Biogas-fuel cell based cogeneration in the pulp & paper industry

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ABSTRACT

This paper introduces a novel concept for cogenerating heat and electricity through biogas generated from treatment of paper mill effluent and a phosphoric acid fuel cell (PAFC) system. The organic content of mill effluent is first converted to a methane rich biogas in high rate anaerobic digesters, This biogas is reformed with steam and fed to the PAFC where it is converted into electricity and heat at very high efficiency. The integrated system not only leads to pollution abatement but also recovers energy from waste which can be utilized to meet some of the electricity and steam requirements of the mill,

Introduction :

The pulp and paper industry is an energy-intensive industry. Energy costs constitute about 20 to 30 percent of the total cost of production of paper in the Indian industry. Energy is required in the form of heat (steam) as well as electricity. About 70 percent of the large and medium size mills have captive power generation facilities. On-site power is mainly generated through condensing turbine generators coupled with coal-fired boilers. However, captive power generation is associated with low conversion efficiency and high cost. Balancing of power generation with steam demand is also difficult due to the variation in electrical load and the intermittent nature of certain processes utilizing steam. The combined heat and power requirements of pulp and paper mills can be met through cogeneration systems. There are several alternatives for cogeneration such as back pressure turbine, extraction cum back pressure turbine, double extraction and condensing turbine, etc. Another cogeneration which has not yet been explored by the pulp and paper industry, but which promises very high efficiency is the Phosphoric Acid Fuel Cell (PAFC) system.

Fuel cells are electrochemical energy conversion devices that convert the chemical energy fuel directly into electrical energy and heat. Since no combustion is involved in a fuel cell, the conversion efficiency is extremely high. The PAFC is the most advanced of all fuel cells in terms of commercialization prospects. The PAFC utilizes oxygen from air as an oxidant and hydrogen or a hydrogen-rich fuel which, in turn, can be derived from suitable primary fuels such as natural gas, digester gas, methanol etc. A PAFC power plant comprises three principal subsystems: a fuel processor, a power section (fuel cell), and a power conditioner. The fuel processor removes impurities from the fuel and converts into H_2 rich gas, the power section converts the H_2-rich gas into electricity and heat, and the power conditioner converts the DC output of the fuel cell into AC. The advantages of the PAFC system are : high fuel conversion efficiency, modular construction, good load-following characteristics, and low environmental emissions.

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In the pulp and paper industry, the feedstock for a PAFC system are available as by-products or process waste and hence a PAFC cogeneration option can be viable. Many integrated pulp and paper mills have their own chlor-alkali plants. Hydrogen produced in these plants, as a by-product, is usually flared. This can instead be used efficiently in a PAFC plant to generate additional electricity and heat. Another product of the mill, i.e. sludge, can be converted into gas via anaerobic digestion. This gas can be suitably processed and fed as fuel to a PAFC power plant to cogenerate electricity and heat. Anaerobic treatment of the effluent from a 50 TPD capacity paper mill would yield gas that could fuel a 300kW PAFC stack and provide an equivalent amount of heat. In this paper, the technical details of an integrated anaerobic digester - phosphoric acid fuel cell (AD-PAFC) system are discussed.

Effluent from the pulp and paper industry :

The pulp and paper industry is amongst the 20 most polluting industries in India. The characteristics of the effluent i.e. combined waste water and sludge from large (LPM) and small paper mills (SPM) in India are given in Tables 1 and 2 respectively (1). In general, the levels of pollution are greater from small mill effluent than from large mill effluent.

Table 1: Characteristics of combined waste water from Indian pulp and paper mills.

Parameters	Agro residue based		Waste paper based (SPM)
	LPM	SPM	
Flow m^3/t paper	167-281 (220)	187-383 (252)	72-159 (107)
pH	6 6-10	6 6-8.5	7.1-7.7
Suspended solids, mg/l kg/t paper	620-1120 (764) 168	400-1115 (615) 155	350-885 (542) 58
BOD_5 20°C mg/l kg/t paper	240-380 (295) 65	220-1067 (698) 176	100-273 (187) 20
COD mg/l kg/t paper	840-1160 (1118) 248	2120-4763 (2940) 741	472-876 (654) 70
COD/BOD	2.95-4.37 (3.8)	2.94-5.4 (4.2)	2.7-5.7 (3.5)

The treatment of effluent and wastes has always posed problems to pulp and paper industry. This is due to the high cost involved, both capital as well as recurring, and the high energy requirement. Presently, in most mills, the practice is to use aerated lagoons followed by activated sludge treatment system for the removal of dissolved solids. Some mills also use anaerobic lagoons.

