INVESTIGATIONS OF CHARACTERISTICS OF BIOGAS GENERATION USING BIOMASS WASTES

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By

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"INVESTIGATIONS OF CHARACTERISTICS OF BIOGAS GENERATION USING BIOMASS WASTES"** in fulfilment of the requirement for the award of the Degree of **DOCTOR OF PHILOSOPHY**, submitted in **ALTERNATE HYDRO ENERGY CENTRE** of the UNIVERSITY OF ROORKEE, ROORKEE, is an authentic record of my own work carried out during a period from July 1986 to November 1989, under the supervision of Dr.J.S.Saini, Dr.I.M.Mishra and Dr.M.P.Sharma.

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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ABSTRACT

The vast majority of rural people in the developing and under-developed nations, which make together around half of the world's population, are totally dependent on **biomass** for their fuel requirements.

On the basis of extensive literature survey it has been found that most of the biogas plants use cattle dung as feedstock and this technology is well established. The rapid mechanization of farm practices has resulted in the decline of cattle population and hence short fall in cattle dung availability. This has necessitated the need to look for the alternative materials for biogas generation. Agricultural and forest residues have been thought to be the viable alternatives that could replace or supplement the conventional cattle dung for biogas production but very little work on biogas generation from agricultural and forest residues has been reported. Thus in order to promote and enhance the biogas production, a systematic study of biogasification characteristics of these materials is necessary.

Based on the availability in large quantities, eight biomass materials which are often wasted/burnt or composted were selected for experimentation. These biomass materials were Ipomoea fistulosa plant stem (IFPS), Ipomoea fistulosa leaves (IFL), Cauliflower leaves (CFL), Rice straw (RS), Mirabilis leaves (ML), Banana peeling (BP), Wheat straw (WS) and Dhub grass (DG). Cattle dung (CD) was used for comparative studies. The

physico-chemical analyses of these biomass materials show that thses have low lignin to cellulose ratio (in the range of Ø.14 to Ø.45) in comparison to cattle dung (Ø.6Ø). This suggests better digestibility of these materials through anaerobic digestion in comparison to that of cattle dung. The nitrogen content of these materials is also satisfactory (except that of RS and WS), to fulfil the requirements of nutrient availability for microbial growth. In the course of extensive laboratory scale experimentation carried out to investigate the biogasification characteristics, all these materials have been found to be suitable for biogas production with or without supplementation of cattle dung. The biomass materials investigated, with the exception of WS and DG, have been found to yield gas more than two times of that produced from cattle dung. Blending of these biomass materials with cattle dung, shows improvement in the methane content of the gas as well as volume of biogas per unit mass of substrate with the increase in the percentage of these materials in the blend.

During anaerobic digestion, under the controlled mesophilic temperature, there is need to control pH and total volatile fatty àcids (TVFA) concentration for IFPS, IFL and CFL to obtain satisfactory digestion. It has been seen that, in general, a judicious control of pH and TVFA concentration results in the enhancement of biogas production.

Particle size of the feedstock has been seen to have a profound effect on the digestibility of biomass materials, the size reduction upto certain (optimum) level has been found to enhance the biogas generation. The study on the effect of temperature of the slurry on biogas generation (in the range of 20°C to 45°C) has shown that the biogas production has a linear variation with the logarithm of inverse of temperature upto 37.5°C. Beyond 37.5°C the gas production begins to decline and totally stops at 45°C.

Adjustment of carbon to nitrogen ratio to bring it to a value around 25 by the addition of nitrogen compounds enhances the gas production to some extent but the materials resistant to microbial attack are not digested satisfactorily regardless of their carbon to nitrogen ratio. Thus the role of nitrogen present in-situ in the biomass materials has been seen to be significantly different from that of the nitrogen added externally. In this context, the contention of some of the previous investigators regarding optimum carbon to nitrogen ratio of around 25 could not be confirmed because IFPS, RS, DG and CFL with carbon to nitrogen ratio of 155.7, 73.5, 34.0 and 12.1, produced 485, 487, 282 and 520 litres of biogas/kg of total solids, respectively.

Preincubation of agricultural and forest residues with water and alkali treatment has been found to enhance the biogas production upto 16%. The laboratory results have also shown that the stirring of the digester substrate can enhance the gas production upto around 11%.

The methane production during eight weeks of digestion from unincubated biomass materials under controlled conditions were found to vary in a wide range. The relative importance of the biomass materials in terms of methane production in the descending order is found to be:

IFL, CFL, BP, IFPS, RS, ML, WS, DG and CD.

On the basis of this study, it can be stated that a number of crop/plant residues could be successfully used as substitutes or supplement to cattle dung for biogas generation and an appreciable improvement in biogas production could be brought about by judicious blending of biomass materials, preincubation, pretreatment, stirring and control of pH, TVFA, temperature and particle size of the substrate.

