Biogas Production in Paper Mills: Existing Technologies and Modern Approaches

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ABSTRACT

Pulp and paper mills have been categorized amongst one of the major energy intensive and highly polluting sectors. Energy cost accounts for more than 30% of total cost of paper production and on comparison with other industries this sector consumes twice the amount of fuels. The release of untreated or partially treated cellulose rich black liquor, having very high organic pollution load of waste chemicals by the small scale or agrobased paper mills, where chemical recovery is a major constraint, poses severe threat of water pollution and simultaneously causes loss of bio energy potential. In this context, the biomethanation process has been identified as a promising technological solution to the dual problems of high energy demand and environmental pollution. The present paper discusses the existing biomethanation technologies in some of the major paper mills and some improved approaches regarding enhancement of biogas production from the paper mill wastes.

INTRODUCTION

Production of biogas, an eco-friendly renewable biofuel, from the pulp and paper mill effluents has various advantages such as, reduction in use of conventional fossil fuels, electricity production, minimization of SO_x, NO_x and green house gas emissions, reduction of appreciable percentages of BOD and COD (70-80%), generation of diminished amounts of stable biosludge, etc. Biomethanation is well feasible for effluents originating from recycle paper mills, mechanical pulping (peroxide bleached), semichemical pulping and sulphite and kraft evaporator condensates. Application of anaerobic treatment in closed circuit further saves on cost of fresh water intake and effluent discharge [1]. Biogas (55-70% methane, 35-45% CO_2, some trace gases, e.g., H_2S, NH_3, etc., calorific value 4700-6400 kcal/m³) is produced through anaerobic microbial digestion of waste organic feedstock (agroindustrial wastes, paper mill effluents and municipal wastes) in anaerobic digesters. Upflow anaerobic sludge blanket (UASB) and internal circulation reactors (ICR) are frequently used in the paper mills for biomethanation while other reactors for biogas production include fluidized bed reactor (FBR), fixed bed reactors, expanded sludge bed reactors (ESBR) and down flow fixed film anaerobic filters, etc. Some of the major paper mills which have already adopted biomethanation technology are Satia Paper Mills Ltd. (SPML) Muktsar, Punjab; Tamilnadu News Print and Papers Ltd. (TNPL) Karur, Tamilnadu; ABC Paper Mill, Punjab; Pudamjee Paper Mills, Pune; Oudegem Papaier, Belgium; Klingele Paper Mill, Weenner, Germany and some other paper mills in North America [2,3,4,5,6,7]. The production of biogas from organic matter requires action of various hydrolytic, acidogenic and methanogenic bacteria under anaerobic conditions at 30 - 38°C or 49 - 57°C for mesophilic bacteria or thermophilic bacteria, respectively within the pH range of 6.2 - 7.0 . Methanogenic bacterial genera include *Methanobacillus, Methanococcus, Methanobacterium* and *Methanosarcina* while nonmethanogens include *Clostridium spp., E.coli, Lactobacillus spp., Corynebacterium spp. a*nd other groups like proteolytic, lipolytic, cellulolytic and ureolytic enzyme producers [8]. The anaerobic treatment of paper mill effluents not only reduces pollution but also leads to cogeneration of biogas to be used as biofuel. Anaerobic system performances of different type of pulp and paper mill effluents are given in Table 1.

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Existing Technology in various Paper Mills

Satia Paper Mills (SPML) : Satia Paper Mills, Muktsar (Punjab), was generating large amount of organic waste materials and also using about 20 tonnes of rice husk per day in their boiler, leading to substantial emission of green house gases. Establishment of biomethanation plant in 1997 as a part of UNDP-supported project, "Development of high rate biomethanation processes as a means of reducing GHG's emission" implemented by Ministry of non-conventional energy resources (MNES), provided a break through to the problems of effluent treatment and high energy requirement. The new anaerobic digestion technology has brought down the pollution levels with 81% reduction in BOD and 54% reduction in COD while the biogas produced (about 10000 m³/day) serves as alternate biofuel saving 20% total fuel requirement in boiler. Cofiring of biogas with rice husk helped in improving boiler performance as well as reduced environmental pollution [9]. The biomethanation plant consists of two UASB reactors of 2623 m³ capacity, sump tank, equalization tank, clariflocculator, clarifier and buffer tank. It could treat about 53 tonne COD load. In the UASB reactor there was unique-3-phase separator system for separation of biogas, entrained biosolids and digested effluent. Due to, high silica and lignin the quality of biosludge bed deteriorated in 3 years, so about 30% fresh biomass was added in reactor replacing equal amount of

