DEVELOPMENT OF A HIGH-RATE ANAEROBIC BIOREACTOR FOR ENERGY PRODUCTION FROM RICE-MILL EFFLUENT

By
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THESIS

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2009

DECLARATION

I hereby declare that this thesis entitled '**Development of a High-rate Anaerobic Bioreactor for Energy Production from Rice-mill Effluent'** is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, fellowship or associateship or other similar title of any other University or Society.

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CERTIFICATE

Certified that this thesis entitled '**Development of a High-rate Anaerobic Bioreactor for Energy Production from Rice-mill Effluent'** is a record of research work done independently by Sri. JoeJoe L. Bovas under my guidance and supervision and that it has not previously formed the basis for the award of any degree, diploma, fellowship or associateship to him.

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SYMBOLS AND ABBREVIATIONS

^{0}C - Degree Celsius
% - Percentage
Ø - Diameter
AAFEB - Anaerobic Attached Film Expanded Bed
ABR - Anaerobic baffled reactor
AFFR - Anaerobic fixed film reactor
ASAE - American Society of Agricultural Engineers
AUBF - Anaerobic Upflow Bed Filter
BOD - Biochemical Oxygen Demand
COD - Chemical Oxygen Demand
CSFE - Cassava starch factory effluent
d - day
DO - Dissolved oxygen
GSS - Gas Solids Separator
h - hour
HUASB - Hybrid Upflow Anaerobic Sludge Blanket
HLR - Hydraulic loading rate
HRT - Hydraulic retention time
ID - Internal diameter
ℓ - litre
LED - Light emitting diode
m - Metre

mg	-	Milligram
mℓ	-	millilitre
mm	-	Millimetre
nm	-	Nanometre
OLR	-	Organic loading rate
PSS	-	Pseudo Steady State
RME	-	Rice mill effluent
SRT	-	Solids retention time
TKN	-	Total Kjeldahl Nitrogen
TOC	-	Total Organic Carbon
TS	-	Total solids
TSS	-	Total suspended solids
UAF	-	Upflow Anaerobic Filter
UAHR	-	Upflow Anaerobic Hybrid Reactor
UASB	-	Upflow Anaerobic Sludge Blanket
ULV	-	Upflow liquid velocity
v/v	-	Volume/volume
VFA	-	Volatile Fatty Acids
VLR	-	Volumetric loading rate
VS	-	Volatile solids
VSS	-	Volatile suspended solids

INTRODUCTION

Chapter I

INTRODUCTION

Unmanaged organic waste fractions from farming, industry and municipalities decompose in the environment, resulting in large-scale contamination of land, water and air. The industries alone contribute millions of litres of effluent every year. These wastes not only represent a threat to environmental quality, but also possess a potential energy value that is not fully utilised despite the fact that they are abundant in most parts of the world. Methane (CH_4) and carbon dioxide (CO_2) emitted as a result of microbial activity under uncontrolled anaerobic conditions at dumping sites are released into the atmosphere and contribute to global warming (Bohdziewicz *et al.,* 2008). The Kyoto Protocol of 1997, signed by more than 60 countries, calls for specific steps to be taken by the different parties involved (Morrissey and Justus 1999). The developed nations which contribute approximately 80% of global greenhouse gas emissions are committed to reducing CO_2 equivalents by an average of 5.2% by 2008-2012, compared with 1990 emissions.

In the past 10 years, the industrial use of bioprocesses has increased drastically. Biological processes are widely applied in wastewater treatment and play an important role today (Liu *et al*., 2005). The production of methane via anaerobic digestion of agricultural residues and industrial organic wastewaters would benefit society by providing a clean fuel from renewable feed stocks. This would reduce the use of fossil-fuel-derived energy and reduce environmental impact, including global warming and pollution. The spiraling costs of imported fuel oil and natural gas have prompted nations to conserve their own limited fuel increasingly used for appliances, vehicles and power generation. Better waste management will also lead to other environmental benefits, such as reduction of surface water and groundwater contamination, transformation of organic waste into high-quality fertilizer and preventing wastage of land and resources (Ayalon *et al.*, 2001, Kashyap *et al*., 2003).

For a country like India where energy continues to be precious, anaerobic digestion has far greater relevance than it has to many other regions of the world. Conversion of organic matter to methane by anaerobic digestion has several advantages over gasification procedures since it is applicable to most types of high-moisture content organic feeds and is operated at low temperature and pressure with relatively high overall thermal efficiencies. The biogas technology is a relatively simple one and research on the utilization of biogas for thermal, electrical and mechanical power generation is well advanced (James and Kamaraj, 2002).

1.1 High Rate Anaerobic Digesters

Anaerobic treatment is a process where organic matter is digested to methane and carbon dioxide in the absence of oxygen. Although the process has been recognized for its ability to treat organic wastes for decades, until recently its application in industrial organic liquid wastes was not promoted (Araujo et al., 2008). The reason for the lack of popularity for its application in industrial organic (effluent treatment) had been due to the slow rate and process instability of anaerobic digestion. The slow rate means large digester volumes resulting in greater costs and more space requirements. Process instability means lack of assurance of steady energy supply (Andras et *al*., 1989; James and Kamarj, 2004). But this situation is poised to change dramatically as a result of a string of breakthroughs which have occurred in recent years. Introduction of anaerobic filter, up-flow anaerobic sludge blanket reactor, expanded / fluidized bed anaerobic reactor and hybrid bioreactors have brought down the hydraulic retention times (HRTs) of anaerobic digesters from 35-40 days of typical unstirred reactors (like conventional biogas digesters) to a few hours. Such drastic reduction in HRT has a dramatically favorable impact in terms of smaller digester sizes and consequently lesser digester costs. Further, it has opened the possibility of treating high-volume low-strength wastes such as industrial waste water and sewage by anaerobic process. Such wastes earlier could be speedily treated only by the aerobic processes which were considered as faster than anaerobic processes.

The high rate anaerobic treatment, however, is one of the most effective ways of minimizing the concentration of organic matter in the wastewater. This is achieved by immobilizing the microbes inside the reactor. One of the most efficient and quite flexible designs available is an upflow anaerobic hybrid reactor (UAHR) which combines the advantages of both anaerobic filter and upflow anaerobic sludge blanket designs. Attempts to retain and extend the existence of the active biomass inside the reactor is indeed desirable as it enables the anaerobic bio reactors to overcome the most important handicap ie., slow rate of waste water treatment. The UAHR essentially use media located in the upper part of the reactor to which anaerobic bacteria gets attached.

1.2 Production of parboiled rice

Rice is consumed as raw rice and par boiled rice. Accordingly, rice mills process paddy to produce one or a combination of both. In par boiling process the cleaned paddy is soaked in hot water for about six hours and then steam is bubbled into the soak tank for 15 minutes. After steaming the water in the soaking tank is drained out as effluent. Parboiled rice production generally requires large amount of water for soaking of paddy. This effluent if not properly treated could result in water pollution and odour nuisance to residents. Pollution to ground water is an important menace caused by high levels of organic material present in rice mill effluent.

1.3 Rice mill effluent and its environmental significance

The continuous discharge of rice mill effluent in and around the rice mills end up in soil sickness affecting the normal growth of the natural flora. Although the effluents discharged from rice mills do not contain any toxic compound or pathogenic bacteria, repeatedly discharging them into the open pose a public health hazard, as the stagnant water not only encourages a variety of organisms but also emits bad odours which are carried long distances by wind (Ramalingam and Raj, 1996). Rice mill effluent requires treatment to reduce its uncontrolled degradation at disposal sites and subsequent greenhouse gas and order emissions. At the same time most rice processing industries experience energy shortages. Anaerobic digestion has high significance due to its positive environmental value arising from its waste treatment ability which combines pollution control along with energy production.

1.4 Objectives

The objectives of the present investigation were to make available the recent breakthroughs in anaerobic digestion in the treatment of rice mill effluent (RME) through high rate biomethanation. This is expected to overcome the technological and economical barriers that prevent the popular acceptance of this technology by small scale as well as large scale rice processing industries. The following were the specific objectives of the study:

a) To study the characteristics of RME.

b) To conduct preliminary studies on anaerobic digestion of rice mill effluent (RME).

c) To design a high rate anaerobic bioreactor and fabricate lab scale models for anaerobic digestion of RME.

d) To evaluate the developed laboratory scale bioreactors at varying operating conditions.

REVIEW OF LITERATURE

Chapter II

REVIEW OF LITERATURE

A review of the research work on rice mill effluent production and its characteristics, biomethanation of industrial effluents and development of high rate anaerobic bioreactors is attempted in this chapter.

2.1 Production of effluent form rice mills and its characteristics

Currently, rice is the most important cereals in the World, being the basic constituent of the diet in Asia. Rice is the stable food of Keralites and the annual rice production in Kerala is 641575 tones in 2006-07 (FIB 2009). In India the rice for human consumption is processed in the form of raw rice and Parboiled rice. Accordingly the mills process paddy to produce one or a combination of both. Parboiling is one of the most important improvement process before milling of paddy. The parboiling process involves significant water consumption resulting in a considerable volume of effluent. These effluents are organic in nature and the characteristics of this effluent are suitable for biological treatment (Queiroz *et al.*, 2007).

2.1.1. Paddy parboiling process and water requirement.

Paddy is milled raw or after parboiling. Parboiling is an ancient method of pre-milling treatment given to paddy to improve the milling characteristics. The process involves soaking, steaming and drying. The conventional rice mills follow the traditional cold-soaking and double steaming methods, wherein paddy is soaked for 2

Queiroz *et al.* (2007) stated that the parboiling process involves significant water consumption and on an average it consumes 4 m^3 of water per ton of processed grain thus resulting in production of a considerable volume of effluent produced.

2.1.2 Characteristics of waste water from rice mills

Ramalingam and Raj (1996) studied the soak water characteristics in various paddy parboiling methods in which they found that, in the traditional cold-soaking and double steaming method, the paddy is soaked for 2-3 days resulting in the development of a characteristic off-odour due to fermentative changes during soaking. In modern rice mills where hot soaking is used, the soak water is discharged repeatedly over a localised area which stagnates and emanates an off-odour. The soak water from hot soaking showed higher level of reducing and total sugars, amino nitrogen and phenol content compared to traditional process.

Queiroz *et al.* (2007) studied the wastewater treatment from rice parboiling and found that total nitrogen in the waste water varies between 25.40–95.04 mg/ℓ and COD in the range 2578– 5022 mg/ℓ. The average C/N ratio was 73.84, higher than that required for development of the micro-organisms.

2.2 Biomethanation of food processing and agro-industrial effluents.

Biogas is produced by the anaerobic fermentation of organic materials. Biomethanation or anaerobic fermentation can be described as the biological process that takes place in the absence of air. The biogas consists of 60 to 70 per cent methane, 30 to 40 percent carbon dioxide (CO_2) and traces of ammonia, hydrogen sulphide, and other gases like hydrogen. The phenomenon of biomethanation was first observed by Alessandro Volta of Italy in 1776. In 1806 William Henry reported that the gas observed by Volta was similar to methane. Humphrey Davy in the early 1800's conducted the first laboratory experiments to produce methane from organic wastes. The micro-organisms involved in the production of biogas are anaerobic bacteria. As organic matter and action of anaerobic bacteria on the substrate are complex in nature, it is difficult to predict the behaviour of such wastes in the digester (Chawla, 1986). A review of past experiences in the anaerobic digestion of agro-industrial effluents and food processing wastes are essential for the system design as well as fixing the process parameters like HRT, HLR and organic loading rates for evaluation of the system.

The anaerobic digestion involves the consecutive but simultaneous phases of operation of the solubilising, acidification and methanogenesis. In the solubilising phase, the bacteria break down the complex organic matters in the feedstock. In the second phase the bacteria reduces the soluble organic materials from the first step to soluble simple organic acids and in the final phase the methanogenic bacteria reduce the organic acids to methane and CO_2 (Chawla, 1986; Mittal, 1996) .

Toxic substances like heavy metals and cyanide can inhibit the micro-organisms (Chawla, 1986; Mathur and Rathore, 1992). Cenni *et al.* (1982) conducted anaerobic digestion studies on tannery wastes in laboratory scale reactors. They found a slow rate of gas production possibly due to the inhibition of toxic substance added in tannery processes. Food processing wastes are in general organic in nature with practically little inhibitory materials.

Landine *et al.* (1983) conducted a lab treatability study of high strength, high solids potato processing wastewater. They observed a COD removal of over 96 per cent at a loading rate of 1.16 $kg/m^3.d$ at an HRT of 4.5 days. Yang *et al.* (1984) examined the bio gasification of papaya processing wastes and found that HRT can be reduced by sludge recycling.

Calzada *et al.* (1984) experimented with one and two phase anaerobic systems for biomethanation of coffee pulp juice. They found that a bi-phasic system with 0.5 and 8 day HRTs respectively for acidogenic and methanogenic phases produced stable condition.

Ranade *et al.* (1989) could obtain a biogas yield of 261 ℓ from confectionery wastes generated by biscuit and chocolate manufacturing plant in 180 ℓ capacity plants at a HRT of 40 days.

Sarada and Joseph (1994) studied the influence of HRT, OLR and temperature on methane (CH_4) production rate and yield during anaerobic digestion of tomato processing waste. They could get a biogas production of 0.7 m^3/m^3.d.

Borja *et al.* (1996) studied the anaerobic digestion of wash waters derived from the purification of virgin olive oil. The HRT ranged from 0·20 to 1·02 days under normal operating conditions after the start-up. COD removal efficiencies of more than 89 per cent were achieved at an OLR of 8·0 kg COD/m^3 day.

Kalyuzhnyi and Davlyatshina (1997) observed that among the factors influencing the process kinetics in anaerobic digestion of glucose, hydrogen concentration and pH value have the primary significance.

Chaiprasert *et al.* (2003) evaluated the ability to remove organic compounds in cassava starch wastewater through anaerobic digestion. When the OLR was increased stepwise from 0.5 to 4.0 kg COD/m^3.d and the HRT shortened to 5.4 days, with a COD removal efficiency of 87 per cent.

James and Kamaraj (2004) treated cassava starch factory effluent (CSFE) in anaerobic conditions. They reported that initial neutralization is not necessary for the biomethanation of CSFE and reported a TS reduction of 54.3 percent.

Chelliapan *et al.* (2006) conducted anaerobic digestion studies on pharmaceutical wastewater containing macrolide antibiotics and found that anaerobic digestion could considerably reduce the antibody population in the effluent.

A laboratory-scale study conducted by Kumar *et al.* (2007) on anaerobic biodegradation of distillery-spent wash demonstrated that at optimum HRT of 5 days and an OLR of 8.7 kg COD/m^3.d, the COD removal efficiency of 79 per cent could be achieved.

Zhu *et al*. (2008) conducted a laboratory-scale study on the anaerobic digestion of soybean protein processing wastewater. It was found that the COD removal efficiencies were 92–97 per cent at a feed rate of 1.2–6.0 kg COD/m^3.d.

Krishna *et al.* (2008) conducted an anaerobic digestion study on the treatment of a low strength complex wastewater operated at HRTs of 20, 15, 10, 8 and 6 h with OLRs of 0.6, 0.8, 1.2, 1.5 and 2 kg COD/m^3.d. It was inferred that even at the maximum OLR of 2 kg COD/m^3.d, COD and BOD removals exceeded 88 per cent.

The study conducted by Gannoun *et al*. (2008) on cheese whey wastewaters could reveal that 80 – 90 per cent of COD removal was possible from it, if the effluent is pre-treated. Otherwise, inhibition caused by fats and proteins could lower the reactor performance. Pre-treatment removed about 50 per cent of COD and 60 per cent TSS. On an average total COD removal achieved was 80–90 per cent at 2 day HRT.

2.2.1 Anaerobic digestion of rice mill effluent

The parboiling process involves significant water consumption, the average equal to 4 m^3/ton of processed grain, resulting in a considerable volume of effluent. (Queiroz *et al.*, 2007) studied the biomethanation characteristics of the rice parboiling effluent in a 4.5 ℓ cylindrical batch bioreactor operated at 30^{0}C. He found that biological treatment of rice mill effluent was possible.

2.3 High rate anaerobic bioreactors

Biological processes for wastewater treatment are generally classified as aerobic processes and anaerobic processes (Barnes and Fitzgerald, 1987). The choice between aerobic and anaerobic processes has tended to favour the former in the past because the systems were considered to be more reliable, more stable and better understood in spite of the positive energy recovery aspect of the latter. But, with the advent of anaerobic high rate processes, the waste water treatment scenario has witnessed a tremendous change in favour of anaerobic processes (Lettinga, 1984).

In the anaerobic fixed film reactors like Up flow Anaerobic Filters (UAFs), the biological solids or active biomass become attached to the support surfaces and are also entrapped as flocs in the void spaces between the support matrix particles (Young and McCarty, 1969). In the UASB reactor (Lettinga *et al*., 1980), biological growth is in the form of granules which grow initially around a tiny support particle and are retained at high concentration within the reactor by a gas-solids separator device.

Jewell *et al*. (1981) attempted to develop an optimum biological reactor that would accumulate a maximum active attached biomass, the process referred to as Anaerobic Attached Film Expanded Bed (AAFEB) system.

Anaerobic Hybrid digesters are among the newer designs instigated by Guiot and Van der Berg (1984). This process combines the advantages of both the anaerobic fixed film reactor and the UASB.

Biomass accumulation on supporting media in a form of bio film is a complex process. Physicochemical and microbial forces are significantly involved in the initiation and stabilization of the bio film. For a microbial cell to attach to a surface properly, hydrodynamic shear force played a key role on the bio films characteristics (Connauyhton *et al*., 2006) and contributed directly to its qualities such as density, shape, thickness, and strength (Jianlong *et al*., 2000). Both liquid and gas up flow velocities are regarded in this category and can promote both the attachment and detachment of the film depending on the intensity of the flow and surface characteristics.

The fluidized bed process relies on the retention, within the reactor of a fluidized bed of bio-layer covered particles (Heijnen *et al*., 1989). The bio-layer covered particles are maintained in a fluidised state by an upwards directed flow of water. The fluidised bed anaerobic bioreactors are highly engineered systems and require expertise in operation and maintenance (James and Kamaraj, 2002).

2.3.1 Development of different anaerobic high rate reactor designs

In the last four decades, much progress has been achieved in understanding the fundamentals of the anaerobic process as well as in the in the design of bioreactors. A review of these developments is essential in designing new high rate bioreactors for rice mill effluent. A brief summary of the research and development activities in the area of anaerobic high rate reactors are outlined in this section.

2.3.1.1 Up flow Anaerobic filter (UAF)

The anaerobic filter systems initially developed by Young and McCarty (1969) consists essentially of a column packed with an inert support material such as gravel, ceramic, fired clay etc. If the feed inlet for the anaerobic filter is at the bottom of the unit, thereby creating an upward flow through the submerged matrix, the system is referred as Up flow Anaerobic Filter (UAF). The biomass in the reactor is attached to the media surfaces as a thin bio film as well as entrapped within the media matrix.

The application of the UAF design to a variety of soluble wastes was subsequently investigated by El-Shafie and Bloodgood (1973), Jennet and Dennis (1975), Mueller and Mancini (1977), Mosey (1978), Donovan (1981) and Young (1981). Newell (1981) experimented with a waste containing milk washings from a dairy plant and waste from a pig fattening unit. The percentage COD removal was 82 per cent with an average methane content of 82 per cent CH_4 at a HRT of 0.5 days for dairy plant wastes. The digestion of pig slurry supernatant at a HRT of 3 days could yield 20 m^3/m^3 biogas with 80 – 85 per cent CH_4. The average COD and BOD removals were 88 per cent at a loading rate of 19.6 kg COD m^3/d. Corrondo *et al.* (1983) studied the performance of anaerobic filters for treating molasses fermentation waste water at loading rates varying from 2 – 12 kg COD/m^3.d corresponding to HRTs 2.5 to 5 day. They could achieve 57 – 79 per cent COD reduction. Wastewater from a sugar refinery plant with a COD of 6000 – 13000 mg/ℓ has been successfully treated by Tesch *et al.* (1983). At a hydraulic retention time of 27 hours, a COD removal of

75 per cent has been obtained. To reduce the cost, clay media was used as biomass support.

Young and Dahab (1983) reported treatment of waste water from an alcohol producing plant in UAF with different media and reported a specific biogas yield of 0.38 m^3 CH_4/kg COD added at loading rates above 2 kg COD/m^3.d. Badrinath and Kaul (1984) reported on studies with two anaerobic filters operated in series for primary treatment of distillery waste waters at organic loads varying from 2 to 90 kg COD/m^3.d corresponding to HRTs 11.8 – 0.26 day. The first filter gave 83 – 36 per cent COD removal and the second 72 – 28 per cent.

Sanna *et al*. (1984) experimented with a pilot scale UAF to treat sugar refinery waste water. They got a maximum gas production of 11.5 volume/ reactor operating volume/ day with a reduction of BOD and VS up to 80 per cent and COD up to 70 per cent at a HRT of less than one day.

Wheatley *et al*. (1984) experimented with a UAF of 10 m^3 capacity to treat the waste from a sweet factory. They found that COD removals of up to 80 per cent can be achieved at economic HRTs of 24 – 30 hours at loads of 5 – 15 kg COD/m^3.d. Gas yields were between 0.5 – 0.7 m^3/kg COD removed with 50 – 70 per cent CH_4.

Lo and Liao (1985) could operate lab scale fixed film reactors receiving screened dairy manure at HRTs from 15 to 1 day. The highest methane yield of 0.104 litre CH_4/g VS_{added} occurred at 10 day HRT and 3.40 g VS/ ℓ.d loading rate. The corresponding COD and VS reduction efficiencies were 17.2 per cent and 21.3 per cent respectively.

Start-up characteristics of anaerobic fixed bed reactors were investigated by Nordstedt and Thomas (1985[a]). They used two media types viz., pine wood chips and plastic rings. The test HRT was 2 days for regular feeding which commenced after the experimental incubation periods of 5, 10 and 10 day with pH control. The reactor did not achieve stable operation or indicate that start-up would occur within 30 days without pH control. They found that a 20 per cent mixture of seed inoculum with the feed stock was sufficient to start a fixed bed reactor when a 10 day incubation period was provided with pH control.

Henry (1985) described the commercial venture of SGN anaerobic digestion process. They constructed industrial demonstration plants for treatment of distillery spent wash and pig manure. The reactors operated at loading rates of 5 – 22 kg COD /m^3.d with BOD reduction 85 – 90 per cent. A BOD reduction of 98 per cent was achieved after a secondary aerobic treatment. The plant capacities ranged between 100 m^3 to 4400 m^3. The media used were 3 inch diameter plastic rings.

Gadre and Godbole (1986) while treating distillery effluent by laboratory scale upflow anaerobic filters, at a HRT of 15 days with stone rubble of 25 mm mean diameter as filter media, the COD removal was 60 per cent and 44 per cent for dilute and raw effluent respectively.

Subrahmanyam and Sastry (1989) described the secondary treatment of effluent from a primary anaerobic lagoon treating distillery wastewater in a two stage UAF. They used the COD loading rates of 8.33, 12.50, 16.65, 25 and 50 kg COD/m^3.d corresponding to HRTs 144, 96, 72, 48 and 24 hours respectively. Filter I and II gave 76.5 to 49.5 per cent and 70.2 to 47.7 per cent COD removals. Even at 144 hour HRT, the effluent had a high COD of 3500 mg/ℓ due to non-biodegradable constituents in the waste water. The specific biogas yield for the unit was 0.484 to 0.326 m^3 CH_4/kg COD_{added}.

Andreoni *et al.* (1990) experimented with UAFs having two different packing media (wood chips and PVC media) to treat swine slurry mixed with pyrolignitic acids. The two digesters had almost the same efficiency when treating swine slurry containing 6.5 per cent pyrolignitic acids. Higher concentrations reduced the performance of both reactors and wood chips reactor was found to be more resistant.

Lo and Liao (1990) studied the treatment of baker's yeast waste water in a fixed film reactor with PVC fixed film supports roughened by sand blasting. Even after a four months operating period they could obtain only 0.46 ℓ CH_4/ℓ.d. They found that the presence of high sulphate concentration in bakers yeast wastewater prolonged the start-up process in the fixed film reactor which had no biomass attached to it.

Marques *et al.* (1990) used two lab scale anaerobic filters to study the anaerobic biodegradation of milk factory waste water. They used randomly packed PVC pipe pieces as media. The range of COD loading was between 0.75 g COD/ℓ. day to 4.5 g COD/ℓ. day. The study was performed on HRT basis, which covered 24 – 48 hours with COD removal efficiencies 77 – 93 per cent.

The effect of temperature on treatment of dairy waste water was investigated by Viraraghavan and Kikkeri (1990). The reactors were operated at HRTs of 1 – 6 days at 12.5°C, 21°C and 30°C. It was found that the UAF could be started up at 21°C without any adverse effects. Temperature effects were not pronounced at long HRTs. At a HRT of 4 days, average COD removals in the three UAFs were found to reduce from 92 per cent at 30°C to 78 per cent at 12.5°C. Gas production was also low at lower temperature but the gas had higher CH_4 content.

Weiland and Thomsen (1990) reported that distillery slops from a multi-crop ethanol plant, for which the composition and load changes throughout the year, could be treated in a fixed film reactor of 1800 m^3 reactor volume. The load applied was up to 10 kg COD/m^3.d at a HRT of 5 days with COD removals of 85 – 90 per cent.

Sharma and Bandyopadhyay (1991) used a lab scale UAF for treatment of pulp and paper mill effluent. Effluent was fed to UAF at different COD concentrations from 1000 to 6000 mg/ℓ and the performance studied for different hydraulic loading rates. Maximum COD removal of 84.38 per cent was achieved for an influent COD concentration of 4182.5 mg/ℓ at a hydraulic loading rate of 129.92 ℓ/m^3d. A methane yield of 0.425 ℓ/g COD destroyed was obtained at a COD loading rate of 0.431 kg/ m^3.d.

Yap *et al.* (1992) used a 20 litre anaerobic bio-filter, packed with expanded clay pellets to treat 2-EHA, a component in a pharmaceutical plant effluent. The bio filter was operated at HRTs from 20 to 0.83 days with an influent 2-EHA concentration of 8200 mg/ℓ. The performance was optimum in terms of COD removal rate at 1.1 day HRT. COD removal efficiency was 92.8 per cent and the biogas production rate averaged 128.7 ℓ/d with 83 per cent methane. The COD removal efficiency was 20.1 per cent when the system failed at a HRT of 0.83 day.

Jianmin *et al*. (1993) reported that bacterial acclimation in anaerobic phenol bearing waste water treatment process is very difficult in general. The study revealed that adopting suitable acclimation methods, digestion of high concentrated phenol bearing waste water was feasible and was advantageous over other methods. They could get 89.3 – 97 per cent phenol removal efficiency when the influent phenol concentrations ranged from 1635 – 2200 mg/ℓ.

Monroy *et al*. (1994) presented the results from a pilot scale UAF for the treatment of the waste water from ice cream manufacture. The reactor was completely mixed by gas production but the solids or sludge held within the reactor was shown to be affected by the liquid velocities. Daily loading rates varied from 0 – 18 kg COD /m^3.d with an average load of 5.5 kg/m^3.d and the mean COD removal was 70 per cent.

Anaerobic treatment of waste water from a seafood processing plant was conducted by Prasertsan *et al*. (1994) at organic loading rates ranging from 0.3 to 1.8 kg COD /m^3.d at HRTs ranging from 36 to 6 days. PVC rings were used as packing media in the lab scale anaerobic filter. More than 75 per cent COD reduction could be maintained up to an OLR of about 1 kg COD /m^3.d at a HRT of 11 days. An OLR of 1.3 kg COD/m^3.d corresponding to a HRT of 6.6 days gave maximal biogas productivity of 1.5 m^3/m^3.d or 1.3 m^3/ kg COD with a 65 per cent COD reduction.

Anaerobic treatment of phenol bearing dyestuff waste water in UAFs was investigated by Kanekar and Kelkar (1995). The reactors were initially stabilized on cattle dung and the feed was gradually replaced by dyestuff waste water. The treatment resulted in 91 – 94 per cent removal in phenol and 61 – 54 per cent in COD.

The biogas production was 481.3 – 502.8 mℓ/ ℓ of feed and 114.4 to 120.7 ℓ /kg COD with 67 per cent CH_4.

Anaerobic fixed film reactors like UAF reactors are considered stable in operation. The responses of an anaerobic fixed film reactor to hydraulic shock loadings were studied by Chua *et al.* (1997). The AFFR was started up with a synthetic waste water of 3000 mg COD/ℓ at 5 d HRT achieving 98 per cent COD removal efficiency. When stable operation was attained, the HRT was sporadically adjusted to 2.5, 1.25, 1 and 0.5 d to simulate hydraulic shock loading of 2, 4, 5 and 10 times respectively. The COD removal efficiency was temporarily reduced at 2, 4 and 5 times shock loadings and the AFFR could recover from the inhibition. But 10 times shock loading resulted in the failure of the reactor.

The continuous treatment of fish meal processing waste waters was carried out by Guerrero *et al.* (1997) in a mesophilic UAF. They found that recycle ratio was a key factor in performance. Around 90 per cent of the total COD could be anaerobically degraded with 80 per cent COD removal efficiency.

Umana *et al.* (2008) evaluated laboratory-scale anaerobic fixed bed reactors by treating with dairy manure in an upflow mode and semi-continuous feeding. The effluent quality improved when the hydraulic retention time (HRT) increased from 1.0 to 5.5 days. Methane yield was also found to be a function of the HRT.

Acharya *et al.* (2008) studied the anaerobic digestion of wastewater from a distillery industry in a continuously fed, upflow fixed film column reactor under varying hydraulic retention time and organic loading rates. The seed consortium was prepared by enrichment with distillery spent wash. At 8 d HRT with an organic loading rate of 23.25 kg COD m^{-3} d^{-1}, the COD removal efficiency was found to be 64 per cent with a biogas production of 7.2 m^3 m^{-3} d^{-1}.

Gannoun *et al.* (2008) investigated the anaerobic digestion of cheese whey wastewaters in an upflow anaerobic filter. A pre-treatment was conducted to solve the inhibition problems during anaerobic treatment of cheese whey caused by fats and proteins and the major problem of clogging in the reactor. The pre-treatment of diluted cheese whey induced removal yields of 50 per cent of COD and 60 per cent of TSS at 32 °C. The average total COD removals achieved was 80–90 per cent. Significant methane yield of 280 ℓ/kg COD $_{\text{removed}}$ was obtained at an HRT of 2 days.

2.3.1.2 Development of Upflow Anaerobic Sludge Blanket (UASB) Reactor Systems:

The UASB reactor concept (Lettinga *et al*., 1980, Lettinga *et al*., 1983, Lettinga *et al*., 1984, Lettinga and Hulshoff pol, 1986) is based on the inherent settling properties of anaerobic sludge and relies on the formation of well settleable flocculent or granular type of anaerobic sludge.

The biomass in the anaerobic sludge blanket reactor is immobilized in the reactor by development of highly settleable bacterial granules of 1 to 5 mm diameter. It was possible to achieve high loading rates once the granular sludge was formed. But the granulation process did not occur with all wastes, like slaughter house wastes and raw sewage. A UASB system could be started up easily if reactors could be seeded from granulated sludge from an existing system.

Application of the UASB reactor for anaerobic treatment of paper and board mill effluent was examined by Habets and Knelissen (1985). They studied the feasibility at lab scale and pilot scale and found that the anaerobic seed sludge granulated at 31 and 17 weeks respectively. Organic loadings of 8 – 18 kg COD/m^3.d was applied with COD removals from 60 to 70 per cent with 0.39 m^3 biogas production per kg COD removed. The minimum HRT attained was 2.5 hours. In a full-scale plant of 70 m^3 they could obtain granulation within 10 weeks, by the use of 20 m^3 of pre-granulated sludge as seeding material.

Even though earlier workers reported difficulties in granulation with dairy waste waters, Yan *et al*. (1988) could treat cheese whey in a 17.5 litre laboratory scale UASB reactor over a wide range of HRTs and organic loading rates. At constant influent strength, the methane production rate (litre CH_4/g COD) decreased with decreasing HRT. At constant HRT, the methane production rate increased with influent strength. A high treatment efficiency of 98 per cent COD removal was achieved.

Goodwin *et al.* (1990) experimented with a set of 10 laboratory scale UASB reactors for digestion of ice-cream wastewaters. An alternative carbon source and other additives were tried. The results showed that the waste itself was capable of being treated by UASB process at a low retention time of 18.4 h with around 87 per cent TOC removal efficiency. Granulation commenced after 60 – 70 days in the lab scale reactors.

Kosaric *et al.* (1990^a) operated laboratory scale UASB reactors with a synthetic wastewater with a mixture of acetic, propionic and buteric acids in the ratio 4:1:1 (w/v). They seeded the reactors with granules from a pilot plant. They found that the granules were maintained in the reactors in an active state and COD conversion up to 100 per cent was obtained. The specific organic loading rate of 1.5 g COD/g VSS. d was found to be optimum.

Wambeke *et al.* (1990) studied the performance of a UASB reactor treating potato processing waste water. The waste water was passed through a primary settler and an equalization tank before it passed on to the UASB reactor. The 1000 m^3 reactor was initially seeded with 300 m^3 sludge. They could achieve a 90 per cent removal of soluble COD with 2.6 m^3/m^3.d biogas production with 88 per cent methane. In spite of the high OLR applied and strong fluctuations in flow and influent concentration the reactor exhibited a stable and efficient performance.

The sludge and substrate profiles in the digestion of cheese whey using UASB process was investigated by Yan *et al.* (1990). The results indicated that two sludge distribution regions, a sludge bed and a sludge blanket as well as two distinct reaction phases, acidogenic and methanogenic were formed. The acidogenic region extended into the methanogenic region in the upper portion, when the substrate loading was increased. When the whole region became acidogenic, the reactor failed.

Vieira and Garcia (1992) also reported on the satisfactory performance obtained from a 120 m^3 UASB reactor for domestic waste water treatment. The HRTs ranged from 5 to 15 hours, resulting in an effluent with 50 to 150 mg COD/ℓ and 40 to 85 mg BOD/ℓ.

Berruta and Castrillon (1992) treated leachates from the solid urban wastes land fill in UASB reactors. The gas production was up to theoretical values with 84 per cent CH_4 content. The highest percentage of COD removal was 88 per cent at a HRT 2.4 days.

Shin *et al.* (1992) reported the anaerobic digestion of distillery waste water in a two phase UASB system. The phase separation was achieved by adjusting pH in each reactor. Loading rate up to 44 kg COD/m^3.d could be applied in the methanogenic phase while removing 80 per cent of influent COD with a specific gas production of 16.5 ℓ/ℓ. day.

Fang *et al.* (1995) treated wastewater with concentrated butyrate in a 2.8 ℓ, UASB reactor. The process consistently removed 97 to 99 per cent of COD for loading rates up to 31 g COD/ ℓ.d. Of all the COD removed, 94.5 per cent was converted to methane and the average sludge yield was 0.037 g VSS/g COD.

Singh *et al.* (1996) investigated the treatment of a low strength synthetic waste water by a semi pilot scale UASB reactor. Under ambient temperature conditions (20 to 35°C) with a HRT of 3 h and OLR of 4 kg COD/ m^3.d, 90 to 92 per cent COD and 94 to 96 per cent BOD reductions were achieved. Methane production was found to be about 141 ℓ /kg $COD_{removed}$.

The performance of a pilot scale UASB reactor at a HRT of 7.6 hours was tested by Behling *et al.* (1997) for the treatment of domestic sewage. In spite of the use of a pre-granulated sludge as inoculum, the start-up period was about 90 days. Alkali was added to the reactor to attain stability. The COD removal efficiency was 85 per cent with a specific methane yield of 0.34 m^3/kg $COD_{removed}$.

Anaerobic treatment of waste water from citric acid industry was investigated by Fernandez (1999) in two sets of experiments. The first set was in single phase operation and the second set in two phase operation. They used a fluidized bed reactor for acidogenic phase. A COD conversion efficiency of 95 per cent was obtained with an average methane yield of $6m^3$ CH_4 /m^3 of waste water. They could reduce the HRT of 3 days in single phase operation to 1 day in the two phase operation.

The performance of a bench scale UASB was evaluated by Buzzini and Pires (2002) with diluted black liquor from a kraft pulp plant. The average COD removal efficiency during the entire experiment was 80 per cent. It was found that the microbial consortium became acclimated to the substrate, even though black liquor is potentially toxic for methanogenic cells.

