Bioenergy Generation from Pulp and Paper Mill Waste through High Rate Biomethanation

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(Paper presented in IPPTA Zonal Seminar held at Bhubaneswar, on 5-6 July, 2002)

ABSTRACT
This paper highlights the potential of bioenergy available in the pulp and paper mills wastes which can be tapped through high rate biomethanation to supplement the energy requirement of the mills to a certain extent and help Indian mills in improving their economy and make them competitive in open global market.

INTRODUCTION
In India, around 500 pulp and paper mills are in existence accounting for five million tonnes of paper production. For producing this quantity of paper more than 10 million tonnes of raw material is consumed. Of this roughly five million tonnes of raw materials goes as either as liquid or solid waste. In large mills, having chemical recovery system, only 12% of raw material used is discharged as waste with major fraction as non-combustible waste. However in small agro based mills (without chemical recovery system) more than 60% of the raw material consumed is discharged as waste with high proportion of organic matter. Energy management/conservation is today on the top agenda of pulp and paper industry so as to minimise the overall production cost and thus become competitive in today's era of open market economy. One of the major factors which adversely influence the competitive ability of Indian pulp and paper industry is the high percentage of energy component (around 30%) in total production cost. A comparison of the energy scenario in paper industry of developed countries and India indicates that while the mills dependence on purchased energy in developed countries is only 20-25% of the total energy requirement, the Indian mills purchase energy to a tune of around 60-70% of the total energy requirement. A comparative energy consumption pattern in pulp and paper industries of India and developed countries is indicated in Fig. 1. Thus in addition to giving high priority to efficient energy management, there is a need to find alternate fuels to supplement the energy requirement of the mills to reduce the consumption of conventional fuels and dependance of Indian mills on purchased energy.

Sources of Biomass available in Indian Pulp and Paper sector
It is estimated that around five million tonnes of paper is produced per annum by around 500 mills in India consuming more than 10 million tonnes of raw material. In case of large paper mills having chemical recovery system (which contributes 30% of the total production) only 12% of the raw material used ends up as waste mostly as inorganic and noncombustible. However in small and medium size mills based on agro residues (which contributes 36% of the total paper production), due to absence of chemical recovery system the quantity of waste generated is quite high (around 60% on the basis of the raw material consumption). A close evaluation of the wastes generated from the paper industry reveals that in certain cases these wastes have a good potential for generation of bioenergy which if utilized...
Table 1. Different biomass generated in pulp and paper industry and their energy potential.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Quantity, million t/annum</th>
<th>Recovered, million t/annum</th>
<th>Waste discharged, equivalent to coal million t/annum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent Liquor</td>
<td>1.5-2.5</td>
<td>0.75-1.0</td>
<td>0.75-1.0</td>
</tr>
<tr>
<td>ETP Sludge</td>
<td>0.18-0.20</td>
<td>-</td>
<td>0.09-0.10</td>
</tr>
<tr>
<td>Evaporator condensates and others</td>
<td>0.02-0.03</td>
<td>-</td>
<td>0.01-0.2</td>
</tr>
</tbody>
</table>

Table 2. Different routes for energy recovery in agro based paper mill (basis: 40 tpd).

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Chemical recovery</th>
<th>Gasification</th>
<th>Wet cracking</th>
<th>Anaerobic treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass recovery in form of energy, %</td>
<td>75</td>
<td>60</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>a) Thermal energy, %</td>
<td>70</td>
<td>50</td>
<td>75</td>
<td>-</td>
</tr>
<tr>
<td>b) Electrical energy, %</td>
<td>30</td>
<td>50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chemical recovery, %</td>
<td>90</td>
<td>75</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>Pollution reduction, %</td>
<td>90</td>
<td>95</td>
<td>75</td>
<td>55</td>
</tr>
<tr>
<td>Investment, Rs. Million</td>
<td>200</td>
<td>150</td>
<td>250</td>
<td>25</td>
</tr>
</tbody>
</table>

Table 3. Market share of various anaerobic technology.

