Energy recovery from bagasse/straw black liquor as biomethane by modular reactor systems

RAO V.V.*

ABSTRACT

Industrial wastewaters with a significant pollutant load are normally considered for end of-pipe treatment by an anaerobic aerobic sequence to meet stipulated regulatory standards of treated water Among the high strength wastewaters, distillery spentwash based on sugarcane molasses and weak black liquor from bagasse or straw based minipaper mil's, are particularly notable owing to their potential as sources of biogas which can be g nerated during anaerobic treatment. Biological processes based on a combination of anaerobic aerob:c methodologies also offer substantial savings in energy, space and nutrient requirements About 80-90% of the biochemical energy potential expressed as BOD is released as biogas While several options are available for anaerobic reactor or digester design, this investigation deals with the attached growth biofilms reactor in which specially designed plastic media are utilised to develop a permanent film of active biomass These reactors have been successfully developed for distillery spentwash. Salient features of some full scale installations using the patented BACARDI fixed film process for the generation of biogas from distillery spentwish are described Bioreactors of the fixed film type have also been developed for the anaerobic treatment of segregated weak black liquor from mini-paper mills This paper also highlights a n·w design of biogas generation system developed by our organisation for handling black liquor

Introduction

Anaerobic treatment of industrial wastewaters is a mature technology today with the development of different types of high-rate reactors. Design and operation of full scale biogas generation systems suitable for a variety of complex industrial wastewaters is now possible with a better understanding of the microbiology and mechanisms of anaerobic reactions, nature of biomass, characteristics of wastewaters and process monitoring as well as rational design of reactors incorporating principles of chemical reaction engineering.

The new designs of industrial anaerobic reactors, can be regarded as a three phase system consisting of wastewater as substrate, biomass of growing micro-organisms and biogas generated during bioconversions. The three important aspects of reactor design include (a) Ability to retain biomass, (b) Provide good contact of biomass with wastewater and (c) Facilitate efficient separation of biogas from the system Commercial designs of reactors incorporate proprietary features to achieve these requirements The basic configurations of the different reactors include the following : Contact Reactor (CR), Anaerobic Filter (AF) reactor, Downflow Stationary Fixed Film (DSFF) reactor, Upflow Stationery Fixed Film (USFF) reactor, Upflow Anaerobic Sludge Blanket reactor (UASB), Fluidized Bed (FB) or Expanded Bed (EB) reactor and hybrid reactor combinations.

The various high rate process configurations have recognised the roles of hydraulic retention time (HRT)

*The Dharamsi Morarji Chemical Company Limited,
Regent Chambers, 8th Floor,
208-Nariman Point, Bombay-400 021

and solids retention time (SRT) which have a significant effect on reactor size and process stability respectively. Commercial reactors are designed to provide high SRT values through high biomass concentrations accomplished by the development of flocs/granules with good settling behaviour as in UASB systems or a biofilm developing on the surfaces of a supporting medium as in anaerobic filters and fluidized/expanded bed systems. The effective separation of SRT and HRT has enabled significant improvements in the anaerobic process leading to higher organic loadings requiring smaller reactor volumes. Systems with high SRT provide good process efficiency while ensuring good process economy at relatively low HRT.

Anaerobic bioreactors have been successfully adopted for the treatment of industrial wastewaters owing to significant savings in energy requirements compared to the aerobic processes. The energy demand of the aeration devices used in aerobic treatment far exceeds the mixing energy requirement of the anaerobic processes. Another major advantage is the reduced sludge generation in anaerobic treatment processes and savings in nutrient and chemical doses.

The recent trend integrates anaerobic treatment of medium/high strength industrial wastewaters with the overall facilities for handling different process effluents. A survey of current literature high-lights reports of world wide application of anaerobic processes in full scale wastewater treatment for handling effluents from process industries like food, dairy, brewery, distillery, yeast, starch, paper, chemical, pharmaceutical, petrochemical etc. In this context, the sugarcane molasses based alcohol industry in India has readily adopted global developments in anaerobic technology providing a viable biogas energy recovery option for handling the dark colo ed high strength spentwash, a wastewater generated after recovery of alcohol by distillation. World-wide developments also indicate the potential application of anaerobic treatment methodologies for handling process effluents from integrated paper mills. Many minipaper mills in this country based on agro-residues like straws and bagasse are now looking to anaerobic treatment of pulp mill black liquors as a viable proposition for significantly reducing (upto 80-85%) the pollution loads while recovering the biochemical energy potential as biogas for use as fuel.