Table 1 : Removal percentages of BOD and COD from pulp and paper mill effluents

Sources of effluents	COD Removal (%)	BOD Removal (%)
Recycle paper	65 - 80 %	80 - 90 %
NSSC Pulp	50 - 60 %	80 - 90 %
TMP / CTMP Pulp	45 - 55 %	55 - 70 %
Kraft Pulp	75 - 85 %	> 90 %

Table 2 : Comparison between anaerobic / aerobic combined bioteatment system and biotreatment by aerobic system alone

	Anaerobic/aerobic combined system		Aerobic system
1.	Total suspended solids	5-10 mg/L	50-85 mg/L
2.	Organic matter removed		
	BOD	20-40 mg/L	4-7 mg/L
	COD	220-250 mg/L	50-85 mg/L
3.	Biogas production	Yes	No

Table 3 : Digestibility of different paper fractions

	TS, %	VS, %	l biogas/kg VS	l biogas /kg TS	% conversion
Newsprint I	91.7	94.2	139	131	13.6
Newsprint II	92.8	91.8	218	200	27.7
Woodfree Paper	94.6	81.6	636	519	80.8
Computer Paper	94.3	83.6	710	594	90.1
Magazines	93.8	72.7	327	238	41.5
Brochures	94.9	73.8	208	154	26.4
Packing Paper	93.9	94.5	381	360	48.4
Recycled Paper	93.6	90.5	246	223	31.2
Packing Cardboard	92.3	98.0	440	431	55.9

sludge. The feed rate was increased gradually and it operated on 100% loading in one month's time [2].

Tamilnadu News Print & Paper Ltd. (TNPL) : TNPL, Tamilnadu is bagasse based pulp and paper industry, where the bagasse with 3-4% residual sugars is kept in bagasse yard (for 3- 9 months) with water sprays to maintain quality [3]. The wastewater from bagasse yard with high COD is being used for biomethanation. For anaerobic treatment of wastes two UASB reactors of 5Ml capacity were commissioned in March 2003 replacing the conventional anaerobic lagoon for treating bagasse wash water. For treatment, the bagasse wash water is passed from bagasse clarifier to equalization tank and then to neutralization tank where the pH of 4 4.5 is adjusted to 6.5 7.0 by applying $Ca(OH)_2$. Now the neutralized wastewater is passed through clarifier where suspended solids are removed and the clarified water passes to buffer tank. Then after addition of urea and diammonium phosphate the wastewater is pumped into UASB reactors with the help of reactor feed pumps. The treated effluent is further sent towards activated sludge treatment process. The resulting biogas is supplied from the gas holder to the lime kiln using gas blowers at ambient temperature. The reactors are operated at 5.75 kg COD/m³/d organic loading rate at 20 h hydraulic retention time and the plant is designed to treat 12Ml/d of waste water [10].

Benefits of Anaerobic Treatment to TNPL: (1) 80-85% COD Reduction with biogas production factor of 520 l/Kg COD reduced. (2) 34.12 lakh m³ methane gas from biomethanation plant in the year 2004-05. (3) The use of same biogas in lime kiln saves 1886 kL of furnace oil worth 2.02 crores and 10 kL of furnace oil is saved every day. (4) Besides significant saving in furnace oil, reduction of 6.4 Gg CO_2 emissions was achieved.