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Market Share, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>UASB Reactor</td>
<td>61</td>
</tr>
<tr>
<td>Contact Reactor</td>
<td>12</td>
</tr>
<tr>
<td>Anaerobic Filter</td>
<td>6</td>
</tr>
<tr>
<td>Hybrid Reactor</td>
<td>4</td>
</tr>
<tr>
<td>EGSB Reactor</td>
<td>3</td>
</tr>
<tr>
<td>Fluidized Bed Reactor</td>
<td>2</td>
</tr>
<tr>
<td>Fixed Film Reactor</td>
<td>2</td>
</tr>
<tr>
<td>Anaerobic Lagoon</td>
<td>7</td>
</tr>
</tbody>
</table>

Effectively, can affect the overall economics of the paper production. The sources of biomass available in large and small scale paper mill and their energy potential is indicated in Table 1.

Prospects of Energy Recovery in Pulp and Paper Mills

The total biomass generated varies from mill to mill depending upon its size, the raw materials used and the pulping process employed. There exists a huge potential in the Indian pulp and paper mills particularly in agro based mills for cogeneration of energy from liquid wastes. Spent black liquor constitutes the major source of energy in terms of organics and chemicals. The various routes available for energy recovery from black liquor are Chemical Recovery. Gasification, Wet Cracking and Anaerobic Treatment. A comparative picture of these processes is indicated in Table 2. Though the best option for cogeneration is chemical recovery small agro based mills have limitations to adopt it due to size constraints and requirement of huge investment. For these categories of mills, biomethanation of black liquor holds the most promising option of energy recovery in the form of methane which can be used as a fuel in boilers for steam generation.

High strength streams generated during cleaning of raw materials evaporation of black liquor i.e. evaporator condensate and weak washings of pulp have also been found as good sources of high rate biomethanation since these streams contain easily degradable constituents like organic acids, methanol etc. The basic advantage of biomethanation process is reduction in pollution load (around 50%) along with cogeneration of energy in the form of methane rich biogas which can supplement 25-30% of the total energy requirement in a typical 40 tpd agro based mill.

Present Status of Biomethanation Technology

Though biomethanation is a century old process, it has gained popularity in last few decades due to development of high rate reactor configurations through increased understanding of basic fundamentals, mechanism, microbiology etc. The biomethanation technology has undergone tremendous
changes in recent times especially in design of high rate bioreactors with compact size, making them more technoeconomically viable for treatment of low and medium strength waste water. A variety of process and reactor designs are available but the basic biology and biochemistry are same in all the systems. The technological developments in the field of biomethanation has taken place with the following objectives:

• Flexibility in operation.
• Handling of wide variety of effluents.
• Handling of higher organic loading rate (20-40 kg COD/m³/day)
• Biological scrubbing of biogas to remove hydrogen sulphide.
• Efficient conversion of biogas into electrical energy.

Some of the recent developments in high rate bioreactors based on different configurations are Expanded Granular Sludge Bed (EGSB) Reactor, Internal Circulation (IC) Reactor and Hybrid Reactor. At present UASB and Contact process are most widely used anaerobic treatment process by the paper industry worldwide as evident from the market share of these technologies (Table 3).

**Potential of Biomethanation Technology in Pulp and Paper Mills**

The various substrates generated in large and small scale pulp and paper mill which have potential to generate bioenergy through biomethanation process are as under:

**(A) Large Scale Pulp and Paper Mills**

• Rayon grade pulp mills

  Prehydrolysate liquor (pH liquor) generated during prehydrolysis of wood chips and evaporator condensates generated during concentration of black liquor in chemical recovery system have a good potential for bioenergy recovery through biomethanation.

**(B) Small Scale Agro Based Pulp and Paper Mills**

Most of these mills are discharging their black liquor laden effluent either without or with partial treatment since the conventional chemical recovery process is not techno-economically viable. This discharge of black liquor in effluent stream not only results in increase pollution load but also loss of valuable biomass which has a good potential to recover energy through biomethanation process.