Anaerobic digestion : energy recovery from mill effluent

The major drawbacks of the existing treatments can be overcome by using anaerobic digesters which provide a combination of energy-efficient waste water purification and energy recovery in the form of biogas production. Low power consumption and nutrient demand and lesser sludge generation are the other major advantages of these anaerobic digesters.

In the anaerobic digestion process, the organic component of the mill effluent is first converted to soluble compounds by hydrolytic bacteria. The product is next transformed into simple organic acids by acidogenic bacteria. The acids are then reduced to evolve methane and carbon dioxide (biogas or digester gas) by methanogenic bacteria. This process takes place in simple reactors or digesters. The limitations of the conventional anaerobic reactors are long hydraulic retention time (30-50 days), low conversion rate, low specific gas yield (0.3-0.9 m^3/m^3 of digester volume per day), etc.

These limitations can be overcome in newer reactor designs like Upflow Anaerobic Sludge Blanket (UASB) reactors, Anaerobic Fixed Film reactors (Anaerobic Filters) as well as Anaerobic Fluidized Bed reactors. High rate anaerobic reactors work on the principle of retention of the active bacterial mass and viable sludge for more efficient contact with the effluent so that effective digestion time is reduced. Recirculation of digester gas as well as digester liquor increase rate of gas production and methane content. Thes high rate reactors have a very low hydraulic retention period (4-6 hours), high COD/BOD reduction capacity, high specific gas production (4-6 m^3/m^3 of digester volume per day), and the capability to overcome sudden upsets.

Industry has gradually started shifting from the resource—destroying aerobic to the resource conserving anaerobic waste water treatment. Mac Millan Bloedal Ltd. has installed a high rate anaerobic waste water treatment system for its paper and pulp mill at Stirgon Falls, North America. About 10-15 per cent of the mill's steam requirements are met by the biogas generated during treatment of waste water. This results in savings of US$ 0.75-1.1 million annually from its natural gas fuel bill [2]. An anaerobic treatment plant employing a mixed reactor is working in The Pudumjee Pulp and Paper Mill Ltd. Pune(60 TPD). BOD and COD reduction efficiencies of about 80% and 60% respectively have been achieved with specific gas production ranging from 0.45-0.5 m^3/kg-COD destroyed and a methane: CO_2 ratio of 75:25 in biogas. Net savings in oil are Rs. 10,000 per day, and in power and chemicals are Rs. 15 lakhs every month [3).

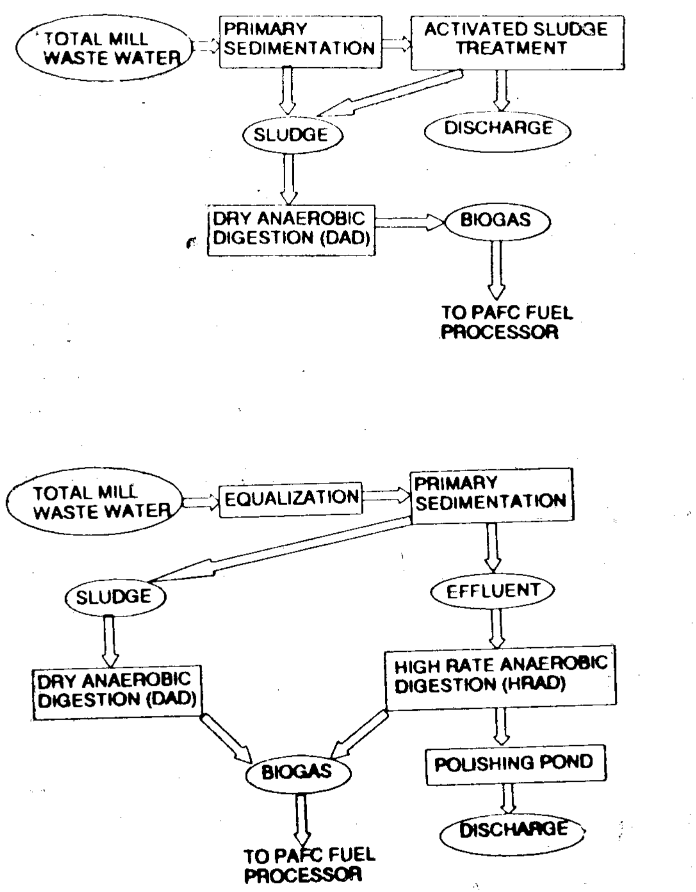
An integrated anaerobic digester-PAFC system