This paper high-lights developments in attached biomass growth biofilm reactor systems for the treatment of industrial wastewaters and in particular the patented 'BACARDI' process for the generation of biogas from distillery spentwash and a novel adaptation of the design developed by our organisation for handling black liquor from straw or bagasse based mini-paper mills.

Anaerobic Biotechnology

Anaerobic digester handling industrial wastewaters can be regarded as a bioreactor for a set of complex biochemical transformations brought about by a consortium of anaerobic bacterial groups. A multi-step process consisting of several interacting series and parallel reactions has been postulated by several authors for describing the pathways of bioconversions during anaerobic degradation of complex substrates consisting of both particulate and dissolved organic compounds/polymers present in industrial wastewaters. The complex microbial processes during anaerobic treatment of a multi-substrate medium leading to the generation of biogas (methane and carbon dioxide) are now regarded to involve upto four stages consisting of Hydrolysis, Acidogenesis, Acetogenesis and Methanogenesis.

HYDROLYSIS : Extracellular enzymes hydrolyse complex polymeric materials such as polysaccharides, proteins and lipids (fats and grease) to simple soluble monomeric constituents.

ACIDOGENESIS (FERMENTATION) : The relatively simple soluble compounds are fermented to formate, acetate, propionate, butyrate and other short chain fatty acids, alcohols, carbondioxide, hydrogen and ammonia.

ACETOGENESIS : Acetogenic micrcorganisms convert the metabolic products of fermentation step especially the short chain fatty acids and aromatics to form mainly acetate, hydrogen and carbondioxide. The hydrogen consuming acetogenic bacteria also lead to acetate formation.

METHANOGENESIS : Methanogenic bacteria convert the acetate into methane and carbon dioxide (aceticlastic methanogens) besides carbon dioxide reduction by hydrogen to form methane (reductive methanogenesis).

In addition to the above, during anaerobic treatment of wastewaters containing a high sulfate concentration, like distillery spentwash (SO_4=4000—6000 mg/l) the sulfate reducing bacteria (SRB) also compete with the methanogens for hydrogen and acetate producing sulfide/hydrogen sulfide with an inhibiting effect on methane generation.

The aggregation of different anaerobic bacterial metabolic groups into microbial flocs/granules or as biofilm under optimal environmental conditions (pH, temperature, buffer capacity, nutrients, redox potential) in the reactor leads to the overall substrate conversion to biogas during anaerobic digestion. Process design and control of anaerobic processes essentially integrates several inter-related recent developments in microbiology including microbial growth dynamics and biomass characterization, biochemical mechanisms, reactor hydrodynamics, mass transfer and mathematical modelling to meet the needs of practical applications.

The sequential nature of the bioconversions involving hydrolysis fermentation, acetogenesis and methanogenesis steps during anaerobic degradation of a complex multisubstrate medium has been utilised to develop mathematical models to describe reactor performance. However, at the present time, these models have rather limited direct applicability to full scale industrial bioreactors, though they have widened the knowledge of the engineering and technological aspects of the process.

Among the various high-rate anaerobic treatment systems, the anaerobic filters offering significant improvements in process stability and reliability have been reported to be operating successfully handling distillery spentwash. These reactors have been generally adopted for single phase operating mode under mesophillic temperature range (35-37°C), in this country. There are a few installations operating in the thermophitic temperature range (55-60°C). Some are operating in a diphasic mode segregating the acidogenic and methanogenic stages of the overall process with two separate reactors, the acidogenic reactor leading to the formation of intermediate volatile fatty acids (mainly as acetic acid) and the methanogenic reactor for biogas generation. The phasing of the reactor system into two stages operating under optimum environmental conditions for acidogenic and methanogenic reactions will be beneficial particularly for high strength wastewaters giving operational flexibility and higher efficiency for BOD/COD removal with comcormitant increase in biogas yields. The technical benefits of diphasic operation have not been adopted in industry owing to additional investment and operating cost implications.