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BP	Banana peeling
CD	Cattle dung.
CFL	Cauliflower leaves
DG	Dhub grass
IFL	*Ipomoea fistulosa* leaves
IFPS	*Ipomoea fistulosa* plant stem
ML	*Mirabilis* leaves
RS	Rice straw
WS	Wheat straw
TS	Total solids, gm
TVFA	Total volatile fatty acids, mg/l
VS	Volatile solids. %
pH	Logarithm of receprocal of hydrogen ion concentration
C/N	Carbon to nitrogen
KVIC	Khadi and Village Industries Commission

LIST OF NOTATIONS

C_A	Effluent carbon concentratio,	moles/l
C_{AO}	Influent carbon concentration,	moles/l
C_m	Micro-organism concentration,	mg/l
K	Reaction rate constant,	$(Day)^{-1}$
K_d	Methane decay coefficient,	$(Day)^{-1}$
K_1	Constant,	$(Day)^{-1}$
K_M	Constant,	mg/l
r_A	Reaction rate,	mole carbon/l/day.
T	Retention time,	$(Day)^{-1}$
Q	Total biogas production,	l/kg TS
Q_o	Ultimate value of biogas production	l/kg TS
Q_M	methane production rate,	l/kg/day
Q_{MO}	maximum methane production rate,	l/kg/day

CHAPTER I

INTRODUCTION

1.1 ENERGY CONSUMPTION PATTERN

Energy needs of the industralized countries are mostly met from fossil fuels - coal and petroleum. Natural gas has been used as domestic fuel and to some extent for the production of chemicals and power. In most of the third world countries, energy needs of the domestic sector are almost entirely met from biomass; with over 2 billion population dependent on biomass.

Countrywise, Ethopia and Nepal meet nearly all; Kenya three fourths; India around one half; China one third; Brazil one fourth, while Egypt and Morocco about one fifth of their total energy needs from biomass [49].

Biomass is the material that is directly or indirectly derived from plant life and is renewable in very short time periods. Petroleum, coal, kerosene and tar-sands bitumen, though derived from plants, are not renewable and hence are not grouped as biomass. Animal and human wastes are also included in biomass because these are indirectly derived from plants consumed in the form of food by animals and human beings. Biomass contains carbohydrates, proteins, lipids, nucleic acids, non-protein nitrogeneous compounds, and salts. The nitrogen and sulphur in proteins and other compounds are (in so far as energy production is concerned) only a source of impurities in the fuels which eventually lead to problems of pollution or corrosion in the use of fuels. Carbon, hydrogen and oxygen present in compound forms are useful components for energy production. Only about 1/4 % of the solar energy penetrating and incident on earth's atmosphere is converted to biomass. This small fraction is equivalent to energy produced by 75 billion tonnes of coal/year [131]. About 40% of all potential natural biomass production is either used directly by humanity or diverted into human-dominated ecosystems [144].

The energy consumption in the form of biofuel is about 33% in developing countries. The pattern of consumption of different energy sources in rural India is as follows:

Non-commercial sources	
Fuel wood	68%
Cattle dung	8.3%
Agricultural residues	4%
Commercial energy sources	
Oil	14%
Coal	3%
Others	4%

Thus around 80% of the rural energy needs is met from traditional sources.

1.2 WORLD SCENERIO OF BIOMASS RESERVES

1.2.1 Agricultural Residues

Agricultural residues and manure are often returned to the soil. Apart from providing essential plant nutrients, organic material improves, protects and stabilizes the structure of the soil, facilitates the soil's uptake of water, increases the ability to retain that water, and provides a suitable environment for the sustanance of micro-organisms. When crop residues and cattle dung are burnt instead of being recycled to the soil, crop land can become impoverished, to give reduced yields, degraded soil structure and erosion, and eventually to malnutrition.

The world potential of agricultural residues is shown in the Table-1.1, while the main and by-product ratios of some of the important crops have been listed in Table-1.2. Wheat straw is the most important agricultural residue which contributes 43% of all agricultural residues from crop production. From Table-1.1, it is also clear that Asia produces the highest quantity of residues.

1.2.2 Forest residues

The total global area under forest cover is about 3800 million hactare. According to FAO, in 1978, about 1160 million people in the world were using fuelwood. Natural forest are being destroyed at the rate of about 11 million hactare/year [75]. India is losing forest area at the rate of 1.5 million hactare/year. Shortage of fuel wood in all the developing countries signifies a major crisis. The major consequences of the rapid depletion of this "green cover" are the aggravation of soil

TABLE 1.1 QUANTITY OF AGRICULTURAL RESIDUES (IN '000 TONNES) [49]

Crop	Africa	Asia	Latin America	North America	Europe	USSR	Oceania	World
Wheat	12047	229085	27195	124970	167970	98800	24538	678187
Rice	12015	606476	23586	11929	2743	10	921	657943
Barley	4398	19182	1482	28651	95342	5460	7271	205962
Maize	22201	100157	51742	218437	60264	13000	549	449255
Sugarcane	9592	48835	64746	25250	49	---	4226	131008
Peanut	3832	13840	846	2196	24	2	60	20611
Oilseed	8910	80196	15968	30690	22046	26802	1180	181629

TABLE 1.2 MAIN AND BY-PRODUCT RATIO OF AGRICULTURAL CROPS

Crop	Main product	By-product	Ratio (by weight)
Wheat	Grain	Straw	1:1
Paddy	Grain	Straw	1:1
Barley	Grain	Straw	1:1
Maize	Grain	Straw	1:1
Sugarcane	Sugar	Bagasse	1:2
Potatoes	Tuber	Stalk	1:0.9
Pea	Grain	Straw	1:1.2

erosion, floods, siltation and desertification. The world wood production is presented in Table-1.3.

In most of the under developed and developing countries fuel wood is the single largest source of energy (Table-1.4). Even in oil producing Nigeria, it accounts for over 80% of the total national energy consumption [48, 78]. Per capita fuel wood consumption figures of upto 2.865 tonnes/year have been reported from Nicaragua [68] and about 2.6 tonnes/year in some areas of Tanzania [42]. A survey report of Social Forestry Monitoring Advisory Board, [5] shows per capita fuel wood consumption in the range of 344-676 kg/year for 17 villages of Tamil Nadu in India Samanta [109] reported per capita fuel wood consumption in the range of 509-826 kg/year in five villages of the state of Orissa stae in India.