Pudamjee Pulp and Paper Mills: The first commercial scale anaerobic treatment plant for pulp and paper mill effluent was commissioned in India at M/s Pudumjee Pulp and Paper Mill Limited, Pune in 1988. The average biogas generation/day has increased from 6500 to 9000 m³ over eight year period through design and process optimization [11]. This biogas plant consists of two anaerobic mixed bed type reactors of 6200 m³ with gas holding capacity of 400 m³ each. The digestors are fed from top to bottom, resulting in counter current distribution in central inlet and two lateral agitators are provided for adequate mixing of components. The system has lamella clarifiers and siphon for solid-liquid and liquid gas separation. The whole process is regulated by micro processor based auto control [5].

Benefits of bio methanation plant: (1) Average biogas production 6500 to 10000 m³/d (from 1991 to 1996) with calorific value 6400 kcal/m³. (2) Reduction of 85-90% in BOD. (3) Reduction of 70-75% in COD. (4) Saves 15% of total fuel oil requirements.

Operating conditions: Organic loading rate is 5 kg/m³ (at biogas volume 6200 m³) pH range 6.8 to 7.6, temperature 37°C with retention time of 50h. For inoculation, digested municipal sludge and fresh cowdung slurry was used. Pulping section black liquor is being used for biomethanation [5].

ABC Paper Mills: ABC paper mill, Hoshiarpur (Punjab) is an agrobased paper mill which produces fine quality paper from Sarkanda (*Saccharum munja*), Kahi (*Saccharum spontaneum*) and wheat straw (*Triticum aestivum*). In December 1999, UASB reactor of 3925 m³ was installed for biomethanation of alkaline sulphite black liquor.

Operating conditions: (1) During the initial startup of the reactor the reactor was inoculated with inoculum from distillery installations and cowdung which was later supplemented with commercial cultures and sludge. (2) The organic loading rate gradually increased from 0.5 kg to 12 kg COD/m³/d for a period of about 8 months. (3) Optimum temperature range for biogas production is 38° - 45°C, pH 6.8 7.5 and H.R. time of 50 hours for treatment of alkaline black liquor.

Benefits of Biogas to ABC Paper Mills: (1) Reduction of COD 45-48% and BOD 72-80%. (2) Production of 8000-9000 m³ of biogas. (3) Biogas is being used in co-firing the boilers along with the rice husk. (4) Reduction of fuel costs by 15% [4].

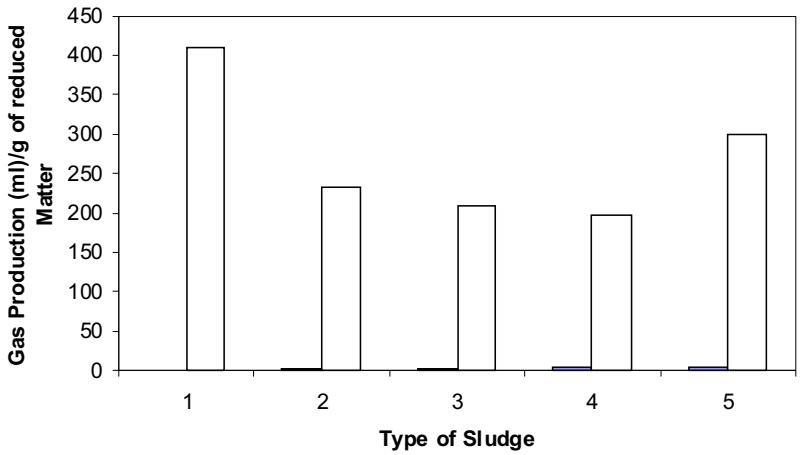
Paper Mills Abroad: The biomethanation process at Oudgem Papier, Belgium, utilizes thermophilic internal circulation reactor (ICR) for clearing its internal water loop. The anaerobic treatment process is operated at 55°C using anaerobic thermotolerant bacteria that treat the clarified mill water at 385 m³/h. The biogas produced is applied in biolers to produce steam. The treated water is returned to the mill circuit after purification [6]. Since the digestion temperature is 55°C the mill water (around 55°C) to be treated does not need any cooling.