Features of Anaerobic Modular Biofilm Reactors

Development in fixed film reactors during the past two decades have successfully addressed the following issues of reactor design :

* Surface characteristics of biomass support media.
* Type, selection quantity and arrangement of packing material - random packed media or stacked modular packing.
* Formation of stable biofilm layers
* Feed and recycle arrangements.
* Bed hydro-dynamics. feed characteristics, permissible organic (COD) loading rates, selection of inoculum, startup, monitoring and process control.

The selection of an ideal support media for fixed film reactors is based on the following criteria :

* High Surface area per unit volume.
* Surface texture to promote bacterial adhesion.
* Inertness to chemical and biological action, high porosity to prevent choking.
* Low specific mass to reduce structural support requirements, media orientation - tubular media, cross - flow media and random media.

The characteristics of the media are very important since they influence both biofilm development and reactor hydro-dynamics which together influence process efficiency and stability.

Modular high rate biofilm reactors are now available which are robust against hydraulic and organic over-loads/shock loads and capable of handling many dilute to high strength wastewaters with reduced risk of clogging or channeling. Some of the significant advantages of the newer anaerobic filter reactors include the following :

* Adaptability to many wastewaters.
* High organic loading rate reducing reactor volume
* Short HRT
* High BOD/COD removal efficiency
* Tolerance to overloads/shock loads.
* Low energy demand.
* Savings in alkali and nutrient requirements.
* High process reliability.
* Quick start-up and re-start after shutdowns.
* Easy operation and control.
* Ability to handle wastewaters with high TSS after preclarification.
* Periodic backwash of reactor bed.

Many of the above benefits can be realised in well operated properly designed full-scale plants and can often off-set the additional cost of the support media. The absence of expensive media is often quoted as a major advantage of UASB systems. However, many full scale operating plants are often reporting difficulties in the formation and maintenance of flocculated or granular sludge necessary to provide a sludge blanket in the UASB reactor. The reactor is sensitive to hydraulic and organic over-loads/shock loads and sudden changes in wastewater properties. A major limitation of the UASB reactors appear to be related to hydraulic factors and their sensitivity to suspended solids in the wastewaters.

Anaerobic filters are considered to be the most 'robust' to toxicant and organic overloads since the thick growth biofilm can offer protection to the lower layers which can accelerate subsequent recovery after a toxic load.

Variables generally monitored include : pH, volatile fatty acid (VFA), bicarbonate alkalinity, COD, BOD, VSS, wastewater and gas generation rates and composition depending upon the availability of reliable off-line or on-line instrumentation facilities. Even though, the application of automatic control system for anaerobic reactors is rather limited, simpler proportional controllers requiring inexpensive sensors are increasingly used for effective process control of key process variables like pH, temperature and flow rate. Volatile fatty acid and alkalinity concentrations in the reactor are often used as indicators of reactor performance besides the sustained generation of biogas at the design rate and desired composition.

DMCC/BACARDI Modular Biofilm Reactor System For Spentwash

Bacardi Corporation, Puerto Rico has developed and installed a full scale anaerobic filter for handling vinasse (rum slops) a strong wastewater of rum distillery based on fermentation of sugar-cane molasses. This reactor designed as a down flow stationary fixed film (DSFF) reactor and commissioned a decade ago is probably the largest installation of its kind operating in the world handling a high strength waste derived from cane molasses.

Andhra Sugar Limited (ASL), Tanuku, Andhra Pradesh are among the pioneers in this country to adopt the technology of Bacardi Corporatian in late eightees. The technology package is now being offered in India by our organisation. The first plant is installed at Kopargaon Sahakari Sakhar Karkhana Limited, Maharashtra and presently commissioning of this plant is in progress.

DMCC Modular Biofilm Reactor System For Black Liquor

Weak black liquor from pulp washing at 1-1.5% (Black Liquor Solids) is seggregated as a separate stream and sent to a primary clarifier for the removal of fibrous suspended matter. The overflow from the clarifier with Suspended Solids below 100-150 mg/l at 35-45°C is pumped to the anaerobic-upflow stationery fixed film (USFF) reactor as the feed (Figure 1). Experience of the mini-paper mills pulping bagasse/straws shows that the pH of the black liquor would be 7-8 after the sedimentation step and marginal neutralisation may be needed during start-up but not on a continuous basis during plant operation.