1.2.3 Domestic Garbage

Another source of the production of energy may be domestic garbage and house-hold refuse. The high moisture content of the garbage makes it unattractive for use as a boiler-fuel. According to an estimate, the total household refuse from 174 class-I cities of India alone is 32,450 tonnes/day which is expected to reach a level of more than 60,000 tonnes/day by the year 1991. In India, seven major metropolitan cities alone contribute around 18,000 tonnes/day of refuse. The combined refuse generation rate of cities in the population range of 5-20

TABLE 1.3 WORLD ANNUAL WOOD PRODUCTION [99]

Forest type	Annual production of wood Area (Million ha.)	Volume of wood (m^3/ha.)	Mass of wood (Tonnes/ha.)
Cool coniferous	800	4.1	3.0
Temperate mixed	800	5.1	4.0
Warm temperature	200	5.5	4.0
Equatorial rain	500	8.3	6.0
Tropical moist	500	6.9	5.0
Deciduous dry	1000	1.4	1.0
	3800 (Total)	4.7 (Average)	3.4 (Average)

TABLE 1.4 CONSUMPTION OF WOOD IN DIFFERENT COUNTRIES
[48, 78]

Country	Fuel wood consumption (% of total energy consumption)
Anglo	74
Benin	86
Brazil	33
Central African Rep.	91
Ethopia	93
Ghana	74
Guinea	74
India	36
Kenya	70
Madagascar	80
Morocco	19
Nepal	98
Nicaragua	25
Nigeria	82
Pakistan	37
Somalia	90
Sri Lanka	55
Sudan	81
Thailand	63
Zimbabwe	28

lakhs amounts to 7370 tonnes/day. Indian refuse has a low percentage of paper, plastics, metals and glass contents in comparison with those of developed nations. The calorific value of Indian refuse is in the range of 3349 to 10048 kJ/kg, which is 2-2.5 times less than those of developed nations. Table-1.5 presents the composition of domestic garbage for different countries.

1.2.4 Aquatic based Residues

Aquatic plant matter such as marine algae, water hyacinth and sea weeds can be utilised for energy production. The total coverage of water hyacinth, in India, is around 200,000 hactare. Out of this area, West Bengal accounts for 12,000 hactare and Bihar for 80,000 hactare. It can be cultivated in drainage water, ponds, lakes, rivers and in sewage effluent ponds. Water hyacinth can be utilised as fertilizer, fodder-food for cattles, raw material for paper making industries, source for fuel gas, proteins and other chemicals.

1.2.5 Animal Wastes

Cattle dung is considered an imporatnt source of fuel and fertilizer. Out of 150 million tonnes of dry cattle dung cakes used in the world every year for burning in domestic sector, 40% is used in India alone [2]. Burning of dung as cakes in open hearth ovens (chulhas) gives a very low energy efficiency of around 10-12% only. It produces large amount of smoke and affects

TABLE 1.5 COMPOSITION OF DOMESTIC GARBAGE [110]

Composition	India						
	Bombay	Delhi*	Madras	Calcutta	USA	UK	Europea countries
Paper %	8.0	8.9	4.8	3.2	42	43	45
Plastic %	0.6	1.5	0.6	0.6	1.5	5.0	6.0
Metals %	1.0	0.4	0.7	1.0	6.0	9.0	9.0
Glass %	0.3	0.4	0.4	0.4	6.0	9.0	9.0
Ash & Fines %	26.5	32.5	24.1	35.2	--	12.0	18
Carbon %	24.5	37.5	21.5	19.2	28.0	--	33.8
Nitrogen%	0.8	0.4	0.7	0.5	0.3	--	1.2
Calorific value (kJ/kg)	8374	6280	6699	6280	11388	14654	15826
Per capita generation (kg/day)	0.52	0.5	0.56	0.51	1.25	0.91	0.82

* As analysed by the author for the year 1989.

adversely the health of housewives in rural and suburban areas. Besides, the diversion of dung to make fuel cakes reduces its consumption as manure (after composting) to enrich the organic and nutrients, levels of the soils. The fuel efficiency can be raised upto 60% by making use of dung in biogas digesters. The highest quantity of dung is produced in Asia followed by Latin America (Table-1.6). The annual production of animal and human wastes in India is shown in Table-1.7. If the total waste is processed through biogas plants, more than 77,400 million m^3 of biogas with around 60% methane content could be produced.