Tham and Kennedy (2004) used a central composite design to methodically investigate anaerobic treatment of aircraft de-icing fluid (ADF) in bench-scale UASB reactors. A total of 23 runs at 17 different operating conditions were conducted in continuous mode. It was found that the biomass-specific acetoclastic activity was improved two-fold from 0.23 g COD/g VSS/d for inoculum to a maximum of 0.55 g COD/g VSS/d during ADF treatment in UASB reactors. The COD removal efficiencies were higher than 90 per cent.

Biogranulation is the process of cell to cell attachment, representing in self immobilization that culminates in the formation of granules. The biogranules are dense microbial consortia packed with several species and typically contains millions of organisms per gram of biomass (Najafpour *et al.*2006)

Buzzini and Pires (2007) evaluated the performance of a UASB reactor by treating diluted black liquor from a kraft pulp mill under different operational conditions, including partial recycling of the effluent. The study showed that without recirculation, the reduction of the HRT from 36 to 30 h did not significantly affect the average COD removal efficiency. The parameter displaying the greatest variation was the average concentration of effluent volatile acids. With recirculation the reduction of the HRT from 30 to 24 h increased the average COD removal efficiency from 75 per cent to 78%.

2.3.1.3 Anaerobic Hybrid Reactors

The effort of scientists to combine the advantages of two different designs of anaerobic reactors, resulted in the development of the concept ‘hybrid bio reactors’. Guiot and Van den Berg (1984) developed such a new design viz. the Upflow Sludge Bed-Filter reactor which hybridizes the UASB concept and random packing of plastic rings floating in the top third of the reactor column.

A series of lab scale studies were conducted by Kennedy and Guiot (1986) to evaluate the performance of this new design. They reported that this configuration combined the advantages of both UASB and UAF while minimising their limitations. They found that the reactor was efficient in the treatment of dilute to high strength waste water at high OLR and short HRT. The use of packing media only in the top portion of the reactor minimises channelling problem associated with UAF and loss of biomass due to floatation associated with poorly performing UASB reactors. Additionally, the packing material enhanced the development of granular sludge.

Calzada *et al* (1988) used an upflow two section hybrid reactor, consisting a sludge section in the lower part and a packed section in the upper part for the treatment of coffee pulp juice. They got gas production rates of 0.44 to 1.00 ℓ/ℓ.d when operating at 1.8 day HRT.

A similar design was developed by Choi *et al*. (1989). They were investigating the effect of packing media placement in identical lab scale bioreactors and developed an Anaerobic Upflow Bed Filter (AUBF) reactor that was free of plugging and channelling and possessed all merits of the UAF. The reactor which had packing only on the top half performed equally well as a fully packed reactor.

Britz *et al*. (1990) treated a high strength leachate from a municipal land fill site using a lab scale hybrid digester which could reduce the COD of the leachate by

90 per cent at loading rates of 14.53 kg COD/m^3.d. Total biogas yields ranged between 5.11 and 6.89 m^3/m^3 respectively at HRTs 1.2 and 0.9 day. The methane content of biogas was 65 – 75 per cent. They used a porous polyethylene foam as the fixed film support to the inside reactor wall.

Hong (1990) used a porous cuboid phenol resin in the size of 2 cm^3 as biomass support material in another hybrid design. He could obtain a COD reduction of 87 per cent at a loading rate of 10.6 g COD /ℓ.d and biogas yield of 107.3 ℓ/d with a methane content of 53 per cent. He found that many granules were formed at the UASB zone of the reactor. The results indicated that the operation of the system at 4.7 day HRT was effective to reduce pollution load while 3 day HRT was appropriate for maximum biogas production. Young (1991) reported that most of the new installations of UAF reactors were of the hybrid type and the media heights ranged from 50 per cent to 70 per cent of reactor height.

Yugu *et al.* (1992) studied the performance of lab scale hybrid reactors in treating alkaline straw pulp effluent. With the reduction of HRT from 6 days to 1 day, the OLR increased from 1.5 g/ ℓ.d to 11 g/ ℓ. d. During this period, COD and BOD removal rates were stable at 70.5 – 77.6 per cent and 87.3 – 93.1 per cent respectively. They reported that they could get 0.36 – 0.51 and 0.33 – 0.49 litre biogas per gram COD$_{\text{removed}}$ from the two reactors.

Ozturk *et al.* (1993) experimented with similar lab scale reactors in the treatment of dairy effluents. The reactor had a total height of 140 cm with the upper 60 per cent filled with plastic rings having a specific surface area of 190 m^2/m^3. They could operate the reactor at HRTs ranging from 0.21 to 0.96 days. COD removal efficiencies of more than 87 per cent were achieved at an OLR of 8.5 kg COD/m^3.d.

Lo *et al.* (1994) used a hybrid design with rope matrix as fixed film medium in its mid sector. The UAHR could be used without seeding at moderate OLRs to treat screened swine waste water. They reported that additional bio film on the fixed film of the UAHR increased stability of the reactor and maintained steady methane production.

Cordobo *et al.* (1995) developed a hybrid anaerobic reactor converting the flow mixing chamber of an anaerobic filter into an USAB which resulted in a 92 per cent increase in efficiency.

Malaspina *et al.* (1996) investigated the treatment of cheese whey in a different anaerobic system. They could increase the OLR to the target value of 10 g COD/ℓ.d after only 40 days from start up and granulation was noticed 20 days after start-up. The reactor was first fed with undiluted raw whey on 42nd day, which caused failure due to high VFA concentration. Thereafter, regular addition of alkali was required to keep the reactor stable. Then they switched over to a 2 phase system and eventually came out with a down flow-up flow Hybrid reactor in which phase separation was obtained within the same reactor.

Borja *et al.*(1996) operated a laboratory-scale hybrid anaerobic reactor to study the anaerobic digestion of wash waters derived from the purification of virgin olive oil. The HRT ranged from 0·20 to 1·02 days under normal operating conditions after the start-up. COD removal efficiencies of more than 89 per cent were achieved at an OLR of 8·0 kg COD/m^3 day. The anaerobic reactor performances did not change significantly when the OLR was gradually increased from 2·6 to 7·1 kg COD/m^3 day within 16 days.

James (2000) developed a hybrid anaerobic bioreactor for the treatment of cassava starch factory effluent. The bioreactors had a media filled portion in the upper half.

James and Kamaraj (2002) described different types of high rate bioreactors and opined that hybrid reactors have easy start-up and stability when compared to UASB.

Chaiprasert *et al.* (2003) studied the performances of three anaerobic hybrid reactors with various nylon fibre densities per packed bed volume (33, 22, and 11 kg/m^3) as supporting media to remove organic compounds in cassava starch wastewater. The organic loading rate was increased in stepwise from 0.5 to 4.0 kg COD/m^3/day and the HRT shortened to 5.4 days. The COD removal efficiency and the total biomass in the reactors were higher with greater nylon fibre densities. When the HRT was further shortened to 3 days, however, the efficiency of both reactors demonstrated a declining trend.

James and Kamaraj (2003) studied the performance of an Upflow Anaerobic Hybrid Reactor in treating cassava factory effluent using coconut shell as the media, operating on HRTs from 15 to 1 day. They observed a maximum specific gas production of 908.5 ℓ/kg TS and COD reduction of 98 per cent.

Najafpour *et al.* (2006) conducted studies on the Upflow Anaerobic Sludge-Fixed Film (UASFF) reactors with a tubular flow behaviour. The UASFF was developed to shorten the start-up period at low HRT for palm oil mill effluent treatment. The reactor was operated at 38 °C at an HRT of 1.5 and 3 days. The organic loading was gradually increased from 2.63 to 23.15 g COD/ ℓ day. Granular sludge was rapidly developed within 20 days. The size of granules increased from an initial pinpoint size to reach 2 mm. High COD removals of 89 and 97 per cent at HRT of 1.5 and 3 days respectively were achieved. Methane yield of 0.346 ℓ CH_4/g $COD_{removed}$ was obtained at the highest organic loading rate (OLR).

Kumar *et al.* (2007) studied the anaerobic biodegradation of distillery-spent wash on a lab-scale anaerobic hybrid reactor operated in a continuous mode at 5 day HRT and OLR 8.7 kgCOD/m^3.d. The COD removal efficiency of the reactor was 79 per cent. Ramakrishnan and Gupta (2008) investigated the feasibility of anaerobic treatment of complex phenolics in their studies on a simulated synthetic coal wastewater using a Hybrid Upflow Anaerobic Sludge Blanket (HUASB).

James and Kamaraj (2009) investigated the performance of Upflow Anaerobic Hybrid Reactors (UAHR) with two different media viz. PVC pall rings and coconut shells with regard to the energy production from cassava starch factory effluent. They found that the coconut shell bioreactor performed marginally better than the PVC pall rings bioreactor with a volumetric gas production of 2.038 m^3/m^3 reactor volume at an OLR of 4.53 kg $COD/m^3.d$

2.3.1.4 Anaerobic Baffled Reactor (ABR)

Baffled reactors are characterised by the separation of reactors using baffles so as to have an upward and downward liquid flow alternatively. Bachmann *et al.* (1985) developed the anaerobic baffled reactor (ABR) in order to obtain an improved performance of high strength treatment process in anaerobic reactors. This is achieved by the separation between the acidogenesis and methanogenesis (Anderson *et al.* 1994). The ABR encourages phase separation along the length of the reactor (Barber and Stuckey, 1999).

Xing *et al.* (1991) conducted a study on the anaerobic treatment of high strength molasses waste water using hybrid anaerobic baffled reactor at an OLR of 20 kg COD/m^3d and achieved soluble COD removal in excess of 70 per cent.

Nachaiyasit and Stuckey (1997) studied the effect of transient and step hydraulic shock loads on reactor performance in terms of COD removal and microbial responses to hydraulic shocks in each compartment of an ABR. The reactors were operated at 20 h HRT with a feed strength 4 g/litre COD at 35°C. The reactor could achieve 98 per cent COD removal. When the HRT decreased to 10 h removal dropped to 90 per cent, where as the removal was only 52 per cent at 5-h HRT. Hydraulic shocks with an HRT of 1 h, 10 h and 5 h were applied to the reactors for 3 h, 2 weeks and 3.5 weeks respectively, and a variety of key intermediates monitored over time in each compartment. It was found that the ABR was very stable to large transient shocks.

Grover *et al*. (1999) reported the use of ABR in the continuous anaerobic digestion of black liquor from pulp and paper mills and its performance at different pH, temperatures, HRT and OLR. A maximum COD reduction of about 60 per cent was achieved at an OLR of 5 kg m^{-3} d^{-1} at hydraulic retention time of 2 d, pH 8.0 and temperature 35°C. The OLR above 6 kg m^{-3} d^{-1} was found to be toxic and destabilised the reactor system.

Faisal and Unno (2001) studied the kinetic analysis of palm oil mill wastewater treatment by a modified anaerobic baffled reactor under steady-state conditions. The methane gas production was in the range of 0.32–0.42 l-CH_4 (g-COD)$^{-1}$ removed.

Baloch and Akunna (2003) conducted a study on a granular bed baffled reactor by operating the reactor from 1 to 20 kg COD/m^3 d at 6 hour HRT and found that the COD removal efficiency was over 95 per cent. Kuscu and Sponza (2005) evaluated the performance of an ABR by treating synthetic waste water containing p-nitrophenol and found that the COD removal efficiency varied between 90 to 99 per cent.

Zhu *et al.* (2008) studied the anaerobic digestion of soybean protein processing wastewater on a laboratory-scale ABR. It was found that the COD removal efficiencies were 92–97 per cent at a loading rate of 1.2–6.0 kg COD/m^3 d.

2.3.1.5 Comparative performances of high rate reactors for wastewater digestion

A Variety of designs of anaerobic high rate bioreactors have been evolved in the last three decades and many workers conducted investigation on comparison of these designs.

Stronach *et al*. (1987) investigated the start-up of UAFs, anaerobic fluidized beds and UASB reactors on two types of pharmaceutical wastes. Fluidized beds proved superior to UASB reactors and filters in COD removal capacity and pH stability during start-up. The methane production was found better in the UASB.

Rintata (1991) compared the anaerobic mesophilic treatment of a synthetic and thermo-chemical pulping wastewater in lab scale UASB reactors and UAFs. The reactors were inoculated with non-granular sludge. The start-up proceeded faster in the filters than the UASB reactors with both wastewaters. However, there were no major differences in the loading rates and removal efficiencies when the runs were continued. The superiority of a hybrid reactor over UASB reactor in biogas production as well as its tolerance to high OLRs in treating baker's yeast factory waste water was reported by Lo *et al*. (1991).

A comparative evaluation done by Macarie *et al*. (1992) with terephthalic acid plant waste water using two UASB reactors and a down flow tubular fixed film reactor revealed the comparable efficiencies with rather low COD removal. The performance of the fixed film reactor was much higher due to better resistance to toxicity caused by the aromatics present in the waste water.

Van der Merwe and Britz (1993) treated a high strength effluent from a baker's yeast factory using a UAHR and UAF under mesophilic conditions. The feed had high variations in composition with high sulphate concentration. They reported that both digesters behaved in a similar manner with a COD removal efficiency and methane yield of 67 per cent and 0.207 m^3/kg COD $_{removed}$ for the UAF and 65 per cent and 0.208 m^3/kg COD $_{removed}$ for the UAHR at a HRT of 3 day.

Chen and Shyu (1996) operated four types of anaerobic reactors, viz. CSTR, UASB, UAF and a baffled reactor for treatment of dilute dairy waste water between HRTs 18.8 and 2 days at OLRs between 0.117 and 1.303 g VS/l. d. The establishment of methanogenesis was slower for CSTR and baffled reactor. The feasibility of slaughter house waste water treatment in UASB reactors and UAF was assessed by Ruiz *et al*. (1997). The COD removal for UASB was 90 per cent for OLR up to 5 kg COD/m^3.d and 60 per cent for 6.5 kg COD/m^3.d. For similar organic loading rates the UAF showed lower removal efficiencies and lower percentage of methanisation.

2.3.2 Design concepts of anaerobic fixed film bioreactors

The high rate reactor to be developed for RME is likely to be a fixed film reactor and a detailed review of the design concepts were very relevant. Young (1991) has made a comprehensive review of the factors affecting the waste treatment performances of anaerobic filters and made recommendations for taking these factors into consideration for the design of fixed film bioreactors.

2.3.2.1 Reactor configuration and media characteristics.

Full scale UAF configurations have generally cylindrical and rectangular tanks of diameter/width in the range 6 to 26 m and with 3 to 13 m height (Young and Yang, 1989). Volumes for full scale reactor systems had ranged from 100 to 10000 m^3.

Young (1991) observed that media:height ratio is important and reactors having 50 per cent or less media volume generally have experienced increased solid loss and reduced efficiency. He recommended that the media be placed in the upper two thirds of the height of up flow reactors with a minimum height of 2 m for full scale reactors.

Young and Dahab (1983) opined that bacterial retention seems to be related to media shape and void size as well as specific surface area. The accumulation of suspended solids or biomass in the packing often leads to plugging and channelling which eventually deteriorates the reactor efficiency (Young, 1985).

The purpose of the media as observed by Young (1991) is to retain biological solids within the reactor either as a fixed film attached to the media, as solids entrapped within the media matrix, or suspended within or beneath the media as a granulated or flocculent sludge mass. Therefore, the media acts as a gas-solids separator, helps to provide uniform flow through the reactor, improves contact between the waste constituents and the biomass contained within the reactor, and permits accumulation of the large amount of biomass needed to produce a long solids retention time (SRT). During the course of development of anaerobic filters, a wide variety of media have been investigated and used. The concept of retention and maintenance of biological growth on an inert support media formed the theoretical basis of almost all second generation immobilised cell bioreactors (James and Kamaraj, 2002). The internal packing creates a suitable environment to accelerate bio granule formation by particle recirculation.

2.3.2.1.1 Use of natural inorganic materials as media

Natural and inorganic materials were used as packing media by several workers. It has been reported that quartzite stones (Young and McCarty, 1969), drain pipe pieces (Smith *et al*., 1977), limestone chips (Barry and Colleran, 1982), and fired clay media (Kennedy and Van den Berg, 1982) were used in the treatment of various wastes.

Gadre and Godbole (1986) used stone rubbles of 25 mm mean diameter. Sharma and Bandyopadhyay (1991) reported on the use of earthenware rings of potter’s clay having an average length 1.88 cm, outer diameter 1.20 cm and internal diameter 0.80 cm with a specific surface area of 133.2 m^2/m^3 as medium. Yap *et al*. (1992) and Chua *et al*. (1997) also reported that they got satisfactory performances with fire expanded clay media. Porous media enhances bio film considerably when compared to more smooth media (Patel and Madamwar, 1995). Acharya *et al*. (2008) conducted studies using charcoal to use its porous property to treat distillery spent wash and noticed better start-up.

2.3.2.1. 2 Use of biological materials as media

In a study conducted by Nordstedt and Thomas (1985[a]) on fixed film reactors using pine wood as media, some inhibition was observed which could be overcome by soaking the media for a longer time. Andreoni *et al*. (1990) also got a similar result with wood chips media when used for the treatment of residues from wood pyrolysis along with swine slurry. Prasad (1992) reported on the good performance of eucalyptus bark as medium in a down flow filter for treatment of a bagasse-paper mill wastewater.

James and Kamaraj (2004) conducted investigations to use of coconut shells as media for cell immobilization in aerobic bioreactors. They found that coconut shells inhibited methanogenic bacteria in anaerobic batch digesters due to the leaching of phenols in the batch digestion studies. They advised the pre-treating of coconut shell to overcome this problem.

James and Kamaraj (2007) reported that the start-up of the Up flow Anaerobic Hybrid Reactors (UAHR) took 28 day with the coconut shell media. They found that once the bioreactors are started up, the coconut shell media reactor performed marginally better than a similar PVC pall ring media reactor.

Acharya *et al*. (2008) used coconut coir to make use of its high porosity as the bio film formation by the micro-organisms is influenced by the porosity of the media. The reactor showed efficient COD and BOD removal and higher gas production.

2.3.2.1. 3 Use of synthetic media

Jones *et al*. (1981) found clogging problems when they used nylon fabrics as media. Henry (1985) used high void volume plastic media with a surface of 250 m^2/m^3 in commercial anaerobic reactors. Ng and Chin (1987) used random packed plastic media made of PVC tubing 25 mm long, 12 mm diameter and 1 mm wall thickness with a total depth of 105 cm in 140 cm tall lab scale reactors for piggery waste water treatment. Aivasidis and Wandrey (1988) reported on the use of porous sintered glass with a porosity of 50 per cent in a fixed bed loop reactor. Marques *et al*. (1990) used randomly packed PVC pipe pieces in a UAF while Breitenbucher *et al*. (1990) developed an open sintered glass material for use in bio film reactors.

Pascik (1990) recommended the use of modified porous polyurethane carriers as packing media. Hill and Bolte (1992) investigated bacterial retention by polypropylene felt, polyurethane foam and nylon mesh. They found that polypropylene felt gave a higher methane productivity and VS reduction. Anderson *et al*. (1994) found that a porous sintered glass medium with its high surface to volume ratio gave a better overall performance than non-porous PVC medium. While Kanekar and Kelkar (1995) used polypropylene rings for treatment of dye stuff wastewater, Prasertsan *et al*. (1996) used PVC rings for fishery waste water treatment.

Oktem *et al*. (2007) used poly propylene pall rings of internal diameter 25mm, density 70 kg/m^3 and a specific surface area of 206 m^2/m^3. Acharya et *al*. (2008) used nylon fibres as media to treat distillery spent wash and found that the nylon fibre is not a perfect media due to its smooth surface.

2.3.2.1. 4 Comparison of media

The microscopic observation of bio films formed on various materials during pig slurry treatment showed that bio films found on the various supports do not differ significantly in microbial content or overall aspect (Robinson *et al*., 1984). The bio film varied in the range of 1-3 mm thick and displayed a rough and uneven surface with many mineral precipitates containing Ca, Mg and P embedded in it. A higher density of material is present towards the base of the film, lower layers being characterized by the presence of a thick matrix. Even though the bacterial population was quite heterogeneous, methanogens (*Methanosarcina* Sp. and *Methanothrix*) were the prevailing micro organisms.

Hudson *et al*. (1978) found that the reactors packed with whole oyster shell media performed better than those with rock media. They opined that the higher specific surface area and porosity are the major factors responsible for better performance.

Nordstedt and Thomas (1985^b) operated bench scale UAFs containing oak, cypress and pine wood block media at HRTs as low as 2 days using supernatant from settled swine waste as feed stock in comparison to plastic media and no media reactors. They reported that the wood block media reactors performed as well as plastic media and showed no visual signs of deterioration after one year of operation.

Sorlini *et al*. (1990) investigated the microbiological aspects of swine slurry digestion in UAFs with different packing media viz., PVC supports, wood chips and expanded clay. The composition of the microbial consortia in the bio film attached to wood chips and PVC supports were not significantly different. Biogas, ℓ /kg VS_{added} was highest for wood chips media reactor and expanded clay media reactor produced very low biogas. Andreoni et al. (1990) found that wood chips reactor showed better resistance compared to PVC media to pyrolignitic acid present in the feed while treating wood pyrolysis wastewater.

Vartak *et al.* (1997) investigated the performance of different packing media in lab scale attached film bioreactors, with limestone gravel, pieces of non-woven polyester matting, combination of limestone gravel and polyester pieces, and no packing. The digesters were started up at 37°C and the temperature was lowered to 10°C and held at that temperature for 5 weeks to study the performance at psychrophilic conditions. They found that the biogas production, VS reduction and COD reduction were significantly higher for the polyester medium with its high porosity and surface : volume ratio.

James and Kamaraj (2004) conducted a comparative study by using both raw and treated coconut shells in semi continuous anaerobic digesters and found that the treated media showed better performance than the untreated media. Acharya et *al.* (2008) used coconut coir in comparison to charcoal and nylon fiber and found that the coconut coir had better performance than the other two.

James and Kamaraj (2009) found that coconut shell media was equally good or marginally better than PVC media for the treatment of cassava starch factory effluent in an Up flow Anaerobic Hybrid Reactor.

2.3.2.1. 5 Criteria for Selection of media

Young (1991) recommended that the specific surface area of media used in full scale anaerobic filters averages about 100 m^2/m^3 regardless of the type of media. He opined that site specific consideration, economics and operating factors should ultimately be the determining factors in the selection of media. He clarified that media specific surface area seemed to have only a minor effect on waste treatment performance and it is unlikely that the additional cost of high density media can be justified by the slight improvement in efficiency and the increased potential for plugging. He opined that a specific surface area of about 100 m^2/m^3 is sufficient to avoid plugging.

2.4 Process parameters of high rate reactors

A major consideration in designing full scale UAF, is the proper distribution of wastes across the base of the unit.

2.4.1 Hydraulic Retention time

The study conducted by Marques *et al.* (1990) revealed that COD removal efficiency varied from 93 to 77 per cent when HRT was varied from 48 h to 24 h in a lab scale reactor. Young (1991) reported that his studies from 1965 through 1968 revealed that the COD removal performance of laboratory scale UAFs was inversely related to the HRT. Prasertsan (1994) also observed that the COD removal efficiency decreased from 75 to 65 per cent when HRT was reduced from 11 to 6.6 days.

James and Kamaraj (2009) found that the COD reduction reduced from 98 per cent at 15 day HRT to 97 percent at 1 day HRT in treating cassava starch factory effluent in a UAHR.

2.4.2 Influent waste concentration and other hydraulic factors

Based on the results of his pioneering studies Young (1991) reported that changes in influent waste concentration ranging from 3000 to 12,000 mg COD/ℓ had no significant effect on COD removal efficiency for reactors operating at HRTs of 18 – 36 h. He further clarified that anaerobic filters could accept large variations in waste flow and load without being upset, and the time required for recovery increases as the magnitude and duration of the change in flow and load increases.

He opined that recycle has essentially the same effect as changing the influent waste strength and HRT because the COD of the recycle stream contributes to the net applied organic loading. He recommended that recycle is not necessary when treating wastes having COD concentration less than about 8000 mg/ℓ, but may produce some benefit in reducing alkalinity and nutrient requirements.

Hydraulic limits of piping and orifice diameter also should be considered as well as a provision for sludge withdrawal (Young, 1991).

2.4.3 Other process parameters.

It is well known that the optimum pH for methanogenesis is 6.8 – 8.0 (Baloch *et al.*, 1979). Chawla (1986) described pH as a function of alkalinity, CO_2 concentration and bicarbonate of the system.

The concentration of volatile acids and alkalinity depend on the concentration of the wastewater and on its composition. The volatile acid to alkalinity ratio is an important criterion for the stability of anaerobic reactor which has more relevance than their absolute values. Kaspar and Wuhrmann (1978) reported that a ratio of total volatile acids (as acetic) to total alkalinity (as $CaCO_3$) less than 0.1 was desirable.

If the pH is allowed to drop too much, the methanogenesis will be inhibited. Anaerobic filters have a higher tolerance against lower pH than suspended growth systems (Frostell, 1979). Russo *et al.* (1985) also reported that the advantage of UAF was that they showed better stability as far as acidity and alkalinity are concerned. The parameters, pH, volatile acids and alkalinity could be treated together since they are closely interrelated and a high level of alkalinity is desirable (Frostell, 1985).

2.4.4 Start-up of high rate anaerobic reactors

Lo and Liao (1985) reported that the fixed film reactor would take three to four months to develop an active biomass in the support structure even though the start-up can be very fast.

Nordstedt and Thomas (1985[a]) found that a 20 per cent mixture of seed inoculum with the feed stock was adequate for start-up of fixed bed reactors when a 10 day incubation time was provided prior to regular feeding. Peck and Hawkes (1987) started up a lab scale UAF in 15 days by adding 10 litre of cattle slurry, 8 litre of deionised water and 2 litre of seed inoculum.

Full-scale anaerobic reactors are generally batch inoculated for practical reasons (Albanac, 1990). Digester sludge up to 50 per cent is added and progressively adapted to the waste water to be treated. Bazile and Bories (1990) ruled out the use of pure strains to inoculate food industries waste water digesters due to the complexity of the ecosystem. They advised seeding from existing eco-systems. A proper seed sludge shortens the start-up period. A fast start-up can be achieved when the inoculum originates from another anaerobic reactor treating a similar type of waste water under comparable conditions (Rintala, 1991).

Cho *et al*. (1996) recommended that a step wise seeding schedule for up flow reactors. They could get a faster acclimation of added sludge and effective build up of biomass by multiple seeding.

James and Kamaraj (2007) studied the start-up characteristics of an Up flow Anaerobic Hybrid Reactor with coconut shell media and a PVC media for treating cassava starch factory effluent. They adopted step-wise seeding schedule and found that the reactors took 5 weeks for start-up without addition of alkali even though CSFE was acidic (pH 4.7 to 5.3).

MATERIALS AND METHODS

CHAPTER III

MATERIALS AND METHODS

The procedure adopted for the analysis of physico-chemical characteristics of waste water samples, the methodology for batch and semi-continuous anaerobic digestion studies of rice mill effluent (RME), as well as the design, fabrication and evaluation procedures for batch, semi-continuous and lab scale high rate bio reactors are outlined in this section.

3.1 Physico-chemical characteristics

The following methods were adopted for estimating different physico-chemical characteristics of the wastewater samples and biogas.

3.1.1 Total solids (TS)

The total solids were determined by the procedure outlined by American Public Health Association (APHA), (1989). A measured volume of well mixed sample was transferred to a pre-weighed dish (A) and evaporated to dryness in a drying oven. The evaporated sample was dried for one hour in the oven at 103 - 105°C. The dish was then cooled in a desiccator and weighed. The process of drying, cooling and weighing was repeated till concordant weights were obtained.

$$\text{TS} = \left\{ \frac{W_1 - W_2}{\text{Sample volume, m}\ell} \text{ x1000} \right\} \text{mg}/\ell$$

W_1 = Weight of the dried residue with dish, mg

W_2 = Weight of dish, mg

3.1.2 Chemical Oxygen Demand (COD)

COD was determined photometrically by Lovibond COD-reactor ET108 (Plate 3.1). It measures the COD concentration by photometric detection employing a linear relationship between absorbtance and concentration. The COD-setup comprises the measure COD in the range from 0 to 15,000 mg/ℓ by two light emitting diodes (LEDs) for emitting light with long-term stability ($\lambda_1 = 605$ nm; $\lambda_2 = 430$ nm, according to ISO 15705:2003-01). The sample is added to the 'Lovibond COD vario tube' and is digested in the reactor for 120 minutes. Then it is analysed in the 'Check it direct COD vario photometer'.

3.1.3 Biochemical Oxygen Demand (BOD)

Five day BOD test was conducted by filling to overflowing 300 mℓ air tight BOD bottles with diluted sample and incubating it at 20°C for 5 days in a BOD incubator (Plate 3.2). Dilution water was prepared by adding to 1ℓ of distilled water, 1 mℓ each of phosphate buffer, $MgSO_4$ solution, $CaCl_2$ solution and $FeCl_3$ solution prepared by the standard procedures (APHA, 1989). The dissolved oxygen (DO) was measured initially and after incubation and the BOD_5 was computed by the relation.

$$BOD_5 = \frac{D_1 - D_2}{P} \ \text{mg}/\ell$$

Where,

BOD_5 = Five day Biochemical Oxygen Demand, mg/ℓ

D_1 = DO of diluted sample immediately after preparation, mg/ℓ

D_2 = DO of diluted sample after 5 days' incubation at 20^0C, mg/ℓ

P = Decimal volumetric fraction of sample used

3.1.4 pH value

The pH values of the samples were estimated using the electrometric method (APHA, 1989). The pH meter used was Eutech instruments make, model-WD-35617-00 (Plate 3.3), pH range- 0.00 to 14.00 pH, with an accuracy- ±0.01 pH.

Plate 3.1 Lovibond COD-reactor ET108

Plate 3.2 BOD incubator

3.1.5 Estimation of Total Organic Carbon (TOC)

The TOC was estimated following the wet digestion method of Walkley and Black as described by Piper (1966). The diluted 20 mℓ sample was digested with 50-75 ml of 1 normal $K_2Cr_2O_7$ with 20 mℓ of concentrated H_2SO_4. After 30 minutes 10 mℓ of ortho-phosphoric acid was added. This was titrated against 1 normal ferrous ammonium sulphate (FAS) with diphenylamine as indicator. A blank was also run.

$$\text{TOC, \%} = \frac{(B_v - S_v) \text{ x NFAS x } 100 \text{ x} 0.03}{V_s}$$

B_v = Blank titre value

S_v = Sample titer value

NFAS = Normality of FAS

V_s = Volume of test sample

3.1.6 Total Kjeldahl Nitrogen (TKN)

Available nitrogen was estimated in the samples by microkjeldahl method. To 1 mℓ of sample, 2-3 mℓ of 25 per cent $KMnO_4$ solution was added followed by few drops of concentrated H_2SO_4. To this 10-15 mℓ of diacid (H_2SO_4 and $HClO_3$ in the ratio 5:2) was added and digestion carried out in a Kjel plus digestion unit. Five mℓ each of the digested samples was distilled with 20 to 50 mℓ of 40 per cent NaOH and the distillate titrated against 0.05 N H_2SO_4.

$$\text{TKN, mg/}\ell = \frac{\text{Titre value x 14 x volume of acid make up}}{\text{Volume of acid pipette}} \text{ x } 100$$

3.1.7 Gas measurement

The volume of gas was measured using water displacement method (Lo and Liao, 1986, James and Kamaraj, 2004). A 3-liter graduated jar was used for the purpose (Plate 3.4).

3.1.8 Methane content of biogas

The methane content of the biogas produced was estimated using Sacharometer (Plate 3.5). A measured quantity of biogas was passed through the saturated KOH solution in the sacharometer. The volume of the gas collected at the top of the sacharometer is methane and the rest is absorbed by the solution. The methane content is calculated as follows.

$$\text{Methane content, \%} = \frac{100 \text{ x volume of gas collected at the top}}{\text{Total volume of gas injected}}$$

3.2 Preliminary biomethanation studies

Most organic effluents are amenable for biomethanation and the possibilities for biological treatment of RME was evident from the fact that no chemical additives are added in the process. But little published data is available on the anaerobic digestion. Hence in order to obtain a clear information on the biomethanation characteristics and select the process conditions for high rate bioreactors, preliminary studies were conducted as detailed below.

3.2.1 Batch digestion studies on RME

Batch digestion study was carried out to study the biomethanation characteristics of RME. Anaerobic digestion of RME samples was done in 10 liter plastic digesters attached with 3 liter capacity water displacement meters. Cow dung was used as the inoculum and was mixed with RME in the ratio 1:1. The TS, pH, COD and BOD were noted for the digester liquid before and after digestion. The gas production was monitored daily. The experimental set-up is shown in Fig. 3.1.

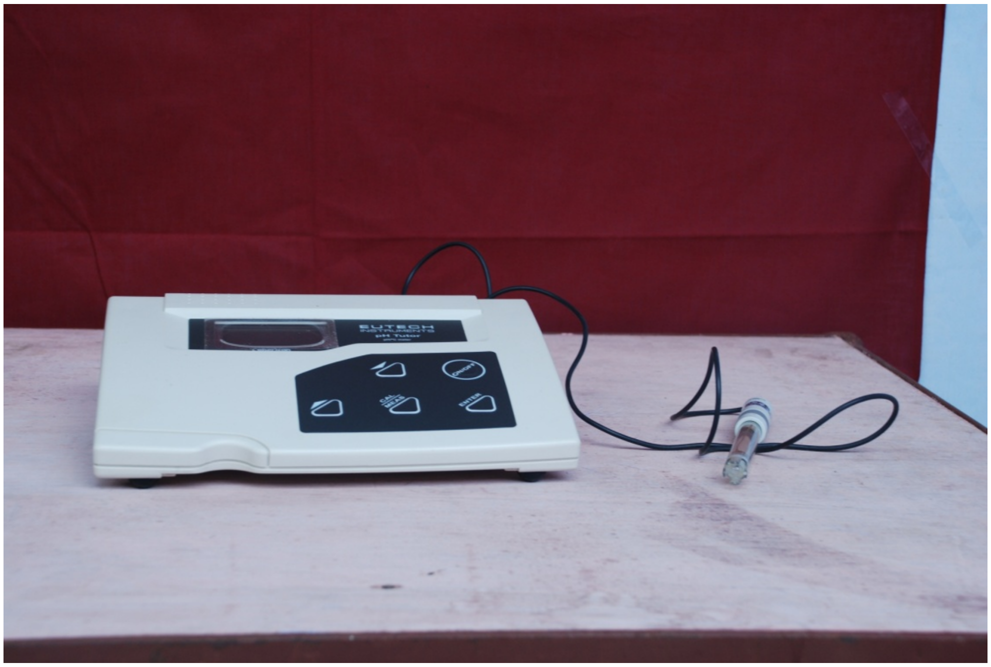


Plate 3.3 pH meter

Plate 3.4 Digester with water displacement meter

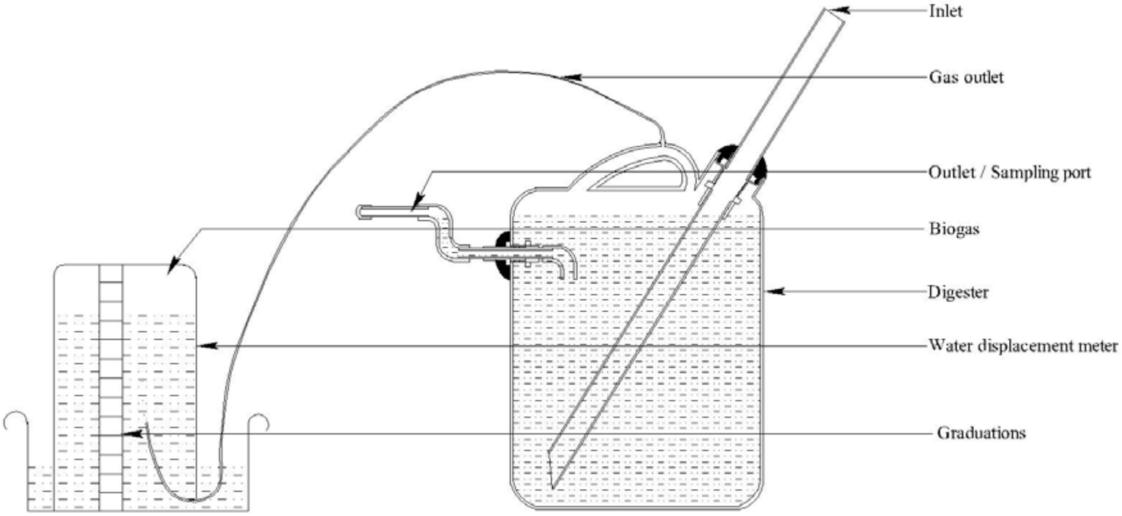


Fig 3.1 Experimental setup of batch digester.