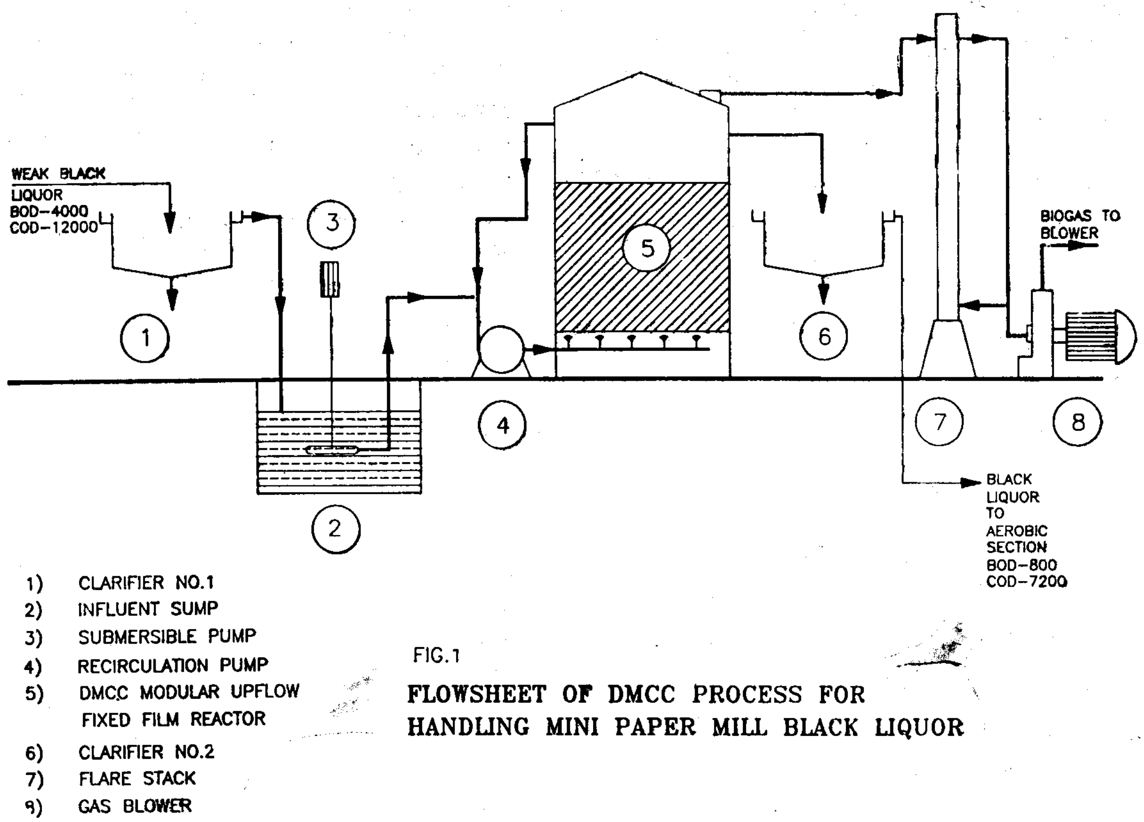

FIG.1

FLOWSHEET OF DMCC PROCESS FOR HANDLING MINI PAPER MILL BLACK LIQUOR

The system designed as an upflow stationery fixed film has a sophisticated distribution system which ensures uniform coverage of the media surface for growth of biofilm. The anaerobic reactor is packed with specially designed media modules which provide a very high specific surface area for the growth of immobilised anaerobic micro-organisms. The specially designed modules contain about 95% voids and provide a zig-zag path for the black liquor flow. This configuration of modules would ensure a better interaction of the organic material and micro-organisms resulting in a high BOD removal efficiency.

The reactor is provided with a set of recirculation pumps and the contents of the anaerobic reactor are kept under constant recirculation. The bottom of the reactor slopes outwardly towards the ports through which the liquid is recirculated by means of recirculation pumps. This helps in increasing solids retention time (SRT) in the reactor. The solids control in the reactor is achieved by maintaining an equilibrium between suspended solids entering and those which are generated in the reactor and then leave the reactor.

