Desilication of agro based black liquor and green liquor using jet loop reactor

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Non-wood fibers represent the largest resource of fibrous materials for many developing countries in the world. Attention is now being focused on cellulose bearing agricultural residues, which can be used as raw materials for production of paper. Though chemical pulping of these raw materials poses no problem, major difficulty arises in the recovery of heat and chemicals from the spent cooking chemical (black liquor). The presence of silica in black liquor obtained from agro based pulp and paper mill causes serious problems at filtration, washing, evaporation, burning, recausticizing and clarification levels of chemical recovery. It is, therefore, necessary to remove silica before the black liquor is concentrated to high solid content. The success of the desilication process by carbonation lies in accurate \( pH \) control otherwise lignin co-precipitation occurs during desilication. In the present work, a high mass transfer efficient, compact Jet Loop Reactors (JLR) or some times called as Highly Compact Reactor (HCR) is used for desilication to obtain exact \( pH \) control. The experiments were carried out in a 15 L reactor at room temperature as well as at higher temperatures. The results obtained in JLR are compared with those obtained by Bubble Column Reactor (BCR). Desilication of green liquor in both the reactors at different temperatures is also studied. The results show that desilication in JLR is more efficient at higher temperatures.

**Keywords**: Black liquor, Green liquor, Desilication, Delignification, JLR, BCR, Carbonation

**IPC Code(s)**: D21C

Black liquor (BL), obtained from paper production units/mills using agricultural residues, contains additional silica, which causes serious problems at filtration, washing, evaporation, burning, recausticizing and clarification levels of chemical recovery. Partial desilication is achieved by raw material cleaning. To make paper industry economical, recovery of spent chemicals from black liquor (BL) is essential. Major difficulty in pulping of non-woody fiber is the recovery of heat and chemicals from the cooking liquor, which contains silica. Straw dedusting, though a simple way of silica reduction, is not efficient. Depithing of bagasse reduces silica in bagasse. Washing of bamboo chips\(^1\) eliminates silica (50%). Wheat straw pretreatment, used in the Italian Foggia straw pulp mill\(^2\), yields BL (80—90%) with a reduction of silica (50%). Green liquor (GL) desilication was also in operation in the Italian Foggia mill\(^2\). Central Pulp and Paper Research Institute (CPPRI), Saharanpur (India) tested\(^3\) straw cleaning in pilot plant scale using a disc mill and achieved 50% removal of silica. Partial desilication of BL is achieved by storing (ageing)\(^4\) at elevated temperature, where silica together with some lignin precipitates. After storage (9 h) of alkaline sulphate BL at 80°C, \( \text{SiO}_2 \) concentration decreased from 4-4.65 to 0.63—0.93 g/L in the clean liquor. Mishra\(^5\) reported desilication of BL by carbonation; partial carbonation followed by lime treatment at 90°C. Froundjian\(^6\) studied desilication of weak BL by acid treatment. This process was also investigated by West Coast Paper Mills in India\(^7\).

Kraftanlagen in Heidelberg & Munich (Germany) worked in late 1970's on a BL desilication process\(^8\). A desilication process was developed by the China Paper Industry Research Institute which was tested in a 15 m\(^3\)/h weak BL pilot plant\(^9\). The weak BL containing silica (6—8 g/L) was treated by flue gas in a Venturi nozzle and \( pH \) lowered to 10.3. CPPRI technology developed in co-operation with UNIDO and SIDA has reached to an operating level within reasonable limits\(^10\). The main problem with this concept is co-precipitation of lignin, resulting in difficulties to separate the precipitate from the liquor and a reduction of BL calorific value. CONOX\(^13\) developed novel plug flow reactor and reported 90% desilication.
Desilication experiments were also carried out in Jet Loop Reactors (JLR), the efficiency of which has already been established in chemical processes\(^{14,15}\). The jet of liquid from the nozzle produces high mixing and turbulence that ensures optimal mass transfer. Vogelpohl & Wachsmann\(^{15}\) achieved a loading rate of 25 kg BOD/m\(^3\)/d with a pilot plant HCR treating brewery wastewater and 44 kg BOD/m\(^3\)/d with a similar plant treating chemical wastewater. Bloor \(^{16}\) achieved an organic loading rate of 50 kg COD/m\(^3\)/d with 97% COD removal of brewery wastewater. Some more studies concerning the hydrodynamics of JLR have also been reported\(^{17-21}\).