3.2.2 Biomethanation studies to investigate media compatibly

Semi-continuous digestion studies were carried out to study the biomethanation characteristics of RME and the effect of media on the digestion process. The studies were carried out in 10 litre plastic digesters attached with 3 litre capacity water displacement meters (Plate 3.6). Three different media were used for the study namely rubber seed inner shell, coconut shell and Rubber seed outer shell (Plate 3.7, 3.8 and 3.9). The use of coconut shell as media were studied by James and Kamaraj, (2004). Rubber is an important crop of kerala and the rubber seed shells are not been utilised properly. Hence it was decided to test the suitability of these agricultural waste materials for use as media in bioreactors.

The following treatments with 3 replications were used for the study. The cow dung mixture used had an approximate TS of 3 per cent.

T_0 - Cow dung mixed with water (3 per cent TS approximately).

T_{01} - Cow dung mixture + Coconut shell media

T_{02} - Cow dung mixture + Rubber seed inner shell media

Plate 3.5 Sacharometer

Plate 3.6   Arrangement of digesters for media selection study

Plate 3.7 Rubber seed inner shell

Plate 3.8 Coconut shell

Plate 3.9 Rubber seed outer shell

T_{03} - Cow dung mixture + Rubber seed outer shell media

T_1 - RME + Cow dung mixture in 1:1 ratio.

T_2 - RME + Cow dung mixture in 1:1 ratio + Coconut shell media

T_3 - RME + Cow dung mixture in 1:1 ratio + Rubber seed inner shell media

T_4 - RME + Cow dung mixture in 1:1 ratio + Rubber seed outer shell media

T_5 - RME neutralized + Cow dung mixture in ratio 4:1

T_6 - RME neutralized + 20% Cow dung mixture in 4:1 ratio + Coconut shell media

T_7 - RME neutralized + 20% Cow dung mixture in 4:1 ratio + Rubber seed inner shell media

T_8 - RME neutralized + 20% Cow dung mixture in 4:1 ratio + Rubber seed outer shell media

3.2.2.1 Estimation of media characteristics

The procedures adopted for the estimation of specific surface area, porosity and bulk density for rubber seed outer shell media, rubber seed inner shell media and coconut shell media were as follows:

To determine the specific surface area of rubber seed outer shells, rubber seed inner shells and coconut shells, 10 numbers of half shells were selected randomly and the surface area was plotted on a graph paper. The graph paper was then scanned and imported into a computer software (autocad) so as to calculate the surface area. The mean surface area of one half shell was then obtained. A known number of rubber seed inner shell and rubber seed outer shells were then filled in a cylindrical measuring jar and the bulk volume occupied was found out. In the case of coconut shells, a known number of half shells were broken to pieces of size in the range of 50 to 100 mm and filled in a cylindrical vessel of diameter 300 mm, so as to obtain the bulk volume, mℓ.

Specific surface area (A_{sp}), m^2/m^3

$$= \frac{\text{Mean surface area of one half shell x No. of shells in the vessel}}{\text{Bulk volume of broken shell}}$$

To determine the porosity, rubber seed outer shells, rubber seed inner shell and coconut shell media were filled in a cylindrical vessel. The vessel with media was then filled with water so that the media is fully submerged.

$$\text{Porosity of media, \%} = \frac{\text{Volume of water filled, m}\ell}{\text{Volume of vessel, m}\ell} \text{ x 100}$$

The bulk density was estimated by finding the weight of a known volume for all the three media.

3.2.2.2 Digester start up

The digester was filled and was run in batch mode for a period for acclimatization. The semi-continuous mode of operation started after 23 days, after the system had stabilized. The system was operated on 20, 15, 10 and 5 day HRT respectively. The TS, pH, COD and BOD were noted for the influent and effluent at every 10 days after the start of the semi-continuous mode. The gas production and ambient temperature were recorded daily.

3.3 Design and fabrication of anaerobic high rate reactors

The methodology adopted for the design and fabrication of the laboratory scale anaerobic high rate reactors are outlined in the following sections.

3.3.1 Selection of reactor configuration

In consideration of the recommendations of Guiot and Vander Berg (1984), Kennedy and Guiot (1986), Chaiprasert *et al.*(2003), and James and Kamaraj, (2004) that a hybrid reactor can combine the advantages of upflow anaerobic filter and UASB, it was decided to design and fabricate an Upflow Anaerobic Hybrid Reactor (UAHR). The expected advantages were an easy start-up and avoidance of possible complications with sludge granulation. Single phase operation was selected considering the recommendations of Lettinga and Hulshoff Pol (1986) that there is no reason to go for a two phase system in the case of soluble wastes.

3.3.2 Media placement and selection

It was decided to place the media on the upper 50 per cent of the reactor height, leaving 1 cm at the top from the liquid surface (Young, 1991; James,2000; Chaiprasert *et al.* 2003 and James and Kamaraj, 2003[a]).

The best performing media in the media selection studies viz. rubber seed outer shell was selected as the media to be compared with an inert material in the UAHR. Polyurethene was selected as the inert media material and rings (Plate 3.10) were fabricated from Polyurethene sheet having dimensions of 45 mm (outer diameter) x 30 mm (inner diameter) x 40 mm (height).

3.3.3 Estimation of media characteristics

The procedures adopted for the estimation of specific surface area, porosity and bulk density for the polyurethene rings (inert media) were as follows:

The actual surface area of the micro structure of biological materials like coconut shells and rubber seed shells is difficult to be estimated by physical methods. Hence the surface area of these materials were measured physically so as to get an appropriate estimate.

To determine the specific surface area of the polyurethene rings, the rings were filled in a cylindrical vessel of 300 mm diameter and the bulk volume was measured for a known number of rings. The surface area of one polyurethene ring was physically determined by linear measurements.

Specific surface area (A_{sp}), m^2/m^3

$$= \frac{\text{Mean surface area of one polyurethene ring x No. of rings (N)}}{\text{Bulk volume occupied by N number of rings}}$$

To determine the porosity, the Polyurethene rings were filled in a cylindrical vessel. Then water was filled into the vessel to the top level of the rings using a measuring jar keeping the rings submerged. A mesh was used to keep the ring submerged by applying pressure against buoyancy. The media were filled in the vessel so that they are submerged and filled up to the water level. The new volume was noted down.

$$\text{Porosity of media, \%} = \frac{\text{Volume of water filled}}{\text{Volume of vessel}} \times 100$$

The bulk density was estimated by finding the weight of the known volume of the media when filled in the cylindrical vessel for porosity estimation.

3.3.4 Dimensions of UAHRs

The procedure adopted for arriving at the dimensions of the lab scale UAHRs are given below.

Design daily feed = 15 ℓ/day

Design HRT = 1 day

Reactor liquid volume = 15 x 1 = 15

The diameter of the reactor was fixed as 200 mm and it was decided to fabricate the reactor with PVC pipes of 200 mm diameter and 10 mm thickness.

Design media height, as percentage
of reactor height = 50 per cent (approx.)

A conical shape was selected for the bottom of the reactor to enable better mixing of feed and easy sludge withdrawal (if necessary). A conical end cap of 200 mm dia and height 100 mm was selected for the purpose.

Volume of the cone (V_c) = $(\pi \times 10^2 \times 10)/3$ = 1046 cc ≈ 1 ℓ

Liquid volume of the reactor cylindrical portion above the cone = V_h

$= 15 - V_c = 14\ \ell$

Height of cylindrical portion of reactor if no media is filled $= 14/\pi r^2 = 45$ cm

Height of the liquid level above the media filled portion $= 1$ cm

Additional height required when media with 56% porosity is filled in 50 per cent height $= (45-1) \times (0.56/2) = 12.3$ cm

50% of reactor height, h_l is set apart for sludge bed zone

$h_l = (44+12.3)/2 \approx 28$ cm

This height was kept same for all bioreactors.

The height of media filled portion, h_2 varied as the porosity of media varied and was calculated as below:

$V_h = \pi r^2 h_l + \{\text{porosity (\%)} \times \pi r^2 h_2\}/100 = 14$ litres

$h_2 = \{(14/\pi r^2)-28\} \times (100/\text{porosity, \%})$

3.3.5 Gas measurement system

The same system as described in section 3.1.7 was used for measurement of gas volume.

3.3.6 Feed inlet, effluent outlet and sludge outlet

The feed inlet was designed such that the chances for blockage by sludge is minimised and a uniform mixing of feed is achieved. The feed inlet was thus positioned at a height of 10 mm from the bottom of the digester. A fluted tube configuration of PVC pipe in a square shape (side 100 mm) with holes (1.5 mm Ø) facing upward, was selected as the feed inlet configuration.

20 mm PVC pipes were selected for effluent outlet, positioned above the media level such that 10 mm length of the horizontal portion of the out let pipe is invariably within the liquid surface so to avoid escape of gas through the outlet. The outlet tube was given to a ‘U’ shape in the portion emerging out as an additional precaution.

The sludge outlet was positioned at the apex of the conical bottom so that sludge can be easily withdrawn, if required. A diameter of 20 mm was adequate for the sludge outlet.

3.3.7 Sampling ports

Two sampling ports were positioned at the middle of the media filled and non media filled portions.

3.3.8 Dispersion plate

Dispersion plates were required to keep the media at proper position in the reactor, and to enable uniform dispersion and flow of feed through the matrix. One plate was required for each reactor, so as to separate the media and non media filled portion. The plate provided had perforations of 2 mm diameter spaced 15 mm centre to centre.

3.3.9 Feed pumping system

A peristaltic pump was selected for pumping the RME to the bioreactors based on the experience of earlier workers. Sorlini et *al*. (1990) used a timing controlled peristaltic pump to pump effluent into the reactor. Bhunia and Ghangerkar (2008) used peristaltic pump to adjust the flow rate of the influent.

The feed rates for different HRT were set in a computer by which the pump was operated. It was possible to pump the RME to four reactors simultaneously and the flow was diverted manually using a three way valve. The feeding pipe line was provided with control valves, and a one-way valve each for each UAHR to prevent back flow when the pump is switched off. The specification of the peristaltic pump used for the experiment is given in Appendix-I. The feeding system setup is shown in Plate 3.11

3. 3.10 Fabrication of the UAHRs

The basic reactor configuration arrived is shown in Fig.3.2. Eight lab scale UAHRs with the two different media were fabricated, after arriving at the design dimensions. PVC well casing pipe of diameter 200 mm (ID) was selected for fabrication of UAHRs. The pipes were cut according to the design dimension. Each UAHR had two pieces of pipe and both ends of each piece were threaded (acme thread). The feed inlet was fabricated as per the design and fixed to the conical end cap to be

Plate 3.10 Polyurethene rings

Plate 3.11 Computer controlled feeding system for the bioreactors

fitted on the lower piece of the pipe. After fixing the end cap with feed in let, the upper pipe was fitted with the perforated PVC plate (to retain the media) placed in between the two pipes. A threaded PVC coupling was used to join the lower and the upper pieces of pipe. Then the media was placed up to the required level. The bottom portion was sealed and 15 liters of water was filled in the reactor. The effluent outlet was fixed at the required level of the reactor height, so as to have exactly 15 liters of liquid volume in the reactor. This was done, as there was difference in the void volume for the two media. Now, the top end cap with the outlet was fitted. A support frame assembly was required to keep the digesters in an erect position. Four legged design with MS angle (25mm x 25mm) iron was selected for the support frame, considering the stability aspects and load.

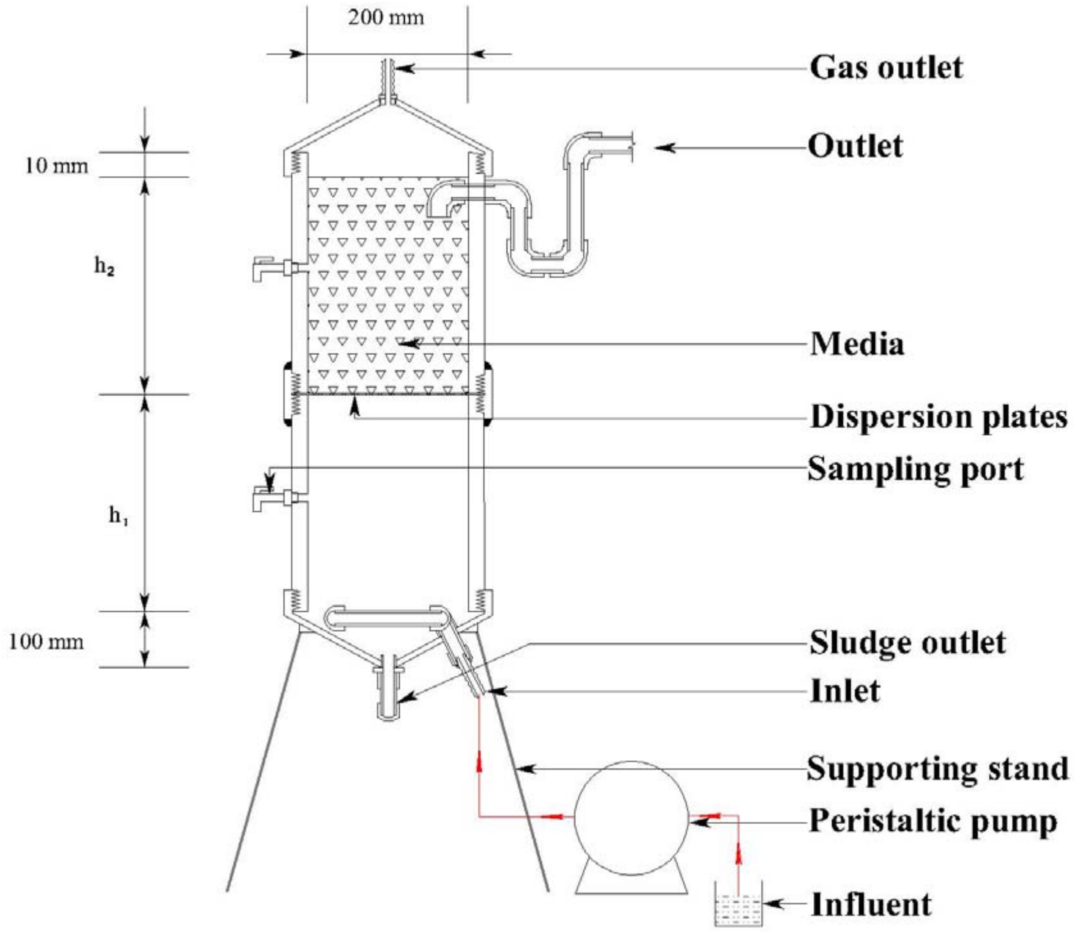


Fig. 3.2 Schematic sketch of UAHR

3.4 Evaluation of lab scale high rate reactors

The performance of the high rate reactors with two different packing media *viz*. rubber seed outer shell and polyurethane rings were evaluated for HRTs of 10, 5, 3, 2 and 1 day. The layout of UAHRs in the laboratory is shown in Plate 3.12. The feeding was done daily in a semi continuous mode at the rate of 2 ℓ/hr. The daily feed volumes for reactors at the respective HRTs were obtained by dividing the volume of the reactor (liquid capacity) by the HRT. The bioreactors were fed at appropriate flow rates and duration so as to get the required inflow volume. Two materials were used as inoculum ie. cow dung (2 per cent TS approximately) and sludge obtained from the semi-continuous digesters used for media compatibility study. The lay

The following treatments with 2 replications were used for the experiment.

T_1 = 80 per cent RME + 20 per cent Cow dung inoculum and rubber seed outer shell as media.

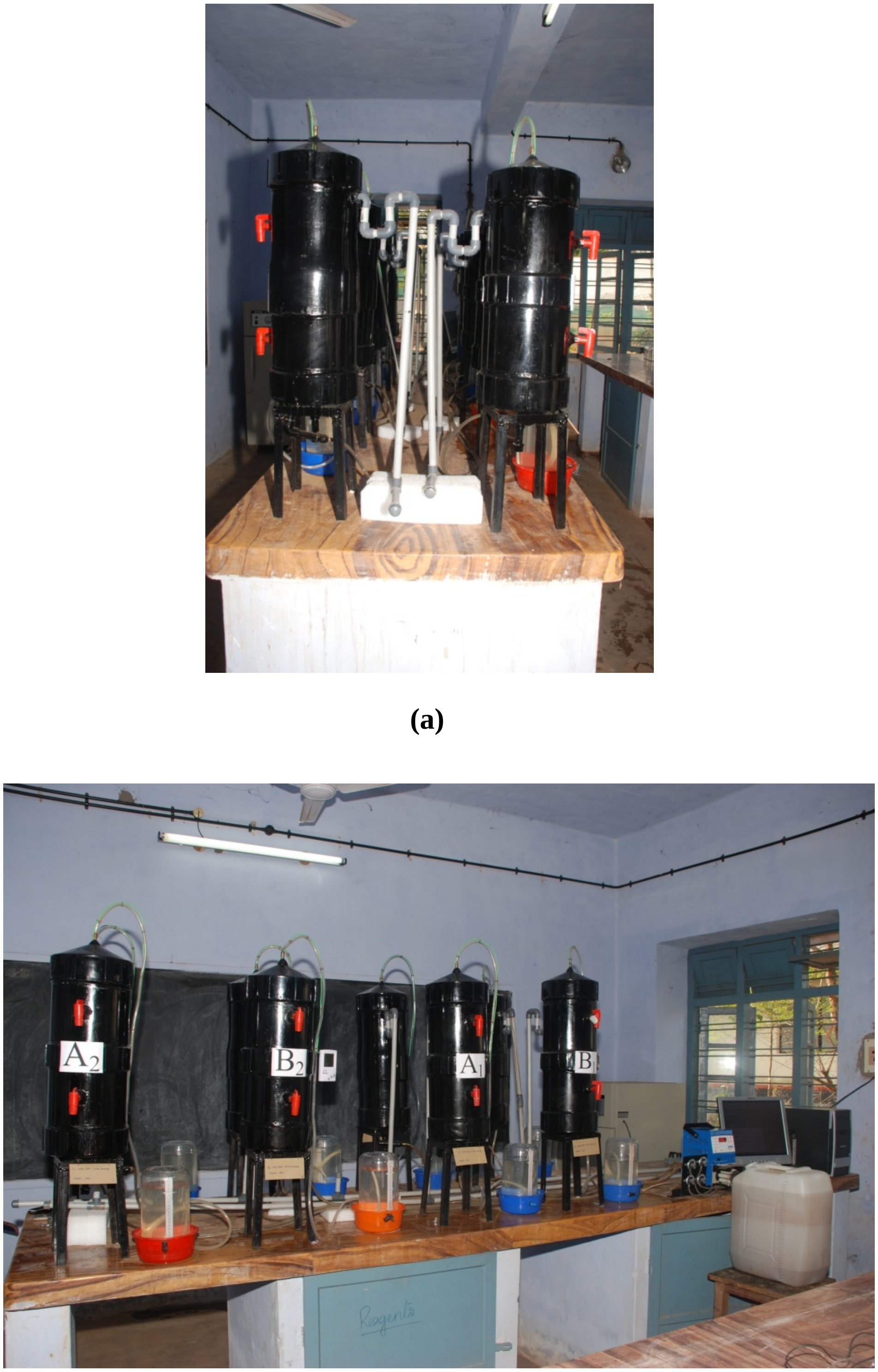
T_2 = 80 per cent RME + 20 per cent Digester sludge inoculum and rubber outer shell as media.

T_3 = 50 per cent RME + 50 per cent Cow dung inoculum and polyurethene rings as media.

T_4 = 50 per cent RME + 50 per cent Cow dung inoculum and rubber seed outer shell as media.

A minimum of 3 volume turnovers (3 HRTs) were allowed and steady state observations were recorded. The following parameters were observed as given below:

Parameter	**Frequency of observation**
Gas volume	Daily
Gas composition	Weekly
pH	Daily during start-up and once in three days thereafter



(a)

(b)

Plate 3.12 Layout of UAHRs in the laboratory

Temperature	Daily
TS of influent and effluent	Weekly
COD of influent and effluent	Weekly
BOD of influent and effluent	Weekly

The respective organic loading rates corresponding to different HRTs were computed by the relation,

$$\text{TS loading rate, kg/m}^3\text{.d} = \frac{\text{kg TS per litre x volume of feed } (\ell/\text{d})}{\text{Reactor volume m}^3}$$

$$\text{BOD loading rate, kg/m}^3\text{.d} = \frac{\text{kg BOD per litre x volume of feed } (\ell/\text{d})}{\text{Reactor volume m}^3}$$

$$\text{Hydraulic loading rate (HLR), } \ell/\text{m}^3 = \frac{\text{Volume of feed } (\ell)}{\text{Reactor volume m}^3}$$

RESULTS AND DISCUSSIONS

CHAPTER IV

RESULTS AND DISCUSSION

The results of the investigations carried out to study the physico-chemical characteristics of rice mill effluent (RME), preliminary biomethanation study, studies for selection of cell immobilization media as well as design, development, start-up, acclimation and performance evaluation of the Upflow Anaerobic Hybrid Reactors (UAHRs) are presented and discussed in this chapter.

4.1 Physico-chemical characteristics of RME

The RME samples were analysed for different parameters and its results are shown in Table 4.1. RME was found to be a very dilute waste water with a TS, BOD and COD values 3090, 3599 and 4100 mg/ℓ respectively. The carbon: nitrogen (C:N) ratio was found to be 22.4:1 with a BOD:COD ratio of 0.88. These results are comparable with the values reported by Queiroz *et al.* (2007). They reported COD values in the range of 2578 - 4090 mg/ℓ, TKN values in the range 25.4 to 88.03 mg/ℓ, pH values of 4.22 to 5.11 and C:N ratio between 32.16 and 197.7 for RME. Timur and Ozturk (1999) reported a BOD:COD ratio between 0.54 and 0.67 for landfill leachate and they opined that this shows better biodegradability. In the present study the COD value was slightly higher, the pH was slightly lower and TKN within the range of the reported value. The high value of BOD:COD ratio in this study indicated a good biodegradability of RME as opined by Gutierrez *et al*., (1991) and Timur and Ozturk (1999). High BOD:COD ratios of 0.45 and 0.57 were observed for distillery spent wash by Acharya *et al.*, (2008) and for cassava starch factory effluent by James and Kamaraj, (2004) respectively, indicating better biodegradability and resulting in higher reduction of TS and BOD. The C:N ratio in the present study was in the optimum ratio of 20-30:1 range for biomethanation recommended by Mathur and Rathore (1992) and indicated that there is no possibility of nitrogen deficiency in anaerobic digestion.

Table 4.1 Characteristics of RME

Sl. No.	Parameters	Mean values
1.	Total Solids (TS), mg/ℓ	3090
3.	Biochemical Oxygen Demand (BOD), mg/ℓ	3599
4.	Chemical Oxygen Demand (COD) mg/ℓ	4100
5.	Total Kjeldahl Nitrogen, mg/ℓ	73
6.	Total Organic Carbon, mg/ℓ	1636
7.	PH	3.87
8.	BOD : COD ratio	0.88
9.	C : N ratio	22.4:1

4.2 Biomethanation Characteristics of Rice mill effluent (RME)

The success of anaerobic treatment depends on proper design, for which the biomethanation characteristics of the feed materials are important. The results of the investigations on the preliminary anaerobic digestion experiments to study the biomethanation characteristics of RME are presented in this section.

4.2.1 Batch anaerobic digestion of RME

The batch anaerobic digestion of RME was carried out to assess the scope for biomethanation of RME as well as to get a basic information on the process conditions. This preliminary experiments were conducted with two treatments, T_0, the control consisting of cow dung (approximately 3 per cent TS) and T_1, a mixture of cow dung (same TS as T_0) and RME in the ratio 1:1. The study was continued for a period of 135 days till the biogas production ceased in the treatment T_1. The initial and final parameters observed are shown in Table 4.2. Total TS reductions of 59.8 and 60.2 per cent were obtained for T_0 and T_1, respectively. These values were higher than the TS reduction of 50 percent reported by James and Kamaraj

(2004) for cassava starch factory effluent due to the long duration of digestion ie. 135 days. The BOD showed a reduction of 93.1 per cent and 92.7 percent respectively for T_0 and T_1, which were also higher than the reported value of 90 percent by Araujo *et al*. (2008) for household waste water and 89% by Acharya *et al.* (2008) for distillery spend wash. An increase of pH from 7.74 to 8.4 was also noted for T_0 and 6.6 to 8.3 for T_1 in the present study, similar to the variation reported by Queiroz *et al*. (2007) for RME. This may be due to the conversion of volatile acids to methane and CO_2, which improved the alkalinity.

Table 4.2 Initial and final parameters of RME in the batch digestion study

Sl. No.	Parameters	T_o			T_1		
		Initial	Final	Per cent reduction	Initial	Final	Per cent reduction
1	Total solids (TS), mg/ℓ	31153	12512	59.83	17121	6812	60.21
2	Biochemical Oxygen Demand (BOD_5), mg/ℓ	8695	599.9	93.10	6147	449	92.69
3	PH	7.74	8.4	NA	6.6	8.3	NA

The RME - cow dung mixture (T_1) could generate a considerable amount of biogas and the performance was consistent, as depicted in Fig. 4.1. The peak gas production of 1.01 ℓ in the control (T_0) occurred on the 28th day and considerable amount of gas production was observed up to 50 days. After the 58th day, the gas production was very low (below 100 mℓ per day). In the case of T_1 the maximum gas production of 0.7 ℓ was achieved on the 14th day. The trend of good gas production continued until the 45th day and thereafter it dipped to low levels below 100 m ℓ. The gas production was found to have almost ceased (below 10 m ℓ per day) on 132nd day for T_0 and 107th day for T_1. The difference in the biomethanation characteristics of T_0 with T_1 is due to the difference in the physico-chemical characteristics. RME contains mostly soluble organics where as cow dung contains more of partially soluble or insoluble compounds.

The cumulutative biogas production for both T_0 and T_1 are shown in Fig. 4.2. The total gas produced in T_1 is 14.20 litres where as it was 25.92 litres for T_0.

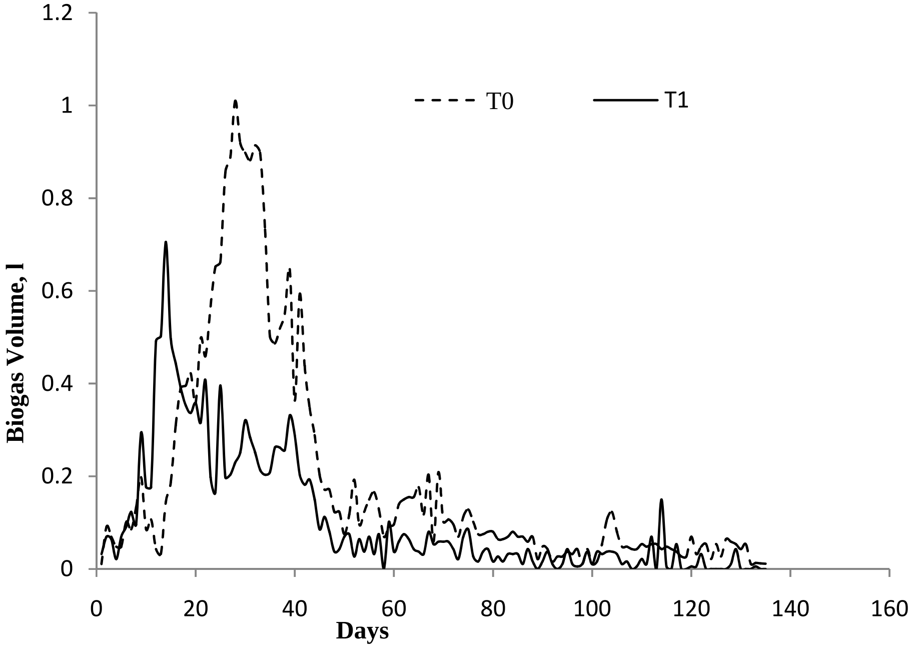


Fig . 4.1 Daily gas production during batch digestion

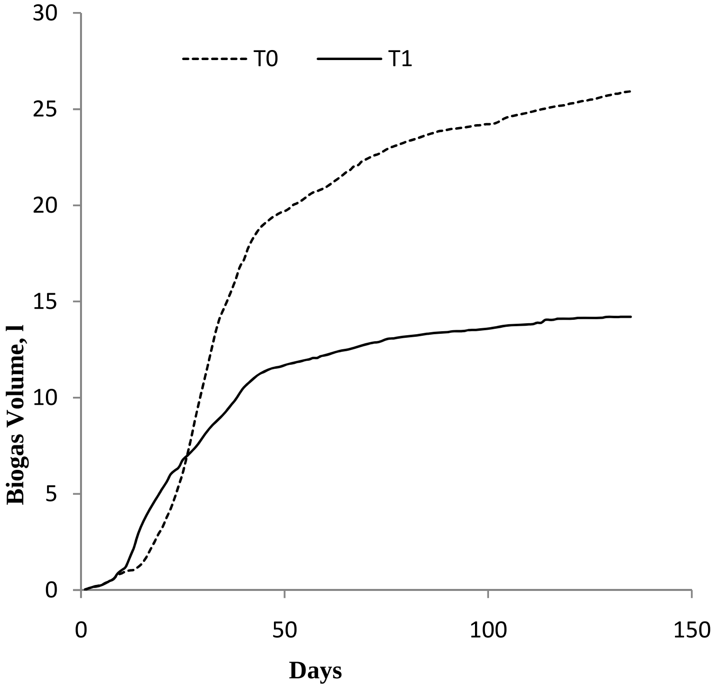


Fig . 4.2 Cumulative gas production in batch digestion

A biogas productivity of 2.59 and 1.4 ℓ/ℓ was observed for T_0 and T_1 respectively. This difference is due to the fact that T_0 contained more solids compared to T_1.

This study could ascertain the scope for biomethanation of RME indicating that energy (methane) could be effectively generated from it.

4.2.2 Biomethanation studies to investigate media compatibly

Suitability of the media for cell immobilization for the high rate bioreactors were examined in this study. This investigation was also aimed at ascertaining chances of inhibition to anaerobic bacteria by leachates from media as described by Nordstedt and Thomas (1985^b). The three media selected for the study viz. coconut shell, rubber seed inner shell, and rubber seed outer shell had significant differences in their physical characteristic.

4.2.2.1 Characteristics of the media

The physical characteristics of packing media selected are shown in Table 4.3

Table 4.3 Media characteristics

Sl. No	Parameters	Coconut shell	Rubber seed outer shell	Rubber seed inner shell
1	Bulk density kg/m^3	405.9	231.5	281.1
2	Porosity, per cent	57.5	58.8	56.1
3	Specific surface area, m^2/m^3	111.9	132.7	412.2

The specific surface area of the rubber seed inner shell was the highest and was nearly 3 and 3.6 times higher than that of rubber seed outer shell and coconut shell respectively. The physical appearance of the rubber seed inner shell was very smooth both on the inner and outer side, while the rubber seed outer shell had a porous and rather rough surface. A rough and porous surface enhances the biofilm development compared to smooth media surface (Patel and Madamwar, 2002; James and Kamaraj, 2003; Acharya *et al*., 2008). All these media had a specific surface area of more than 100, which is the minimum requirement for the effective biofilm formation (Young, 1991; James and Kamaraj, 2003^b; James and Kamaraj, 2004)

The porosity of the rubber seed outer shell media is lower than rubber seed inner shells and higher than coconut shell. The coconut shells are broken into small pieces in order to accommodate in the digester used for the study and resulted in a higher bulk density. The bulk density of coconut shell was nearly 75 and 44 per cent higher than rubber seed outer shell and rubber seed inner shell respectively. Considering the high porosity, moderate specific surface area as well as bulk density, rubber seed outer shells seemed to be a good candidate for utilization as media in the high rate bio reactor.

4.2.2.2 Start up of semi-continuous digesters

The investigation comprised of 12 treatments with 3 replications in 10 litre digesters for the media compatibility study as outlined in section 3.3

Start-up characteristics of RME were observed in different treatments by comparing their biogas production. The cell immobilization media viz. coconut shell, rubber seed inner shell and rubber seed outer shell were tested for their compatibility using 12 treatments. There were treatments with 100 per cent cow dung mixture (T_0, T_{01}, T_{02} and T_{03}), RME with 50 per cent cow dung inoculum (T_1, T_2, T_3 and T_4) and neutralized RME with 20 per cent cow dung inoculum (T_5, T_6, T_7 and T_8).

When the gas production performance of media filled digesters started up with 100 per cent cow dung mixture was observed, the maximum gas production of 2.98 ℓ occurred in the digester with rubber seed outer shell as media (T_{03}) on the 14th day, followed by the digester with coconut shell (T_{01}) and rubber seed inner shell (T_{02}) respectively (Fig. 4.3). During the initial days the digester with coconut shell showed poor performance indicating possible inhibition as reported by James and Kamaraj (2004). The digester with rubber seed inner shell showed better performance than the other two in the start-up period. Gas production from digesters with rubber seed outer shell was comparable to no media reactor throughout the start-up period. Even though digesters with rubber seed inner shell showed better performance in the beginning, slight inhibition in the later stage could be observed. The average gas production was maximum for the treatment T_{02} (1.06 ℓ/d), followed by T_{03} (0.98) and T_{01} (0.69 ℓ/d). The control (T_0) had an average gas production of 1 ℓ/d, close to T_{02} and T_{03} indicating that both inner and outer shells of rubber seed are more compatible than coconut shell for biomethanation, at least in the start-up period.

The gas production of digesters with the different (three) media, started up with the mixture of cow dung and RME in the ratio 1:1 is depicted in Fig. 4.4. The treatment with rubber seed outer shell as media (T_4) showed the peak value of 1.5 ℓ on the 11th day, followed by digester with the rubber seed inner shell as media (T_3) with 1.44 ℓ on the 11th day. The treatment with coconut shell (T_2) showed its peak value of 1.27 ℓ on the 12th day. It is evident that the treatment with rubber seed outer shells performed better than the other two media in not only attaining the peak value fast but also in the quantity of biogas.

The performance characteristics of the treatments with the three media, started up with the mixtures of 20 per cent cow dung and 80 per cent neutralized RME is illustrated in Fig.4.5. The maximum of the peak values was exhibited by the digester with the rubber seed outer shell (T_8) as media with the gas production of 0.88 ℓ on the 15th day but had a slow start-up. The gas production picked up only after the 9th day. This was closely followed by the coconut shell media digester (T_6), with a gas production of 0.74 ℓ on the 15th day. The digester with rubber seed inner shell as media (T_7) did not show any starting problem and showed a maximum gas production of 0.7 ℓ on the 10th day. The average gas production from the no media treatment T_5 was 0.17 ℓ/d where as T_7 recorded the highest value of 0.47 ℓ/d followed by T_8 and T_6 both having 0.23 ℓ/d gas production. This erratic behaviour was different from the trend shown for other treatments and this might have occurred due to the insufficiency of the inoculum volume of 20 per cent.