Treated effluents from the anaerobic reactor bottom is taken by an overflow pipe out of the reactor to a clarifier.

The biogas generated during the process bubbles out and is collected at the top of the reactor. This gas, which is a readily usable fuel and partly substitutes the fuel required for the mill boiler. The boiler retrofitting would chiefly consist of modifying the burner system and combustion controls for the use of this biogas.

A flare stack provided in the system is connected to a bypass on the outlet gas conveying line to burn any excess biogas that is generated whenever there is a plant shut down.

Performance of operating installations

The salient features of these three installations for spent-wash are summarised in Table 1, which highlights some of the design, operation and performance aspects of the installations at Andhra Sugar Limited, Kopargaon Sahakari Sakhar Karkhana and Bacardi

Corporation. There are additional installations in India based on this technology at Kesar Sugar Works and Indian Turpentine and Rosin Corporation in U.P.

The steam generated through utilisation of biogas as fuel essentially meets the full steam requirement of the distillery in each case. The performance of the Modular Upflow fixed Film Reactor for Black Liquor is given in Table 2.

An estimate of the steam generation potential of a 30 TPD mini-paper mill, as illustrated in Table 2 shows that biogas generated from black liquor by anaerobic treatment can meet about one fifth of the total stream demand assuming steam consumption of 7 ton per ton of paper production. A block diagram for the total treatment scheme inclusive of downstream aerobic processing recommended for handling black liquor is shown in Figure 2. The total scheme shown in Figure 2 will satisfy all the major criteria stipulated by the Central/State Pollution Control Boards with the exception of residual color and COD parameters which will require add-on tertiary treatment facilities with significant recurring expenses.