The Klingel Paper MIll (Weener), Germany has commissioned Jenbacher biogas engine in April 2006, which

Table 4 : Investigation of anaerobic treatment on different types of sludges from paper mills

	Secondary sludge 100 ml 1 (IWE)	Secondary sludge 200 ml 2 (IWE)	Deinking sludge 3 (MM)	Fine rejects 4 (SKRP)	Fine rejects (Enzyme Treated) 5 (SKRP)
Total gas production from mixture (ml)	541	530	617	354	502
Gas production /g of reduced matter	410	234	208	197	299
Percent of reduction in DS (dissolved solids)	6.8	8.7	20.6	20.4	19.1

Figure 1 : Biogas production from sludge



operates on biogas produced through biomethanation of mill wastewater. It produces electricity and operates at 81.5% efficiency [12].

Experimental Studies

Immobilized cell systems have been extensively studied in anaerobic reactors. The application of anaerobic baffled reactor together with immobilized cell culture has been proposed for methanogenesis of black liquor from pulp and paper mills in a continuous system. An organic loading rate of 7 kg/m³/d showed maximum COD reduction of 50% and biogas generation of 10 litres/day containing 66% (v/v) methane [13]. Two stage bi-phasic reactor system accompanied with the use of immobilized cell system has been studied for anaerobic treatment of black liquor from pulp and paper mills. The reactor system was operated continuously for 340 days at 8 kg/m³/d organic loading rate which resulted in 55% reduction in COD and biogas generation at the rate of 11 dm³/d containing 71% (v/v) methane. In the two stage reactor system, the methanogenesis step can be separated from hydrolysis and acidogenesis that may prove beneficial for biomethanation in pulp and paper industry [14]. As per a comparative study conducted at a paper mill in Hedera, Israel, the anaerobic treatment of wastes followed by activated sludge treatment (AST) serves as better proposition for bio treatment than with (AST) alone. The anaerobic / aerobic system provided steady operation performance while, individual (AST) system produced effluent characterized by oscillatory values. The results in Table 2 indicate much lower total suspended solids and higher organic matter removal in anaerobic/aerobic combined system.

A combination of rumen micro organisms and colonized polyurethane support particles in a two phase digester resulted in efficient anaerobic decomposition of the paper mill sludge [16]. The reticulated polyurethane foam acts as a support material for the immobilization of methanogenic associations of bacteria. A project has been carried out at Domtar Paper in Windsor, Qebec, Canada, to investigate the potential for anaerobic treatment of contaminated kraft mill condensates. It showed that undiluted foul condensates at Windsor mill were toxic to anaerobic biomass due to high concentration of sulphides. Treatment of combined condensates at a loading of 10-12 g/L/d, resulted in 0.35 l biogas/g COD removed and 95% methanol removal. The biogas produced was of excellent fuel quality having about 90% methane [17]. Application of thermophilic anaerobic - aerobic moving bed biofilm reactors was investigated for treatment of thermomechanical pulping (TMP) white water. Both the reactors, anaerobic and aerobic, were of 15 l capacity. The anaerobic reactor was mixed by gas circulation while aerobic reactor was mixed by air. Before actually applying the TMP white water the reactor was operated with molasses water for one and half year till the suspended and attached growth total biomass concentrations were 3.3 g VSS/l in anaerobic reactor while it is 1.6 g VSS/L in aerobic reactor. The Kaldnes moving bed biofilm reactor is a continuously operated biofilm area where biofilm grows on cylindrical polyethylene carrier elements that move along with water in reactor due to biogas circulation in anaerobic reactor or air circulation in aerobic reactor. Methane production was in the range of 100-350 ml CH_4/g soluble COD removed [18].

Many of mill solid wastes consist of different types of papers. Besides cellulose, lignin and ink, the newsprint paper also contains $CaCO_3$, talc, clay minerals which act as buffer in anaerobic reactor. Different types of paper wastes were examined [19] to estimate their biodegradability for anaerobic digestion. The results of digestion have been expressed on VS and TS basis as shown in Table 3.