1.3 ENERGY PLANTATION AND ENERGY CONTENT OF BIOMASS

Biomass is evidently an ecologically most acceptable renewable source of energy, providing means to recycle nutrients and carbon-dioxide into the atmosphere with plentiful solar radiation available permanently. Out of total solar energy received by earth ($3x10^{21}$ kJ/year), the plant life utilizes a meagre 0.1%, leading to an annual net production of $2x10^{11}$ tonnes of organic matter possessing an energy content of $3x10^{9}$ kJ. Energy plantation to produce fuel wood is thought to be a viable substitute to fossil fuels. There is about 80 million hactare of wastelands in India which is lying barren owing to a number of reasons. Development of wasteland by multiple cropping energy plantation can yield multiple benefits beside solving energy problems. The choice of plant species and site is very important for sucess of energy plantation programme. Tropical countries

TABLE 1.6 TOTAL AVAILABILITY OF ANIMAL WASTE IN THE WORLD [49]
(DRY WEIGHT BASIS, MILLION TONNES/YEAR)

Animal	Africa	Asia	Latin America	North America	Europe	USSR	Oceania	World
Cattle	189.6	403.8	337.2	201.8	144.9	129.2	33.1	1439.6
Pig	1.1	36.7	7.8	9.2	18.1	7.9	0.5	78.7
Horse	13.2	20.5	7.8	3.5	1.3	0.4	0.01	43.1
Chicken	8.2	33.2	12.3	9.4	14.8	12.8	0.7	87.7
Sheep	18.9	32.3	7.8	2.0	14.6	7.9	21.0	114.0

TABLE 1.7 ANNUAL AVAILABILITY OF ANIMAL AND HUMAN WASTES

Animal/Human	Population million	Wet dung (million tonnes/year)	Urine (million tonnes/year)
Cattle	182.0	752.6	488.9
Buffalo	61.5	260.4	180.0
Sheeps & goats	113.6	12.44	8.29
Pigs	10.2	7.4	7.4
Poultry	147.0	3.65	---
Other live-stocks	3.2	5.9	3.9
Human beings	700	33.9	306.6

have ideal environmental conditions for growing biomass as an alternate energy source in the quickest possible time. The heating value of a particular biomass depends upon its carbon and ash content. The effective heat which can be obtained from any substance, depends upon its mode of burning. Heating value of agricultural and forest residues is presented in Table-1.8.

1.4 BIOMASS ENERGY UTILIZATION

1.4.1 Biomass Conversion Process

Biomass can be utilized in the form of solid, liquid or gases. Conversion technologies for producing fuels from biomass can be divided into three categories, namely, combustion, dry chemical process and aqueous process. In combustion, biomass is burnt directly and heat content can be used as such or indirectly by generating high pressure steam to produce electricity.

Dry chemical processes include pyrolysis, gasification and hydrogasification through which one may get oil, combustible gases, methanol and ammonia. Electricity can also be generated via gas engines.

Aqueous process includes anaerobic digestion, alcoholic fermentation and chemical reduction, and the products are methane, ethanol and solvents, respectively.

Out of all the above processes, anaerobic digestion is found to be the best as it utilizes feedstock of high moisture content and can operate at ambient temperatures.

1.4.2 Anaerobic Digestion

Anaerobic digestion is the decomposition of any organic

TABLE 1.8 HEATING VALUE OF DIFFERENT FUELS

Fuel	Heating value (kJ)
Biogas* (m^3) (60% methane)	19679
Wood* (kg)	19679
Cattle dung* (kg)	8792
Kerosene (litre)	38185
Charcoal* (kg)	29099
Soft coke* (kg)	26378
Coal gas (m^3)	16748
Electricity (kWh)	3600
LPG (butane)*(m^3)	45554
Wheat straw* (kg)	17020
Rice straw* (kg)	14361
Hybrid poplar* wood (kg)	20788
*Ipomoea fistulosa** plant stem (kg)	17501
Ipomoea leaves* (kg)	5485
Mirabilis leaves* (kg)	4982
Cauliflower leaves* (kg)	5254
Banana peelings* (kg)	9253

*Determined by the author in the laboratory.

material by the metabolic action of bacteria in the absence of oxygen. Methane and carbon-dioxide (biogas) are the main products of the decomposition. Oxygen requirement for the formation of carbon-dioxide in biogas, is met from the oxygen available in the organic molecules and water. The process is completed in three stages.

Stage I

First stage consists of solubilization of insoluble material, either into soluble polymeric material - oligomers - or into low molecular weight or monomeric compounds. Solubilization depends upon the type - quality and size of the material.

Stage II

Soluble organic matter, either initially present in the substrate or formed by the solubilization of insoluble organic matter, consists of proteins and amino acids, polysaccharides and sugars, lipids, glycerol and fatty acids and some other compounds present in small quantities. These compounds are utilised as substrate by the non-methanogenic bacteria or acid forming (acidogenic) bacteria, producing volatile fatty acids (mainly acetic acid), carbon-dioxide, hydrogen, alcohol etc.

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

Stage III

The products of stage II are used as substrate by methane forming bacteria or methanogens to produce methane and carbon-dioxide. The hydrogen produced in the second stage is not evolved as a main product but remains in the substrate in dissolved form for the synthesis of methane, as follows:

$$2CH_3COOH \longrightarrow 2CH_4 + 2CO_2$$

$$4H_2 + CO_2 \longrightarrow CH_4 + 2H_2O$$

1.4.3 Different Designs of Biogas Plants

The first Indian biogas plant for producing methane was installed at Dadar, Bombay in 1900. Since then considerable amount of work has been done and several designs developed by different group of research workers are available. Two of the earlier models of plants are Gram Laxmi model (developed by J.J.Patel, 1951) and IARI design (given by C.N.Acharya of IARI). The Planning Research and Action Division (PRAD) started work on biogas in 1957 and established a permanent research station called Gobar Gas Research Station at Ajitmal, in Etawah district of U.P (India) in 1960. Khadi and Village Industries Commission, Bombay produced the most popular design known as KVIC model. Community and Institutional biogas plants installed in India are based on this KVIC design. Another design having fixed dome is called Janata model.