James and Kamaraj (2004) observed that coconut shell media had an inhibitory effect during batch digestion studies in their investigation on cassava starch factory effluent. They reported this inhibition of coconut shells are likely to be caused due to production of phenolic compounds. They expected that this effect need not be persistent in semi-continuous and continuous systems. Further studies

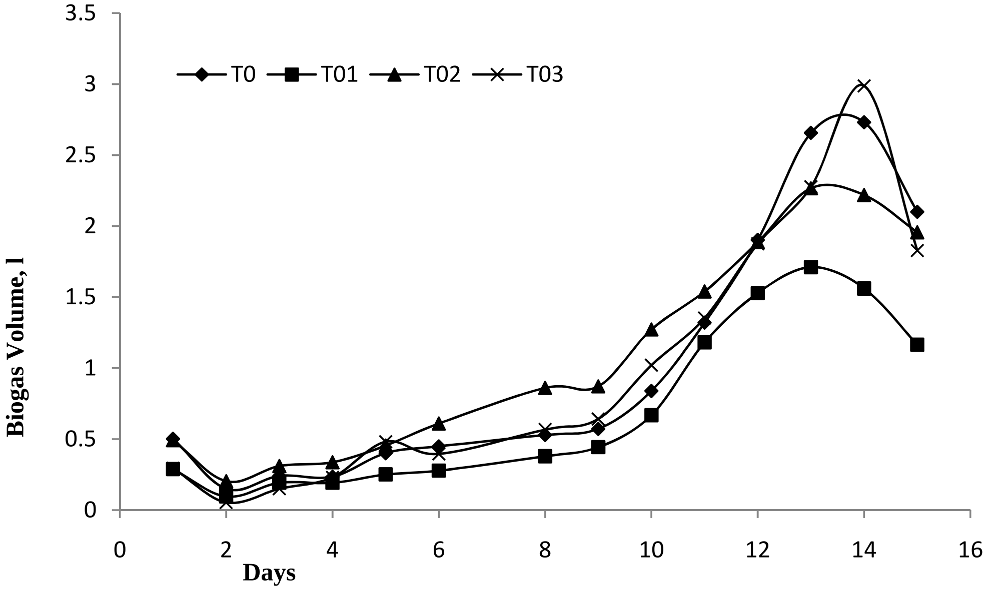


Fig 4.3 Daily gas prodiction during start-up from cowdung in digesters with different media

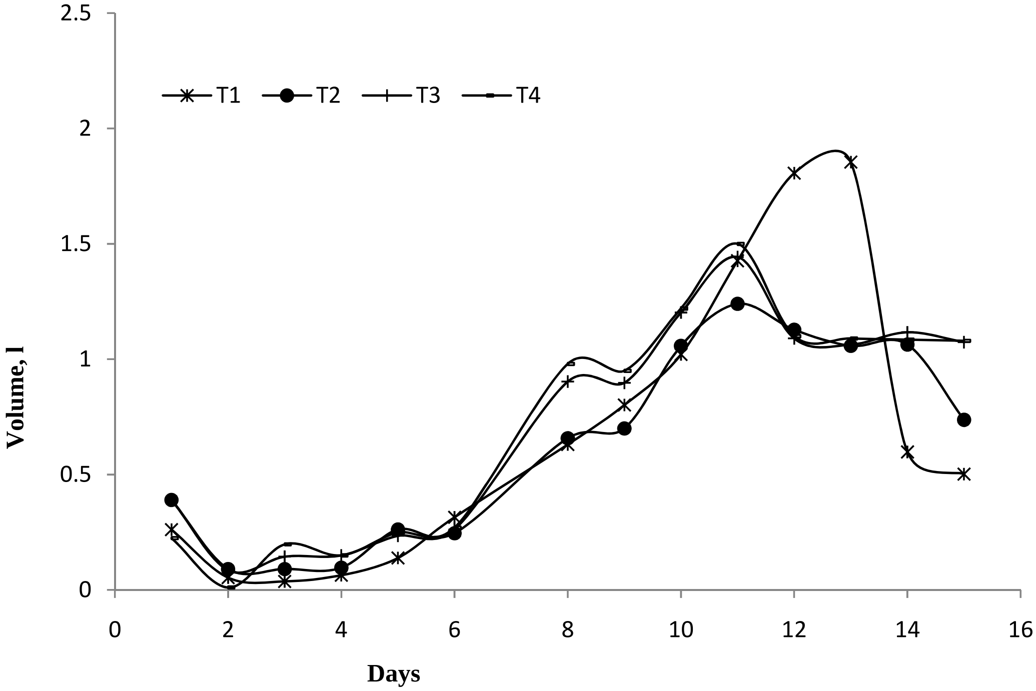


Fig 4.4 Daily gas prodiction during start up from cow dung and RME in the ratio 1:1 in digesters with different media

could prove that their observation was correct in which they found that in the long run the inhibitory compounds got washed out in the pretreatment as well as by the flushing occurring in high rate reactors(James and Kamaraj, 2009).

Acharya *et al.* (2008) while treating distillery spent wash took 35 to 40 days for the digester to stabilize whereas tobacco industry effluent took three months for the digester stabilization (Araujo *et al.*, 2008). The behaviour of digesters shown in Fig. 4.3 to 4.5, indicates that the digesters started up between the 8th and 12th day while operating in batch mode for start-up. Steady increase in gas production was seen due to the presence of readily degradable soluble carbohydrates resulting in easy fermentation to biogas (Noike *et al.,* 1985 and Oktem *et al.* 2007). It is also reported that RME contains nearly 9 to 10 mg/ℓ of glucose (Ramalingam and Raj, 1996), which is also a readily fermentable material. The performance of digesters in the start-up phase revealed that the treatments with rubber seed inner shell and rubber seed outer shell as media showed better gas production than the treatments with coconut shell as media. The poor start-up of digesters with coconut shell as media indicates possible inhibition from the media as coconut shells contain high lignin resulting in the leaching of phenols which inhibit the growth of methanogens as already reported by James and Kamaraj, (2004).

4.2.3 Acclimation of digesters by daily feeding.

Daily feeding of the digesters was started from the 16th day after first charging the digesters and were run for 72 days at this HRT. The influent TS was 3083 mg/ℓ and BOD of 3559 mg/ℓ with a pH of 3.87. Before the start of daily feeding, T_{02} showed the maximum TS of 20252 mg/ℓ while the lowest was for T_7 (4973 mg/ℓ). The BOD before start of daily feeding was observed to be lowest for T_{01} (976.1 mg/ℓ) and the remaining treatments had values ranging between 1083 and 1131 mg/ℓ. The pH values were in the range between 6.88 and 7.23 (Table 4.4), the similar range of pH was reported as favorable for start of daily feeding by Acharya *et al.* (2008). The daily gas production of the treatments are illustrated in Fig. 4.6 It was clear from the figure that there were two phases in the gas production, an unsteady phase and a steady phase, which is referred as pseudo steady state (PSS) by Podruzy and Mc Lean (1989). A true steady state condition cannot be

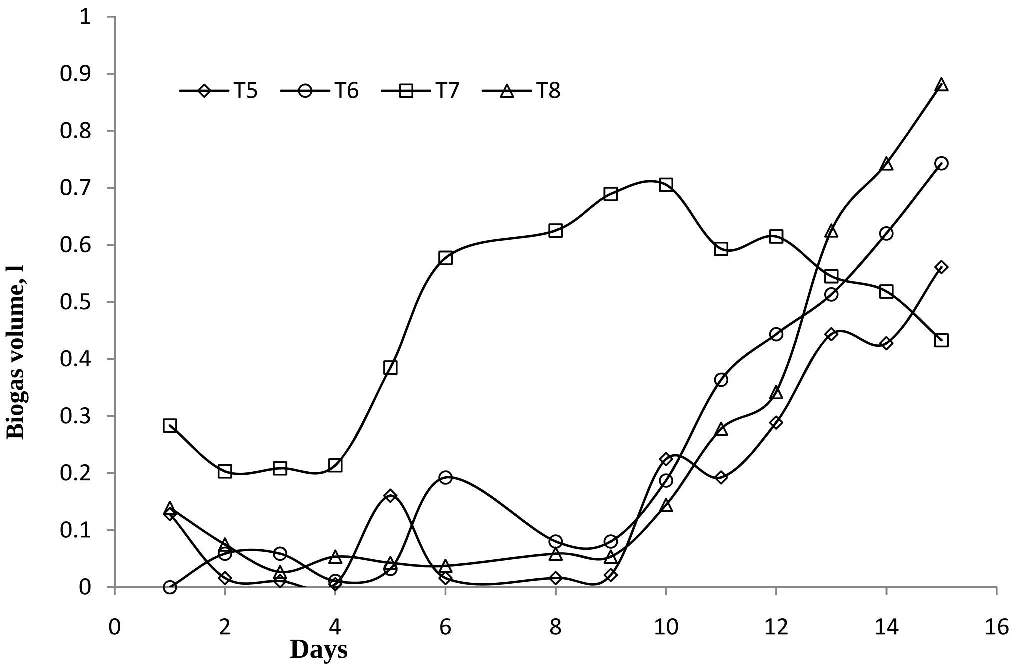


Fig 4.5 Daily gas production during start-up from digesters with 20 per cent cow dung and 80 per cent neutralized RME.

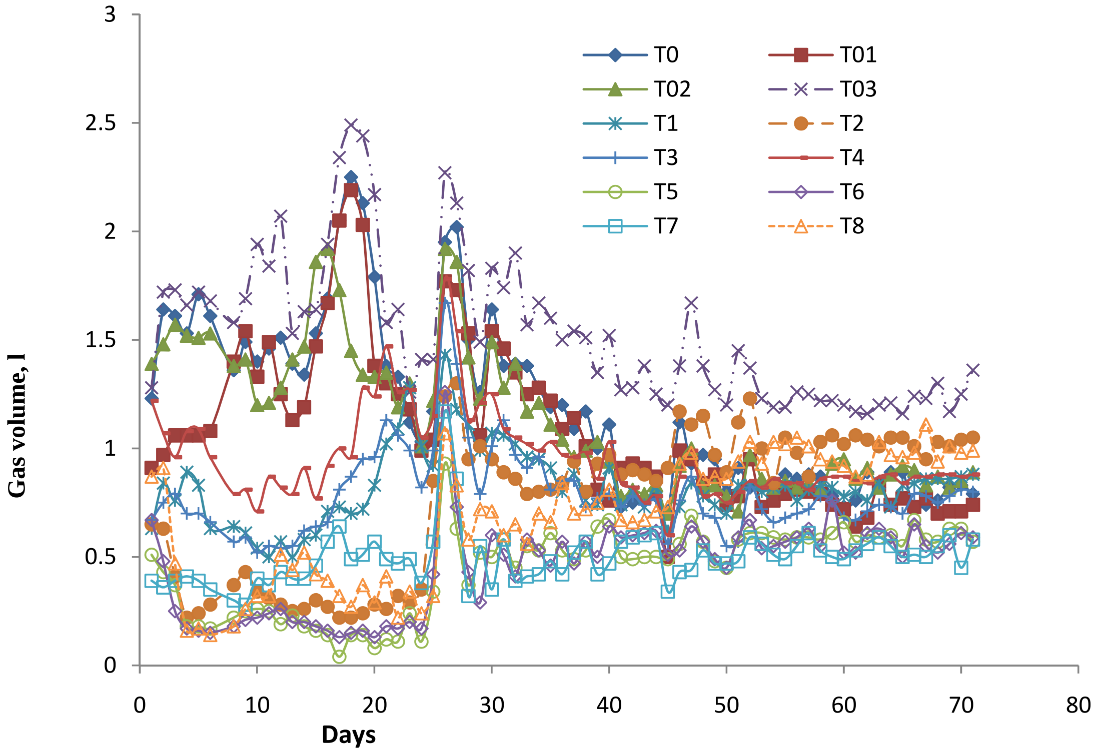


Fig. 4.6 Daily gas production by different treatments at 20 day HRT

achieved since bioreactors are designed for gradual accumulation of biomass. The amplitude of variation of biomass accumulation is negligible when compared to the biomass content in the reactor and does not contribute much to the reactor dynamics and such a state is referred as pseudo steady state (PSS) (James and Kamaraj, 2007). The digesters took 50 to 56 days to achieve PSS phase as indicated by daily biogas production. The maximum daily gas production in the unsteady phase (APPENDIX I) was 1.22 ℓ/d for the treatment T_{03} and a minimum value of 0.53 ℓ/d in T_7.

Table 4.4 TS, BOD and pH of RME at 20 day HRT period in semi-continuous digester

Sl. No.	Treatment	TS, mg/ℓ			BOD, mg/ℓ			pH		
		initial	Before the start of daily feeding	20 day HRT	initial	Before the start of daily feeding	20 day HRT	initial	Before the start of daily feeding	20 day HRT
1	T0	28900	10707	1129	8696	1083	1231.0	7.7	7.2	7.2
2	T01	28900	11447	1058	8696	976	1067.7	7.7	7.1	7.1
3	T02	28900	20252	1138	8696	1107	1081.1	7.7	7.2	7.2
4	T03	28900	10972	1122	8696	1131	1061.1	7.7	7.2	7.2
5	T1	15995	7536	1130	6147	1119	1301.3	6.6	7.2	7.2
6	T2	15995	13670	1183	6147	1131	1174.5	6.6	7.2	7.2
7	T3	15995	14857	1111	6147	1107	1147.8	6.6	7.2	7.1
8	T4	15995	7354	1086	6147	1107	1027.7	6.6	6.9	6.9
9	T5	16058	5100	1091	4619	1101	1308.0	7.1	7.1	7.1
10	T6	16058	5726	1000	4619	1107	1181.2	7.1	6.9	7.0
11	T7	16058	4972	1154	4619	1107	1341.3	7.1	7.4	7.3
12	T8	16058	5361	1147	4619	1131	1101.1	7.1	7.0	7.1

4.2.3.1 Biomethanation performance of treatments at the start up HRT of 20 days

The different treatments could be assessed for their biomethanation performance by observing their biogas production capacity as well as solids reduction ability. The daily feed rates of 0.5 ℓ corresponding to a hydraulic loading rate (HLR) of 50 ℓ/m^3.d for all reactors, were constant throughout the 72 day period. The organic loading rates in terms of TS and BOD were 0.154 kg/m^3.d and 0.177 kg/m^3.d respectively and are low due to the long HRT as well as low TS of the RME. The Fig.4.7 shows the per cent reduction of TS and BOD during the PSS phase of 20 day HRT. The results showed that among the digesters filled with cow dung mixture only the maximum TS reduction of 65.8 per cent and BOD reduction of 71.6 per cent was sighted in T_{03} (treatment having rubber seed outer shell). In the treatments with cow dung and RME in 1:1 mixture, the treatment T_4 (also with rubber seed outer shell media) had the maximum reduction of 64.9 and 72.2 per cent in TS and BOD, respectively. The treatment with 20 per cent cow dung and 80 percent neutralized RME mixture (T6) showed the maximum reduction of 67.6 and 70 per cent for TS and BOD respectively. As evident from Fig. 4.7 the treatments with rubber seed outer shell media had the highest performance in organic reduction followed by those with rubber seed inner shell media, and those with coconut shell media. This indicated that there was some inhibition with coconut shell even though it was not significant. Among the treatments with media, the highest reductions of 67.6 and 72.2 per cent was demonstrated by T_6 for TS and BOD.

The specific gas production and volumetric gas production of different treatments are illustrated in Fig. 4.8. During PSS the maximum specific gas production of 1044.3 ℓ/kg TS and 904.7 ℓ/kg BOD in T_{03} while the minimum value of 253.0 ℓ/kg TS and 219.1 ℓ/kg BOD was seen in T_6. But considerable variation was not observed for different treatments as depicted in Fig. 4.8.

4.2.4 Performance Evaluation of the digesters.

Subsequent to the start-up HRT of 20 days, the digesters were evaluated by operating at HRTs 15, 10 and 5 day. They were allowed to reach the PSS condition at each HRT by maintaining the reactors at the respective HRTs for a minimum duration of three volume turnovers.

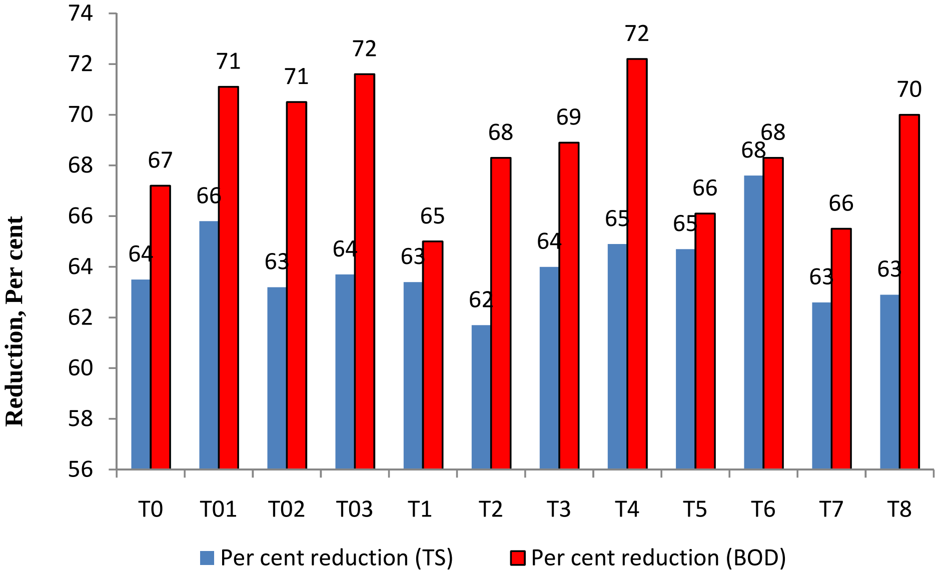


Fig. 4.7 Reduction of TS and BOD for different treatments during 20 day HRT

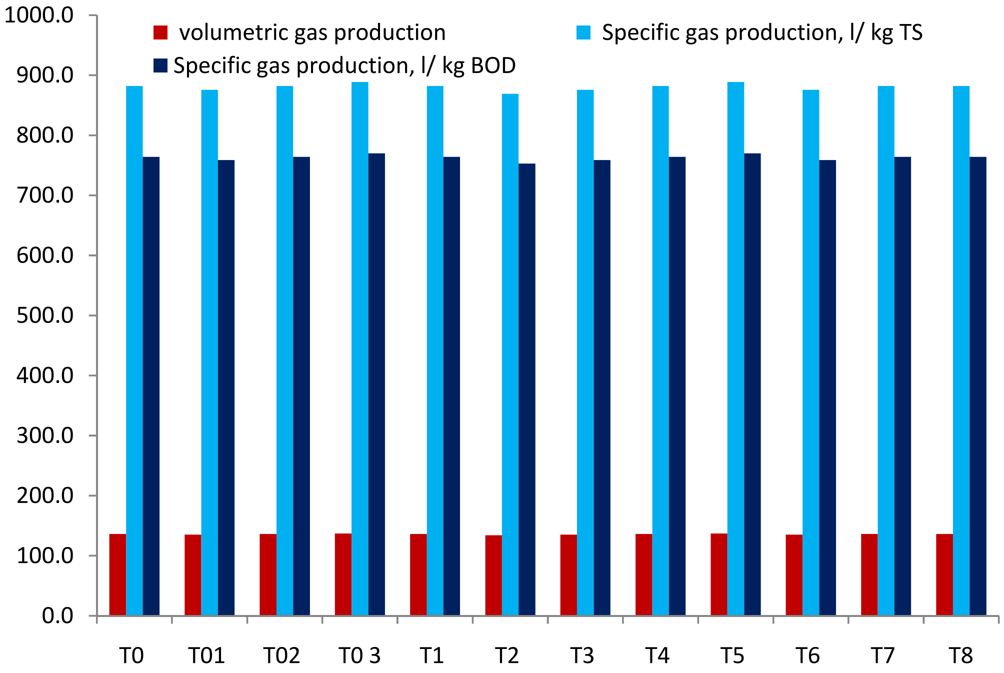


Fig. 4.8 Specific and volumetric gas production by different treatments at 20 day HRT

4.2.4.1 Influent and effluent characteristics of at different HRTs

The influent and effluent characteristics, viz. pH, TS and BOD were regularly monitored. Tables 4.5 show the mean values for the influent RME at various HRTs. The RME was periodically collected from the rice mill and slight variation in the values could be observed. The effluent characteristics at PSS of 20, 15, 10 and 5 day HRT were shown in Table 4.6

Table 4.5 Influent characteristics at various HRT

Parameter	20 day	15 day	10 day	5 day
TS, mg/ℓ	3083	3125	3150	3150
BOD, mg/ℓ	3559	3479	3551	3639
pH	3.87	3.9	3.8	3.8

Table 4.6 Effluent characteristics at different HRT

Treatments	BOD, mg/ℓ				TS, mg/ℓ				pH			
	20 day	15 day	10 day	5 day	20 day	15 day	10 day	5 day	20 day	15 day	10 day	5 day
T_0	1231	1141	1181	1261	1129	1215	1321	1365	7.2	6.9	7.0	6.9
T_{01}	1068	1121	1181	1281	1058	1204	1327	1358	7.2	6.9	7.0	6.9
T_{02}	1081	1161	1201	1261	1138	1272	1344	1402	7.2	7.0	6.9	6.9
T_{03}	1061	1101	1161	1241	1122	1060	1331	1351	7.2	6.9	6.9	6.9
T_1	1301	1261	1321	1401	1130	1148	1391	1415	7.2	6.9	6.9	6.9
T_2	1175	1221	1281	1321	1183	1267	1296	1400	7.2	6.9	6.9	6.9
T_3	1148	1101	1161	1261	1111	1045	1320	1374	7.1	6.9	6.9	7.0
T_4	1028	1121	1181	1241	1086	1097	1392	1350	6.9	6.9	6.7	7.0
T_5	1308	1241	1281	1341	1091	1248	1325	1422	7.1	6.9	6.9	6.9
T_6	1181	1201	1241	961	1000	1122	1331	1403	7.0	6.9	6.9	7.0
T_7	1341	1311	1361	1421	1154	1269	1347	1293	7.3	6.8	6.9	7.0
T_8	1101	1186	1261	1321	1147	1315	1318	1357	7.1	6.8	6.7	6.9

4.2.4.1.1 pH and TS

While pH of the influent varied between 3.8 and 3.9, the effluent pH values remained almost neutral (pH 6.9-7.3) during the entire period of investigation (Fig. 4.9). This is an indication of the stable operation of the reactors throughout the period of operation. (Acharya *et al*., 2008 and Kumar *et al.* 2009) have also reported that pH is the most effective indicator with regard to the stability of the system. A general trend of decrease in the pH was observed in all the treatments with the decrease in HRT.

Fig.4.10 illustrate the variation of effluent TS. The effluent TS values for all treatment were between 1402.6 mg/ℓ to 1000 mg/ℓ. In general, the effluent TS is likely to go higher and higher as HRT is reduced (Chaya *et al*., 2008). Acharya *et al*., (2008) verified that this is true in the case of an industrial effluent they investigated. But in this study, the transition from 20 day to 15 day HRT shows an erratic behaviour. Some of the treatments viz. T_{03}, T_1, T_3 and T_4 had a low effluent pH at 15 day compared to 20 day HRT. These digesters probably had an increased biomass accumulation in the transition period so as to counter act the effect of increased hydraulic loading. But the transition from 15 day HRT caused a hike in effluent TS in all treatments. The reduction of HRT from 10 day to 5 day also had similar effect except for T_{01} and T_4 which again could be due to the increased biomass accumulation on media surface during the period. The influent TS varied between 3083.3 mg/ℓ and 3150.3 mg/ℓ.

4.2.4.1.2 BOD

Fig. 4.11 shows the variations in effluent BOD values for all the reactors at various HRTs. During the period, influent BOD slightly varied between 3479 mg/ℓ and 3639 mg/ℓ. The effluent BOD also registered an erratic behaviour similar to TS during transition from 20 day to 10 day HRT. In general the lowest effluent BOD value of 1028 mg/ℓ was found in the treatment T_4 at 20 day HRT and the highest value 1308 was found in T_5 at 20 day HRT. Thus it was clear that the general trend was an increase in BOD as the HRT was reduced, the maximum values seen in 5 day HRT period. Acharya *et al.*(2008) also reported a similar trend.

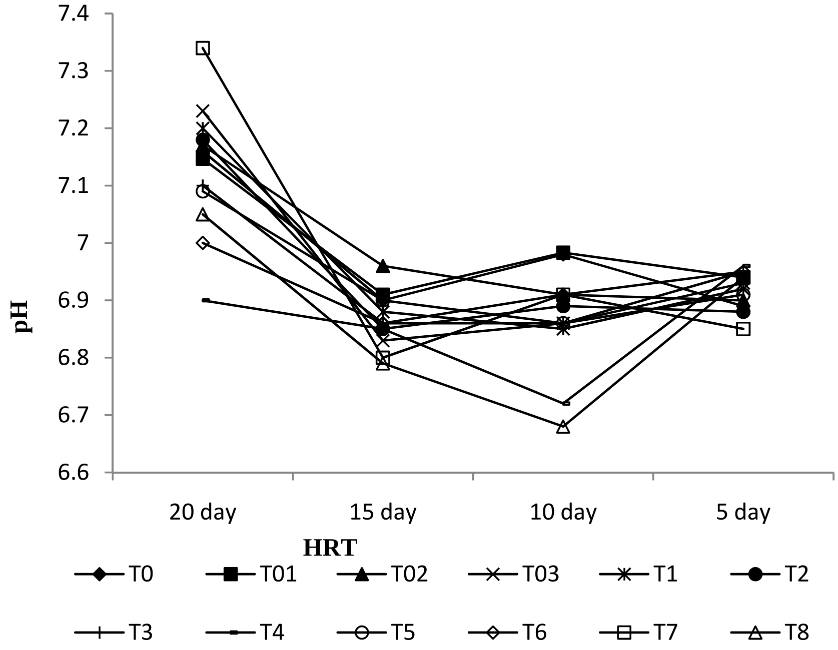


Fig 4.9 Variation of effluent pH at different HRT

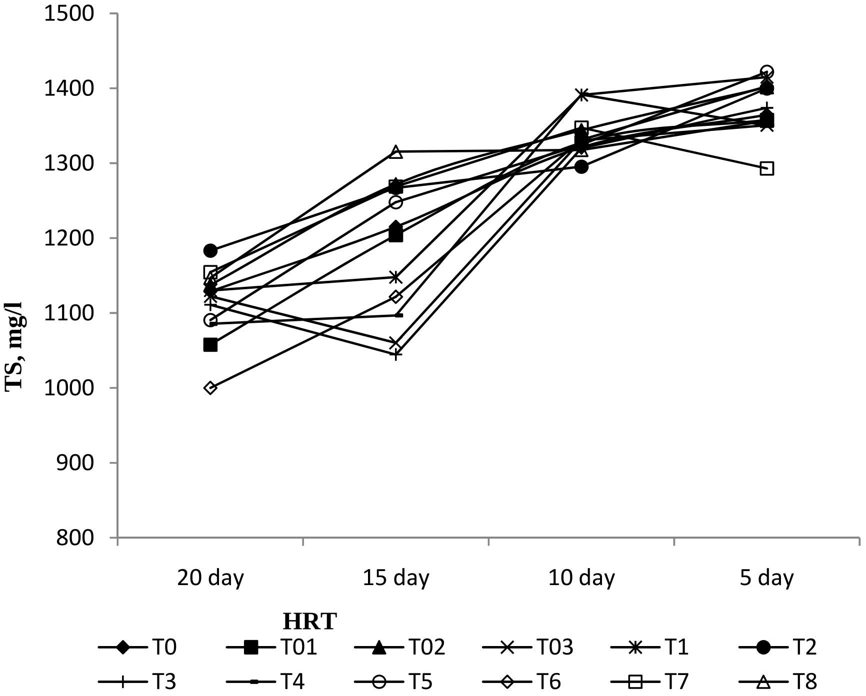


Fig 4.10 Variation of effluent TS at different HRT

4.2.4.2 Performance of digesters at different HRTs

The performances of the digesters as described by different parameters like gas production, TS and BOD reduction during different HRTs are presented in this section.

4.2.4.2.1 Gas production

Gas production rates are the most important indicators for the performance for anaerobic reactors (James and Kamaraj, 2002). Table 4.7 shows the average daily gas production of the various treatments at PSS period of different HRTs. Among the treatments started up with 100 per cent cow dung, the treatment with rubber seed outer shell media (T_{03}) exhibited the maximum gas production at all HRTs with a mean daily gas production of 1.37, 1.75, 2.27 and 2.58 ℓ/d respectively for 20, 15, 10 and 5 day HRT periods. T_{03} was closely followed by T_{02} and shared the same gas production at 10 day and 5 day HRT while the control T_0 had a similar gas production to T_{03} at 10 day HRT. The values for T_0 was higher than T_{01} on all HRT periods except on 10 and 5 day HRT during which both the treatments were similar. Fig.4.12 depicts the trends of daily gas production at different HRTs, which made it evident that the daily gas production increased steadily for all treatments as the HRT was reduced.

Table 4.7 Daily gas production at PSS periods of different HRT for semi-continuous digestion study

Treatments	20 Day HRT	15 Day HRT	10 Day HRT	5 Day HRT
T_0	1.36	1.64	2.27	2.57
T_{01}	1.35	1.64	2.24	2.57
T_{02}	1.36	1.64	2.27	2.58
$T_{0 3}$	1.37	1.75	2.27	2.58
T_1	1.36	1.64	2.22	2.59
T_2	1.34	1.64	2.22	2.57
T_3	1.35	1.64	2.23	2.58
T_4	1.36	1.65	2.26	2.60
T_5	1.37	1.64	2.23	2.59
T_6	1.35	1.63	2.22	2.59
T_7	1.36	1.64	2.27	2.59
T_8	1.36	1.64	2.29	2.59

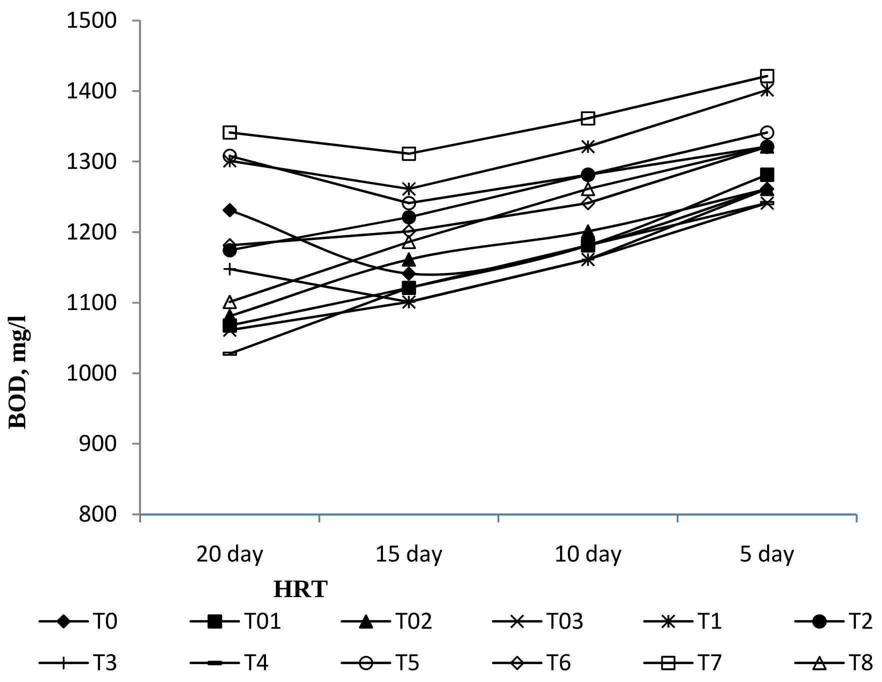


Fig 4.11 Variation of effluent BOD at different HRT

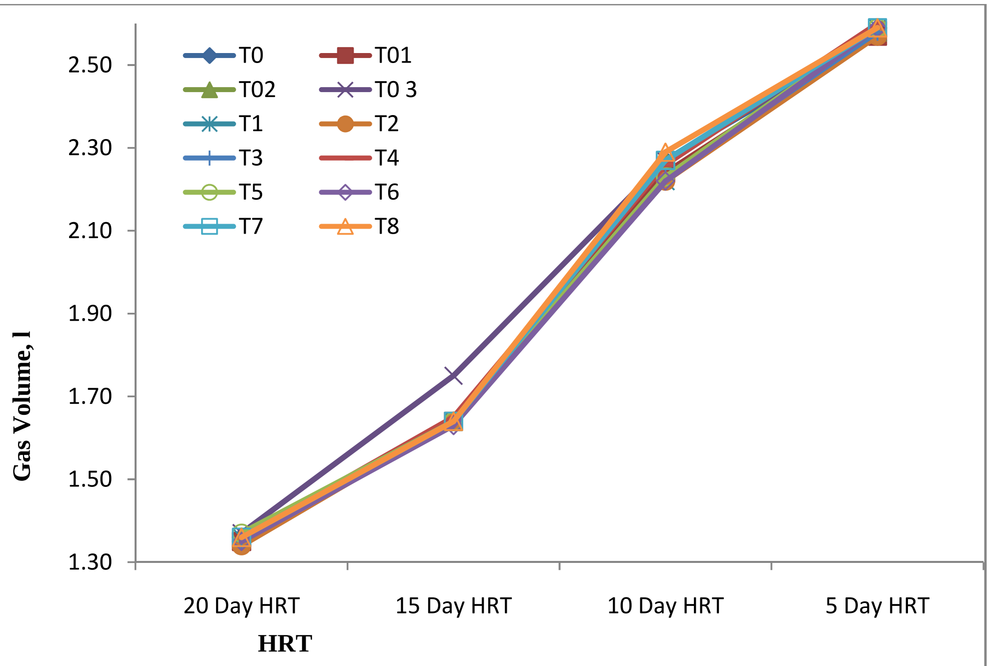


Fig. 4.12 Mean daily gas production at PSS periods of different HRT

Among the digesters filled with a mixture of cow dung and RME in the ratio 1:1, the highest gas production was observed in T_4 on all HRTs with values 1.36, 1.65, 2.26 and 2.60 ℓ/d. At 15 day HRT, the gas production of T_1 was equal to T_4. T_4 was closely followed by T_3 but T_1 had higher gas production than T_3 on 20 day and 5 day HRT periods and same gas production as T_3 on 15 day HRT. At 15 day HRT all treatments expect T_4 has the same gas production of 1.64 ℓ/d. This indicated that at long HRT, the treatments did not differ significantly.

The gas production data of digesters filled with 20 per cent cow dung and 80 per cent neutralized RME showed that the maximum daily gas production on all the HRTs except on the 20 day HRT was observed for T_8. T_4 had the maximum value at 20 day HRT. T_7 had the same daily gas productions as that of T8 at 20, 15 and 5 day HRT. At 5 day HRT, all the treatments had the same gas production of 2.59 ℓ/d. The maximum gas productions at different HRTs were 1.37, 1.64, 2.29 and 2.59 ℓ/d.

It was also clear from Fig. 4.12 that the performance of the digesters containing the rubber seed outer shell as media was marginally higher than the other two media. The rubber seed inner shell followed the rubber seed outer shell which in turn was followed by coconut shell. This indicated a slight inhibition by coconut shell media even though it was not prolonged. James and Kamaraj (2004) also experienced poor performance due to the release of phenols which inhibited the methanogenic bacteria resulting in poor gas production in coconut shell media filled batch digesters. But they also observed that the inhibition was insignificant in the long run when coconut shells were used in a high rate bioreactor (James and Kamaraj, 2003[b]).

4.2.4.2.2 Specific gas production

The specific gas production in terms of TS and BOD are illustrated in Table 4.8. Among the digesters containing 100 per cent cow dung, the treatment T_{03} had the maximum specific gas production in terms of TS and BOD throughout the study as depicted in Fig. 4.13 and 4.14. The highest specific gas production in terms of TS and BOD were 769.8, 762.1, 639.2 and 354.5 ℓ/kg TS and 736.8,

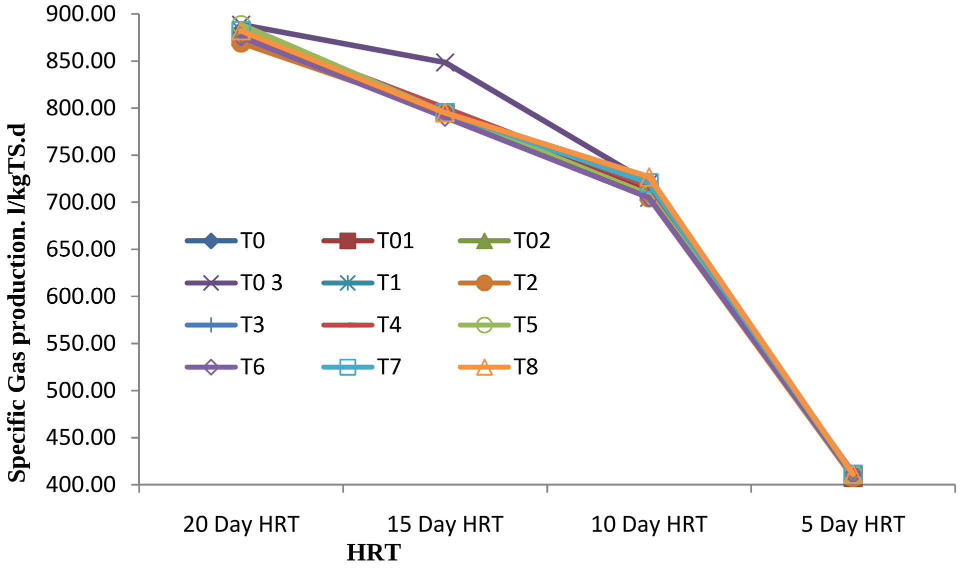


Fig . 4.13 Specific gas production in terms of TS at different HRT

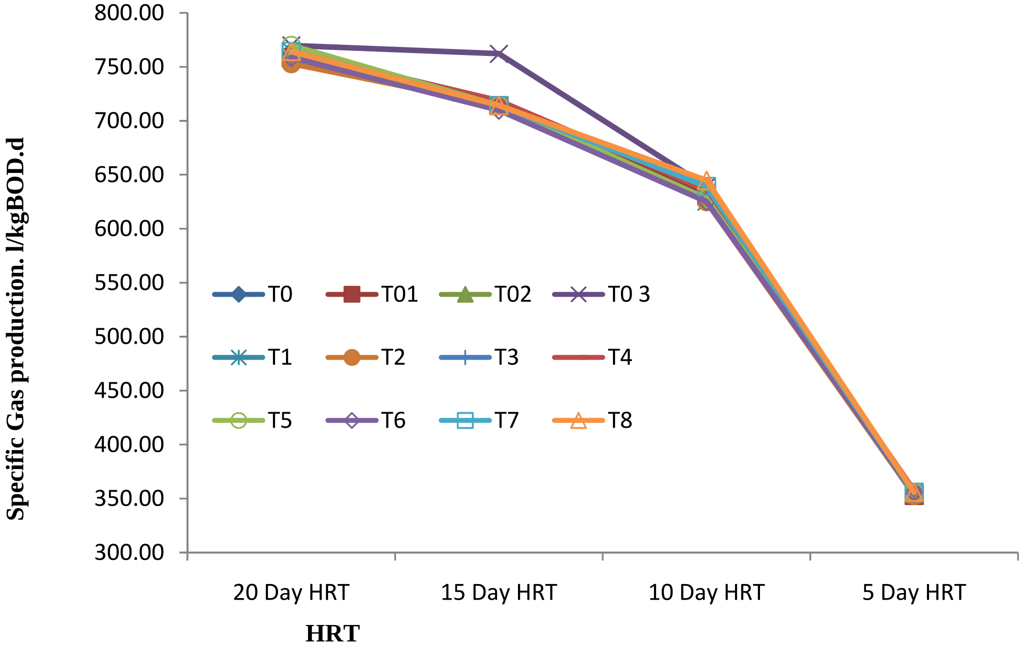


Fig . 4.14 Specific gas production in terms of BOD at different HRT

762.1, 639.2 and 354.5 ℓ/kg BOD respectively for 20, 15, 10 and 5 day HRT. The treatments T_{02} and T_0 had the same specific gas production in terms of both TS and BOD at 10 day HRT.