MODERN APPROACHES AND TECHNOLOGIES:

A wide spectrum of modern or improvised technologies are available that bear potential for enhancing biogas production by the pulp and paper mills as described below.

Anaerobic Digestion of Less Utilized Wastes: The wastes such as paper fines (from recycled paper) kraft mill condensates, sludges etc. from pulp and paper mills have the potential to be converted to biogas. When paper is recycled, paper fines result and approximately 10 to 15% of the recycled paper has to be purged because the fibres are too short to be used. It can be blended with industrial biosludge. The wastes are first treated with lime to enhance reactivity then they are converted to volatile fatty acids (acetic, propionic and butyric) utilizing mix culture of microbes from anaerobic

waste treatment plant. The paper fines provide energy and the industrial biosludge provides nutrients to microbes. The neutralizers (lime or $CaCO_3$) are added to the fermentor to maintain the pH near neutral. From this stage, through a proprietary technology (Mix Alco Process) owned by Texas A & M University, alcohols may be produced [20]. Use of proper methanogenic bacterial cultures at this stage will lead to biogas formation. The National Renewable Energy Laboratory (NREL) has used Simultaneous Saccharification and Fermentation (SSF) technology on pulp mill sludge to get 19% conversion of total sludge weight to ethanol. This also shows that application of suitable acidogenic and methanogenic microorganisms under anaerobic conditions can provide biogas from these sludges. Samples of various types of sludge from different paper mills were studied for energy recovery in the form of biogas through biomethanation. Secondary sludge from Industriewater Eerbeek (IWE), Deinking sludge of Mayr-Melnhof Eerbeek a recycling paper mill (MM) and fine rejects from Smurfit Kappa Roermond Papier (SKRP) have been used for biogas production. Effect of enzyme treatment was also seen [21]. The results are shown in Table 4. Figure 1 shows that in comparison to other sludges, secondary sludge has higher potential for biogas generation.

Some paper mills such as Domtar Papers, Quebec, Canada, have started biogas production from the kraft mill condensates [17]. A 42 liter pilot UASB reactor at Jackson, AL, mill was operated for 3 months. Pilot plant studies have also been conducted in mills at St. Helens and Wallula WA on Kraft foul condensates in internal circulation reactors (ICR) that resulted in significant biogas formation, accompanied with more than 80% BOD and COD reduction and 98% methanol removal [22]. This system had capacity to treat twice the COD loading of conventional UASBs and could tolerate shock loads and recover at two hours hydraulic retention time.

Use of Bioengineered Microorganisms: The biotechnological approaches of genetic engineering and metabolic engineering can be applied to enhance the growth, hydrolysis, acidogenesis and methanogenesis which ultimately lead to higher biogas production. Cellulolytic properties of *Clostridium cellulolyticum* have been improved for higher cellulose up take by metabolic engineering. Wild strain of *C. cellulolyticum* at high carbon flux lead to pyruvate accumulation which is responsible for growth cessation. This condition can be controlled by heterologous gene expression of pyruvate decarboxylase and alcohol dehydrogenase from *Zymomonas mobilis*. The recombinant culture of *C. cellulolyticum* showed 150% increase in cellulose consumption which resulted in 93% increase of acetate required for biomethanation. The required gene from *Z. mobilis* were carried by expression shuttle vector pMT500F to the cells using the electroporation method [23]. Thus the increased uptake of cellulose by bioengineered bacteria is a potentially suitable option for enhancing biogas production.

Use of Thermotolerant Microorganisms: Strains for thermotolerance must be isolated and applied in biomethanation of pulp and paper mills effluents. The mill effluents in the temperature range from 50-60°C usually have to be cooled then treated anaerobically. But the presence of suitable thermotolerant strains that can carry anaerobic digestion at around 55°C - 57° C thus eliminating the need of cooling step and reheating of treated effluent (for use in internal mills circuit) [6,18].