For developing countries like India, biogas can be considered to have considerably higher energy value. One of the major benefits from the use of biogas is the improvement in the quality of life of the rural population in the form of relief from many environmental problems coupled with wastes disposal and energy utilization. There are a number of potential benefits by using agricultural residues through anaerobic digestion, as given below:

1) Production of smokeless, inflammable fuel gas - methane
2) Control of air and water pollution
3) Destruction of pathogens
4) Production of nutrient rich manure
5) Stabilization and reduction of organic solids to more favourable and acceptable forms.

Biogas can be used for cooking, lighting and electricity generation.

1.5 BIOGAS PROGRAMME WORLDOVER

The earlier that fossil fuels, particularly oil, were apparently able to supply energy needs of mankind conveniently and efficiently made the search for other source of energy almost worthless, particularly as the other energy sources were seen to be much more expensive as compared to oil. But the growing awareness in the last two decades that oil supplies will not last for ever, and that even while many new sources of oil remain to be exploited, the oil will not last for long, has led to increased interest in the production of energy from the inexhaustible sources - sun, either directly or indirectly through plant and animal kingdom.

While search for inexhaustible and renewable energy sources as alternatives to the fossil fuels to meet the growing future energy demands is still continuing, production of biogas through anaerobic digestion seems to be one of the best alternatives for meeting rural energy needs.

Rural China utilizes a considerable portion of obtained from a variety of simple but efficient waste digestion units. The advent of biogas technology has resulted in the setting up of 7 million digesters since 1970 in China [70]. More than 1,00,000 technicians were said to have been trained in digester construction by 1975, of both fixed and floating dome types. Several large and medium sized digesters have been installed near distilleries, slaughter houses, city sewage treatment plants and other factories disposing organic wastes. Nightsoil and urine are considered as a valuable commodity in China. China Resources Limited, spent US $ 250,000, in 1976, in importing nightsoil from Hong Kong's Urban Services Department.

Korea has about 29,000 small biogas plants which have similar design as those of Indian KVIC models.

The Indian KVIC drum type biogas plants are not successful in Nepal due to cold climate, especially in winter; and the Chinese fixed dome type biogas plants produce around 75% gas during winter as compared to summer production. Heat exchangers are used in some biogas plants which use the exhaust air from biogas powered engines for heating the digesters, during winter periods.

In central America biogas production feedstocks include poultry litter, water hyacinth, municipal wastes, cattle and piggery wastes, straw and coffee processing residues. One of the largest plants is at Guymon, Oklahoma, where two digesters, each with a capacity of 7575 m^3, have been installed, processing about 500 tonnes of dung/day.

According to a report of the Department of Non-conventional Energy Sources (DNES), New Delhi, [6], upto the end of 1988, more than one million family size (average capacity: $4m^3$/day) and 433 community/institutional biogas plants (average capacity: 100 m^3/day) have already been installed in India. Most of the biogas plants in India are operating on cattle dung using floating dome type KVIC model and fixed dome Chinese or Janata model. Some of the agencies involved in the promotion of biogas programme in India are: DNES, New Delhi; KVIC, Bombay; PRAD, Lucknow; AFFRO, New Delhi; State Energy Development Agencies and Sulabh International, Patna. The Government of India has started National Project for Biogas Development (NPBD) in respect of family size biogas plants. Under this project, financial assistance is provided for the installation of biogas plants.

1.6 SCOPE, AIM AND OBJECTIVES OF PRESENT STUDY

Due to mechanization of farm practices, the tradition of keeping animals excepting those for dairy and meat products is waning and consequently the quantity of available animal wastes is decreasing. In India and also in other countries the conventional biogas plants are operating on cattle dung while the demand for this relatively pollution free gaseous fuel has been steadily increasing.

Keeping above in view the search of alternative raw materials to cattle dung for its replacement and/supplementation is necessary. The alternative materials should be within the reach of people in rural areas (because most of the domestic biogas plants in India are in villages); should be easily and cheaply available in abundance; and could be collected and transported to the plant site and above all must have good digestibility in the digester. In addition to agricultural residues, the other plant matter should be of the type which are available almost universally and uniformally round the year in drought as well as rainfed areas, self propagaated either through seeds or through roots. As could be seen from chapter II, not much work has been reported in literature on the identification and characteristization of different biomass materials - both agricultural plants and forest residues including weeds for the purpose of biogasification. Therefore the present study includes the selection of such materials followed by the investigation of most suitable strategies to be adopted for easy digestion of such materials in a biogas digester, also includes the systematic and extensive investigation of the parameters which affect the rate of biogas generation. The major objectives of the present study include:

1. Identification of suitable biomass materials including agricultural and horticultural crop residues, weed plants and other locally available biomass wastes.

2. Determination of physico-chemical properties of these materials, especially those properties that determine the digestibility of the biomass.

3. Biogasification of these materials in laboratory scale digesters under uncontrolled/controlled conditions to investigate the biogasification characteristics related to quality and quantity of biogas generation.

4. Investigation of the effect of blending of biomass materials with cattle dung and other substrate of relatively different physico-chemical characteristics, on the quality and the rate and amount of gas production.

5. Investigation of the process and operating parameters like preincubation, particle size, C/N ratio, pH, TVFA and temperature on gasification characteristics.

6. Investigation of the kinetics of biogasification to develop suitable expression for the rate of degradation of biomass materials.