Among the digesters initially charged with a mixture of cow dung and RME in the ratio 1:1, highest specific gas production both in terms of TS and BOD was observed for T_4. The values were 882.2, 800, 717.5 and 412.7 ℓ/kg TS and 764.2, 718.5, 636.4 and 357.2 ℓ/kg BOD corresponding to 20, 15, 10 and 5 day HRT.

Among the digesters initially charged with 20 per cent cow dung and 80 per cent neutralized RME, T_8 showed the maximum specific gas production in terms of both TS and BOD. The trend shown by various treatments at different HRTs in Fig. 4. 13 and Fig. 4.14 indicates that all the treatments behaved similarly at the shortest HRT of 5 day

Table 4.8 Specific gas production at different HRT during semi-continuous digestion

Treatments	Volume, ℓ/ kg TS				Volume, ℓ/ kg BOD			
	20 Day HRT	15 Day HRT	10 Day HRT	5 Day HRT	20 Day HRT	15 Day HRT	10 Day HRT	5 Day HRT
T_0	882.2	795.2	720.7	407.9	764.2	714.2	639.2	353.1
T_{01}	875.7	795.2	711.2	407.9	758.6	714.2	630.8	353.1
T_{02}	882.2	795.2	720.7	409.5	764.2	714.2	639.2	354.5
T_{03}	888.7	848.5	720.7	409.5	769.8	762.1	639.2	354.5
T_1	882.2	795.2	704.8	411.1	764.2	714.2	625.1	355.8
T_2	869.2	795.2	704.8	407.9	753.0	714.2	625.1	353.1
T_3	875.7	795.2	707.9	409.5	758.6	714.2	627.9	354.5
T_4	882.2	800.0	717.5	412.7	764.2	718.6	636.4	357.2
T_5	888.7	795.2	707.9	411.1	769.8	714.2	627.9	355.8
T_6	875.7	790.3	704.8	411.1	758.6	709.8	625.1	355.8
T_7	882.2	795.2	720.6	411.1	764.2	714.2	639.2	355.8
T_8	882.2	795.2	727.0	411.1	764.2	714.2	644.8	355.8

From the above observations its clear that the digesters containing rubber seed outer shell media had the highest specific gas production in terms of both TS and BOD compared to the other two media, even though the difference is not very significant. Manilal *et al.* (1990) was able to get only 20 to 60 ℓ/kg TS indicating that the feed used by them was only partly biodegradable. James and Kamaraj (2009) while treating cassava starch factory effluent reported a specific gas production as high as 908.5 ℓ/kg TS. However in the present study the maximum specific gas production is 882.2 ℓ/kg TS, lower than the value reported above.

4.2.4.2.3 Volumetric biogas production and biogas productivity

The volumetric gas production of different treatments are illustrated in Table 4.9 and the trend followed by different treatments are illustrated in Fig. 4.15. Among the digesters initially charged with 100 per cent cow dung, the treatment T_{03} showed the maximum volumetric gas production at all HRTs, with values 136.0, 164.0, 227.0 and 258.0 ℓ/m^3 of the reactor. In the digesters initially charged with the mixture of cow dung and RME in the ratio 1: 1 the treatment T_4 depicted best performance on all HRTs. The volumetric gas productions were 136.0, 165.0, 226.0 and 260.0 ℓ/m^3 of the reactor. Among the digesters charged with a mixture of 20 percent cow dung and 80 per cent neutralized RME the treatment T_8 showed the highest volumetric gas production on all HRTs expect 20 day HRT. The volumetric gas productions steadily increased for all treatments when the HRT was shortened.

From the study, it fairly evident that the digesters containing the rubber seed outer shell as media had higher volumetric gas production than the other two media. The rubber seed inner shell followed the rubber seed outer shell which in turn was followed by coconut shell media.

Biogas productivity of various treatments are shown in Table 4.10. It is very clear that the biogas productivity per litre of RME has displayed a decreasing trend when HRT was shortened, in the case of all treatments.

4.3 Media and process parameters for Laboratory-scale Upflow Anaerobic Hybrid Reactors

The results of the studies outlined in section 4.2 has indicated that rubber seed outer shell is compatible with anaerobic digestion. The porosity and bulk density parameters also indicated that the rubber seed outer shell was a better media than the other two media used for the study. Thus rubber seed outer shell was selected as the media to be used for the UAHRs.

Among the treatments the digesters started up with 100 per cent cow dung solution showed the best gas production in terms of specific gas production and volumetric gas production. They were very closely followed by digesters with the mixture of cow dung and RME in the ratio 1:1. Whereas the neutralized RME digesters inoculated with 20 per cent cow dung showed poor performance. This indicated that volume of cow dung to be inoculated is 50 per cent or more for better start up and continued stability of the reactor. It is not practically feasible to use 100 per cent cow dung solution for commercial UAHRs and hence it was decided to use the mixture of cow dung and RME in the ratio of 1:1. Inoculum from digesters fed with same or similar material is likely to be advantageous. Hence it was also decided to study the performance of rectors inoculated with 20 per cent seed sludge taken from the most active digesters used for the media compatibility study.

Table 4.9 Volumetric gas production at different for semi continuous digestion study

Treatments	20 Day HRT	15 Day HRT	10 Day HRT	5 Day HRT
T_0	136.0	164.0	227.0	257.0
T_{01}	135.0	164.0	224.0	257.0
T_{02}	136.0	164.0	227.0	258.0
T_{03}	137.0	175.0	227.0	258.0
T_1	136.0	164.0	222.0	259.0
T_2	134.0	164.0	222.0	257.0
T_3	135.0	164.0	223.0	258.0
T_4	136.0	165.0	226.0	260.0
T_5	137.0	164.0	223.0	259.0
T_6	135.0	163.0	222.0	259.0
T_7	136.0	164.0	227.0	259.0
T_8	136.0	164.0	229.0	259.0

Table 4.10 Biogas productivity at different for semi continuous digestion study

Treatments	20 Day HRT	15 Day HRT	10 Day HRT	5 Day HRT
T_0	2.72	2.46	2.27	1.29
T_{01}	2.70	2.46	2.24	1.29
T_{02}	2.72	2.46	2.27	1.29
T_{03}	2.74	2.62	2.27	1.29
T_1	2.72	2.46	2.22	1.30
T_2	2.68	2.46	2.22	1.29
T_3	2.70	2.46	2.23	1.29
T_4	2.72	2.47	2.26	1.30
T_5	2.74	2.46	2.23	1.30
T_6	2.70	2.44	2.22	1.30
T_7	2.72	2.46	2.27	1.30
T_8	2.72	2.46	2.29	1.30

4.4 Design, Fabrication and Installation of Laboratory-scale Upflow Anaerobic Hybrid Reactors (UAHR)

The reactors were fabricated after obtaining the required design parameters outlined in section 3.4 and the results are described in the following sections.

4.4.1 Packing media characteristics

The characteristics of the media to be used in UAHRs are to be obtained as they are among the important parameters required for the basic design. The physical parameters were obtained as per the procedure outlined in section 3.4.3 and is shown in Table 4.11.

Table 4.11 Packing media characteristics used in UAHRs.

Sl. No.	Parameters	Polyurethene rings (Inert media)	Rubber seed outer shell media
1	Bulk density kg/m^3	13.3	231.5
2	Porosity, per cent	72.3	58.8
3	Specific surface area, m^2/m^3	153.4	132.7

The bulk density of rubber seed outer shells were much higher than that of Polyurethene. The porosity is also below 60%. The specific surface area even though sufficiently higher than the minimum requirement of 100 m^2/m^3 (Young, 1991; James and Kamaraj, 2002) is lower than that of the inert media.

4.4.2 Reactor dimensions

The reactor dimensions were obtained by the design procedure described in section 3.3.4 to 3.3.9 and the dimensions were as shown in Fig. 4.16

The basic configuration of laboratory-scale bioreactors are described in section 3.4.1 and fabrication was done as described in section 3.4.10.

The void volume of reactor with rubber outer shell as media and reactor with Polyurethene media were slightly different due to the difference in porosity of the packing media. The effluent outlet of all the reactors were fixed correcting their respective liquid volumes to 15 ℓ. The height of the media filled portion in the

UAHRs with rubber seed outer shell and polyurethane rings were 280mm and 230mm respectively. (calculated as described in section 3.3.4)

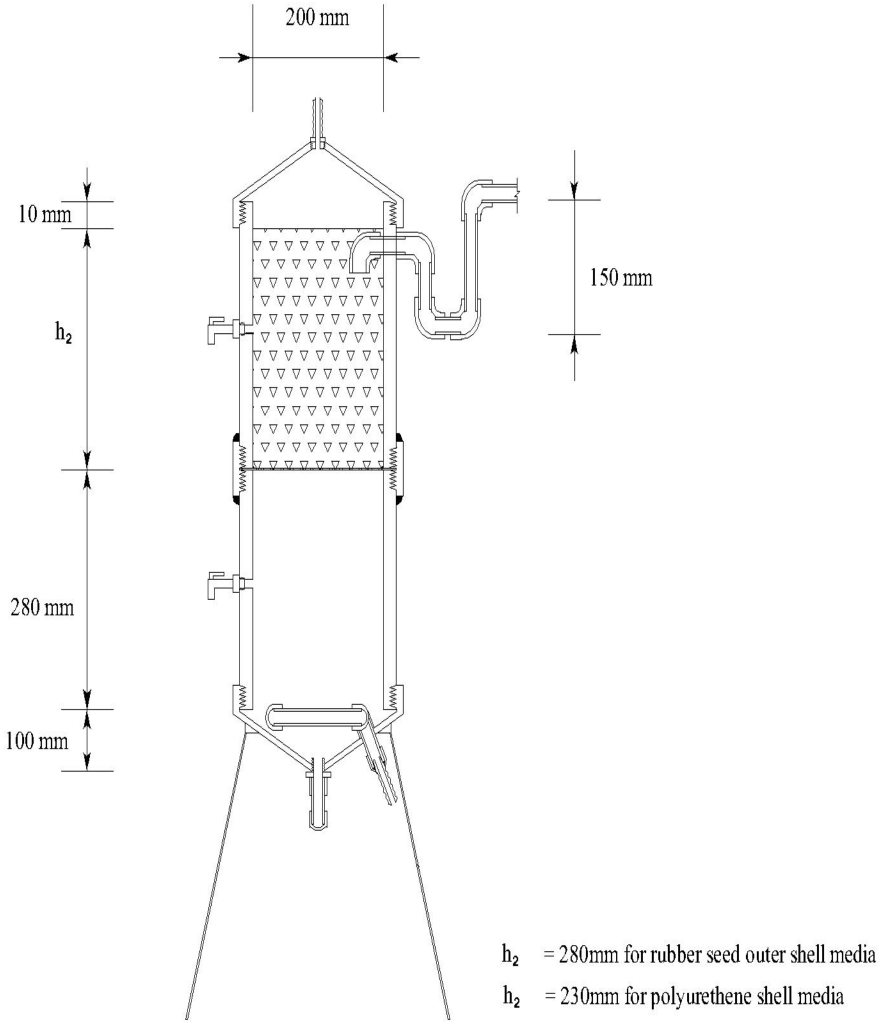


Fig. 4.16 Dimensions of UAHR

This was similar to the design developed by James and Kamaraj (2003^a) in which they compared PVC pall rings and broken coconut shells as media in pilot scale. Najafpour *et al.* (2006) designed a bioreactor to treat palm oil mill effluent with 1/5th of the total volume filled with media and placed it in the central portion of the reactor. A 14 ℓ capacity laboratory-scale up flow hybrid reactor used by Oktem *et al.* (2007) to investigate the treatment of pharmaceutical waste water had media in the upper half of the reactor. Araujo *et al.* (2008) also filled 50 per cent volume of the reactor with media to treat low strength industrial effluent. Umanna *et al.* (2008) packed 18 ℓ of a reactor treating dairy waste water with media out of the total volume of 26 ℓ.

4.5 Installation, start-up and acclimation of the UAHRs.

The UAHRs were installed in the bioenergy lab of Kelappaji College of Agricultural Engineering and Technology, Tavanur. All the eight reactors were fed from the common peristaltic pump and the flow was diverted by way of flow control valves. The salient results of the studies conducted to study the start-up of the lab scale Upflow Anaerobic Hybrid Reactors (UAHRs) and their performance during the start-up HRT of 15 days are presented and discussed below.

4.5.1 Seeding and start up

The study comprised of 8 UAHRs, ie. The 4 treatments replicated twice. The feed mixtures were prepared for the first charging of the reactors as detailed below. The inoculum was diluted cow dung in R_1, R_3 and R_4. The inoculum used in the reactor 2 (R_2) was taken from active digesters of the semi-continuous digestion studies. R_1, R_2 and R_4 had rubber outer shell as media while R_3 had polyurethene rings (inert media). An inoculum volume of 20 per cent of the total liquid volume of bioreactor was used in R_1 and R_2 where as 50 per cent of the total liquid volume was used in R_3 and R_4

The parameters of RME and inoculum mixtures used for charging of the reactors is given in Table 4.12. The RME used in the reactor had a TS of 1625 mg/ℓ with a pH of 3.8. The reactor sludge used as inoculum had a TS of 1200 mg/ℓ and pH of 8.2 and the cow dung used as inoculum had a TS of 17275 mg/ℓ and a pH of 7.7. R_1 was filled with a mixture of 80% RME and 20% diluted cow dung and the resulting TS was 1950 mg/ℓ. R_2 was also charged similarly but with reactor sludge as inoculum and hence had a lower TS. R_3 and R_4 were charged with a mixture of cow dung and rice effluent in the ratio of 1:1, and hence the resulting TS was higher. The reactors were initially operated in batch mode and the pH was closely monitored.

Table 4.12 Parameters of RME and inoculum used for charging UAHR

Sl. No.	Sample	pH	TS, mg/ℓ	BOD, mg/ℓ
1	Cow dung used as inoculum	7.7	17275	1550
2	RME	3.8	1625	3599
3	Digester sludge used as inoculum	8.2	915	1200
4	RME + Cow dung mixture (1:1 ratio)	6.6	9450	2042
5	RME + 20 per cent Cow dung mixture	6.2	1950	2222
6	RME + 20 per cent digester sludge	6.8	1483	2943

The pattern of variation of pH during the start up period of 24 days is shown in Fig. 4.17. It was observed that there was a steady increase in pH for the first 10 days in R_2. The system reached a more or less steady stage with a pH in between 7.1 and 7.3. The pH of R_1 also showed a sharp and steady increase up to the 11th day and then remained stable in the range of 7.1 and 7.3. R_3 had no change in the pH up to the 7th day and thereafter the pH sharply increased to 7 and then remained stable in between 7 and 7.3. R_4 showed no signs of pH increase up to the 6th day but then started steady increase and reached a pH of 7.1 on the 14th day and then remained stable in the range between 7.1 and 7.3.

The temperature profile and daily gas production of UAHR are illustrated in Fig. 4.18. The ambient temperature inside the laboratory, where the UAHRs were installed was in range of 28 ± 3^0C. Gas production in R_1 and R_2 started on the second day. R_1 showed a gas production of 0.024 litres on the second day reaching the value of 0.46 litres on the 24th day, which was equivalent to a volumetric gas production of 1.6 ℓ/m^3 and 46.67 ℓ/m^3 respectively. R_2 showed a gas production of 0.064 litres on the second day and 1.13 litres on the 24th day, which were equivalent to volumetric gas productions of 4.27 ℓ/m^3 and 76 ℓ/m^3 respectively. There was no gas production in R_3 till the 8th day. R_3 produced 0.26 litres of gas which slowly increased to 0.77 litres on the 21st day, which was equivalent to volumetric gas production of 17.33

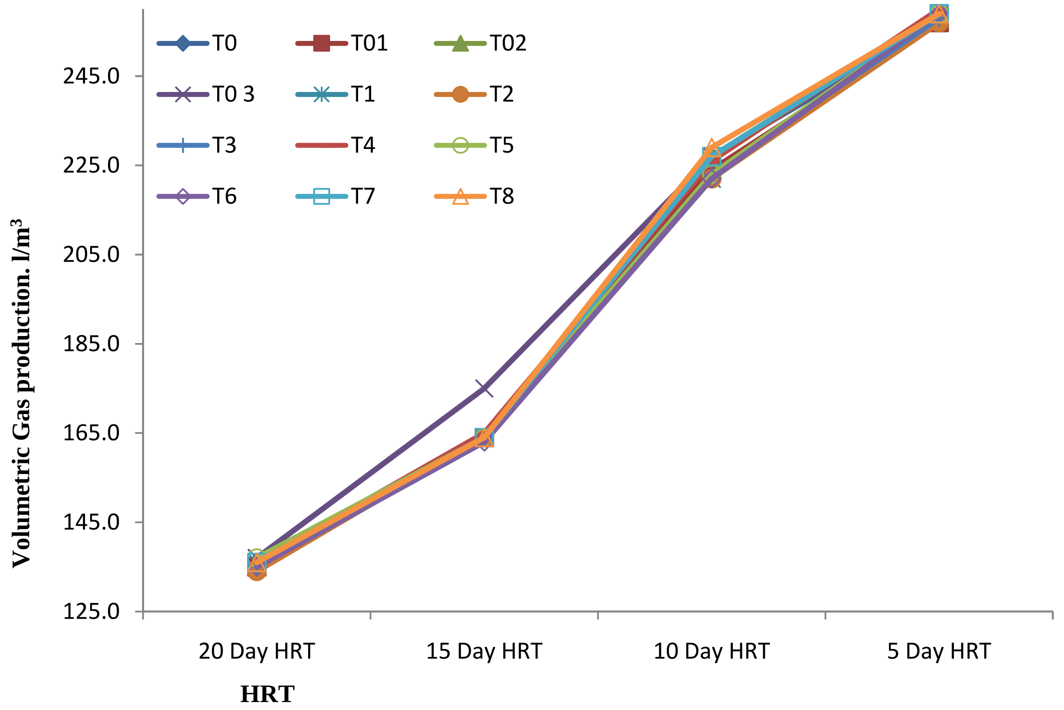


Fig . 4.15 Volumetric biogas production at different HRT

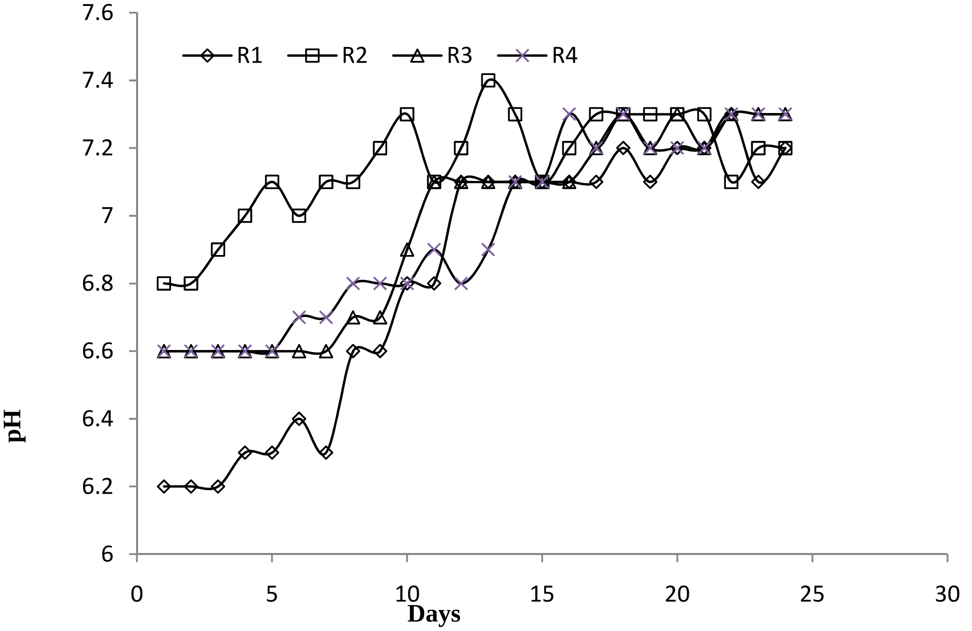


Fig. 4.17 pH variation during the start-up of the UAHR

ℓ/m^3 and 61.33 ℓ/m^3 respectively. Hanaki *et al*. (1994) observed delayed gas production during the start-up of high rate anaerobic reactors. R_4 started gas production on the 4th day (0.08 litres) and slowly increased to 1.16 litres on the 24th day, which was equivalent to a volumetric gas production of 5.33 ℓ/m^3 and 77.33 ℓ/m^3 respectively. All the reactors apart from R_4 showed peak gas production in between the 18th and 21st day and then showed a decreasing trend. This should have been due to the depletion of organic substrate as reported by Acharya *et al*. (2008) and was an indication to start daily feeding. Behling *et al.* (1997) observed a start-up period of 90 days for a pilot scale UASB reactor. Peck and Hawkes (1987) could commence daily feeding after 15 days of charging. James and Kamaraj (2000) and Acharya *et al.* (2008) observed a start-up period of 35 to 40 days. Araujo *et al.* (2008) was able to start the daily feeding in 12 days for a hybrid bioreactor treating house hold waste water. Kumar *et al.* (2008) was able to start the daily feeding in five days while treating low strength Industrial waste water.

Table 4.13 shows the initial and final TS and BOD values of reactor liquor during start-up of UAHR. The maximum BOD reduction of 43.87 per cent was observed in R_2 during the start-up, closely followed by R_4 with 30.14 per cent. R_3 showed the least reduction of 14.7 per cent. The TS reduction also followed a similar trend with the maximum reduction by R_4 (46.9 per cent), followed by R_2, R_3 and R_1 (25.05, 15.1 and 14.39 per cent reduction respectively).

Table 4.13 TS and BOD values of RME samples during start-up of UAHR

Sl. No.	BOD, mg/ℓ				TS, mg/ℓ		
	Reactor	Initial	Before the start of daily feeding	Per cent reduction	Initial	Before the start of daily feeding	Per cent reduction
1	R_1	2222.	1682	24.3	1950	1669	14.3
2	R_2	2943	1652	43.9	1483.3	1112	25.0
3	R_3	2042	1742	14.7	9450	8022	15.1
4	R_4	2042	1426	30.1	9450	5017	46.9

4.5.2 Performance of UAHRs at the start up HRT of 10 days

Daily feeding of the UAHRs was commenced on the 25th day after first charging the reactors and run for 31 days at an HRT of 10 day. The influent characteristics and operating parameters are given in Table 4.14. The average influent TS was 1640 mg/ℓ and BOD of 3604 mg/ℓ, with a C:N ratio of 22.4:1 and a pH of 3.87. The C:N ratio is in the optimum range of 20-30:1 for biomethanation recommended by Mathur and Rathore (1992) and indicated that there is no possibility of nitrogen deficiency in the anaerobic digestion. The influent pH was low but the system performed without any problem. A similar experience was also reported by Acharya *et al.* (2008) while treating distillery spent wash having a pH of 4.5 which was feed into the reactor without neutralization. James and Kamaraj (2007) also successfully started up the hybrid anaerobic bioreactor with un-neutralised cassava starch factory effluent. The reactor at the start up HRT of 10 day had HLR of 100 ℓ/m^3.d, TS loading rate of 0.164 kg/m^3.d and BOD loading rate of 0.36 kg/m^3.d.

Table 4.14 Influent characteristics and operating parameters at 10 day HRT in UAHRs

Sl. No.	Parameter	Quantity with unit
1	Influent TS	1640 mg/ℓ
2	Influent BOD	3604 mg/ℓ
3	Total Kjeldahl Nitrogen	73 mg/ℓ
4	Total organic carbon	1636 mg/ℓ
5	pH	3.87
6	C:N ratio	22.4
7	HLR	100 ℓ/m^3.d
8	TS loading rate	0.164 kg/m^3.d
9	BOD Loading rate	0.36 kg/m3.d

The gas production performance of the reactors are illustrated in Fig. 4.19 that there was an unsteady phase and a PSS phase in gas production as in the case of

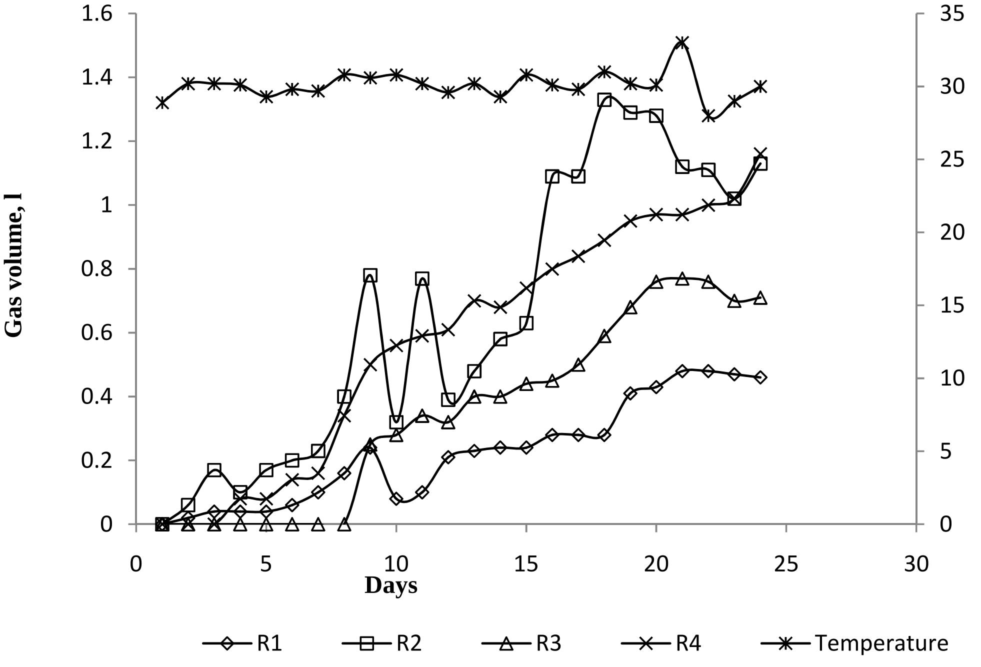


Fig. 4.18 Daily gas production during the start-up of the UAHR

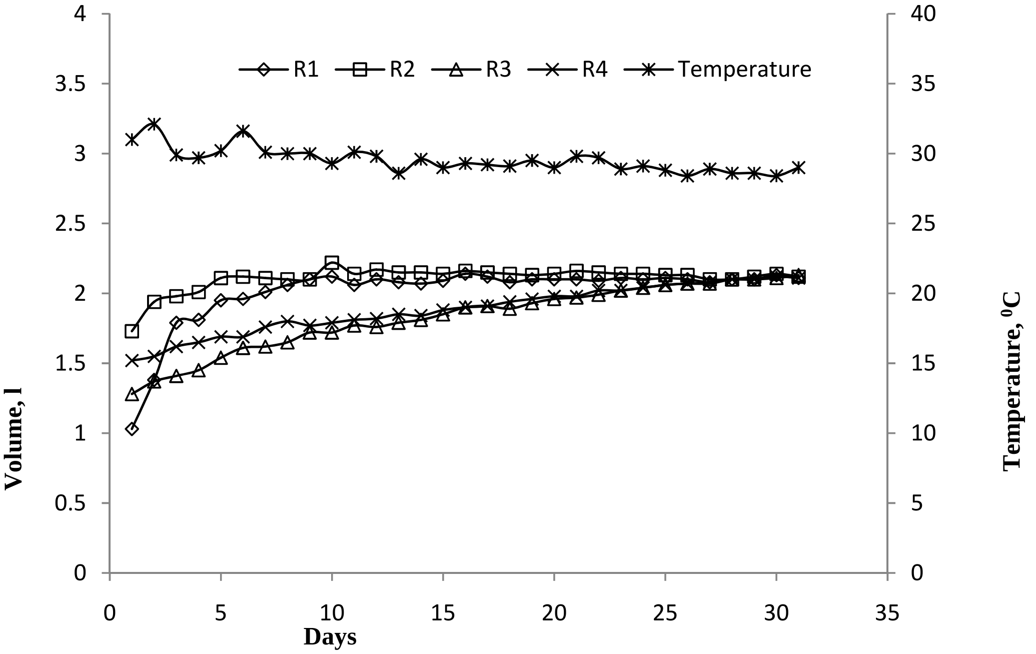


Fig. 4.19 Daily gas production variation during the start-up HRT of 10 days

semi-continuous digesters described in section 4.2.3. The reactors took 3 to 22 days to reach the PSS phase but there was no abrupt variation in gas production. The specific gas productions in all the cases are well above 1000 ℓ/kg TS and were higher than most of the reported values (James and Kamaraj, 2009). This should be due to the reason that RME is easily bio degradable and very dilute.

The performance of UAHRs as indicated by specific gas production is shown in Table 4.15. The specific gas productions in terms of TS during the unsteady period varied between 1006.09 and 1146.34 ℓ/kg TS with the maximum in R_2 and the minimum in R_1. During this phase the maximum value of specific gas productions in terms of BOD was also seen in R_2 and the minimum value in R_1. The specific gas production during this unsteady period was not a clear indication of reactor performance, since gas production from accumulated biomass due to delayed or part digestion, also was possible. Hence, the substrate kinetics and reactor dynamics during this unsteady period was difficult to interpret on the basis of these observations as reported by James and Kamaraj, (2007). The variations of volumetric gas production follow the same trends as that of daily gas production.

Table 4.15 Reactor performance at PSS of 10 day HRT

Sl. No.	UAHR	Unsteady phase			PSS Phase		
		Daily gas production, ℓ	Specific gas production		Daily gas production, ℓ	Specific gas production	
			ℓ/kg TS	ℓ/kg BOD		ℓ/kg TS	ℓ/kg BOD
1	R_1	1.65	1006.1	458.0	2.09	1274.4	580.1
2	R_2	1.88	1146.3	521.8	2.13	1298.8	591.2
3	R_3	1.72	1048.8	477.4	2.08	1268.3	577.3
4	R_4	1.79	1091.5	496.8	2.07	1262.2	574.5

From Table 4.16 it can be seen that the highest effluent TS was 681.15 mg/ℓ, in R_3 and the lowest value of 638.19 mg/ℓ was seen in R_1. The maximum TS reduction was seen in R_4, with a reduction of 60.65 per cent and the minimum in R_3 with 58.46 per cent. From Table 4.17 it was observed that the BOD of the sample taken from the bottom sampling port is slightly higher than that of the sample taken from the top sampling port for all reactors. This is due to the fact that in the upper portion of the reactor the effluent is in contact with the microbes attached to the media thus resulting in more digestion than the bottom portion of the reactor.

Considering the overall performance in BOD reduction the maximum reduction of 82.9 per cent was displayed by R_4. The reactor R_1 was the second with a reduction of 82.7 per cent. R_2 and R_3 were very close in BOD reduction parameters which showed reductions of 82.1 and 81.7 per cent respectively.

Table 4.16 TS, TS reduction, BOD and BOD reduction at PSS of 10 day HRT

Sl. No.	UAHR	TS, mg/ℓ	TS reduction, percentage	BOD, mg/ℓ	BOD reduction, percentage
1	R_1	638.2	61.1	638.2	82.7
2	R_2	649.1	60.4	649.1	82.1
3	R_3	681.2	58.5	681.2	81.7
4	R_4	645.2	60.7	645.2	82.9

Table 4.17 TS and BOD of reactor liquor at 10 day HRT

Sample		TS, mg/ℓ	BOD, mg/ℓ
R_1	Top sample port	617.2	600.6
	Bottom sample port	659.2	645.6
R_2	Top sample port	665.7	630.6
	Bottom sample port	632.4	660.7
R_3	Top sample port	663.2	660.7
	Bottom sample port	699.1	660.7
R_4	Top sample port	652.3	600.6
	Bottom sample port	638.1	630.6

The methane content of biogas over 5 day interval at 10 day HRT period is shown in Table 4.18. The methane content during the first five days in R_1 and R_2 were found to be 50 per cent while for reactor R_3 and R_4 it was as low as 40 per cent.

Gradual hike in methane content was observed in all the UAHRs and towards the end of 10 day HRT period the methane content in R_1 and R_2 reached 65 per cent where as that in R_3 and R_4 was 60 percent.

Table 4.18 Methane content of biogas during 10 day HRT period

Sl. No	Reactor	5 day period					
		1	2	3	4	5	6
1	R_1	50	55	60	60	65	65
2	R_2	50	50	60	60	60	65
3	R_3	40	45	50	55	55	60
4	R_4	40	40	45	50	55	60

4.6 Performance Evaluation of the UAHRs.

Subsequent to the start-up HRT of 10 days, the UAHRs were evaluated by operating at HRTs 5, 4, 3, 2, 1 and 0.8 day. The results of these investigations are presented and discussed in this section. They were allowed to reach the steady state condition at each HRT by maintaining the reactors at the respective HRTs for a minimum of three volume turnovers. Based on the results, a comprehensive set of guidelines for the design and operation of a pilot scale bioreactor is also presented.

4.6.1 Influent and effluent characteristics of UAHR's at different HRTs

The influent and effluent characteristics, viz. pH, TS and BOD were regularly monitored during the different HRTs.

4.6.1.1 pH, TS and BOD

The average influent pH (Table 4.19) varied from 3.84 to 3.91 and the pH of the effluent varied from 6.98 to 8.62. R_4 showed the lowest pH of 6.98 at 0.8 day HRT and the remaining reactors had a pH above 7. This indicates that all the reactors were stable during the entire period of operation. Merwe and Britz, (1992) had reported that pH values above 7.5 will promote digester efficiency. Higher pH provided a good environment for the methanogens resulting enhanced gas production (Kim et *al*., 2002). These findings are in agreement to the present study and a similar range of pH was seen during HRTs longer than 1 day. The influent and effluent characteristics viz. TS and BOD are depicted in Table 4.19. The influent TS varied between 1640 and 1734 mg/ℓ and the influent BOD varied between 3503 and 3643 mg/ℓ. The stable nature of effluent TS and BOD shows the stability of the reactors.

Table 4.19 Influent and effluent pH at PSS of different HRT periods

HRT	Influent	R_1	R_2	R_3	R_4
10 day	3.9	8.6	8.6	8.6	8.6
5 day	3.9	8.4	8.4	8.3	8.3
4 day	3.9	8.2	8.2	8.1	8.1
3 day	3.9	8.1	8.1	8.1	8.1
2 day	3.9	7.7	7.7	7.8	7.8
1 day	3.8	7.4	7.4	7.3	7.3
0.8 day	3.8	7.1	7.1	7.0	7.0

The maximum effluent TS was noted at the shortest HRT of 0.8 day in R_3 while the minimum was seen at 10 day HRT in R_1. The maximum effluent BOD (810 mg/ℓ) was observed in the shortest HRT of 0.8 day on all reactors and the minimum value was at 5 day HRT in R_1. The variation of effluent TS and BOD in comparison with that of influent at different HRTs are depicted in Fig. 4.20 and 4.21.