Desilication of BL is a mass transfer operation with chemical reaction associated. In earlier attempt the authors have studied the desilication of BL using bubble column reactor\(^{22}\). Attempts were also made to study the filtration characteristics of carbonated BL\(^{23}\) and modeling of desilication of green liquor\(^{24}\) and black liquor\(^{25}\) using ANN. Here, it was decided to conduct desilication of BL in high mass transfer efficient gas-liquid contacting equipment. Taking into consideration higher residence time, lower interfacial area and poor dispersion of gas in bubble column the attention was focused towards the newly developed highly energy and mass transfer efficient JLR. In present work, desilication of BL by carbonation was carried out in a Jet Loop Reactor (JLR) to study the desilication as a function of pH, time of carbonation and temperature.

**Experimental Procedure**

**Bubble column reactor (BCR)**\(^{14}\)

A bubble column, as reported earlier\(^{22,24}\), with a flat base having height 800 mm and diameter 90 mm was fabricated using acrylic tube. Provision to pass carbon dioxide as very fine bubbles was made through a perforated rubber mat. The column was filled with BL up to the measured volume and carbon dioxide from a high-pressure gas cylinder was bubbled through a perforated rubber mat fitted at the bottom of the column. Data was generated for pH, silica, lignin and residual active alkali (RAA) content with respect to time.

**Jet loop reactor (JLR)**

The reactor (height 1000 mm and diameter 140 mm) was made of hollow cylindrical acrylic tube of making a volume of 15 L. A central coaxial draft tube (height 750 mm and diameter 55 mm) was placed inside the column for circulation of gas liquid mixture within the reactor (Fig. 1). A two fluid nozzle was fitted at the top of the column for admitting the BL into the reactor. When the liquid forces through the nozzle, it sucks in the gas, (carbon dioxide) through the fine metal tube fitted inside the nozzle. Primary dispersion of the gas and the liquid occurs as the mixture enters the draft tube. The mixture is forced downward due to the inertia and as it reaches the bottom of the column it is deflected back through the annular space between the draft tube and the column. Due to the difference in velocity of the downgoing fluid inside the draft tube and the upcoming fluid in the annular space, secondary dispersion takes place at the top of the reactor and part of the gas-liquid mixture is sucked back into the draft tube from the annular space there by creating the first loop in the reactor. From the bottom of the reactor a portion of the liquid is withdrawn and pumped into the top of the reactor through the two fluid nozzle which forms the second loop.

Fresh BL was mixed with the recirculation BL and pumped through the two fluid nozzle at the top. Provision to withdraw carbonated BL was made at the top of the column. The complete experimental setup is shown in Fig. 2. The hydraulic residence time inside the reactor was maintained by properly adjusting rate of inflow of fresh BL and rate of outflow of carbonated BL under steady state condition.

**Results and Discussion**

**Desilication of BL**

The desilication was carried out in BCR as well as in JLR. Figure 3 gives a comparison between the percentage silica removal in the JLR and BCR as a function of time under otherwise similar conditions at room temperature. The percentage silica removal is around 80% for the JLR. The figure also shows that under the given condition the BCR takes 30% higher retention time for the same degree of desilication as in JLR. The experiments were carried out at 40°C. Figure 3 shows that even at 40°C the JLR is more efficient than BCR under otherwise identical conditions. It is clear from the figure that % silica removal increases with retention time and is favoured by increase in temperature.

It is well understood that lignin in BL also precipitates as pH is lowered. In BL, phenolic
hydroxyl group of lignin are present in the form of -O-Na group. These charged colloidal lignin particles are stable at p\(\text{H}\) greater than 7. As \(\text{CO}_2\) is passed the \(\text{pH}\) of the solution reduces and -O-Na bond breaks; therefore lignin precipitates and sodium goes into the solution. After sufficient treatment with \(\text{CO}_2\) almost all of the sodium compounds are converted to \(\text{Na}_2\text{CO}_3\) and lignin settles in fragmented form. The co-precipitation of lignin with silica is studied. The objective of the work is to have selective silica precipitation at minimum lignin co precipitation. Figure 4 shows the comparison between the % lignin removal as function of time in BCR and JLR. The % lignin precipitation is around 20–25% in JLR which further reduces at higher temperature. JLR shows higher efficiency than the BCR in desilication as well as in delignification. It is clear from the results that at higher temperature in JLR the 80–85% silica removal is achieved at the cost of 20% lignin.
Desilication of agro based liquors using jet loop reactor

Desilication of green liquor

The operation and control of carbonation of GL is easier because of absence of co-precipitation of lignin. Silica is present in the GL in the form of Na$_2$SiO$_3$. Carbonation precipitates the silica from the solution. The operation efficiency was tested in BCR and JLR under identical conditions. Figure 5 shows similar trends for GL as are obtained for black liquor.