CHAPTER II

LITERATURE REVIEW

2.1 GENERAL:

The literature available on various aspects of biogas generation from different raw materials is vast and varied. The process of anaerobic degradation of organic matter including organic wastes resulting in gas formation (methane, carbon dioxide, etc.) has been known for a very long time. This process was used as the principal treatment technique for the waste water and polluted effluents from the food and fruit processing industries, sugar mills, distilleries and municipal sewage. However the energy conciousness generated due to fuel crises has provided impetus to the recovery of energy-rich gas from the anaerobic organic waste treatment processes.

In this chapter, a critical appraisal of the available literature relevant to biogas generation (biomethanation) due to anaerobic biological treatment of biomass has been attempted. Here, the biomass refers to all the organic wastes available in plenty from the agricultural and forestry resource base. Industrial resource base has not been considered here, except where the mechanism of the gas formation or effect of environmental parameters has a direct relevance to the methanation of agricultural/forest resource biomass.

2.2 BIOMASS MATERIALS

The literature on biomass of animal, agricultural and forestry origin used for biomethanation by various research workers can be grouped as follows:

a) Animal Waste/Residues:

1. Cattle dung [15, 36, 44, 52, 69, 76, 81, 94, 95, 104, 124, 126, 129]
2. Piggery waste [63, 98]
3. Rabbit waste [7].
4. Sheep waste [66, 92].
5. Poultry waste [15, 52, 60]
6. Horse stable waste [59].

b) Agricultural Residues:

1. Rice straw [55, 59, 64, 94].
2. Wheat straw [69].
3. Bagasse [77, 91]
4. Rice husk [128]
5. Banana peel and leaves [23, 89]
6. Coffee pulp [19]
7. Barley straw [59]
8. Tomato pomace [59]

9. Rice hulls [59]

10. Castor oil cake [83]

11. Coconut husk [55]

12. Fruit skin [86]

13. Cauliflower leaves [148]

14. Corn stalks [18, 26, 55]

c) Forest Residues:

1. Green leaves [86]

2. Grass [59, 140]

3. Saw dust [125]

4. Water hyacinth [140]

2.3 ENVIRONMENTAL AND OPERATING PARAMETERS:

Environmental and operating parameters have been reported to have profound effects on biomethanation characteristics. Large number of researchers have reported the effect of these parameters on the anaerobic digestion of above mentioned animal, agricultural and forest residues.

2.3.1 Solid Concentration:

Wujicik and Jewell [147] carried out investigations on the effect of high solids concentration in the feed on biogasification. They reported that upto a solid concentration of

30%, gas formation remained at a steady level and beyond total solid concentration of 35%, methane production rate declined sharply. Bousfield et al., [15] found that cattle waste digestion is better at higher solids concentration while the reverse is true for poultry waste. Rastogi et al., [104] showed the effect of dilution of cattle dung slurry on the gas evolution rate as well as on the total volume of biogas. The maximum biogas production rate was observed when the total solid content was 6.4%.

Hills [58] and Hills and Roberts [59] carried out investigations on the digestion of undiluted dairy manure and a combination of dairy manure and barley straw at high solids concentrations. He reported that 40-80% of the volatile solids were reduced during a retention period of 45 days for undiluted dairy manure. The conversion rate was reported to be 0.73 m^3 of gas per kg of volatile solids (VS) consumed for the combination of dairy manures as compared to 0.83-0.93 m^3 per kg of VS consumed for the combination of dairy manure and barley straw. Aubart and Bully [7] carried out experiments on anaerobic digestion of rabbit waste and pig manure mixed with rabbit waste in a 6-litre digester at 37°C with manual loading once a day and stirring for 3 minutes for each hour. The results showed the optimum total solid content as 6% and the optimum methane yield as obout 0.215 m^3 per kg VS.

Biogas production from cattle waste using daily fed digesters was carried out by Singh et al., [128] at solid concentrations in the range of 2.25 to 18% (W/V). At a loading rate of 3.8 g/litre/day and a constant retention time of 30 days, they reported that optimum solid concentration could be obtained at a solid concentration of 13.5%. Pathak et al., [94] carried out experiments in batch digesters to study the effect of solid concentration on gas production using 3 digesters with 7.7%, 10.2% and 14.8% solid concentration, with cattle dung as the basic feed. They carried out another experiment with a combination of cattle dung and rice straw, which had been soaked in water for 5 days, having 15.2% solid concentration. The cattle dung digesters were run for 65 days while the rice straw mixed digesters were operated for 80 days. Their results showed that the anaerobic digestion is not adversely affected if the total solid concentration in the substrate is increased to above 15%. The gas production rate was comparable with that produced at lower solid concentrations. Summers [138] reported that with cattle waste feed having 5-7.5% solid concentrations, 32% degradation could be achieved.

2.3.2 Loading Rate:

Loading rate is found to depend upon the substrate composition, temperature, the digester volume and the type of digester design.

Fischer et al., [41] suggested an optimum loading rate of 4.0 kg/VS/m^3/day with retention time of 15 days. Taiganides [139] has reported that controlled digestion could be obtained by using loading rates between 0.5 and 2.0 kg of VS/m^3/day in normal digesters. In high rate digesters, the loading rate of 2 to 6 kg

VS/m³/day could be used with agitation for keeping the solids under suspension. Hills [60] recommended an organic loading rate of 4.91 kg VS/m^3/day with a retention time of 11.5 days.

