at the end of the year 1996 slightly below the design capacity, mainly due to restrictions in the recovery area.

- Cooking: the cooking plant was operating very reliably from the beginning. To our big surprise we reached very soon a kappa number of 5, although with low viscosity but without problems in the digester circulation as well as during washing and bleaching. Anyway to my knowledge, this should be one of the lowest kappa numbers ever reached from an industrial scale kraft digester.

But there are still two major limitations from the cooking process. On the one hand, the consumption of effective alkali is around 15% higher than predicted. This means an important restriction in production capacity, which was lifted this month by increasing caustizing capacity. On the other hand the viscosity on a given kappa number is slightly lower than expected from the lab tests. Lower viscosity losses in the bleaching process and a higher ageing resistance of our pulp can compensate this effect but anyway, we are still working on an improvement. The big question mark, the vapour phase prehydrolysis, proved to work very well, which allows us to adjust the pentosane content in a wide range.

- Fiber Line: The fiber line is keeping its promises concerning quality and chemical consumption. Especially the oxygen delignification is reaching the remarkable lignin reduction of more than 72%. It can also to a big extent smoothen the variation in kappa number and viscosity.

The ozone stage is also fulfilling the expectations in terms of delignification, brightening and activation for the following peroxide bleaching. Only the viscosity control in a wide range via ozone dosage is not working as well as predicted. In this point we will make some further improvements together with the supplier by increasing gas mixing efficiency.

Concerning transition metal removal the mill is exceeding the design values, so we can easily obtain a low metal content. The final peroxide bleaching is gaining more than 10% of brightness due to the previous activation.

After some problems in the start up phase and some minor modifications, the drying machine with the tetraformer is now operating very well and has proved to be a good solution for a low energy dewatering system.

We have also installed a rewinder, so we are selling our product in form of bales as well as reels.

4. Pulp Quality

In the first year of operation we could very well establish a good quality pulp for the viscose fiber market. Besides that Bacell is also developing dissolving pulp qualities for other branches like acetate, filament, nitrocellulose and others together with clients.

The normal range of our quality is:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brightness:</td>
<td>88 - 90.5 % ISO</td>
</tr>
<tr>
<td>Viscosity:</td>
<td>400 - 650 ml/g</td>
</tr>
<tr>
<td>Alpha cellulose content:</td>
<td>&gt; 94.5%</td>
</tr>
<tr>
<td>R 18:</td>
<td>&gt; 96.5%</td>
</tr>
<tr>
<td>R 10:</td>
<td>&gt; 92.0%</td>
</tr>
<tr>
<td>Kappa number:</td>
<td>&lt; 0.5</td>
</tr>
<tr>
<td>Extractives (DCM):</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Ash:</td>
<td>&lt; 0.12% including sodium oxide</td>
</tr>
<tr>
<td>Metals:</td>
<td></td>
</tr>
<tr>
<td>Fe:</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>Ca:</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>SiO₂:</td>
<td>&lt; 80 ppm</td>
</tr>
<tr>
<td>Mn:</td>
<td>&lt; 0.5 ppm</td>
</tr>
<tr>
<td>Mg:</td>
<td>&lt; 80 ppm</td>
</tr>
<tr>
<td>Cu:</td>
<td>&lt; 1.5 ppm</td>
</tr>
<tr>
<td>Na:</td>
<td>&lt; 300 ppm</td>
</tr>
<tr>
<td>Dirt:</td>
<td>&lt; 5 mm²/m²</td>
</tr>
</tbody>
</table>

But we are always open to discuss variations of specific parameters within the bounds of our possibilities:

- It is evident that the brightness ceilings are lower for a TCF pulp than for a chlorine dioxide bleached one. But investigations could prove that the preservation of brightness during the whole viscose process is the highest for Bacell pulp compared to all others tested. Probably this is due to the very low content of carboxylic and reducing end groups in our pulp.

- In comparison with our competitors the viscosity of our pulp is on a lower level. Higher resistance in the ageing stage is compensating this property. Anyway we are working on an improvement of our cooking process to reach a higher viscosity range.
As already mentioned above, the vapour phase prehydrolysis is very efficient, so an increase in alpha cellulose content up to 96% or even more is possible and necessary for acetate grades. R 18 and R 10 are following the same correlation.

The low lignin content, expressed by the kappa number is a benefit of the ozone bleaching technology with its good delignifying properties.

The extractive content of our pulp is extremely low and so far we have not observed in our production line any scaling or deposits caused by pitch. This low level of natural resin makes the addition of a surfactant, for example Berol Visco 388, very efficient in terms of reactivity in the viscose production.

The acid as well as the chelating treatment of the pulp is reducing the metal content substantially, therefore lower values can be achieved also.

The molecular weight distribution of the Solucell is exceptionally narrow with a low portion on short chains, which should give a remarkable advantage concerning fiber quality (Fig. 4).

The fiber length distribution is typical for an eucalyptus pulp and very similar to acid sulfite eucalyptus cellulose (Fig. 5).

Ageing Properties: A comparison with a market pulp of a similar quality (hardwood prehydrolysis kraft with cold caustic extraction = HPKC) showed interesting results. Without using a catalyst the kinetics of both pulps were nearly the same (Fig. 6).

To our surprise the addition of a catalyst (25ppm Mn as KMnO4) changed this relation. Bacell's Solucell proved to be more resistant to catalyzed depolymerization compared to other marked pulps. This behaviour is even more pronounced at higher temperatures (Fig. 7a and 7b).

Viscose Quality: Our pulp gave a good viscose with low turbidity. But there was a very significant further improvement by the addition of surface active chemicals, probably due to the low content of extractives. By dosing 0.07% of Berol Visco 388 the particle concentration could be reduced by 80% (Fig. 8).

5. Experience with SOLUCELL in the rayon process

5.1 Laboratory investigations

At first the Bacell pulp was tested on the so called „Treiber”-Viscose Plant at Lenzing by Dr. H. Sixta to receive basic data for ageing behavior and viscose quality.
5.2 Pilot Plant Tests

- Viscose Quality: Viscose of Bacell pulp showed outstanding filterability properties before and after filtration. Also the particle concentration was the lowest in comparison with other commercial pulp samples (Fig. 9). As a further advantage the content of small, non filterable particles is extremely low; the maximum is shifted towards higher particle diameters.

- Fiber Properties: The strength properties of these fibers were comparable to those made from other market prehydrolysis kraft pulps but clearly better than of fibers produced from sulfite pulps. Remarkable is the preservation of the brightness over the whole production process, which was the highest for Bacell pulp in comparison to all other pulps investigated (Fig. 10).

6. Summary

- BACELL came on stream with a new dissolving pulp mill during 1996 with a prehydrolysis kraft pulp made from eucalyptus, which is already well established for the viscose fiber production.

- The introduction of most modern technologies in cooking and bleaching was successful. BACELL is producing the first and only prehydrolysis kraft dissolving pulp with a TCF-bleaching sequence.

- The results obtained in the first year of operation could, with some small exceptions, prove the design values.

- The quality of the pulp is an excellent one with low amounts of impurities like hemicellulose or ash, good reactivity in the rayon process, low metal concentration, low kappa number and a good and stable brightness.

- Both, the fiber length and the molecular weight distribution are narrow, which results in an advantage for viscose fiber properties.

- Viscose and viscose fibers made out of BACELL pulp in Lenzing’s laboratory and pilot plant showed excellent quality data.

- The feed back from our clients which are using our pulp already some months is very positive.