4.6.1.2 Methane content of biogas

The methane content of biogas has improved from 65% in reactor R_1 and R_2 and 60 per cent in reactor R_3 and R_4 during the 10 day HRT to 75 per cent during 4 day HRT in R_1 and R_2 (Table 4.20). The maximum methane content observed was 75 per cent in R_1 and R_2 during the 4 day HRT and the minimum methane content (57.5 per cent) was observed in R_4 during the 0.8 day HRT.

The methane content of biogas observed in this study is in agreement with earlier studies. Kennedy et *al*., 1998; Chang, 1989 and Hendry *et al*., 1987 reported methane contents in the range of 67 to 81 per cent. Timur and Ozturk (1999) reported methane content in between 58 to 75 per cent, in the anaerobic treatment of land fill leachate. Najafpour et *al*., (2006) reported a methane content of 62 to 82 per cent for palm oil mill effluent digestion. Ramakrishnan and Gupta (2008)

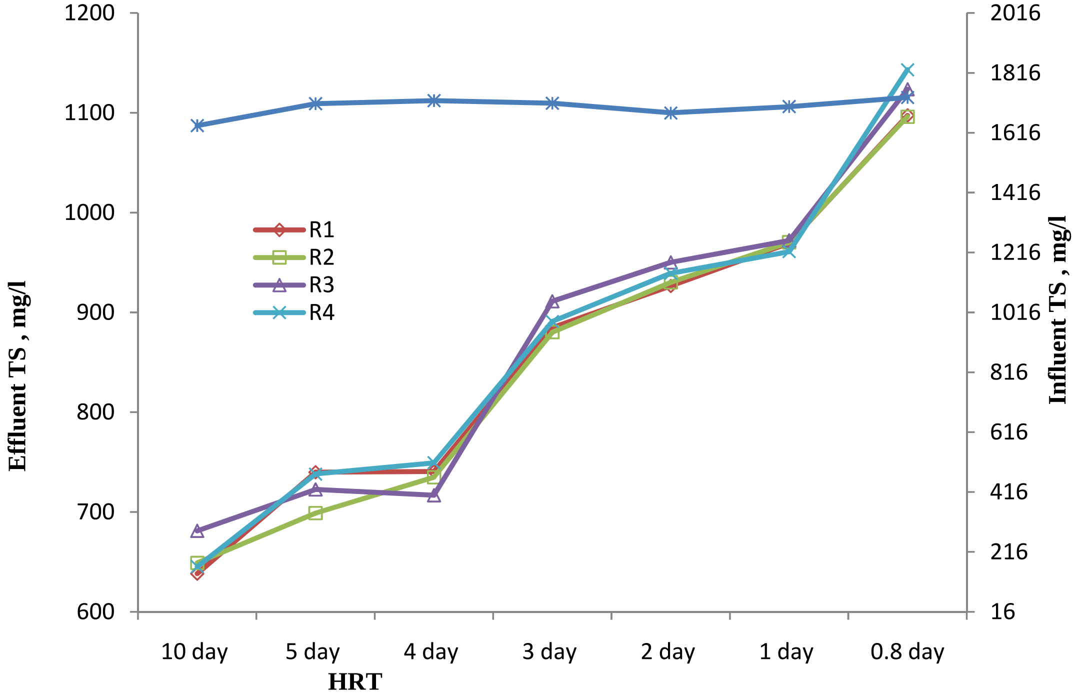


Fig. 4.20 Variation of influent and effluent TS at different HRT in UAHRs

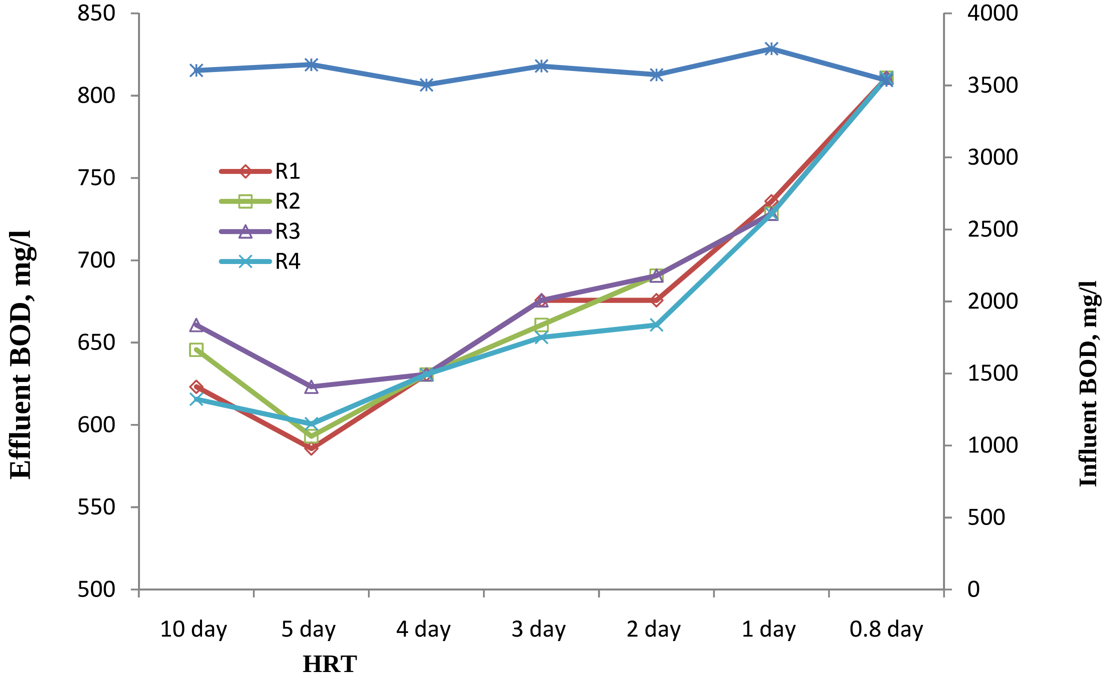


Fig. 4.21 Variation of influent and effluent BOD at different HRT in UAHRs

could get methane content of 65 per cent in the biogas obtained from anaerobic digestion of coal waste water. A similar ranges was reported by Kumar *et al*. (2008) in anaerobic treatment of low strength industrial effluent. The maximum methane content of 65 per cent found in the present study indicated that the quality of biogas generated from RME is fairly good and can be utilized for energy generation.

Table 4.20 Methane content of biogas at different HRT periods

Reactor	10 Day	5 Day	4 Day	3 Day	2 Day	1 Day	0.8 Day
R_1	65	72.5	75	72.5	70	67.5	62.5
R_2	65	70	75	75	70	65	62.5
R_3	60	65	72.5	72.5	65	62.5	60
R_4	60	67.5	70	72.5	65	62.5	57.5

4.6.2 Performance of UAHRs at different HRTs

The performances of the UAHR as described by different parameters during different HRTs are presented in this section.

4.6.2.1 Loading rates

The organic loading rates of the reactors with respect to TS and BOD along with the respective hydraulic loading rates are depicted in Fig. 4.22. During the HRT from 5 days to 2 days, the per cent increase of HLR over the values of the previous HRT were less than 50 per cent. The change from 10 day to 5 day was abrupt but it did not affect the reactor performance. The change from 2 days HRT to 1 day HRT also resulted in sharp increase of 100 per cent but the system was stable. A similar change was observed in organic loading rates also as the influent concentrations were more or less constant.

4.6.2.2 Gas production

Gas production rates are the most important indicators of reactor performance for anaerobic reactors. Table 4.22 shows the gas production data of the UAHRs at PSS of various HRTs.

4.6.2.2.1 Daily gas production

The daily gas production of R_1 increased from 2.0 l (10 day HRT) to 12.8 l (0.8 day HRT) showing 6.4 times increase, R_2 had an increase from 2.1 l to 12.8 (6.1 times), R_3 from 1.8 to 12.8 (7 times) and R_4 from 1.9 to 12.7 (6.8 times). The trend of variation over different HRTs is illustrated in Fig.4.23.

4.6.2.2.2 Specific gas production

The variation specific gas production in terms of TS and BOD are shown in Table 4.21. A maximum specific gas production (858 ℓ/kg TS) occurred at 10 day HRT, for R_2. The minimum value (391.3 ℓ/kg TS) was obtained at 0.8 day HRT for R_4. The variation of specific gas production per kg TS is plotted in comparison to the TS loading rate in Fig. 4.24. It could be observed that as the loading rate increased the specific gas production decreased. The decrease was rather slow for all the reactors up to 2 day HRT. But a sharp decrease in specific gas production can be seen when the HRT was reduced from 2 day to 1 day. The reduction of HRT from 1 day to 0.8 day did not make much difference.

Specific gas productions in terms of BOD also exhibited similar pattern and is depicted in Fig. 4.25. The maximum value of 390.5 ℓ/kg BOD occurred for R_2. The minimum value was obtained at 0.8 day HRT of 192 ℓ/kg BOD in R_4.

It became evident from these parameters that all reactors performed equally good and there was no significant difference. But a marginal better performance could be noticed for R_1 and R_2 at 1 day HRT.

4.6.2.2.3 Volumetric biogas production and biogas productivity

The maximum biogas production obtained per liter of RME was 1.40 ℓ/ℓ (at 10 day HRT) in R_2 (Table 4.21) and the minimum (0.67 ℓ/ℓ) at 0.8 day HRT in R_4. The trend of variation in biogas productivity is illustrated in Fig. 4.26

The volumetric gas productions of UAHRs are shown in Fig. 4.27. In general, the volumetric biogas production increased as the HRT was shortened. This is an important information when biogas production is the important objective and the feed material is in abundance. The biogas produced from a bioreactor will be maximum at the shortest practical HRT. The behaviour of all the four reactors were quite similar. The minimum value of 122 ℓ/m^3 was noticed for R_3 at 10 day

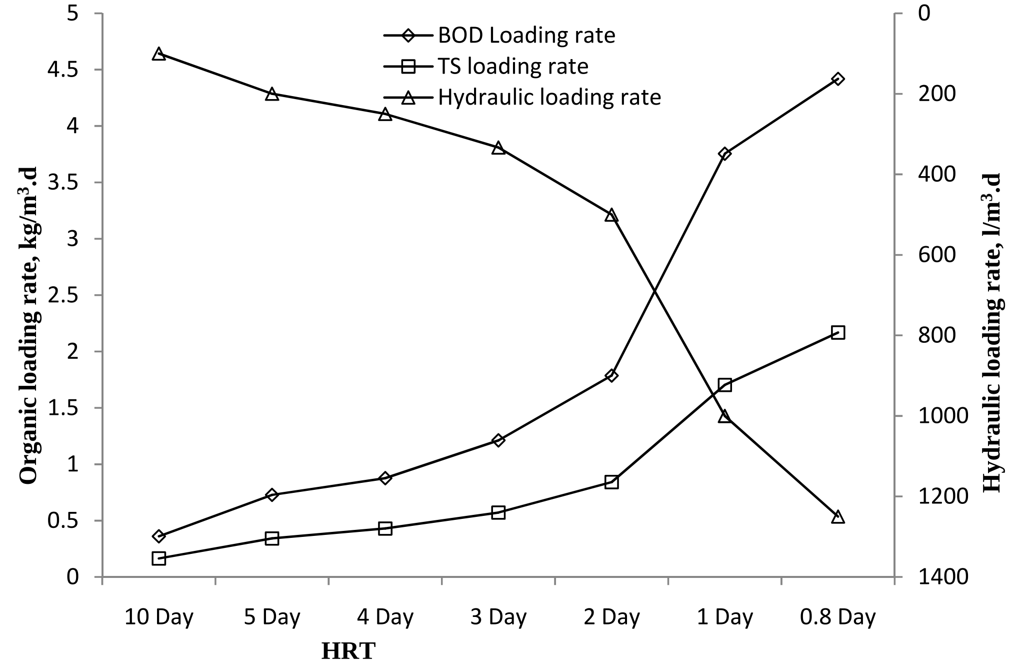


Fig. 4.22 Hydraulic and organic loading rates of UAHRS at different HRT periods

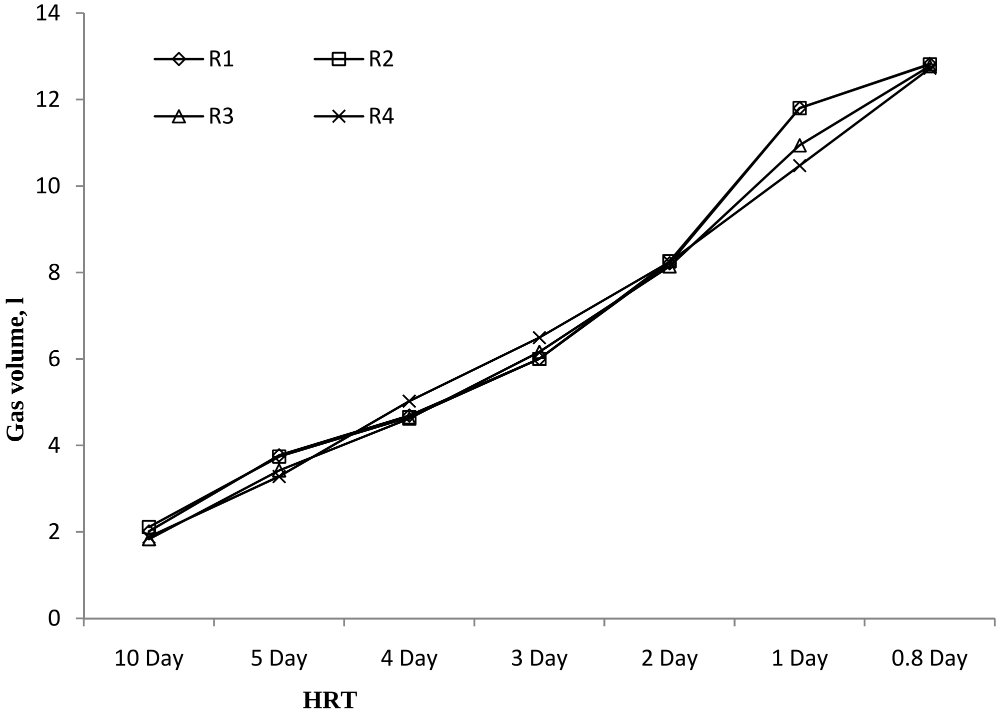


Fig. 4.23 Daily gas production at different HRT periods

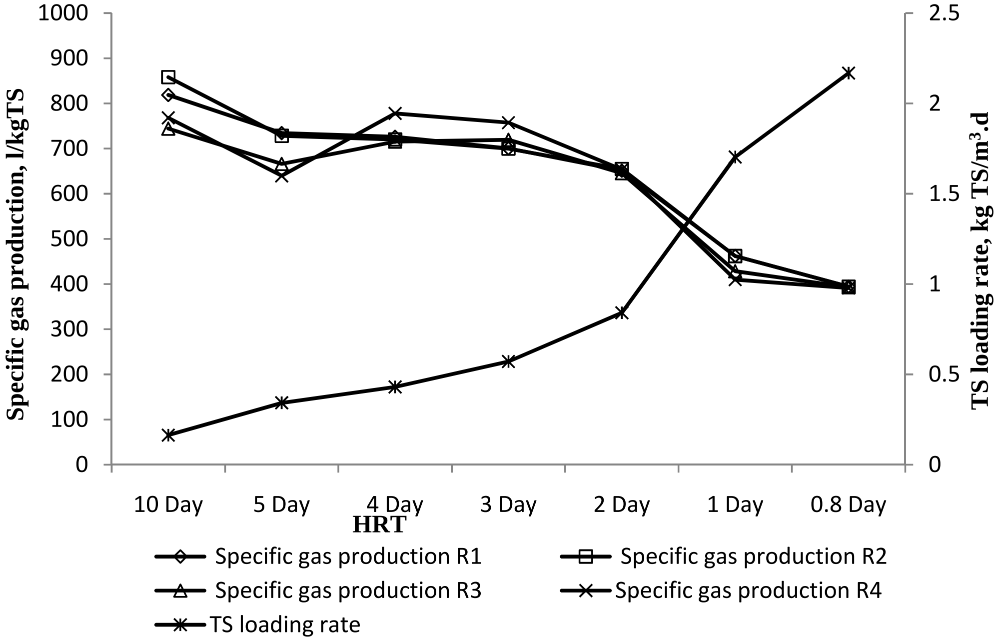


Fig. 4.24 TS loading rate Vs specific gas production at different HRT periods

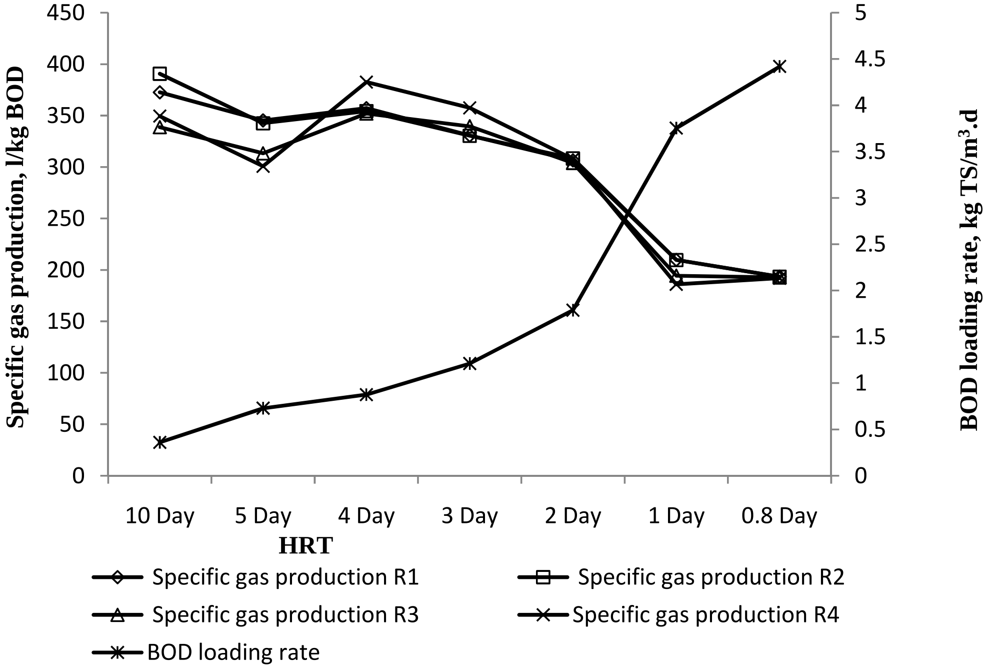


Fig. 4.25 BOD loading rate Vs specific gas production at different HRT periods

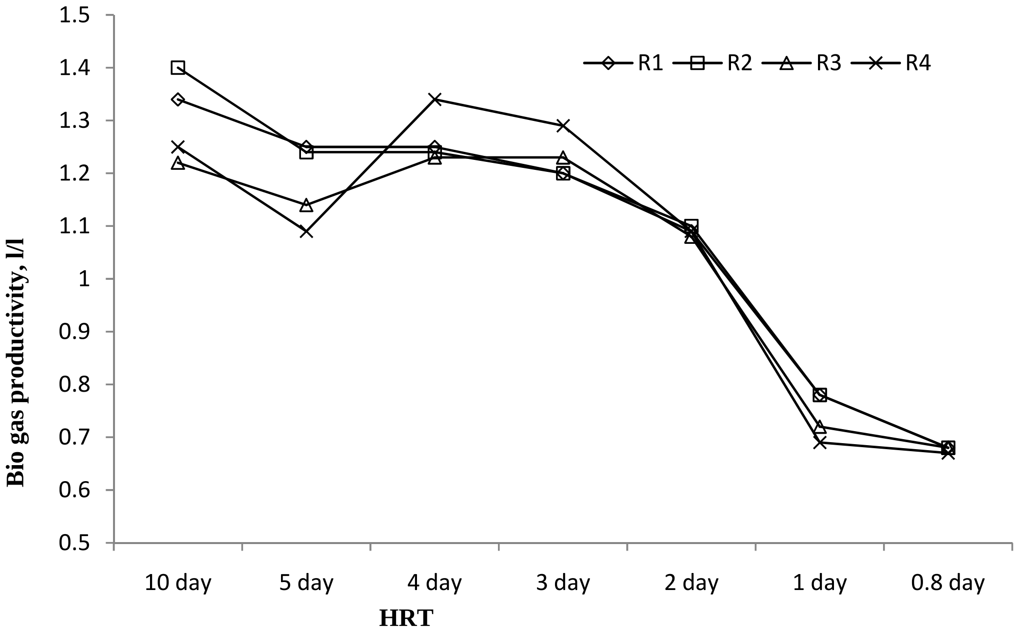


Fig. 4.26 Biogas productivity of UAHRs at different HRT periods

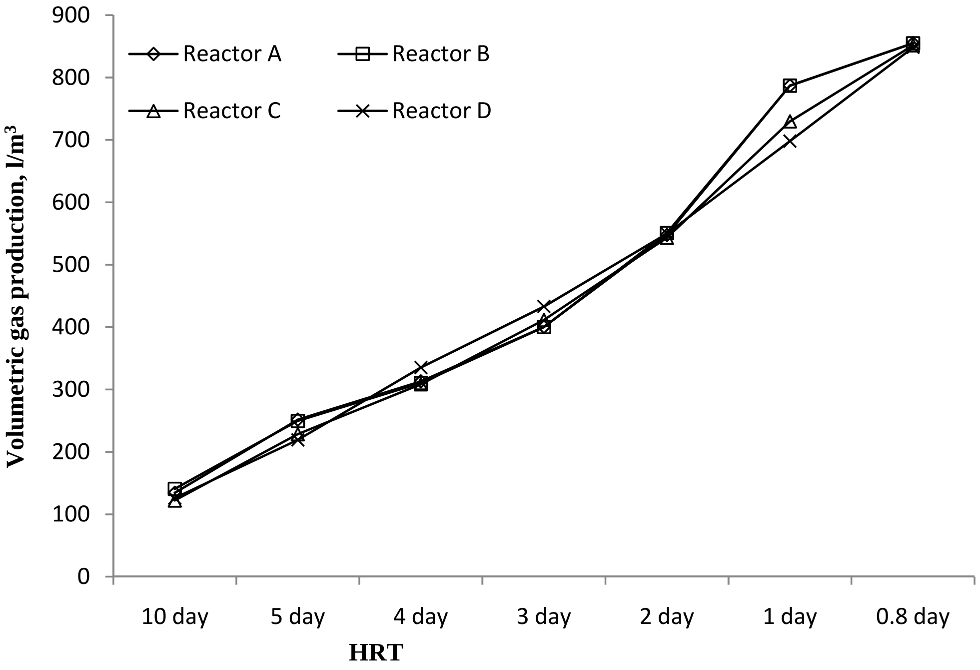


Fig. 4.27 Volumetric gas production of UAHRs at different HRT periods

HRT and the maximum of 855 ℓ/m^3 (0.8 day HRT) for R_1. Najafpour et *al*., (2006) reported biogas productivity of 6.23 ℓ/ℓ .d during the start-up HRT while treating palm oil mill effluent. The reported value of bio gas productivity was very close to the theoretical yield, which is much lower than the above value. James and Kamaraj (2009) reported a volumetric biogas production of 2038 ℓ/m^3 at 1 day HRT for cassava starch factory effluent. The biogas productivity was around 2 ℓ/ℓ at 1 day HRT. These higher values are due to the higher TS content of the feed material.

Table 4.21 Specific gas production, volumetric gas production and biogas productivity of UAHRs at different HRT

Sl. No.	Parameter	UAHR	HRT period						
			10 day	5 day	4 day	3 day	2 day	1 day	0.8 day
1	Specific gas production, ℓ/kg TS	R_1	818.6	734.2	726.1	700.3	650.9	462.0	394.4
		R_2	858.2	728.3	720.3	699.9	654.8	462.0	394.2
		R_3	744.2	666.2	715.5	719.4	645.6	428.3	392.8
		R_4	768.0	639.7	777.8	757.4	653.6	409.8	391.3
2	Specific gas production, ℓ/kg BOD	R_1	372.6	345.2	357.2	330.5	306.4	209.7	193.5
		R_2	390.5	342.5	354.3	330.3	308.3	209.6	193.4
		R_3	338.7	313.3	351.9	339.6	304.0	194.4	192.7
		R_4	349.5	300.8	382.6	357.5	307.7	186.0	192.0
3	Volumetric gas production	R_1	134.2	251.5	312.8	400.3	547.5	787.0	854.9
		R_2	140.7	249.5	310.3	400.1	550.8	786.8	854.6
		R_3	122	228.2	308.2	411.2	543.1	729.5	851.4
		R_4	125.9	219.1	335.0	432.9	549.8	698.0	848.2
4	Biogas productivity	R_1	1.3	1.2	1.2	1.2	1.0	0.7	0.6
		R_2	1.4	1.2	1.2	1.2	1.1	0.7	0.6
		R_3	1.2	1.1	1.2	1.2	1.0	0.7	0.6
		R_4	1.2	1.0	1.3	1.2	1.0	0.6	0.6

4.6.3 TS and BOD

The reduction of TS and BOD as percentage of the influent is shown in Table 4. 22. The general trend of reduction was that as the HRT is shortened, the reduction got decreased.

The maximum TS reduction was seen in R_4 with 60.65 per cent in the 10 day HRT and the minimum value was seen in the same reactor (34.08 per cent) at 0.8 day HRT. The trend followed by various reactors at different HRTs is illustrated in Fig.4.28. James and Kamaraj (2004) reported a maximum TS reduction of 50 per cent, lower than the value reported in the present study. However in the present study TS reduction of more than 50 per cent was seen. This might be due to the better cell immobilization and the high biodegradability of RME compared to cassava starch factory effluent in their study.

The maximum per cent BOD reduction was seen in R_1 (83.92 per cent) while running at 5 day HRT. The lowest reduction of 77.06 per cent BOD occurred at 0.8 day HRT by all the reactors. Up to 1 day HRT, all the reactors exhibited steady performance irrespective of the influent concentrations. Thereafter a sharp decrease was observed at 0.8 day HRT, due to the increased loading rate. The lowest reduction of 77.06 per cent BOD occurred at 0.8 day HRT for all the reactors. R_2 was found superior to R_1 which in turn was superior to R_4, in BOD reduction at all HRTs.

The results of this study are comparable to the BOD reduction reported by Araujo *et al.* (2008) while treating industrial waste water (73-90 per cent). The reduction obtained by Acharya et *al*.(2009) for distillery spend wash and Krishna et *al*. (2009) was higher than the reduction obtained in this study.

The average values of TS and BOD of the samples taken from the top and bottom sampling ports of the reactors at different HRT are given in Table 4.23 and 4.24. It is clear from the tables that both in the cases of TS and BOD the value of the top sample is lower than the value from the bottom sample. This change is due to the fact that RME in the top portion of the reactor is in contact with the micro organisms attached to the media and is easily digested more compared to that of the bottom portion of the reactor. This also indicates the advantage of the hybrid design in which media is provided in the upper half of the bioreactor.

Table 4.22 TS and BOD reduction at different HRT periods

HRT	TS reduction, percent				BOD reduction, percent			
	R_1	R_2	R_3	R_4	R_1	R_2	R_3	R_4
10 day	61.1	60.4	58.5	60.7	82.7	82.1	81.7	82.9
5 day	56.8	59.2	57.8	56.9	83.9	83.7	82.9	83.5
4 day	57.0	57.4	58.4	56.5	82.0	82.0	82.0	82.0
3 day	48.4	48.7	46.9	48.0	81.4	81.8	81.4	82.0
2 day	44.9	44.7	43.5	44.2	81.1	80.7	80.7	81.5
1 day	43.1	43.0	42.9	43.6	80.4	80.6	80.6	80.6
0.8 day	36.7	36.8	35.2	34.1	77.1	77.1	77.1	77.1

Table 4.23 TS of the reactor liquor from top and bottom sampling ports in UAHRs

UAHRs		10	5	4	3	2	1	0.8
R_1	Top sample port	617.2	711.0	730.6	851.6	922.3	966.2	1100.3
	Bottom sample port	659.1	768.7	750.5	918.2	930.6	972.3	1094.6
R_2	Top sample port	665.7	689.2	723.7	854.9	928.8	972.8	1102.6
	Bottom sample port	632.4	708.6	746.0	905.5	931.4	967.6	1089.7
R_3	Top sample port	663.2	691.0	701.3	890.8	949.1	972.1	1125.6
	Bottom sample port	699.1	754.2	732.2	931.6	951.1	971.9	1121.6
R_4	Top sample port	652.3	706.4	726.2	862.6	936.2	958.5	1132.0
	Bottoms ample port	638.1	769.6	772.3	919.4	942.0	963.3	1154.4

Table 4.24 Average BOD from top and bottom sampling ports in UAHRs

UAHRs		10	5	4	3	2	1	0.8
R_1	Top sample port	600.6	555.5	600.6	645.6	630.6	705.7	780.7
	Bottom sample port	645.6	615.6	660.6	705.7	720.7	765.7	840.8
R_2	Top sample port	630.6	540.5	600.6	615.6	660.6	690.6	780.7
	Bottom sample port	660.6	645.6	660.6	705.7	720.7	765.7	840.8
R_3	Top sample port	660.6	585.5	600.6	645.6	660.6	720.7	780.7
	Bottom sample port	660.6	660.6	660.6	705.7	720.7	735.7	840.8
R_4	Top sample port	600.6	570.5	600.6	615.6	630.6	705.7	780.7
	Bottom sample port	630.6	630.6	660.6	690.6	690.6	750.7	840.8

4.6.4 Performance of the UAHRs and biomass attachment

The high performance of all the reactors could be accounted to the hybrid design which incorporated the UASB concept along with media packing. The biomass could grow on the surface of the packing media as attached bio-layer where as it was in the form of suspended sludge in the sludge bed zone (bottom unpacked zone) of the reactor. Cordobo *et al* (1995) also has reported an increased efficiency when he converted an UAF into hybrid type.

Because of the high degree of biomass attachment to the packing media, the process was stable with respect to sharp hike in HLR (2 times) during the change of HRT from 2 days to 1 day. Chua *et al*. (1997) also observed that anaerobic fixed film reactor sustained hydraulic shocks up to 5 times loadings. In the present study when the HRT was changed from 2 day to 1 day the reactors sustained the shock load. The ability of hybrid reactors to recover from shock loadings is due to the prevention of biomass washouts achieved by attachment to the matrix and entrapment in the void spaces. Such a stability was also reported by James and Kamaraj (2009). The suspended biomass in the sludge bed zone also was protected by the packing media which also acted as a GSS device as in the case of UASB reactors.

The methanogenic activity of suspended biomass is likely to be high, since fresh substrate is available at this zone and the sludge is partly fluidized during feeding. Agitation in this zone is also achieved by gas bubbles which carry sludge particles upwards. The biomass flocs are pushed upwards by the gas bubbles to which they are physically attached. The impact between the matrix and the bubble helps the separation of gas from the solids that can fall back in to the sludge bed or be temporarily entrapped within the matrix. Higher is the impact velocity, more efficient is the gas release (Tilche and Vieira, 1991). This process continues enabling a thorough mixing of sludge particles with substrate.

The superiority of reactor R_1, R_2 and R_4 as evidenced by increased performances might be due to the favorable surface configuration of the media. Rubber seed outer shells might have caused minor inhibition during the start-up period and during the first week after commencement of regular feeding. Within a short time, reactor R_1, R_2 and R_4 picked up good performance and overtook R_3, even though the porosity and specific surface area were higher for inert media. One reason is that, the actual surface area made available by the micro structure of rubber seed outer shell surface would have been quite larger than the measurable area. Huysman *et al*., (1983) reported that the surface roughness and leaching of mineral nutrients may also be important factors affecting the performance of packed bed anaerobic reactors. Nordstedt and Thomas (1985[b]) and Prasad (1992) as well as James and Kamaraj (2009) also had similar experiences with wood block media, wood and coconut shells respectively.

4.6.3 Modeling of reactor performance parameters

Interpreting the performance of the reactors in terms of loading rates provide better understanding since OLR is a function of the combination of HRT and influent concentration.

The relationship between TS loading rate kg/m^3.d (x) and specific gas production, ℓ/kg TS (Y) is illustrated in Fig. 4.29. The linear relationship could be expressed by the following equations.

For R_1,

$y = -2E{+}08x + 82140$ ....($R^2 = 0.988$)

For R_2,

$y = -2E{+}08x + 83184$ ....($R^2 = 0.963$)

For R_3,

$y = -2E{+}08x + 78076$ ....($R^2 = 0.946$)

For R_4,

$y = -2E{+}08x + 80863$ ....($R^2 = 0.872$)

The high R^2 values assure the validity of the equations.

Fig. 4.30 illustrates the exponential relationships between BOD loading rate, kg/m^3.d (x) and specific gas production ℓ/kg BOD (Y) which are defined by the equations,

For R_1,

$y = 402.0e^{-0.16x}$ ....($R^2 = 0.992$)

For R_2,

$y = 406.9e^{-0.17x}$ ....($R^2 = 0.990$)

For R_3,

$y = 382.1e^{-0.16x}$ ....($R^2 = 0.93$)

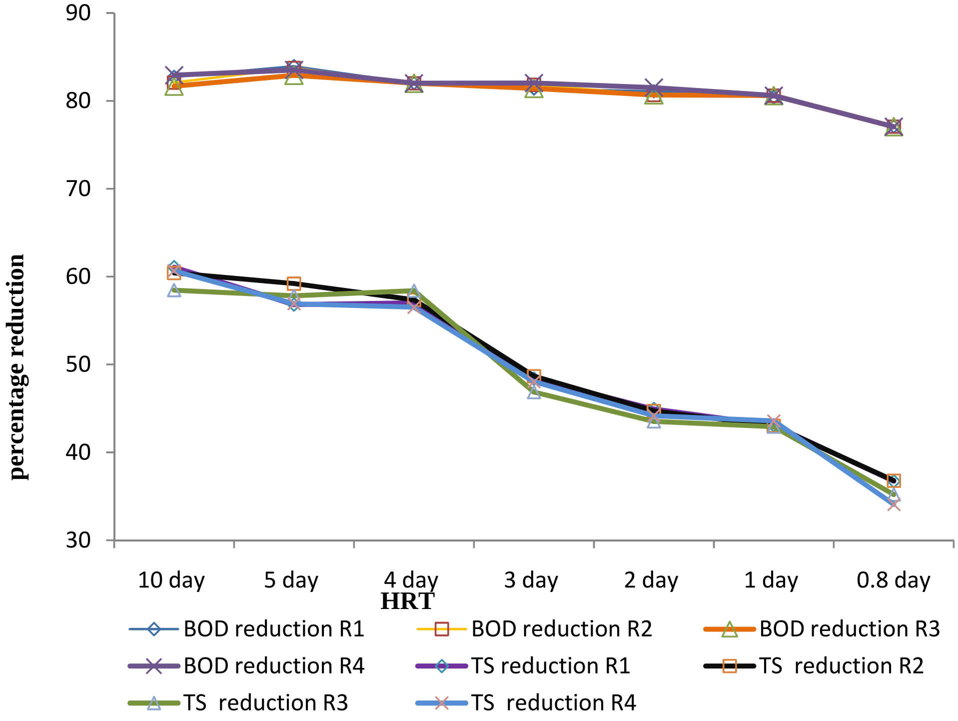


Fig. 4.28 BOD and TS reduction of UAHRs at different HRT periods

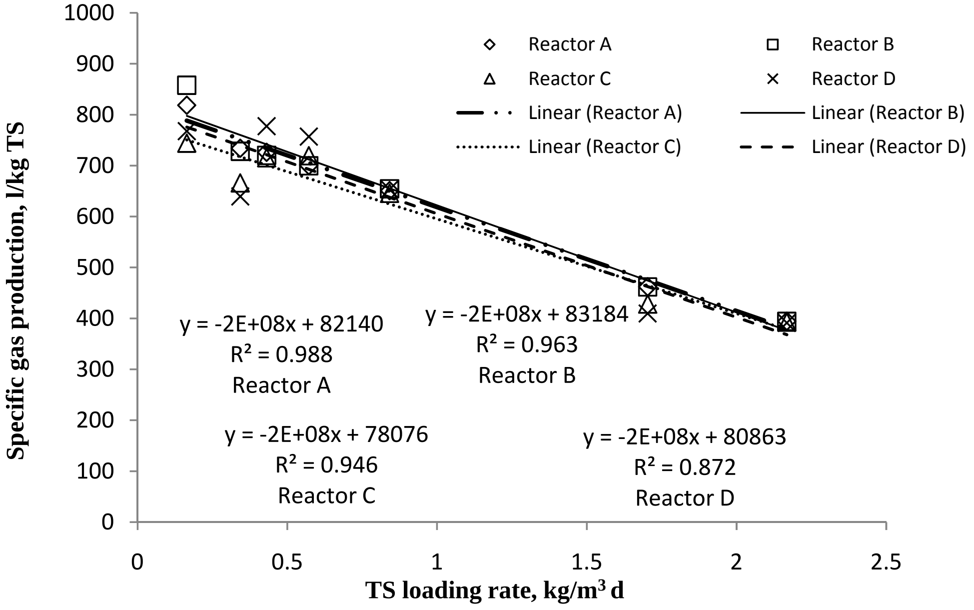


Fig. 4.29 TS Loading rate Vs. Specific gas production

For R_4,

$y = 397.4e^{-0.17x}$ ....($R^2 = 0.872$)

A slightly low value of R^2 was obtained for the relationship of reactor D.