Experiments with one and two phase anaerobic systems using coffee pulp juice were performed by Calzada et al., [19]. In a single phase methanogenic reactor the loading rate varied between 0.5 and 3 kg VS/m^3/day with a retention time of 10 days. When separate acidogenic and methanogenic digesters were used, the first digester was operated at a retention time of 0.5 days with a load of 56 kg VS/m^3/day, while the retention time for the second digester ranged between 5 and 10 days with loading rate of 2.4 to 0.6 kg VS/m^3/day. Results show that two phase anaerobic system is better for treating coffee pulp juice as compared to a single phase unit. Singh et al., [128] carried out the digestion of cattle waste in daily fed digesters at a loading rate of 3.8 kg solids/m^3/day, at a constant retention time of 30 days. Hills [60] stated that for economic reasons, compact digestion system should be designed. Thus, heavy organic loading and relatively short retention time is to be preferred. However, this would tend to make the digestion system unstable. He has shown that when the plant is operating in this region, the method of loading plays a major role in maximising energy output. Even though the digestion system is designed for steady-state loading; while the actual operating conditions are dynamic, the loading of the system actually varies and is never at steady-state. Results indicate that the gross methane production is approximately 33% higher and volatile solids reduction is increased by 28% for the fermentation plant operating with varying retention times when compared to operating the same plant with varying loading concentrations.

2.3.3 <u>Retention Time:</u>

Retention time is dependent upon solid concentration of influent, loading rate and the temperature.

Bousfield et al., [15] carried out the digestion of cattle and poultry waste in a pilot plant and reported an optimum value of retention time of 2Ø days. Singh et al., [124] while working with cattle waste in a batch scale digester, reported that a retention time of 2Ø days is optimum for highest gas production per unit of digester volume. They further reported that rates of reduction of cellulose, total solids and volatile solids were higher in the initial period of digestion but slowed down with increasing period of digestion. Odeyemi and Adewumi [92] studied the batch digestion of cow dung, sheep manure, goat excreta, swine manure and poultry droppings. At peak production which occured on different days during the 4Ø days incubation period, the gas production was found to be Ø.Ø397, Ø.Ø935, Ø.2Ø, Ø.3Ø and Ø.31 m^3/kg/day respectively for the above materials.

Aubart and Bully [7] investegated the digestion of rabbit waste and pig manure at 37°C, with a retention time of 7.5 days. The optimum methane production was obatained as Ø.215 m^3/kg VS with retention time varying between 4 and 2Ø days. The methane production decreased from 1.Ø8 to Ø.39 m^3 of methane per m^3 of digester per day. Erdman [36] carried out studies on fermentation of low solids dairy waste in horizontal, unagitated and isothermally maintained tubular fermenters at different temperatures and at retention times of 1, 2, 4, 6, 8 and 10 days, respectively. Methane production per unit fermenter volume was highest with a retention time of 1 day; however, maximum methane production per unit of substrate feed occured at longer retention time. Singh et al., [129] carried out studies with 2.5 m^3 biogas plant on the anaerobic digestion of cattle waste. The results showed that a retention time of less than half of the usually recommended 50 days is optimum for biogas production. More than 75% of the total gas available with very large retention times, is recovered in 20-25 days. They further reported that decreasing the retention time will reduce the size and thereby the cost of construction of biogas plants. Summers [138] reported the production of 0.17 m^3 of biogas/kg of total solids with 58% methane content at a retention time of 20 days at 37°C from cattle waste.

2.3.4 Total Volatile Fatty Acids:

Total volatile fatty acids (TVFA) or volatile fatty acids (VFA) are formed by the non-methanogenic or acid forming bacteria, by the decomposition of organic matter.

McCarty and McKinney [84] found that an increase in the VFA concentration is one of the first signs of instability of the digester and signals the need for control measures long before a drop in pH and consequent digester failure results. They found that sodium salts are relatively toxic to methane bacteria when added on a slug basis and therefore sodium hydroxide is a poor material to be used for neutralization of excess volatile acids. Deshpande et al., [31] carried out the digestion of cattle dung mixed with water hyacinth and found that besides acetic acid, some other volatile fatty acids such as propyonic, butyric, iso-butyric, valeric, iso-valeric acids are also formed. They also detected ethyl alcohol on the seventh day of digestion.

Singh et al., [125] investegated the digestion of cattle waste (CW), and combination of cattle waste and poultry waste (CW + PW) and mixed cattle waste, poultry waste and saw dust (CW + PW + SD). Supplementation of CW with 10% PW resulted in an increase in VFA concentration and consequently higher gas production. The TVFA concentration in the slurry increased from 1725 to 6639 mg/l at the end of third week; from 1740 to 7890 mg/l at the end of second week and from 1665 to 8325 mg/l at the end of fourth week in case of CW, CW and PW and the mixture of CW, PW and SD, respectively. The analysis of VFA showed that the level of acetic acid decreases after third week for CW and the mixture of CW and PW and after fourth week for the mixture of CW, PW and SD. This shows that acids are usedup for the gas production. The propionic acid content increased gradually during fermentation in CW; and CW and PW mixture upto seventh week and in mixture of CW, PW and SD upto eighth week. The iso-butyric , iso-valeric and valeric acids, when present were found in low concentrations. Addition of PW to CW increased the rate of production of butyric acid as compared to that in CW. Patni and Jui [95] studied the change in VFA content of dairy cattle liquid manure slurry. They stored the slurry in 3m deep, covered, concrete tanks from January to October and similarly from June to November. It was found that temperature affects the VFA concentrations significantly. In all the tanks, concentrations of all VFA except iso-valeric acid, were significantly lower in case of the tanks at Ø.3m depth than those at greater depths, after 5Ø days of storage. However, the concentration of VFA increased in all the tanks. They further reported that the mean concentrations of VFA in all the tanks were substantially in excess of those normally associated with steadily operating digesters. Acetic acid was the dominant VFA in every tank, and changes in its concentration set the trend for changes in the concentration of TVFA in the slurry in that tank. On a molar basis, concentrations decreased in the order of acetic, propionic, butyric, iso-valeric, iso-butyric and valeric acid in all the tanks, the last three acids accounted for only 6-8% of the TVFA.