**(C) Recycled fibre waste Paper based Mills**

The installation of biomethanation plant in an individual recycled fibre based mill (even in a 100 tpd mill) may not be technically and economically feasible owing to low pollution load generation but their effluent has high BOD:COD ratio indicating good potential for biomethanation. However the concept of cooperative biomethanation plant, where the effluents from three or four recycled fibre based mills located in close vicinity can be collectively treated together and the biogas generated may be utilized together among the mills, makes application of biomethanation feasible in this category of mills.

**Table 4. Potential of Biomethanation in pulp and paper mills.**

<table>
<thead>
<tr>
<th>Particulars</th>
<th>Bagasse washings</th>
<th>pH liquor</th>
<th>Evaporator condensate</th>
<th>Agro based black liquor</th>
<th>RCF combined mill effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed Capacity, t/d</td>
<td>600 tpd</td>
<td>300 tpd</td>
<td>300 tpd</td>
<td>50 tpd</td>
<td>3-4 mill of 100 tpd</td>
</tr>
<tr>
<td>COD Load, t/d</td>
<td>50-60</td>
<td>100-120</td>
<td>5.0-6.0</td>
<td>50-60</td>
<td>15-18</td>
</tr>
<tr>
<td>BOD Load, t/d</td>
<td>35-40</td>
<td>75-80</td>
<td>2.5-3.5</td>
<td>15-20</td>
<td>6.0-7.5</td>
</tr>
<tr>
<td>COD Reduction %</td>
<td>65-70</td>
<td>70-75</td>
<td>80-85</td>
<td>40-50</td>
<td>60-65</td>
</tr>
<tr>
<td>BOD Reduction %</td>
<td>85-90</td>
<td>85-90</td>
<td>90-95</td>
<td>75-80</td>
<td>80-85</td>
</tr>
<tr>
<td>Biogas generation m³/d</td>
<td>18,000</td>
<td>36,000</td>
<td>2000</td>
<td>10,00-12,000</td>
<td>4000-4500</td>
</tr>
<tr>
<td>Calorific value, kcal/m³</td>
<td>6000-6500</td>
<td>6000-6500</td>
<td>6000-6500</td>
<td>6500-7000</td>
<td>6200-6500</td>
</tr>
<tr>
<td>Coal equivalent, t/d</td>
<td>22-27</td>
<td>45-50</td>
<td>3.5-4.0</td>
<td>15-18</td>
<td>5-6</td>
</tr>
<tr>
<td>Fuel Oil equivalent, t/d</td>
<td>8-10</td>
<td>20-22</td>
<td>1.5-2.0</td>
<td>6.0-7.5</td>
<td>2.5-3.0</td>
</tr>
</tbody>
</table>

The potential of biomethanation in large and small scale agro and recycled fibre (RCF) based paper mills is summarised in Table 4.

Problems likely to occur during continuous operation of biomethanation plant and their remedial measures

(A) Deposition of recalcitrants in reactor biomass

The presence of recalcitrants like silica and lignin in black liquor causes adverse impact on quality of biomass and performance of reactor due to their deposition on the biomass over a period of operation of the biomethanation plant. This is due to the fact that deposition of these recalcitrants on the biomass substantially reduces the overall contact between microbes and the substrates resulting in poor performance efficiency. As such a part of anaerobic biomass of the reactor should be replenished periodically.

Moreover lignin present in the black liquor is biorefractory and anaerobically nonbiodegradable in nature due to which it is not decomposed by microbial biomass and only contributes to increase in dead load of the sludge biomass. Lignin removal through pretreatment of black liquor before anaerobic treatment offers encouraging results in improving the efficiency of biomethanation process. The studies show an overall improvement in performance efficiency by 15-20% (in terms of COD and BOD reduction %) after lignin removal. Lignin thus separated through lignin removal process can be used for number of industrial applications like grinding aid in cement industry, disperser in dye industry and it can also be used as particle binder in briquetting plants for better combustion.