The energy content of paper mill effluent can be efficient by recovered through the use of a high rate anaerobic digestor coupled to a PAFC cogeneration system. Two treatment alternatives could be followed for recovering high quality digester gas from paper mills for this system. In case of mills with existing effluent treatment plants based on aerobic (activated-sludge) processes, the sludge could be treated in a dry anaerobic digester (DAD) (4) to recover biogas for the PAFC fuel processor. This is illustrated schematically in Fig. 1. The biogas and methane outputs from the sludge generated in large and small paper mills (Table2} using the DAD treatment have been calculated and are given in Table 3. The calculations are based on a conversion rate of. 0.4 m^3-biogas/kg-dry matter, a dry matter conversion of 40 per cent and a CH_4-content of 75 per cent in biogas.

The second alternative is based on direct conversion of mill effluent using high rate anaerobic digesters. In this process, the total mill waste water is first taken into an equalization, tank for pH adjustment, after equalization the effluent is taken to a primary sedimentation system. The effluent, which is rich in carbonaceous compounds and nutrients, is then fed to the digester where gas evolution takes place. Sludge from sedimentation can also be further stabilized in a DAD system, as described above, leading to additional gas recovery. This is shown schematically in Fig.1. The biogas and methane outputs from the total effluent generated in large and small paper mills (Table 2) using this treatment are given in Table 4. These calculations are based on a conversion rate of 0.4 m^3-biogas/kg-COD removed, COD reduction of 75 per cent and a CH_4 - content of 70 percent in biogas (5)

Table 2: Sludge generation (after aerobic treatment) in the Indian Pulp and paper Industry.

Type of sludge	Kg dry solids/t paper	
	LPM	SPM
Primary sludge	159	116
Secondary sludge	34	105



Figure—1: Schematic of biogas production from paper mill wastes using the DAD process (top) and the HRAD process (bottem,.

Table 3: Biogas and methane generation from sludge using DAD plants.

LPM		SPM	
Biogas	CH_4	Biogas	CH_4
m³/T of paper			
77.2	57.9	88.4	66.3

Table 4: Biogas and methane generation from total mill effluent using high rate anaerobic digesters.

LPM		SPM	
Biogas	CH_4	Biogas	CH_4
m³/T of paper			
137.4	96.2	268.7	184.1

Gas generated from the high rate anaerobic digestion of mill wastes based on either of the alternatives described is then taken to the PAFC plant. Since the PAFC utilizes H_2 or H_2-rich gas as a fuel, it is necessary to design a suitable fuel-processing system to convert the methane component of digester gas to H_2-rich gas. The digester gas fuel processor system is shown schematically in Fig.2. Gas generated from the high rate anaerobic digestion of mill effluent, as described above, contains impurities such as H_2S, COS and chloride compounds from the paper-making process. These impurities are detrimental to the fuel processor catalysts and must be removed to tolerance limits within 0.5-15 ppmv. The removal of sulfur species is achieved by using an inexpensive chemical absorbent such as iron sponge or iron oxide followed by ZnO at 400°C. Chloride and other impurities are removed by a guard bed which may be a nearly spent catalyst, a lower cost version of the main catalyst or an absorbent such as activated carbon. Clean gas is sent to the reformer, where the following reaction takes place between CH_4 and steam :