A similar relationships which could be established in the cases of TS loading rate versus TS reduction is depicted in Fig, 4.31.

The TS loading rate kg/m^3.d (x) and TS reduction per cent (Y) are related linearly as,

$y = -5.119x + 59.34$ ..... R_1,

$y = -5.269x + 59.94$ ..... R_2,

$y = -5.243x + 58.94$ ..... R_3,

And, $y = -5.495x + 59.44$ .... R_4

The R^2 values were in the range of 0.835, 0.831, 0.791 and 0.830 for reactor A, B. C and D respectively.

The BOD loading rate, kg/m^3.d (x) was related to the BOD reduction per cent (Y) by the exponential relationship given below (Fig 4.32):

$y = 83.55e^{-0.01x}$ ..... R_1

$y = 83.29e^{-0.01x}$ ..... R_2

$y = 82.82e^{-0.01x}$ ..... R_3

And, $y = 83.69e^{-0.01x}$ .... R_4

The R^2 values were in the range of 0.795, 0.745, 0.730 and 0.818 for reactor A, B. C and D respectively.

4.6.4 Optimisation of reactor design parameters

An effort to arrive at the optimum reactor design parameters on the basis of the results obtained on biogas production and pollution reduction was made.

For maximum biogas production HRTs longer than 2 day is advisable. Even at 2 day HRT a specific biogas production of more than 650.9 ℓ/kg TS was achieved in the present study. The reduction in specific gas production from 3 day HRT to 2 day HRT was only 6.8 per cent (for reactor 1). Hence the minimum HRT recommended for moderate biogas production could be taken as 2 days.

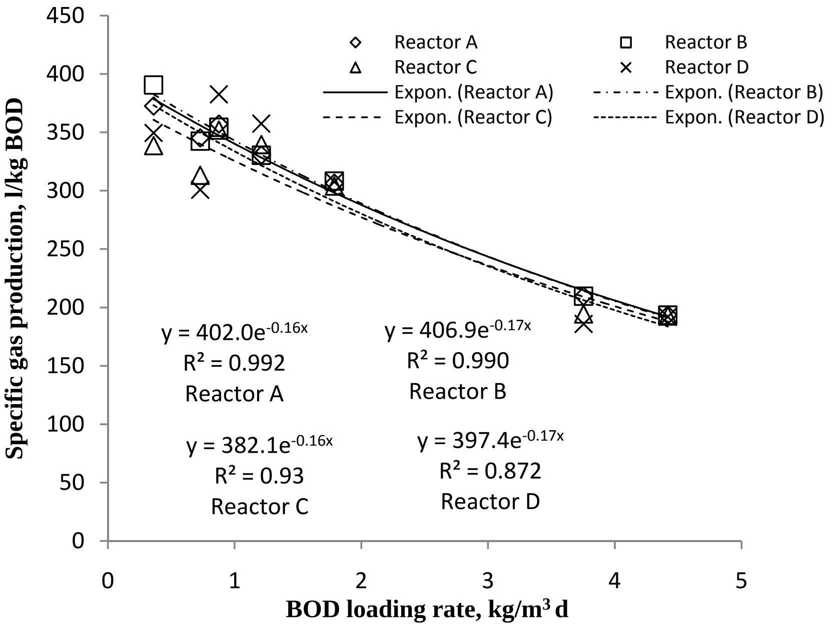


Fig. 4.30 BOD loading rate Vs. Specific gas production

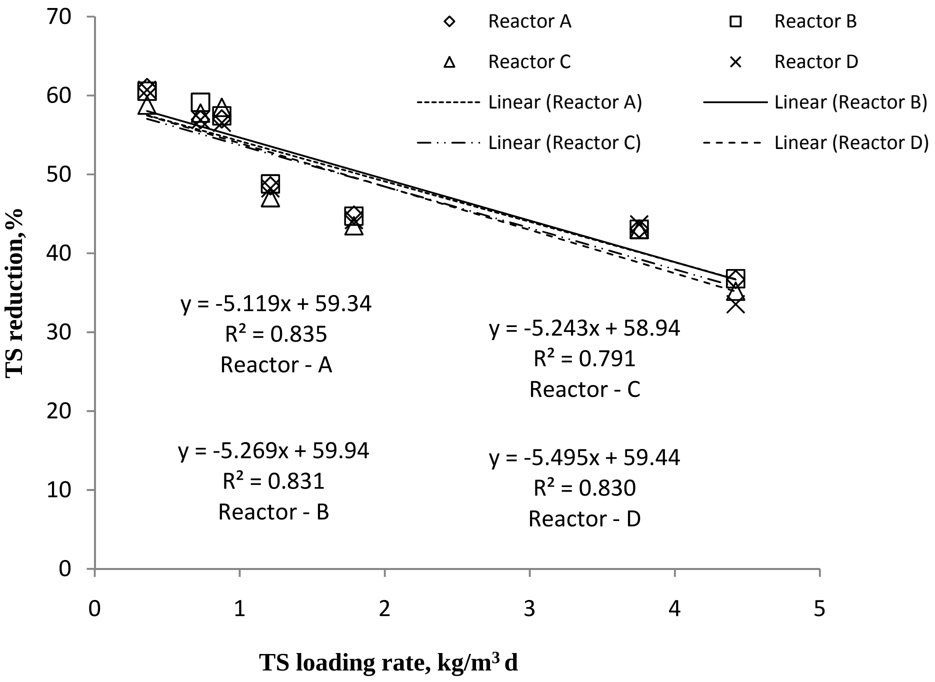


Fig.4.31 TS loading rate Vs TS reduction

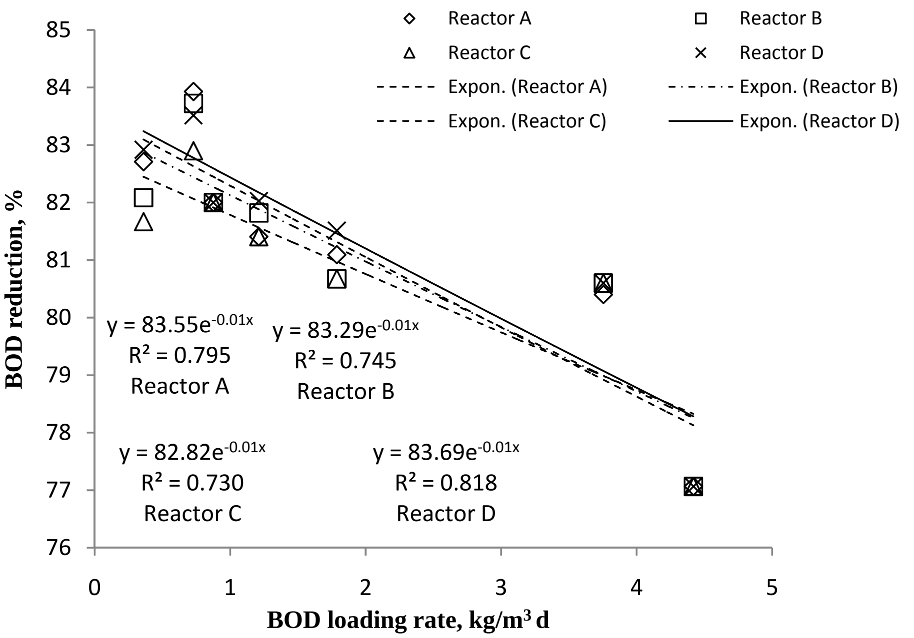


Fig.4.32 BOD loading rate Vs. BOD reduction

It was found difficult to attain the effluent standards of 30 mg/ℓ BOD even at the longest HRT of 10 day. An aerobic polishing treatment can bring down the pollution load to the required levels without high capital investment and energy expenditure. Such a finishing treatment was done by Sanna et al. (1984) for sugar refinery waste and Henry (1985) for sugar distillery wastewater. Lettinga (1984) also has pointed out this aspect as a drawback of anaerobic processes. At 2 day HRT, a reduction of over 80.1 % BOD was achieved in the present study and hence the requirement of aerobic treatment will be nominal.

The average daily effluent discharge from Pavizham rice mill is nearly 4 lakh litres. The total energy which can be generated from biogas produced from 4 lakh litres of effluent could be estimated as 8800 MJ, considering that 1 m^3 of biogas with 60 to 65 per cent methane will yield 20 MJ/m^3 of energy. This energy can either be used for thermal applications or electricity generation.

Biogas could be burnt to produce steam with an overall efficiency of 60 per cent. If this biogas can be used to replace the firewood presently used (average calorific value of 18 MJ/kg, thermal efficiency of 20 per cent) we can replace 264 tonnes of firewood per day. Balance biogas if any can be used to produce electricity.

SUMMURY AND CONCLUSION

CHAPTER V

SUMMARY AND CONCLUSION

Conversion of organic matter to methane by anaerobic digestion has got great relevance in India. Biomethanation of agro-industrial waste provides a means of decentralised energy generation along with waste disposal. Development of high rate bioreactors has opened the possibility of treating high volume, low strength agro-industrial effluents by anaerobic processes. The continuous discharge of rice mill effluent in and around the rice mills end up in soil sickness and pose a public health hazard. Rice mill effluent requires treatment to reduce its uncontrolled degradation at disposal sites and subsequent greenhouse gas and odour emissions. Anaerobic digestion of rice mill effluent has a high significance due to the positive environmental value as it combines pollution control along with energy production. The study was aimed at development of an economically and technologically feasible, high rate anaerobic bioreactor for energy production from RME.

1. The investigation to understand the characteristics of rice mill effluent (RME) revealed its highly polluting nature. The TS of the RME was found to have a TS of 3090 mg/ℓ, BOD of 3599 mg/ℓ and a COD of 4100 mg/ℓ. The carbon : nitrogen (C:N) ratio was found to be 22.4:1 and the BOD:COD ratio was 0.88. The total Kjeldahl nitrogen was 73 mg/ℓ whereas TOC was 1636 mg/ℓ. The pH was in the acidic range and was found to be 3.9. It was also revealed that the high COD: BOD ratio and the optimum C:N ratio is favorable for biological treatment of RME.

surface properties of the rubber seed outer shell would have aided better biofilm attachment and was selected as the media suitable for use in laboratory scale UAHRs. The study also revealed that a TS reduction up to 61 per cent could be attained in the longest HRT of 20 days.

4. The high rate reactor design selected was ‘Up flow anaerobic hybrid reactor (UAHR)’ considering the advantage of such a hybrid design which could combine the advantages of anaerobic filter and sludge bed reactors. Eight lab scale UAHRs were designed and fabricated. Two different media for immobilization viz. polyurethane rings and rubber seed outer shell were used in them. The reactors had a total height of 60 cm and a diameter of 20 cm. The media was placed at the upper half of the reactor, retained at the proper position by dispersion plates and had a height of 29.5 cm for the media filled portion. The sludge bed zone consisted of the bottom 29.5 cm height of the reactors. The gas was measured using water displacement method. The feed (RME) was introduced at the bottom of the reactor by a peristaltic pump through a fluted tube type feed inlet. The effluent outlet was bend into the liquid inside the reactor and was bend to U-shape outside the reactor to avoid the escape of gas through the effluent outlet.
5. The evaluation of the URHRs were done by observing the start-up characteristics and operating the reactors at various HRTs. Four treatments with two replications were used. The inoculum used was diluted cow dung (TS approximately 2 per cent) in the two treatments with rubber seed outer shell as media viz. R_1 and R_4 (inoculum volume of 20 and 50 per cent of the total digester volume respectively). The digester sludge from semi-continuous digesters used for media compatibility study (20 per cent volume) was used in the treatment R_2, also with rubber seed outer shell media. The treatment R_3 with polyurethene media was used to compare the treatments with rubber seed outer shell media and was inoculated with cow dung (50 per cent volume).
6. The results revealed that 25 days were required for the start-up. Bioreactors R_1 and R_2 started biogas production on 6th and 3rd day respectively. R_3 showed a short delay in start-up, while R_4 started gas production from the 4th day.

7. The daily feeding of all the reactors were started on the 25th day at a start-up HRT of 10 day and was operated on that HRT for 31 days. Reactors took 3 to 21 days to reach the pseudo-steady stage (PSS) in gas production. The reactor 2 was the first among the four to reach the PSS on the 3rd day, while Reactor 3 took the longest period of 22 days. The effluent characteristics of all the reactors with respect to TS, BOD and pH were fairly steady over the PSS period showing good stability of the reactors. The effluent pH during this period was above 7 for all reactors even though the influent had a low pH in the range 3.8 – 3.9.
8. The hydraulic retention time (HLR) of the reactors during 10 day HRT period was 100 ℓ/m^3 with a organic loading rate (OLRs) of 0.164 kg $TS/m^3.d$. All the reactors showed good gas production performance during the PSS period and a highest specific gas production of 858.2 ℓ/kg TS and 390.5 ℓ/kg BOD were seen in Reactor 2 and the lowest values of 744.2 ℓ/kg TS and 338.6 ℓ/kg BOD were observed in Reactor 4. The biogas productivities observed in these reactors were 1.25 and 1.19 ℓ/ℓ of feed in R_1 and R_2 respectively.
9. The performance of the reactors with respect to TS and BOD reductions were in the range of 58.5 to 61.1 and 81.7 to 82.9 per cent respectively. R_1 showed the maximum TS reduction. The R_3 remained as the lowest performer in the case of BOD and TS reductions during 10 day HRT.
10. The evaluation of the reactors conducted by operating them at HRTs 10 day, 5 day, 4 day, 3 day, 2 day, 1 day and 0.8 day further confirmed the stability of operation and high performance of the UAHRs.
11. The effluent pH values were almost neutral or slightly alkaline (7.0 – 8.6) during the entire period of operation.
12. The effluent TS, and BOD were found to increase with the reduction of HRT for all reactors.
13. The methane content of biogas reached the peak value of 75 per cents at 4 day HRT in Reactor 1 and 2 and at 3 day HRT in Reactor 2. In general the methane content varied between 57.5 and 75 per cent.

14. The HLR as well as OLR during PSS periods of 10 day to 0.8 day HRT progressively increased to reach the peak values of 2.2 kg TS/m^3.d and 4.4 kg BOD/m^3.d for all the reactors at 0.8 day HRT.
15. The specific gas productions in terms of TS and BOD for all reactors were found to decrease with the reduction of HRT. The maximum values were R_2 (858.2 ℓ/kg TS and 390.5 ℓ/kg BOD) at 10 day HRT and the minimum value was seen in R_4 (391.3 ℓ/kg TS and 192.0 ℓ/kg BOD) at 0.8 day HRT.
16. The biogas productivity also followed a similar trend of specific gas production. The biogas productivity decreased with decrease in HRT. There was a sharp decrease when shifted from 2 to 1 day HRT while the change from 1 to 0.8 day HRT did not affect the biogas productivity so much. The maximum biogas productivity was seen at 10 day HRT by R_2 (1.4 ℓ/ℓ) and the minimum value of 0.6 ℓ/ℓ was seen in all reactors at 0.8 day HRT.
17. The volumetric gas production increased with the decrease of HRT in all reactors. The maximum production of 854.9 ℓ/m^3 was observed in R_1 at 0.8 day HRT while the lowest production (122 ℓ/m^3) was observed in R_3 at 10 day HRT.
18. The TS and BOD reductions followed a decreasing trend with shortening of HRT. The maximum reductions were 61.1 per cent TS at 10 day HRT in R_1 and 82.9 per cent BOD in R_4 also at 10 day HRT. The minimum values were 34.1 per cent (R_4) and 77.1 per cent (all reactors) for TS and BOD respectively at 0.8 day HRT.
19. The high performance of the reactors could be accounted to the high degree of cell immobilisation obtained by the hybrid design which incorporated the UASB concept along with media peaking.
20. The reactors with rubber seed outer shell media was found to perform better than the reactor with polyurethene media, possibly due to the more favorable micro structure of rubber seed outer shell surface which facilitated biomass attachment.
21. Reactor performance models relating the parameters of specific gas productions and pollutant reductions with organic loading rates in terms of TS and BOD were obtained. The relationship had a high degree of fit.

22. HLR or in other words HRT was found to be the most important parameter affecting reactor performance.
23. The UAHR was found to be efficient in energy production from RME and 20 MJ/m^3 of energy could be produced as biogas if the system is operated at 2 day HRT. In the case of Pavizham rice mill 400000 liters of RME is produced per day. The total energy which could be produced amounts to 8000 MJ/d.

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ABSTRACT

DEVELOPMENT OF A HIGH-RATE ANAEROBIC BIOREACTOR FOR ENERGY PRODUCTION FROM RICE-MILL EFFLUENT

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ABSTRACT OF THE THESIS

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ABSTRACT

Anaerobic digestion of agricultural, industrial and municipal wastes has a great relevance in the global renewable energy scenario, since it combines waste stablisation with net fuel production. RME is a low strength, high volume waste for which anaerobic treatment can be economically and technologically made feasible by adopting high rate processes. Hence, an investigation was taken up to develop an anaerobic high rate reactor for biomethanation of RME.

It was revealed that the RME had a low pH along with high BOD and COD. The batch digestion studies proved that it is amenable to anaerobic digestion. The semi-continuous studies to test media compatibility could reveal that the reactor could be feed with RME without prior neutralisation. The study established the compatibility and suitability of rubber seed outer shells as packing media in high rate reactors and hence this was selected to be used in Up-flow Anaerobic Hybrid Reactors (UAHRs).

Eight lab scale UAHRs were designed and fabricated, with two different media for immobilization viz. polyurethane rings and rubber seed outer shell. The daily feeding in the reactors were started from the 25th day after initial charging and operated for 31 days, with a startup HRT of 10 day.

The UAHRs were then operated at HRTs of 10, 5, 4 ,3 , 2, 1 and 0.8 day and the performance evaluated. All reactors were stable in operation and exhibited high process efficiency characterised by good organic reduction and biogas production. This was due to the high degree of cell immobilisation obtained in the hybrid design. The performance deteriorated with reduction in HRT. The methane content of the biogas remained fairly high (60-65 per cent) during the above period with a near neutral effluent pH (7.7 t0 7.8). The reactor performance models showed a high degree of fit within the ranges of loading rates investigated. The major parameter which affected reactor performances was HLR, which is a function of HRT.

The maximum loading rate and volumetric gas production (at 0.8 day HRT) were 2.2 kg/m^3.d and 855 ℓ/m^3 (Reactor 1). The maximum specific gas production was 858.2 ℓ/kg TS observed in Reactor 2 at 10 day HRT. The BOD reduction had the maximum

value of 82.9 per cent at 10 day HRT in R_2 and the minimum reduction was on the 0.8 day HRT during which 77.1 per cent reduction was obtained for all reactors.

The UAHR was found to be appropriate in energy conversion of RME and 0.022 MJ/m3 of energy could be produced as biogas by operating the bioreactor at 2 day HRT, simultaneously reducing the pollution load of RME considerably (81 per cent BOD reduction). A HRT of 2 day was found optimum for moderate biogas production. An aerobic polishing treatment would be required to meet the effluent standards prescribed by the pollution control board. The overall performance of the reactor with rubber seed outer shell media was found to be significantly better than the polyurethane media reactor, possibly due to the enhanced microbial attachment on the more favorable surface.

APPENDICES

Appendix-I

Specification of peristaltic pump

Sl. No.	Description	Specification
1	Make	Miclins
2	Model	PP-20
3	Flow range	2 ml/hr to10 l/hr
4	Number of rollers	4
5	Tube size (ID)	2mm
6	Tube wall thickness	1.5mm

APPENDIX II

Gas Volume (mℓ) of Batch Digestion study

Days	T_0			T_1		
	A	B	C	A	B	C
1	0	0	32.06	0	0	96.20
2	112.20	48.10	112.23	192.40	16.03	0
3	96.20	48.10	64.13	0	80.17	112.23
4	32.10	32.06	80.17	0	64.13	0
5	32.10	48.10	64.13	48.10	64.13	96.20
6	64.10	128.27	112.23	128.27	64.13	80.17
7	96.20	80.17	80.17	96.20	112.23	160.34
8	112.20	128.27	160.34	80.17	160.34	48.10
9	176.30	176.37	240.51	320.68	288.61	272.57
10	96.20	48.10	112.23	224.47	112.23	192.40
11	112.20	96.20	112.23	160.34	160.34	208.44
12	16.0	32.06	80.17	481.02	561.19	432.91
13	16.0	16.03	64.13	577.22	464.98	464.98
14	96.20	192.40	144.30	657.39	753.59	705.49
15	192.40	192.40	176.37	497.05	513.08	481.02
16	240.51	464.98	224.4	416.88	448.95	464.98
17	368.78	464.98	336.71	368.78	384.81	416.88
18	368.782	464.986	352.748	288.612	320.68	448.95
19	497.05	432.918	336.71	288.61	192.40	529.12
20	304.64	448.95	320.68	384.81	352.74	336.71
21	400.85	577.22	513.08	288.61	336.71	320.68
22	432.91	529.12	416.88	448.95	464.98	304.64
23	577.22	721.53	400.85	208.44	176.37	208.44
24	673.42	705.49	577.22	128.27	224.47	144.30
25	625.32	785.66	577.22	497.05	192.40	497.05
26	769.63	962.04	833.76	176.37	224.47	192.40
27	1090.31	913.93	657.39	208.44	160.34	240.51

28	929.97	897.90	1202.55	208.44	256.54	224.47
29	881.87	881.87	994.10	240.51	272.57	240.51
30	737.56	769.63	1186.51	256.54	400.85	304.64
31	849.80	929.97	865.83	288.61	304.64	256.54
32	785.66	994.10	962.04	336.71	224.47	192.40
33	1010.14	849.80	833.76	208.44	176.37	256.54
34	737.56	641.36	817.73	192.40	192.40	224.47
35	464.98	513.08	529.12	208.44	192.40	224.47
36	448.95	545.15	464.98	256.54	240.51	288.61
37	497.05	561.19	497.05	240.51	256.54	288.61
38	400.85	753.59	497.05	256.54	240.51	272.57
39	545.15	609.29	785.66	545.15	176.37	272.57
40	464.98	529.12	96.20	240.51	448.95	176.37
41	448.95	513.08	817.73	224.47	176.37	208.44
42	384.81	545.15	384.81	176.37	192.40	176.37
43	352.74	368.78	320.68	208.44	176.37	192.40
44	320.68	336.71	208.44	144.30	160.34	144.30
45	224.47	208.44	176.37	16.03	112.23	128.27
46	176.37	176.37	160.34	192.40	64.13	80.17
47	160.34	192.40	160.34	64.13	80.17	96.20
48	112.23	144.30	112.23	32.06	32.06	48.10
49	112.23	128.27	128.27	32.06	48.10	48.10
50	96.20	96.20	32.06	96.20	32.06	80.17
51	112.23	128.27	112.23	32.06	128.27	64.13
52	96.20	176.37	304.64	48.10	0	32.06
53	96.20	96.20	96.20	32.06	112.23	48.10
54	128.27	128.27	112.23	48.10	0	64.13
55	144.30	160.34	144.30	48.10	96.20	64.13
56	128.27	256.54	112.23	32.06	0	64.13
57	112.23	144.30	128.27	32.06	112.23	80.17
58	80.17	80.17	48.10	0	0	0

59	96.20	96.20	80.17	16.03	256.54	32.06
60	96.20	112.23	80.17	16.03	64.13	32.06
61	144.30	144.30	128.27	48.10	48.10	80.17
62	144.30	144.30	160.34	64.13	64.13	96.20
63	128.27	176.37	160.34	64.13	64.13	64.13
64	160.34	176.37	128.27	32.06	48.10	48.10
65	112.23	288.61	128.27	48.10	32.06	32.06
66	160.34	80.17	112.23	32.06	16.03	48.10
67	336.71	112.23	160.34	80.17	80.17	80.17
68	112.23	64.13	0	64.13	64.13	32.06
69	96.204	176.37	352.74	64.13	48.10	64.13
70	112.23	128.27	64.13	64.13	64.13	48.10
71	112.23	160.34	48.10	80.17	48.10	48.10
72	112.23	96.20	80.17	64.13	16.03	48.10
73	80.17	48.10	80.17	16.03	48.10	0
74	112.23	96.20	128.27	80.17	64.13	64.13
75	128.27	144.30	112.23	80.17	80.17	96.20
76	80.17	112.23	112.23	48.10	32.06	0
77	80.17	80.17	64.13	32.06	16.03	0
78	64.13	80.17	80.17	32.06	48.10	32.06
79	64.13	96.20	80.17	48.10	32.06	48.10
80	48.10	112.23	80.17	16.03	16.03	16.03
81	64.13	64.13	64.13	32.06	32.06	16.03
82	16.03	96.20	80.17	0	16.03	32.06
83	80.17	64.13	64.13	48.10	32.06	16.03
84	80.17	96.20	64.13	32.06	32.06	32.06
85	48.10	80.17	80.17	32.06	32.06	32.06
86	64.13	80.17	64.13	16.03	0	16.03
87	64.13	64.13	48.10	32.06	80.17	16.03
88	64.13	64.13	80.17	32.06	0	16.03
89	32.06	16.03	16.03	0	0	0

90	48.10	48.10	48.10	16.03	0	32.06
91	64.13	0	64.13	48.10	32.06	32.06
92	0	16.03	32.06	16.03	16.03	0
93	16.03	32.06	32.06	0	0	0
94	0	32.06	48.10	0	16.03	16.03
95	64.13	0	48.10	48.10	32.06	48.10
96	0	48.10	48.10	16.03	0	16.03
97	32.06	48.10	48.10	0	16.03	0
98	0	16.03	16.03	16.03	16.03	0
99	64.13	64.13	0	32.06	32.06	48.10
100	0	32.06	0	16.03	0	16.03
101	0	16.03	32.06	32.06	48.10	32.06
102	48.10	112.23	0	48.10	48.10	0
103	144.30	48.10	128.27	32.06	32.06	48.10
104	160.34	80.17	128.27	32.06	32.06	48.10
105	32.06	48.10	160.34	32.06	32.06	32.06
106	48.10	32.06	64.13	0	16.03	16.03
107	48.10	48.10	48.10	16.03	16.03	16.03
108	32.06	32.06	64.13	0	0	0
109	48.10	16.03	64.13	16.03	0	0
110	48.10	64.13	48.10	48.10	16.03	0
111	48.10	48.10	48.10	0	32.06	0
112	48.10	48.10	64.13	176.37	32.06	0
113	48.10	48.10	64.13	0	0	0
114	64.13	16.03	48.10	0	448.95	0
115	32.06	64.13	48.10	0	16.03	0
116	32.06	48.10	48.10	0	0	0
117	48.10	16.03	48.10	0	16.03	144.30
118	16.03	32.06	32.06	0	0	0
119	16.03	16.03	48.10	0	0	0
120	64.13	80.17	64.13	0	16.03	0

121	32.06	32.06	32.06	0	16.03	0
122	48.10	48.10	48.10	96.20	0	0
123	48.10	64.13	48.10	0	0	0
124	0	16.03	48.10	0	0	0
125	48.10	64.13	48.10	0	0	0
126	32.06	16.03	32.06	0	0	0
127	64.13	64.13	64.13	0	0	0
128	48.10	64.13	64.13	0	32.06	0
129	48.10	64.13	48.10	112.23	16.03	0
130	48.10	16.03	64.13	0	0	0
131	48.10	64.13	48.10	0	0	0
132	16.03	32.06	16.03	0	0	0
133	48.10	80.17	64.13	0	16.03	0
134	16.03	16.03	32.06	0	0	0
135	32.06	32.06	32.06	0	0	0

APPENDIX III

Gas Volume (mℓ) of Media selection study

Sl. No.		Treatments						
		T0	T01	T02	T03	T1	T2	T3
		Volume, mℓ						
1	Start up	502.39	288.61	491.70	293.95	261.88	390.16	390.16
2		149.65	96.20	203.09	53.44	53.44	90.85	85.51
3		240.51	192.40	309.99	149.65	37.41	90.85	144.30
4		235.16	192.40	336.71	229.82	64.13	96.20	149.65
5		400.85	251.19	454.29	481.02	138.96	261.88	235.16
6		448.95	277.92	609.29	395.50	315.33	245.85	261.88
7		374.12	342.05	609.29	491.70	529.12	395.50	438.26
8		529.122	379.47	860.49	566.53	630.67	657.39	903.24
9		571.87	443.60	871.18	641.36	801.7	700.15	897.90
10		839.11	668.08	1272.03	1020.83	1020.83	1058.24	1202.55
11		1320.13	1181.17	1539.26	1352.20	1427.02	1239.96	1443.06
12		1902.70	1528.57	1886.66	1875.97	1806.49	1127.72	1090.31
13		2656.29	1710.29	2266.13	2276.82	1854.59	1058.24	1063.58
14		2731.12	1560.64	2218.03	2987.66	598.60	1063.58	1117.03
15		2100.45	1165.13	1956.14	1827.87	502.39	737.56	1074.27
16	20 day HRT	1239.96	919.28	1394.95	1282.72	630.67	678.77	1223.92
17		1640.81	972.72	1480.47	1726.32	844.45	753.59	1079.62
18		1619.43	1063.58	1576.67	1737.01	769.63	791.01	962.04
19		1539.26	1063.58	1528.57	1667.53	897.90	705.49	1084.96
20		1715.63	1068.93	1512.54	1726.32	839.11	705.49	1095.65
21		1614.08	1084.96	1539.26	1683.57	636.01	662.73	967.38
22		1421.68	1255.99	1464.43	1421.68	625.32	555.84	737.56
23		1362.89	1400.30	1384.26	1587.36	646.70	571.87	791.01
24		1491.16	1544.60	1410.99	1699.60	614.63	593.25	817.73
25		1405.64	1330.82	1207.89	1940.11	545.15	529.12	716.18
26		1469.78	1496.50	1213.23	1843.91	502.39	550.50	876.52

27		1512.54	1250.65	1288.06	2079.07	571.87	545.15	823.07
28		1394.95	1133.06	1410.99	1539.26	507.74	550.50	791.01
29		1341.51	1197.20	1475.12	1630.12	587.91	625.32	919.28
30		1539.26	1475.12	1865.28	1646.15	603.94	646.70	774.97
31		1699.60	1678.22	1929.42	1945.45	710.84	668.08	924.62
32		2052.35	2057.69	1737.01	2346.30	732.21	812.38	1004.79
33		2250.10	2196.65	1459.09	2490.61	700.15	876.52	962.04
34		2132.52	2030.97	1341.51	2442.51	721.53	956.69	1288.06
35		1790.46	1384.26	1336.16	2175.27	833.76	962.04	1245.30
36		1389.61	1304.09	1352.20	1582.02	1026.17	1138.41	1475.12
37		1336.16	1250.65	1197.20	1646.15	1095.65	1068.93	1266.68
38		1127.72	1181.17	1304.09	1266.68	1288.06	994.10	1272.03
39		1031.52	994.10	1010.14	1416.33	1015.48	828.42	1052.89
40		1170.48	1042.21	1229.27	1416.33	929.97	999.45	1154.44
41		1950.80	1774.42	1924.0	2271.48	1437.71	1678.22	1785.11
42		2025.62	1731.67	1865.28	2137.86	1186.51	1394.95	1544.60
43		1507.19	1539.26	1421.68	1827.87	1117.03	1058.24	1138.41
44		1261.34	1068.93	1239.96	1496.50	999.45	791.01	1213.23
45		1640.81	1549.95	1491.16	1833.22	1079.62	1015.48	1250.65
46		1389.61	1464.43	1288.06	1747.70	1063.58	1133.06	1095.65
47		1394.95	1357.54	1394.95	1902.70	1026.17	978.07	1052.89
48		1384.26	1255.99	1175.82	1576.67	967.38	919.28	1026.17
49		1288.06	1282.72	1213.23	1678.22	956.69	967.38	994.10
50		1191.86	1223.92	1117.03	1603.4	913.93	812.38	1036.86
51		1202.55	1090.31	1047.55	1507.19	807.04	855.14	978.07
52		1090.31	1149.10	962.04	1549.95	881.87	855.14	967.38
53		1175.82	1015.48	994.10	1517.88	769.63	737.56	983.41
54		1004.79	812.38	1031.52	1352.20	748.25	774.97	860.49
55		1111.69	769.63	946.00	1528.57	919.28	791.01	1031.52
56		737.56	913.93	785.66	1277.37	748.25	732.21	844.45
57		758.94	935.31	812.38	1288.06	801.7	780.32	823.07

58		769.63	919.28	791.01	1384.26	732.21	742.90	753.59
59		785.66	876.52	839.11	1250.65	823.07	764.28	780.32
60		716.18	502.39	700.15	1202.55	625.32	561.19	609.29
61		1122.38	994.10	924.62	1389.61	732.21	764.28	871.18
62		935.31	956.69	1004.79	1678.22	849.80	876.52	994.10
63		972.72	844.45	823.07	1384.26	780.32	705.49	785.66
64		956.69	887.21	839.11	1277.37	748.25	684.11	791.01
65		801.7	742.90	780.32	1207.89	705.49	555.84	758.94
66		913.93	780.3213	710.84	1459.09	833.76	577.224	807.04
67		823.07	951.35	972.72	1378.92	833.76	823.07	855.14
68		844.45	737.56	860.49	1239.96	801.7	721.53	828.42
69		839.11	764.28	828.42	1197.20	828.42	668.08	865.83
70		881.87	796.35	855.14	1197.20	833.76	684.11	849.80
71		860.49	812.38	828.42	1261.34	769.63	700.15	849.80
72		887.21	807.04	844.45	1255.99	817.73	726.87	812.38
73		876.52	796.35	812.38	1223.92	839.11	780.32	860.49
74		785.66	748.25	936.38	1223.92	823.07	769.63	871.18
75		737.56	726.87	951.35	1202.55	780.32	689.46	871.18
76		769.63	646.70	860.49	1175.82	807.04	678.77	855.14
77		892.55	689.46	913.93	1165.13	764.28	716.18	844.45
78		828.42	839.11	823.07	1202.55	844.45	742.90	871.18
79		897.90	742.90	887.21	1218.58	737.56	737.56	881.87
80		897.90	774.97	924.62	1165.13	833.76	705.49	849.80
81		737.56	737.56	903.24	1245.30	844.45	796.35	876.52
82		742.90	774.97	839.11	1234.61	860.49	785.66	876.52
83		764.28	705.49	876.52	1304.09	865.83	753.59	887.21
84		828.42	716.18	828.42	1175.82	865.83	780.32	881.87
85		833.76	710.84	855.14	1250.65	876.52	817.73	876.52
86		791.01	748.25	892.55	1362.89	881.87	807.04	887.21
87		919.28	657.39	919.28	1239.96	839.11	817.73	913.93