A modified process flow diagram incorporating lignin removal system in biomethanation plant is given in Fig. 2.

(B) Corrosion of Construction Materials

Chances of corrosion of gas pipeline, gas holder, liquid pipeline etc are high specially in mills using sodium sulphide as cooking chemicals due to presence of hydrogen sulphide in higher proportion in the biogas. Moreover sulphur compounds are toxic and cause inhibition to anaerobic microbes. The corrosion problem may be overcome to some extent by using anticorrosive materials or pigments.

Potential of Power Generation from Biogas

Apart from the use of biogas in the boiler for generation of steam, the biogas can also be used for generation of power which can reduce the dependence of the mill on purchased power from the external

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**Table 5. Potential of power generation from biogas in Indian agroresidue based mills.**

| No. of agroresidue based mills of production capacity 30-40 tonne pulp per day | 1,440,000 m³/d |
| Potential for Power Generation | 90 MW |

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grid. It is estimated that in a 30-40 tpd pulp mill biogas generated (~ 12000 m³) may produce 750 kW of power assuming 30% efficiency of the gas engine. The potential of power generation from the biogas in Indian paper mills based on agricultural residues is evaluated and presented in Table 5.

However for generation of power through gas engines, quality of biogas is of utmost importance. Normally the composition of biogas generated from biomethanation constitutes 70-85% Methane, 15-30% Carbon dioxide and 1-5% Hydrogen sulphide depending on composition of substrate used for biomethanation. Methane is known to be one of the best fuels for reciprocating or turbine engines. The presence of CO₂ in biogas does not affect the fuel quality as regards to its usage in the engines (except a small reduction in rate power level of the engine). The hydrogen sulphide is undesirable from the view point of utilisation of biogas particularly in gas engines used for generating electricity where the level of hydrogen sulphide gas should be less than 0.01%. H₂S causes corrosion problems in the system itself thus reducing its life, so it is necessary to make it free from H₂S upto a level for 100 ppm.

Several methods have been developed for H₂S removal. Many metal oxides (eg. ZnO, CuO, Fe₂O₃, etc) are useful in removing H₂S at relatively high temperatures. However the chemical scrubbing of H₂S from biogas have been found to be expensive and not very efficient. Recent development by way of biological scrubbing of H₂S from biogas is a revolutionary invention for purification of biogas containing H₂S.

The ThioPaq Scrubber process, as it is popularly known is based on the biological oxidation of sulphide into elemental sulphur. The distinguishing feature of the process is that the sulphur is not formed in the scrubber itself outside the scrubber (Fig. 3). The removal efficiency of H₂S in this scrubbing process is more than 99% and has high operational safety as there is no risk of blockage which is an additional advantage compared to other conventional methods.

CONCLUSION

The biomass generated in Indian pulp and paper mills have good potential for bioenergy generation. In large scale paper mills high strength effluent streams i.e. raw material cleaning effluent, prehydrolysis liquor, weak washings and evaporator condensates have good potential for bioenergy generation. In small scale mills based on agroresidues pulping spent liquor which causes more than 80% pollution load can become a major source of energy generation through biomethanation and use of biogas in the boiler will certainly reduce mill's dependence on conventional fuels substantially. A 50 tpd pulp and paper mill can supplement at least 25-30% of its energy requirement through high rate biomethanation. Moreover energy generation from high strength effluent streams through biomethanation also results in reduction of pollution loads to conventional effluent treatment plant i.e. activated sludge plant which is highly energy and chemical intensive and thus helps in reduction in energy consumption required for effluent treatment. In all the High Rate Biomethanation is a promising and techno-economically viable process for conversion of biomass generated in pulp and paper sector into an ecofriendly fuel and thus help in supplementing the energy requirement of the mill to a certain extent.

REFERENCES