Again the effect of temperature on percentage silica removal in both the reactors at room temperature and 40°C show identical results as are shown for black liquor.

The data obtained for desilication of BL using JLR (current study) and other previous attempts is given in Table 1. Various Mass transfer equipments like packed bed, submerge bubble reactor, ventury scrubber, plug flow reactor, ventury absorber, bubble column reactor were tried. From the Table it can be concluded that the desilication using JLR at higher temperature is more efficient as compared to many previously tried methods.

Silica is being manufactured for the last two years from rice husk ash by M/s Karthik Chemicals, at their plant located at Gummudipundi, Nellore District, Andhra Pradesh (India) using the technology transfer from ISRO (capacity 1 tonne per day). The silica thus produced and the commercially available silica were compared and found to be at par. The silica was utilized in tyres, paddy dehusking rollers, conveyer belts, shoe soles. The properties of the above product with silica from rice husk were found to be improved than with silica obtained from market. The silica thus precipitated from BL with rice husk as raw material could also be utilized in the same way.

Conclusion

An attempt was made to remove silica from Kraft BL obtained from straw based pulping material by carbonation technique. Batch and continuous experiments were carried out in bubble column reactor and energy efficient and high mass transfer JLR. The results indicate that the technique can be applied to mills having no chemical recovery facility...
Table 1 — A comparison of various attempts for desilication of black liquor

<table>
<thead>
<tr>
<th>Type</th>
<th>Method</th>
<th>Retention time, min</th>
<th>( pH )</th>
<th>RAA as ( \text{Na}_2\text{O} ), g/L</th>
<th>Silica g/L</th>
<th>Silica removal %</th>
<th>Lignin g/L</th>
<th>Lignin removal%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
<td>Final</td>
<td>Initial</td>
</tr>
<tr>
<td>Pack bed at 30°C</td>
<td>Carbonation</td>
<td>75</td>
<td>12.3</td>
<td>10.3</td>
<td>7.2</td>
<td>5</td>
<td>1.4</td>
<td>72</td>
</tr>
<tr>
<td>Pack bed at 30°C</td>
<td>Carbonation + acid treatment</td>
<td>NR</td>
<td>12.4</td>
<td>10.3</td>
<td>6.4</td>
<td>-</td>
<td>5.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Single stage SBR at 30°C</td>
<td>Carbonation</td>
<td>78</td>
<td>12.1</td>
<td>10.4</td>
<td>6.0</td>
<td>1.4</td>
<td>76</td>
<td>NR</td>
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<tr>
<td>Two stage SBR at 30°C</td>
<td>Carbonation</td>
<td>24</td>
<td>12.6</td>
<td>10.7</td>
<td>NR</td>
<td>7.5</td>
<td>2.2</td>
<td>71</td>
</tr>
<tr>
<td>Ventury scrubber at 90°C</td>
<td>Carbonation + lime</td>
<td>Batch</td>
<td>11.5</td>
<td>9.8</td>
<td>NR</td>
<td>NR</td>
<td>NR</td>
<td>75% in carbonation 17-19% in lime treatment 60-90%</td>
</tr>
<tr>
<td>Plug flow with CO₂ injected at 93°C</td>
<td>Carbonation</td>
<td>NR</td>
<td>11.1-11.8</td>
<td>10.3</td>
<td>NR</td>
<td>6-8</td>
<td>1-2.3</td>
<td>83-85%</td>
</tr>
<tr>
<td>Ventury absorber</td>
<td>Carbonation</td>
<td>10-12</td>
<td>12.5</td>
<td>10</td>
<td>2.1</td>
<td>0.3</td>
<td>3.5</td>
<td>0.87</td>
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<tr>
<td>Bubble column reactor at 25°C</td>
<td>Carbonation</td>
<td>8-9</td>
<td>12.0</td>
<td>10.5</td>
<td>1.5</td>
<td>0.7</td>
<td>3.4</td>
<td>0.85</td>
</tr>
<tr>
<td>Bubble column reactor at 40°C</td>
<td>Carbonation</td>
<td>7</td>
<td>12.5</td>
<td>10.4</td>
<td>3.4</td>
<td>0.3</td>
<td>3.2</td>
<td>0.73</td>
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<tr>
<td>Jet Loop Reactor at 25°C</td>
<td>Carbonation</td>
<td>5</td>
<td>12.5</td>
<td>10.4</td>
<td>2.1</td>
<td>0.4</td>
<td>2.8</td>
<td>0.64</td>
</tr>
</tbody>
</table>

NR – Not reported

where precipitation of both lignin as well as silica is possible. Selective precipitation of silica can be carried out for high capacity mills and silica so precipitated can have good byproduct value.

References