$$CH_4+H_2O=CO+3H_2, \quad \triangle H= +223 kJ/mol.$$

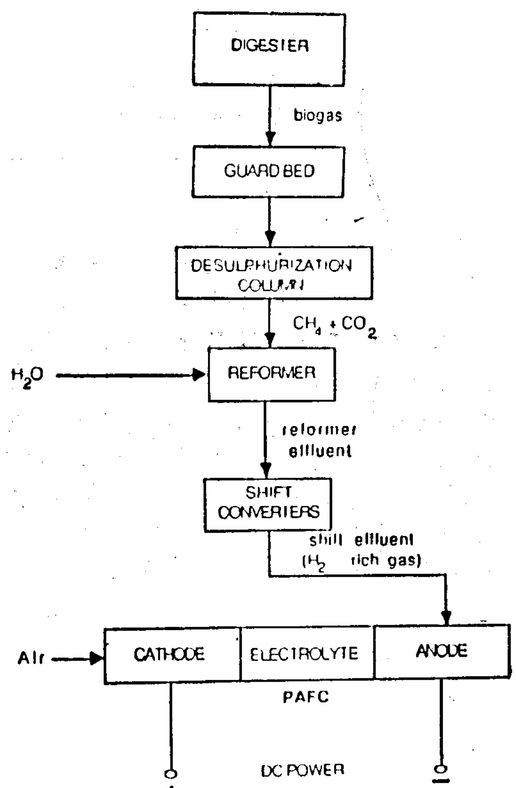


Figure 2: Schematic of the integrated biogas-PAFC system

The reformation reaction is highly endothermic and requires nickel catalysts. It is thermodynamically favored by high temperature and low pressure. A part of the digester gas is burned directly to meet the thermal requirements of the reformer. The steam requirment is met through by-product steam generated from the fuel cell. The reformer is operated at 650-700°C & uses about 1.5 times the stoichiometric amount of steam.

CO produced in the reformer is a poison for the Pt-electrocatalyst employed in PAFC. The tolerable. concentration of CO in the anode feed-gas is about 1.4 vol% at the PAFC operating temperature of 190°C. The CO content in reformed gas is, therefore, converted into CO_2 with additional production of H_2 using steam in a two-stage water-shift converter (employing high and low temperatures), where the following reaction takes place-

$$CO+H_2O=CO_2+H_2, \quad \triangle H=-41 kJ/moi.$$

The water-shift reaction is mildly exothermic. It is favored by low tempera'ure but is unaffected by pressure. In the HTS (high temperature shift), iron oxide catalyst is employed at 450°C, whereas, in the LTS (low temperature shift), CuO/ZnO catalyst on Al_2O_3 is used at 250°C.

The enriched H_2 stream is fed through the anode of a PAFC operating at about 190°C. The electrochemical oxidation of H_2 which generates electricity is:

$$H_2 \rightarrow 2H^+ + 2e^- \text{ (anode reaction)}$$
$$2e^- + (1/2)O_2 + 2H \rightleftharpoons H_2O \text{ (cathode reaction)}$$
$$H_2 + (1/2)O_2 \rightleftharpoons H_2O \text{ (overall reactian)}$$

Hydrogen in the fuel diffuses through the porous anode to reaction sites at the electrode-electrolyte interface, where it is electrochemically oxidized. The electrons are transported through the external circuit and produce electrical work, the hydrogen ions are conducted through the electrolyte to the cathode reaction sites.

Oxygen from air. which diffuses through the cathode, reacts with hydrogen ions and electrons drawn from the external circuit. The product is water, which diffuback out of the cathode. Approximately half of the chemical energy input to the PAFC is converted into useful electrical energy, whereas the remainder is converted into heat. The d.c. power output from a PAFC may be regulated or converted to a.c. power through an inverter. The a.c output can be designed virtually for any frequency and voltage needed to interface with electrical equipment or for connection to existing transmission lines, Heat is recovered from the PAFC using a heat exchanger and steam separator. A part of the steam is fed back to the reformer whereas the remaining can be utilized for process heating in the mill. Low grade heat can be used in the anaerobic digester to attain thermophilic conditions.

The technical parameters of a typical HRAD-PAFC cogeneration system for a 50 TPD paper mill using data from Pandya et al. (6) are calculated in table 5. Such a system could therefore be used for a dedicated or peaking load application without upsetting the steam demand in the mill.

Table 5: Technical parameters for HRAD-PAFC system based on effluent treatment in a 50 TPD paper mill

Effluent Treatment Plant	
System	HRAD + DAD
Biogas output	6870 Nm^3 /day
PAFC Plant	
System heat rate	2550 kcal/kWh
Biogas-to-electricity conversion	0.5 Nm^3 /kWh
Plant utilization factor	0 6
Power output	about 300 kW
Heat recovery rate	about 250 kW at 160°C

At present, prototype development of PAFC stacks is being undertaken by Bharat Heavy Electricals Ltd. and these fuel should be available commercially soon. A demonstration project for an on-site integrated energy system based on biogas from municipal sewage coupled to a PAFC has been executed by the Tata Energy Research Institute at the Okhla SDW in New Delhi (7). A biogas—PAFC cogeneration system has the potential to effectively utilize paper mill wastes in an economic manner. Technical and economic feasibility is dependent on specific application, and would have to be carried out for a particular paper mill.

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