Improved Reactors: Amongst various anaerobic systems the UASB and IC are most applied ones [1]. Many improvised configurations of anaerobic reactors have been tried for paper mill wastes. The UASB reactor has been applied in treatment of waste waters from various industries including paper mills. It has a suspended growth system, where micro organisms develop in well settling flocs or granules and has high loading ranging from 5 to 15 kg COD / m^3 day. The influent is typically equalized, neutralized and partially acidified in separate tank on the head of reactor. The UASB reactor consists of a (1) gas solid separator (2) influent distribution system (3) effluent draw off facilities. The waste to be treated, is introduced from the bottom of the reactor and it flows upward at 0.6 to 0.9 m/s velocity through a sludge blanket composed of biologically formed granules and the resulting biogas formed causes internal circulation. It is collected in the gas collection domes at the reactor top [8]. Fluidized bed reactors (FBR) are especially suitable for treatment of hazardous wastes with recalcitrant compositions. The hybrid reactor is an improved version of the UASB system and combines the merits of the upflow anaerobic sludge blanket and fixed film reactors [24]. The IC reactor, also a modification of UASB process and consists of expanded granular sludge bed and UASB compartments on the top of each other. The special feature of the reactor is separation of biogas in two stages and the gas collected in the first stage causes internal wastewater biomass circulation thus reducing the energy demand of the process [25].

Removal or Reduction of Inhibitory Compounds: It has been reported that the, lignin related compounds, (chlorolignins, phenols, chlorophenols), resin acids and tannins etc. contained in many of the effluent streams from pulp and paper mills are inhibitory to the biomethanation process [26]. Hence the methodologies for partial or complete removal or biodegradation of these inhibitory compounds from the waste streams will be beneficial for biogas production in paper mills. Traditionally, activated carbon adsorption and solvent extraction were most widely used methods for removal of phenolic compounds but recently microorganisms have been considered as promising adsorbents [27]. A study on biosorption capacity of the fungus *Pleurotus sajor caju* (dry and dead) showed maximum adsorptions of (in m mol/g) 0.95 for phenol, 1.24 for o-chlorophenol, 1.47 for p-chlorophenol, 1.89 for 2, 4, 6 - trichlorophenol. Adsorptions of phenol and chlorophenol increased with increasing pH while desorption were achieved with 30% v/v methanol solution [28]. Dried sewage sludge has also been studied for its biosorption capacity of phenols [29]. Tannins are polar phenolic polymeric compounds, its monomers have low toxicity but oligomers bear high toxicity for methanogens. Oxidative polymerisation of bark tannins effectively reduced their toxicity in paper mill effluents. Resin acids are tricyclic terpenes found in tree wood and bark, which get entry into pulping and wood processing wastewaters (several hundred ppm in CTMP waste waters) showed toxicity to methanogens. Mixed group of aerobic and anaerobic microbes have been used

for resin acid degradation, which include *E. Coli, Bacillus sp. Pseudomonas, Alcaligens eutrophus* etc. Pretreatment of effluent with fungus *Phanerochaete chrysosporium*, in a rotating biological contactor for 2 days reduced 42% AOX, 45% COD & 55% of total BOD. Subsequent anaerobic treatment removed additional 40% AOX, 45% soluble COD and 65% BOD at 0.16 kg COD/m^3 day organic loading and 20 days retention time [30] . The chloroorganics can also be minimised in effluents by adopting ECF or TCF bleaching processes or enzyme pretreatments in order to make bleach effluents suitable for biogas production. Removal of lignin before anaerobic treatment by acidification can be beneficial for biogas production. Dual fuel production may also be performed through anaerobic digestion of paper mill effluents. Anaerobic digestion using two stage bioreactors, first one for hydrogen and the second one for methane production provided 35% hydrogen at 139 ml/h and methane at171.4 ml/h [31].

CONCLUSION

From the present study we can conclude that improved biotechnological techniques, suitable reactor design and strategies for minimization of inhibitory compounds in an integrated manner can contribute towards higher production of biogas from the paper mill wastes.

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