88	15 day HRT	769.63	705.49	817.73	1218.58	785.66	678.77	903.24
89		726.87	678.77	785.66	1304.09	844.45	689.46	871.18
90		742.90	662.73	785.66	1357.54	785.66	726.87	908.59
91		737.56	625.32	876.52	1245.30	769.63	705.49	913.93
92		737.56	742.90	881.87	1330.82	812.38	732.21	892.55
93		769.63	716.18	887.21	1352.20	780.32	732.21	860.49
94		764.28	694.80	839.11	1336.16	812.38	748.25	855.14
95		758.94	774.97	839.11	1293.40	839.11	705.49	828.42
96		881.87	764.28	887.21	1336.16	876.52	737.56	839.11
97		887.21	737.56	887.21	1667.53	823.07	705.49	833.76
98		881.87	764.28	881.87	1245.30	828.42	721.53	849.80
99		897.90	769.63	844.45	1234.61	801.7	753.59	828.42
100		849.80	791.01	887.21	1213.23	823.07	732.21	807.04
101		839.11	780.32	807.04	1250.65	801.7	742.90	839.11
102		862.62	748.25	919.28	1320.13	839.11	732.21	844.45
103		876.52	726.87	956.69	1298.75	807.04	726.87	849.80
104		865.83	758.94	887.21	1250.65	807.04	689.46	839.11
105		929.97	753.59	865.83	1202.55	844.45	678.77	839.11
106		865.83	748.25	849.80	1330.82	828.42	678.77	839.11
107		860.49	774.97	855.14	1272.03	796.35	668.08	833.76
108		855.14	764.28	774.97	1309.44	807.04	721.53	860.49
109		833.76	726.87	774.97	1346.85	796.35	641.36	844.45
110		860.49	705.49	774.97	1341.51	796.35	678.77	876.52
111		855.14	689.46	908.59	1239.96	892.55	673.42	865.83
112		887.21	721.53	817.73	1298.75	823.07	636.01	3303.00
113		876.52	721.53	855.14	1245.30	812.38	684.11	823.07
114		865.83	748.25	774.97	1218.58	817.73	668.08	871.18
115		865.83	726.87	796.35	1245.30	849.80	657.39	865.83
116		897.90	668.08	849.80	1181.17	855.14	662.73	860.49
117		881.87	812.38	839.11	1223.92	807.04	673.42	913.93
118		839.11	796.35	833.76	1277.37	801.7	684.11	924.62

119		817.73	721.53	860.49	1272.03	807.04	646.70	871.18
120		839.11	710.84	865.83	1229.27	785.66	694.80	881.87
121		657.39	678.77	812.38	1079.62	614.63	507.74	668.08
122		657.39	742.90	769.63	1052.89	571.87	636.01	646.70
123		716.18	721.53	764.28	1101.00	593.25	523.77	625.32
124		716.18	732.21	780.32	1154.44	614.63	507.74	619.98
125		657.39	726.87	737.56	1149.10	539.81	497.05	652.04
126		646.70	673.42	774.97	1052.89	534.46	507.74	705.49
127		753.59	860.49	748.25	1133.06	700.15	475.67	668.08
128		668.08	758.94	791.01	1095.65	587.91	550.50	689.46
129	10 day HRT	678.77	742.90	764.28	1106.34	593.25	422.22	732.21
130		673.42	716.18	769.63	1101.00	534.46	427.57	726.87
131		668.08	673.42	780.32	1090.31	502.39	438.26	673.42
132		668.08	678.77	769.63	1084.96	577.22	481.02	764.28
133		668.08	705.49	769.63	1138.41	550.50	539.81	673.42
134		774.97	700.15	758.94	1149.10	539.81	566.53	668.08
135		780.32	716.18	812.38	1063.58	545.15	555.84	721.53
136		700.15	780.32	742.90	1117.03	598.60	555.84	662.73
137		673.42	785.66	742.90	1084.96	598.60	678.77	657.39
138		668.08	630.67	801.7	1122.38	534.46	577.22	678.77
139		630.67	716.18	764.28	1101.00	545.15	523.77	657.39
140		662.73	758.94	748.25	1143.75	571.87	571.87	641.36
141		668.08	716.18	791.01	1127.72	529.12	603.94	678.77
142		678.77	705.49	801.7	1084.96	636.01	593.25	657.39
143		689.46	732.21	812.38	1101.00	571.87	545.15	689.46
144		657.39	732.21	694.80	1111.69	636.01	566.53	641.36
145		705.49	774.97	705.49	1133.06	561.19	566.53	828.42
146		705.49	710.84	764.28	1143.75	561.19	550.50	678.77
147		705.49	700.15	892.55	1138.41	561.19	545.15	678.77
148		657.39	705.49	732.21	1111.69	614.63	561.19	646.70
149		689.46	764.28	812.38	1090.31	652.04	571.87	662.73

150		684.11	758.94	774.97	1127.72	710.84	555.84	673.42
151		657.39	764.28	812.38	1058.24	694.80	534.46	668.08
152		662.73	721.53	764.28	1047.55	582.56	582.56	684.11
153		497.05	619.98	534.46	732.21	566.53	459.64	513.08
154		502.39	603.94	625.32	662.73	518.43	448.95	513.08
155		491.70	657.39	507.74	742.90	539.81	523.77	464.98
156		486.36	673.42	518.43	769.63	518.43	470.33	534.46
157		507.74	550.50	545.15	764.28	518.43	432.91	507.74
158		539.81	625.32	561.19	748.25	523.77	443.60	507.74
159	5 day HRT	491.70	598.60	561.19	833.76	481.02	459.64	513.08
160		502.39	603.94	561.19	732.21	513.08	448.95	539.81
161		486.36	614.63	448.95	796.35	491.70	481.02	545.15
162		518.43	662.73	497.05	726.87	523.77	502.39	555.84
163		523.77	625.32	475.67	774.97	497.05	438.26	502.39
164		507.74	678.77	545.15	732.21	523.77	432.91	619.98
165		497.05	662.73	491.70	705.49	529.12	438.26	529.12
166		523.77	630.67	529.12	721.53	486.36	438.26	502.39
167		502.39	673.42	513.08	742.90	545.15	475.67	513.08
168		454.29	684.11	555.84	726.87	507.74	523.77	513.08
169		534.46	678.77	587.91	817.73	529.12	555.84	486.36
170		502.39	630.67	571.87	737.56	539.81	539.81	470.33
171		491.70	587.91	550.50	758.94	507.74	470.33	518.43
172		486.36	598.60	630.67	780.32	539.81	550.50	529.12
173		529.12	619.98	539.81	721.53	561.19	481.02	502.39

Sl. No.		Treatments					Temperature, ^{0}C
		T4	T5	T6	T7	T8	
		Volume, mℓ					
1	Start up	224.47	128.27	0	283.26	138.96	28.7
2		10.68	16.03	58.79	203.09	74.82	29.8
3		197.75	10.68	58.79	208.44	26.72	29.1
4		74.82	5.34	10.68	213.78	53.44	28.5
5		64.13	160.34	32.06	384.81	42.75	29
6		74.82	16.03	192.40	577.22	37.41	28.7
7		32.06	10.68	64.13	507.74	32.06	28.5
8		58.79	16.03	80.17	625.32	58.79	28.2
9		64.13	21.37	80.17	689.46	53.44	28
10		80.17	224.47	187.06	705.49	144.30	28.2
11		208.44	192.40	363.43	593.25	277.92	28.8
12		245.85	288.61	443.60	614.63	342.05	28.8
13		400.85	443.60	513.08	545.15	625.32	28.7
14		539.81	427.57	619.98	518.43	742.90	28.7
15		625.32	561.19	742.90	432.918	881.87	28.5
16	20 day HRT	657.39	518.43	673.42	395.50	876.52	28.4
17		630.67	432.91	481.02	363.43	919.28	28.4
18		411.53	379.47	256.54	390.16	475.67	28.7
19		229.82	181.71	171.02	416.88	165.68	29
20		245.85	187.06	165.68	395.50	171.02	29.2
21		283.26	171.02	154.99	358.09	144.30	28.8
22		347.40	203.09	165.68	309.99	154.99	28.7
23		374.12	229.82	187.06	304.64	181.71	28.7
24		438.26	256.54	219.13	288.61	267.23	29.1
25		347.40	261.88	229.82	406.19	326.02	29.1
26		315.33	251.19	240.51	374.12	326.02	28.9
27		283.26	192.40	267.23	438.26	513.08	28.5
28		251.19	235.16	203.09	400.85	443.60	28.8

29		261.88	187.06	203.09	400.85	529.12	29
30		304.64	165.68	187.06	464.98	427.57	29
31		272.57	144.30	160.34	577.22	390.16	29.5
32		229.82	48.10	138.96	646.70	326.02	28.7
33		229.82	144.30	154.99	497.05	277.92	29
34		240.51	149.65	160.34	518.43	374.12	29.5
35		288.61	80.17	138.96	571.87	293.95	30.1
36		261.88	122.92	187.06	491.70	416.88	30.2
37		320.68	117.58	176.37	475.67	229.82	30.2
38		299.30	245.85	208.44	497.05	342.05	30.5
39		358.09	117.58	171.02	384.81	240.51	30.1
40		855.14	342.05	427.57	577.22	326.02	29.9
41		1245.30	935.31	1266.68	1175.82	1079.62	30.1
42		1304.09	636.01	732.21	865.83	833.76	29.8
43		951.35	379.47	432.91	326.02	582.56	29.7
44		1010.14	529.12	299.30	550.50	721.53	23.33
45		956.69	502.39	603.94	358.09	710.84	29.7
46		897.90	582.56	518.43	587.91	603.94	30.1
47		865.83	459.64	416.88	395.50	652.04	30.1
48		796.35	550.50	587.91	416.88	566.53	30.5
49		807.04	534.46	534.46	422.22	700.15	30
50		817.73	614.63	464.98	481.02	668.08	30.3
51		844.45	534.46	571.87	422.22	844.45	30.3
52		946.00	497.05	475.67	529.12	700.15	30.6
53		801.7	534.46	577.22	577.22	721.53	30.5
54		935.31	641.36	502.39	422.22	758.94	30.3
55		978.07	678.77	646.70	475.67	812.38	30.2
56		887.21	507.74	598.60	577.22	673.42	30.9
57		908.59	491.70	609.29	593.25	668.08	30.4
58		881.87	507.74	619.98	609.29	678.77	30.3
59		855.14	502.39	625.32	619.98	716.18	29.6

60		919.28	491.70	518.43	342.05	737.56	30.5
61		1170.48	566.53	539.81	438.26	935.31	30.8
62		1111.69	694.80	646.70	448.95	988.76	30.6
63		1159.79	577.22	571.87	539.81	860.49	30.1
64		972.72	481.02	497.05	470.33	871.18	28.7
65		897.90	459.64	454.29	470.33	860.49	28.8
66		1127.72	582.56	598.60	481.02	946.00	28.4
67		1239.96	619.98	673.42	593.25	1031.52	29
68		1004.79	614.63	545.15	561.19	935.31	30.6
69		849.80	598.60	555.84	513.08	1036.86	30.5
70		1052.89	582.56	577.22	497.05	1020.83	30.3
71		988.76	598.60	593.25	555.84	1052.89	30.3
72		876.52	593.25	636.01	614.63	1015.48	29.6
73		1036.86	587.91	555.84	539.81	956.69	30.5
74		1068.93	614.63	764.28	507.74	940.66	30.8
75		1020.83	668.08	523.77	497.05	924.62	29
76		1063.58	571.87	523.77	534.46	876.52	30.6
77		1042.21	603.94	614.63	566.53	887.21	30.5
78		1015.48	593.25	636.01	598.60	1031.52	30.3
79		1052.89	609.29	598.60	555.84	972.72	30.3
80		1052.89	550.50	507.74	502.39	967.38	30.3
81		1010.14	673.42	652.04	513.08	988.76	29.6
82		951.35	582.56	550.50	507.74	1117.03	30.5
83		1036.86	571.87	529.12	550.50	940.66	30.8
84		1010.14	636.01	566.53	609.29	1010.14	29
85		1042.21	630.67	614.63	459.64	983.41	30.6
86		1052.89	577.22	598.60	582.56	994.10	30.5
87		1036.86	571.87	609.29	561.19	956.69	30.8
88	15 day HRT	999.45	582.56	539.81	497.05	988.76	29
89		1036.86	400.85	641.36	529.12	983.41	30.6
90		1052.89	646.70	555.84	561.19	1010.14	30.5

91		1010.14	603.94	566.53	534.46	1015.48	30.3
92		1068.93	603.94	587.91	459.64	903.24	30.5
93		994.10	641.36	529.12	603.94	1026.17	30.8
94		978.07	571.87	593.25	448.95	962.04	29
95		1036.86	684.11	561.19	518.43	972.72	30.6
96		1031.52	673.42	577.22	491.70	978.07	30.5
97		1010.14	678.77	566.53	475.67	972.72	30.8
98		1020.83	577.22	561.19	475.67	999.45	30.1
99		1015.48	587.91	561.19	481.02	946.00	29.8
100		1031.52	614.63	534.46	582.56	956.69	29.7
101		1015.48	593.25	577.22	539.81	1020.83	23.33
102		1026.17	534.46	577.22	577.22	1026.17	29.7
103		1026.17	2586.81	582.56	566.53	994.10	30.1
104		1042.21	603.94	593.25	587.91	967.38	30.1
105		1047.55	577.22	534.46	603.94	1079.62	30.5
106		1010.14	507.74	529.12	587.91	1063.58	30.6
107		1031.52	518.43	566.53	507.74	1036.86	30.5
108		1036.86	561.19	545.15	555.84	1031.52	30.8
109		1026.17	630.67	571.87	614.63	978.07	30.1
110		1047.55	598.60	566.53	636.01	913.93	29.8
111		999.45	368.78	577.22	593.25	988.76	30.8
112		1031.52	587.91	555.84	571.87	988.76	30.1
113		999.45	630.67	587.91	561.19	978.07	29.8
114		1015.48	700.15	555.84	571.87	978.07	29.7
115		1010.14	582.56	566.53	582.56	1010.14	23.33
116		1004.79	587.91	555.84	593.25	940.66	29.7
117		1015.48	571.87	571.87	577.22	988.76	23.33
118		1042.21	577.22	539.8113	577.22	972.72	29.7
119		1010.14	555.84	577.224	566.53	1010.14	30.1
120		994.10	609.29	571.87	577.22	972.72	30.1
121		1074.27	555.84	561.19	662.73	1047.55	30.5

122		1079.62	582.56	571.87	641.36	1058.24	29.8
123		1052.89	630.67	545.15	673.42	1031.52	29.7
124		1042.21	587.91	545.15	652.04	1004.79	23.33
125		1026.17	646.70	507.74	684.11	908.59	29.7
126		946.00	561.19	534.46	684.11	1010.14	23.33
127		1095.65	400.85	454.29	668.08	1010.14	30.3
128		1010.14	400.85	481.02	652.0493	1052.89	30.3
129	10 day HRT	924.62	416.88	486.36	710.8407	1042.21	29.6
130		951.35	454.29	555.84	705.49	1015.48	30.5
131		994.10	486.36	529.12	668.08	1047.55	30.8
132		1026.17	475.67	566.53	689.46	1004.79	29
133		994.10	443.60	518.43	748.25	1010.14	30.6
134		1020.83	400.85	491.70	673.42	908.59	30.5
135		1042.21	416.88	507.74	684.11	913.93	29.7
136		1026.17	432.91	571.87	700.15	1063.58	23.33
137		994.10	438.26	555.84	700.15	1058.24	30.3
138		1015.48	422.22	497.05	668.08	1095.65	30.3
139		1047.55	427.57	443.60	668.08	1042.21	29.6
140		999.45	443.60	545.15	603.94	1015.48	30.5
141		994.10	518.43	550.50	657.39	951.350	29
142		1063.58	438.26	481.02	710.84	1015.48	30.6
143		1042.21	523.77	464.98	689.46	1026.17	30.5
144		994.10	507.74	513.08	694.80	1010.14	29.7
145		978.07	454.29	491.70	705.496	972.72	23.33
146		999.45	448.95	566.53	641.36	1068.93	30.3
147		994.10	438.26	534.46	652.04	972.72	30.3
148		1010.14	438.26	523.77	668.08	967.38	29.7
149		1020.83	481.02	534.46	662.73	1020.83	23.33
150		1042.21	513.08	571.87	668.08	1052.89	30.3
151		1010.14	486.36	507.74	636.01	1058.24	30.3
152		940.66	539.81	523.77	668.08	1068.93	29.6

153		694.80	470.33	459.64	513.08	694.80	30.5
154		700.15	438.26	432.91	513.08	694.80	29
155		721.53	529.12	411.53	518.43	700.15	30.6
156		694.80	438.26	416.88	464.98	780.32	30.5
157		694.80	443.60	427.57	491.70	716.18	23.33
158		657.39	422.22	411.53	497.054	518.43	30.3
159	5 day HRT	710.84	448.95	374.12	443.60	742.90	30.3
160		684.11	448.95	379.47	470.33	748.25	29.7
161		705.49	454.29	395.50	502.39	737.56	23.33
162		689.46	454.29	352.74	470.33	764.28	30.3
163		710.84	448.95	454.29	448.95	812.38	30.3
164		668.08	459.64	422.22	475.67	732.21	29.6
165		673.42	475.67	443.60	491.70	721.53	30.5
166		657.39	448.95	438.26	475.67	732.21	29
167		668.08	448.95	411.53	491.70	737.56	30.6
168		673.42	470.33	481.02	481.02	791.01	30.5
169		678.77	491.70	464.98	443.60	742.90	23.33
170		652.04	448.95	443.60	448.95	742.90	30.3
171		689.46	459.64	427.57	475.67	769.63	30.5
172		657.39	448.95	475.67	523.77	753.59	29
173		662.73	320.68	443.60	513.08	764.28	30.6

APPENDIX IV

Gas volume of UAHRs

Sl. No.		Reactor A		Reactor B		Reactor C		Reactor D		Temperature ^{0}C
		A1	A2	B1	B2	C1	C2	D1	D2	
		Volume, ℓ								
1	Start up	0	0	0	0	0	0	0	0	28.9
2		0.3	0	0.4	0.4	0	0	0	0	30.2
3		0.1	0.4	1.4	0.8	0	0	0	0	30.2
4		0.3	0.2	0.8	0.5	0	0	0	1	30.1
5		0.5	0	1.1	1.1	0	0	0	1.1	29.3
6		0.6	0.2	1.4	1.1	0	0	0	1.8	29.8
7		0.9	0.4	1.5	1.4	0	0	0	2	29.7
8		1	1.1	3.6	1.4	0	0	0	4.3	30.8
9		1	2	3.8	6	1.8	1.4	1.7	4.6	30.6
10		1.1	0	2.5	1.5	2.4	1.1	2.2	4.8	30.8
11		1.2	0.1	7.6	2.1	2.7	1.6	2.5	4.9	30.2
12		1.5	1.2	4.2	0.7	2.3	1.8	2.6	5.1	29.6
13		1.6	1.3	4.9	1.1	3	2	3	5.8	30.2
14		1.7	1.3	5.9	1.4	2.9	2.1	3.4	5.2	29.3
15		1.9	1.2	6.5	1.4	3.1	2.4	3.3	6	30.8
16		2	1.6	7.7	6	3.2	2.5	3.8	6.2	30.1
17		1.9	1.7	6.8	6.8	3.7	2.6	4.2	6.4	29.8
18		2	1.6	9	7.7	4.4	3	4.5	6.7	31
19		2.1	3.1	8.1	8	5.5	3.1	4.6	7.3	30.2
20		2.2	3.2	8.9	7.1	6.3	3.2	4.9	7.2	30.1
21		2.5	3.5	7.8	6.2	6	3.3	4.8	7.3	33
22		2.4	3.7	7	6.9	6.2	3.5	4.9	7.6	28

23		2.5	3.5	6.9	5.9	6.6	3.7	5.1	7.7	29
24		2.7	6	7.3	6.9	7.2	4.3	5.5	9	30
25	10 day HRT	5.1	7.8	10.8	10.9	10	6	8.9	10.1	31
26		9	8.3	13	11.2	10.4	6.8	9.1	10.3	32.1
27		12.2	10.2	12.9	11.8	10.6	7	9.9	10.4	29.9
28		12.4	10.3	13	12.1	11	7.2	10.1	10.6	29.7
29		12.2	12.2	13.5	12.9	11.6	7.7	10	11.1	30.2
30		12.1	12.4	13.5	13	12.1	8.1	10.1	11	31.6
31		12.2	12.9	13.4	13	12.3	8	10.6	11.4	30.1
32		13.1	12.6	13.2	13.1	12.3	8.4	11	11.5	30
33		13.7	12.5	13.2	13	12.4	9.1	10.8	11.4	30
34		13.6	12.9	14.5	13.2	12.3	9.2	11	11.4	29.3
35		12.7	13.1	13.7	13.1	12.5	9.6	11.1	11.5	30.1
36		13.1	13.2	13.9	13.2	12.2	9.8	11.2	11.6	29.8
37		13	13	13.6	13.3	12.4	10	11.4	11.7	28.6
38		13.1	12.8	13.7	13.2	12.5	10.1	11.2	11.8	29.6
39		13.2	12.9	13.6	13.2	12.6	10.6	11.6	11.9	29
40		13.6	13.1	13.7	13.3	12.7	11	11.7	12	29.3
41		13.4	13.1	13.8	13.1	12.8	11.1	12	11.9	29.2
42		13.2	12.8	13.7	13	12.7	10.9	12.1	12.1	29.1
43		13.3	12.9	13.4	13.2	12.9	11.2	12.2	12.3	29.5
44		13.3	12.9	13.6	13.1	13	11.5	12.3	12.4	29
45		13.4	12.9	13.7	13.3	13	11.6	12.2	12.5	29.8
46		13.3	12.8	13.7	13.2	12.9	12	12.6	12.7	29.7
47		13.3	13.1	13.7	13.1	13.1	12.2	12.7	12.6	28.9
48		13.4	12.9	13.5	13.2	13	12.5	12.8	12.7	29.1
49		13.4	13	13.5	13.1	13.1	12.6	12.9	12.9	28.8

50		13.4	12.9	13.4	13.2	13.2	12.7	13.1	12.8	28.4
51		13.1	12.9	13.3	12.9	13	12.9	13	13	28.9
52		13.2	13	13.2	13	13.1	13.1	13.1	13.1	28.6
53		13.2	13.1	13.4	13.1	13.3	13	13.2	13	28.6
54		13.3	13.3	13.5	13.2	13.2	13.2	13.4	13.1	28.4
55		13.3	13.1	13.4	13.1	13.3	13.3	13.2	13.2	29
56	5 day HRT	17.2	16.7	17.7	16.6	16.9	17.7	17.2	17.7	28.8
57		18.9	19.3	19.1	18.3	19.5	18	18.9	18.2	28.6
58		19.4	22.3	19.5	19.2	19.8	18.3	19.4	18.3	28
59		20.8	24.1	21	22	21	18.5	20.6	18.4	29.1
60		21.9	23.8	22	22.9	23.5	18.6	20.9	18.5	29
61		23.7	24	24	23.5	24.1	18.7	21.2	18.6	30.6
62		25.1	24.1	25	24.3	24.2	18.9	21.4	18.8	30.6
63		25.4	24.3	25.5	24.3	23.8	19	21.7	18.9	30.1
64		24.8	23.9	24	24.1	24.3	19.1	21.6	19	30
65		25.1	24.1	24	24	24	19.3	21.8	19.2	30
66		23.6	24	23.8	23.8	23.8	19.2	21.9	19.1	28
67		23.8	23.8	22.9	24.1	23.2	19.4	21.8	19.2	27
68		24.6	24.2	24	24.2	24.1	19.5	22	19.3	30
69		24.5	24.1	24.1	24.3	24.3	19.6	22.1	19.4	30.3
70		24.7	24.5	24.7	24.5	24	19.7	22.2	19.5	29.8
71		24.8	24.2	24.5	24.3	24.5	19.7	22.3	19.6	28.7
72		24.6	24.3	24.3	24.2	24.3	19.8	22.4	19.6	28.1
73		24.1	24	23.9	24.1	24	19.7	22.6	19.7	27.6
74		24.6	24.2	24.2	24.2	24.2	20.1	22.7	19.9	27..8
75		24.1	24.6	24.7	24.5	24.5	20.1	22.8	20	27.9
76		24.1	24.3	24.3	24.3	24.3	20.2	22.9	20.1	27.5

77		24.2	24.4	24.4	24.3	24.4	20.3	22.8	20.3	27.6
78		24.3	24.3	24.3	24.5	24.3	20.2	22.9	20.4	27.5
79		24.3	24.1	24.2	24.2	24.2	20.3	23	20.5	28
80		24.3	24.3	24.3	24.3	24.3	20.4	23.4	20.6	28
81	4 day HRT	26.3	26.8	26	26.9	27.1	26.5	28.9	26.4	28
82		27.5	29.3	27.8	28	27.8	27	30	27.5	28.6
83		27.9	28.7	28.2	28.1	28.2	27.3	30.1	28.2	28.9
84		30	29.1	30.1	27.9	28.1	27.5	32	28.3	30
85		31.1	29	30	28.3	28	27.9	32.5	28.4	30
86		30.4	31	30.3	28.1	30.3	28.1	33	28.5	29.8
87		30.2	29.4	30.2	28.4	29.8	28.2	33.1	28.5	29.7
88		29.5	29.6	29.8	28.9	29.5	28.3	33.2	28.6	29.5
89		29.5	29.7	29.7	29.1	29.7	28.4	33.3	28.7	29.6
90		29.7	29.6	29.6	29.3	29.6	28.5	33.2	28.9	29.7
91		29.8	29.6	29.9	28.8	29.4	28.7	33.3	30.1	30
92		29.9	29.5	30.1	29.4	29	28.8	33.3	30.2	29.9
93		28.9	29.1	28.9	28.7	28.9	28.9	33.4	30.1	29.6
94		29.7	29.3	29.4	29.2	29.4	29	33.5	30	28.9
95		29.4	28.9	29.1	29.3	29.1	29	33.4	30.2	29
96		29.3	28.8	29.1	29.2	29.2	29.1	33.5	30.3	29.2
97		29.1	29.1	29.2	29.2	29.2	29.2	33.6	30.4	29.3
98		29.4	29.3	29.5	29.5	29.4	29.3	33.8	30.5	29.6
99		29.4	29.1	28.9	28.7	28.9	29.2	33.9	30.6	29.6
100		29.1	29	29.1	29.1	29.4	29.3	34.2	30.7	29.7
101		29.5	29.1	29.1	29.1	29.1	29.4	34.1	30.8	30
102		29.5	29.3	29.3	29.3	29.2	29.5	34.3	30.9	30.5
103		29.4	29.3	29.3	29.3	29.2	29.6	34.4	31	30.4

104		29.5	29.2	29.2	29.2	29.2	29.5	34.5	31.2	30.1
105		29.3	29.2	29.4	29.4	29.3	29.7	34.6	31.3	30.5
106	3 day HRT	32.9	34.1	33	34.1	32.1	36.9	40.4	36	31.5
107		33.5	34.8	32	35.9	34.8	37.7	41	36.8	31.9
108		34.9	35.8	35	36.7	36.3	38.2	41.6	37.4	32.3
109		36	36.3	34	38.2	37	38.4	41.8	37.7	31.7
110		36.2	38.1	36	37.9	36.9	38.9	42.1	38	32
111		38.1	37.8	37.2	38.1	37.6	39	42.2	38	31.9
112		38.1	38.1	38.1	38.3	38.1	39.1	42.3	38.1	31.93
113		38.6	38.4	38.4	38.4	38.2	39.3	42.5	38.5	32
114		38.2	38.3	38.2	38.2	38.2	39.3	42.6	38.6	32
115		38.1	38.2	38.1	38.2	38.1	39.5	42.7	38.7	32
116		38.4	38.4	38.3	38.1	38.3	39.4	42.8	38.8	31.6
117		38.3	38.2	38.2	38.2	38.2	39.5	42.9	38.7	31.5
118		38.3	38.3	38.3	38.3	38.3	39.6	42.8	38.9	31.6
119		38.1	38.1	38	38.2	37.8	39.7	43	38.8	31.5
120		37.9	38	37.9	38.1	38.1	39.8	43.2	39	31.3
121		38	38.2	38.2	38.2	38.2	40	43.3	39.1	31.5
122		38.2	38.1	38.1	38.1	38.1	40.1	43.4	39.2	31.4
123		38.2	38.1	38.1	38.3	38.3	40.2	43.6	39.3	31.4
124		38.2	38.3	38.2	38.2	38.2	40.2	43.7	39.4	31.5
125		38.1	38.1	38.1	38.1	43.1	40.3	43.8	39.5	31.4
126	2 day HRT	41.1	45.2	42	45.1	45.9	48	50.1	47.2	31.6
127		44.1	43.2	43.5	48.2	43.1	49	51	48.1	31.6
128		46.1	46.1	45.7	49.2	48.5	49.1	51.4	48.5	31
129		50.2	49.8	50.2	50.6	49.3	49.8	52	49.4	32.1
130		50.9	49.7	51.3	52.9	49.9	50.1	52.6	49.3	31.7

131		50.9	50.1	50.9	50.8	50.2	50	52.7	49.6	31
132		51.8	52.1	52.1	52.1	51.1	50.4	53	49.7	31.2
133		53.2	52.2	53.2	52.4	52.9	50.5	53.3	49.8	31.5
134		53.4	52.9	52.9	52.8	52.8	50.6	53.4	49.9	31.2
135		53.1	52.8	53	53.1	52.4	50.5	53.5	50	31.2
136		53.1	51.8	51.8	53.4	52	50.4	53.4	50	30.6
137		52.4	52.4	52.4	53.1	52.4	50.7	53.8	50.2	31
138		52.9	52.7	53	53.1	52.7	50.9	53.4	50.2	31.1
139		53.1	52.9	53.1	52.8	53	50.9	53.9	50.3	31
140		53.4	53.4	53.4	52.9	52.9	51.1	54	50.4	31
141		53.2	53.2	53.2	53.1	53.2	50.9	54.1	50.3	31.1
142		53.1	53	53	52.7	53	51.1	54.2	50.3	30.9
143		53.2	53.1	53.1	52.9	53.1	51.2	54.2	50.4	30.8
144		53.2	53.3	53.2	53.2	53.2	51.2	54.3	50.5	31
145		53.3	53.3	53.1	52.8	53.1	51.3	54.4	50.6	31
146	1 day HRT	59.1	63.3	58.3	64.2	59.1	61	63.9	59.6	31.1
147		64.2	65.2	61.1	66.3	63.2	62.2	65	60.7	31.6
148		66.2	70.1	66.3	66.3	65.8	62.8	65.5	61.7	32.1
149		73.2	71.2	71.2	74.2	69.8	63.3	65.9	62.3	32.4
150		77.4	74.2	77.3	76.1	73.5	63.6	66.2	63.7	30.9
151		75.4	74	74.4	76.2	74.1	63.9	66.4	63.9	32
152		76.1	75.3	78.1	77.1	74.6	64.1	66.6	64.2	31.5
153		76.4	75.2	75.2	75.9	74.5	64.3	66.7	64.3	31
154		75.5	75.3	74.3	75.8	74.2	64.4	66.6	64.4	31
155		75.3	75	75	75.7	74.3	64.5	66.7	64.6	30.9
156		75.1	75.2	76.4	75.8	73.9	64.6	66.8	64.8	32
157		75	75.1	73.1	75.4	74.6	64.7	66.9	65	31.5

158		75	74.9	72.1	74.8	73.4	64.7	66.8	65.1	31.5
159		75.1	74.7	73.1	74.9	74.2	64.8	66.9	65.2	31.6
160		75.2	75.4	75.4	75.1	74.8	64.9	67	65.3	31.1
161		75.6	76.2	76.2	75.4	74.1	64.8	67.1	65.4	31.6
162		75	74	74	75.6	74	65.1	67.2	65.4	32
163		75.4	76.3	76.3	75.6	74.9	65.2	67.3	65.3	32.3
164		75.8	76.3	78	76	74.8	65.2	67.2	65.5	31
165		75.9	76.2	75.9	76.5	74.9	65.3	67.3	65.6	31.4
166	0.8 day HRT	79.1	78.2	78.2	78.2	78	76.8	77.7	76	31.5
167		81.2	78.9	78.9	78.9	78.7	78.1	78.9	77.3	31.4
168		80.4	79	79	80	80.2	78.2	79.5	78	31
169		80.2	78.9	78.9	78.9	79.8	79.1	79	78.3	32
170		80.1	79.8	81.1	81	80.1	79.4	80	78.5	32.1
171		80.2	79.9	79.9	79.8	80	79.5	80.3	78.7	32.1
172		80.3	79.7	80.3	80.1	80.1	79.7	80.4	78.8	32
173		81.1	80.1	81.1	81.1	81.1	79.8	80.3	79	32
174		80.2	79.9	80.3	80.2	80.3	79.9	80.5	79.1	32.3
175		80.1	80.1	80.1	80.1	80.1	79.8	80.4	79.2	31.9
176		80.1	81	80.4	80.3	80	79.9	80.1	79.3	32
177		80.2	80.2	80.2	80.2	80.2	80	80.2	79.4	32.1
178		80.2	79.8	79.8	80.9	80.1	80.1	80.4	80.4	32.9
179		80.1	80.1	80.1	80.1	80.1	80.2	80.4	80.1	32.3
180		80.2	80.2	80.2	80.2	80.2	80.2	80.2	80.2	32.1

APPENDIX V

BOD of UAHRs

		HTR													
		10		5		4		3		2		1		0.8	
Reactor name		BOD, mg/l													
A1	T	600.60	600.60	540.54	600.60	600.60	600.60	660.66	660.66	660.66	660.66	660.66	720.72	780.78	780.78
	B	660.66	660.66	600.60	660.66	660.66	660.66	720.72	720.72	720.72	720.72	720.72	780.78	840.84	840.84
A2	T	600.60	600.60	540.54	540.54	600.60	600.60	600.60	660.66	600.60	600.60	720.72	720.72	780.78	780.78
	B	630.63	630.63	600.60	600.60	660.66	660.66	660.66	720.72	720.72	720.72	780.78	780.78	840.84	840.84
B1	T	660.66	660.66	540.54	540.54	600.60	600.60	600.60	660.66	660.66	660.66	660.66	660.66	780.78	780.78
	B	660.66	660.66	660.66	660.66	660.66	660.66	720.72	720.72	720.72	720.72	780.78	720.72	840.84	840.84
B2	T	600.60	600.60	540.54	540.54	600.60	600.60	600.60	600.60	660.66	660.66	720.72	720.72	780.78	780.78
	B	660.66	660.66	660.66	600.60	660.66	660.66	720.72	660.66	720.72	720.72	780.78	780.78	840.84	840.84
C1	T	660.66	660.66	600.60	600.60	600.60	600.60	660.66	660.66	660.66	660.66	660.66	720.72	780.78	780.78
	B	660.66	660.66	660.66	660.66	660.66	660.66	720.72	720.72	720.72	720.72	720.72	720.72	840.84	840.84
C2	T	660.66	660.66	540.54	600.60	600.60	600.60	600.60	660.66	660.66	660.66	720.72	780.78	780.78	780.78
	B	660.66	660.66	660.66	660.66	660.66	660.66	660.66	720.72	720.72	720.72	780.78	720.72	840.84	840.84
D1	T	600.60	600.60	600.60	540.54	600.60	600.60	660.66	600.60	600.60	600.60	660.66	720.72	780.78	780.78
	B	660.66	660.66	660.66	600.60	660.66	660.66	720.72	660.66	660.66	660.66	720.72	720.72	840.84	840.84
D2	T	600.60	600.60	600.60	540.54	600.60	600.60	600.60	600.60	660.66	660.66	720.72	720.72	780.78	780.78
	B	600.60	600.60	660.66	600.60	660.66	660.66	660.66	720.72	720.72	720.72	780.78	780.78	840.84	840.84

APPENDIX VI

TS of UAHRs

Reactor name		HTR													
		10		5		4		3		2		1		0.8	
		TS, mg/l													
A	T	604.78	629.65	705.40	716.64	726.65	734.66	860.82	842.51	944.88	899.87	955.25	977.24	1092.09	1108.52
	B	633.33	685.01	752.55	784.94	740.14	760.88	928.82	907.62	948.90	912.35	973.13	971.52	1085.11	1104.19
B	T	598.13	733.33	680.31	698.15	707.21	740.31	884.70	825.16	921.17	936.60	970.69	975.10	1074.19	1131.20
	B	669.64	595.23	714.55	702.82	725.36	766.72	923.65	887.37	922.22	940.59	963.75	971.63	1054.04	1125.38
C	T	600.33	726.08	702.60	679.48	720.76	681.97	881.94	899.79	936.72	961.53	965.22	979.06	1128.57	1122.6
	B	638.58	759.61	754.02	754.43	716.28	748.17	921.00	942.24	939.56	962.71	965.37	978.62	1116.67	1126.66
D	T	657.32	647.34	682.17	730.77	718.75	733.71	860.85	864.35	932.51	940.06	938.29	978.87	1159.42	1104.58
	B	619.14	657.14	753.36	785.97	779.49	765.30	899.56	939.32	935.21	948.97	951.17	975.52	1165.50	1143.35