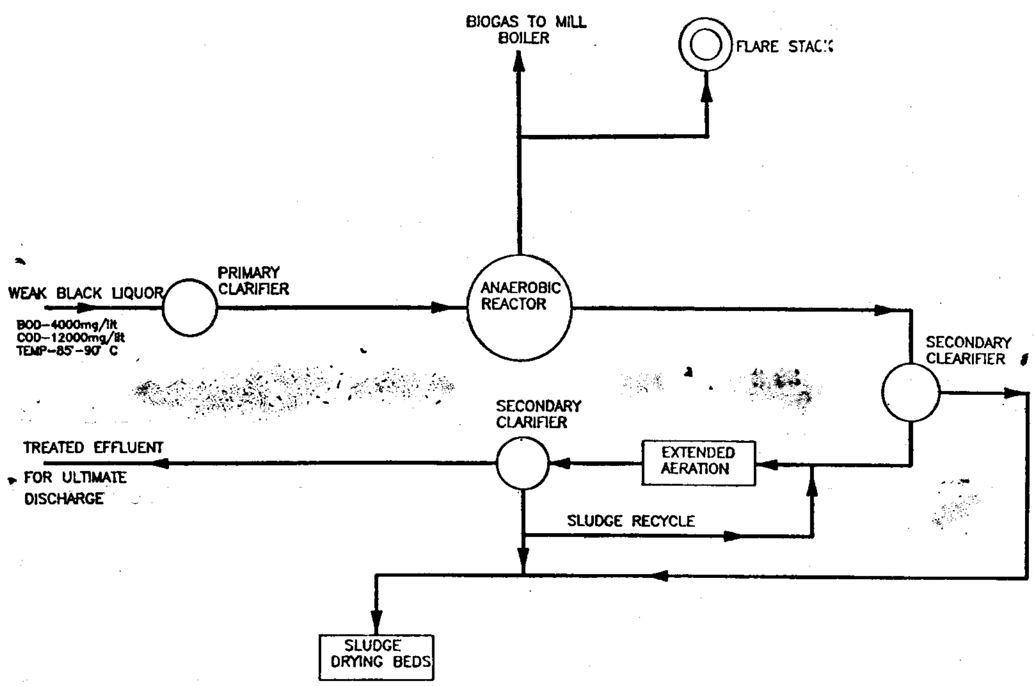

FIG-2
FLOW DIAGRAM OF ANAEROBIC–AEROBIC TREATMENT SCHEME FOR MINI PAPER MILL BLACK LIQUOR

TABLE—1
PERFORMANCE OF BACARDI INSTALLATIONS HANDLING DISTILLERY SPENTWASH

	Parameter	Asl	Kssk	Bacardi
A.	DISTILLERY			
	Alcohol			
	Capacity (KLD)	15	30	100-120
	Spentwash (cum/d)	200-225	450-500	1500-1700
	pH	4-4.2	4.2-4.5	4 2-5
	BOD (g/l)	40-45	40-45	36-42
	COD (g/l)	95-100	90-100	80-105
	TSS (g/l)	3-5	3-5	3-8
	SO_4 (g/l)	4-6	4-6	4-10
	Cl (g/l)	4-6	4-8	—
B	REACTOR			
	Diameter, m	18	24.8	36 6
	Media Height, m	6	6.1	9.1
	Total height, m	12	9.0	12 8
	Media Volume, Cum	1526	3000	9600
	Area Sq. M/Cum	90	100	90
	Loading kg COD/cum/d	10.5	12.5	12.5
C.	BIOGAS			
	Methane (%)	55-60	55-60	50-55
	Rate (cum/kg/COD)	0 5	0.52	0.56
	Generation (cum/d)	6800	13600	48,000
	Energy Potential (Kcal/d)	$33x10^6$	$64x10^6$	$256x10^6$
	Steam Generation (T/d)	40.4	80.8	350
	Steam Demand* (T/d)	37.5	75.0	300
D.	REACTOR PERFORMANCE			
	BOD Removal %	80-82	80-85	75-80
	COD Removal %	67-70	65-70	65-70
	HRT (d)	8-10	8-10	8-10

*Assuming steam requirement of 2 5 kg per kg alcohol production.

It would be relevant to cite here the experience of the Petro Chemical Sector engaged in manufacture of purified terapthatic acid (PTA) - a joint venture of AMOCO and CAPCO at Thailand, who have put up two Down flow Stationery Fixed Film (DSFF) anaerobic filters (volume 10,000 M^3 each) in parallel to generate methane from process wastewater involving a scale-up factor of a million from a ten litre laboratory unit., Incidentally AMOCO got the prestigious biennial Kirkpatrick Chemical Engineering Achievement Award in 1991.

Table—2
DMCC - MODULAR BIOFILM REACTOR SYSTEM FOR BLACK LIQUOR

A.	PULPMILL CAPACITY	30 Tonnes/Day
B	BLACK LIQUOR	
	Cu. M/Day	3500 - 5000
	pH	10.5 - 11
	B. O. D mg/L	3000 - 6000
	C. O. D mg/L	10000 - 20000
	S. S mg/L	1000 - 2000
	SO_4 mg/L	500 - 800
	Cl mg/l	200 - 300
	Color	Dark Brown
	Temperature Degree C	35 - 50
C	DMCC MODULAR BIOFILM REACTOR	
	Diameter, M	33.3
	Total Height M	9.0
	Media Height M	6.1
	Media Volume Cu. M	5300
	Area M^2/M^3	100
	Loading Kg COD / Cu. M Day	9
D	BIOGAS FROM BLACK LIQUOR	
	Methane %	55 - 60
	Specific Rate Cu M/Kg. Cod Removed	0.52
	Generation Cu M/Day	6650
	Energy Potential KCAL/DAY	32 x 10^6
	Steam Generation T/D	40
	*Steam Demand	200
E	DMCC MODULAR FILM REACTOR PERFORMANCE	
	B. O. D Removal %	80 - 85
	C. O D Removal %	60 - 65
	H. R T. D	1.5
	*Steam Demand	6 - 8 Tonnes/Per tonne of paper

CONCLUSION

The anerobic filter, particularly of the downflow stationary fixed film type, has proven itself as a versatile means to treat high strength waste water such as distillery spent-wash and PTA effluents. Application of a modified reactor system with upflow configuration for the treatment of black liquor from bagasse/straw based paper mills is under way. Further possibilities of using this technique can be explored in other industries such as dairies, breweries and organic chemical industries which generate wastewater with high levels of BOD and COD.

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