Erdman [36] detected acetic, propionic, iso-butyric, butyric, iso-valeric and valeric acids at average concentrations of 4.7, 1.4, Ø.5, 1.6, Ø.1 and Ø.2 micro-mole/ml, respectively. He found that the acetic acid was predominant and the lowest concentration of acetic acid was found in fermenters maintained at 3Ø and 4Ø°C as compared to those at higher temperatures. The effect of propionic acid concentration on anaerobic digestion was studied with emphasis on the acidogenic step by Gourdon and Vermande [47]. No inhibitory effect on the methanogenic step was noticed upto concentrations of 6ØØØ mg/l when pH was more or equal to 7.4. Propionic acid when present at 4ØØØ mg/l or more, reduced the rate of the acidogenic step, but the effect was marginal. They concluded that propionic acid accumulation in anaerobic digesters must be considered mainly as a warning and not as a sign for alarm.

2.3.5 Carbon/Nitrogen (C/N) Ratio

During anaerobic digestion Carbon, Hydrogen, Nitrogen and Phosphorus are the major elements required for cell growth. Two of the above namely carbon and nitrogen, are the most important

According to Fraser [43] animal wastes with their relatively low C/N ratio can be improved for digestion by the addition of cellulosic wastes such as straws and other crop residues. Smil [130] reported that in China, generally, the following admixtures of cattle dung, crop residues and night soil are used as biogas digesters feedstocks, to achieve optimum C/N ratio:

i) 10% night soil + 30% cattle dung + 10% crop stalks and grasses + 50% water.

ii) 20% night soil + 30% hog manure + 50% water.

iii) 10% night soil + 10% cattle dung + 30% marsh grass + 50% water.

Hills [57] determined the effect of C/N ratio on anaerobic digestion of dairy manure. Screened dairy cow manure which had a optimun C/N ratio of 8.0 was combined with glucose and, later with cellulose, to obtain C/N ratio varying between 8.0 and 51.7. Six 4 litre digesters were operated for 11 months. The loading rate was varied in the range of 1.0 to 2.0 kg

$VS/m^3/day$. The highest methane production per unit loading rate occured when the C/N ratio of the feed was maintained at 25.

Scharer and Moo-Young [111] stated that carbon and ammonical nitrogen ratio of 25:1 to 35:1 are generally considered optimal. Significantly, low C/N ratio, as obtained in poultry manure, may cause ammonia toxicity, particularly, if the slurry become alkaline. Hills and Roberts [59] carried out the digestion of dairy manure and crop residues to find the optimum non lignin C/N ratio. Dairy cow manure was mixed with barley straw or rice hulls or rice straw and the non lignin C/N ratio of the feed was maintained between 12.3 and 40. Results show that methane production from fresh dairy manure can be enhanced by the addition of chopped field crop residues. The optimum performance has been found to occurs when the non-lignin C/N ratio of these feed mixtures is between 25 and 32. Tumlos [140] used water hyacinth, leaves, sorghum, grass, night soil and rice straw for anaerobic digestion and concluded that while optimizing the biogas production; it is important to consider not only C/N ratio of the wastes but also the relative ease of biodegradation of the waste material involved. The mixture of water hyacinth, sorghum and night soil produced the maximum gas.

2.3.6 Nutrients Concentrations:

The net growth of microbial cells is directly related to the nutrients concentration. To achieve satisfactory biological treatment of waste, it must contain sufficient amounts of nutrients such as carbon, nitrogen, phosphorus, sulphur, alkali metal, etc. Animal manure, generally, contains sufficient amount of nutrients, however, this may not be the case for many other biomass and waste materials.

Speece and McCarty [133] observed exceptionally high rates of acetate utilization as a result of the addition of combination of iron, cobalt, thiamine and organic precursors of vitamin B_{12} to digesters purged of the original seed material. Khan and Taoitier [72] showed that a sulphur source of about Ø.85 mM concentration in the form of sulphate, thio-sulphate, sulphite, sulphide, cysteine or methionine is essential for the degradation of cellulose to methane since sulphur forms an integral part of the ferrodoxin system and coenzyme M. Mineral components of yeast extract have been reported to be highly stimulatory by Berg and Lenty [13]; Baresi et al., [11]; and Mah et al., [85]. They suggested that methanogenesis in the environment may be limited by the non-availability of sufficient amounts of essential inorganic micro-nutrients.

According to Azevedo and Stout [8] only 25% of the nitrogen consumed is retained by the dairy animals. The remainder is excreted, approximately 52% in the urine and 48% in the feaces. The excreted nitrogen is subject to losses, either through volatilisation as ammonia, denitrification, or mechanical separation. Effect of cobalt on biogas production from cattle dung was studied by Wate et al., [145]. Various concentrations of cobalt ranging from 5 to 25 mg/l of reaction mixture were studied for maximum biogas production and acetate utilization. Cobalt addition at 15 mg/l resulted in a significant increase in acetate utilization and consequently the biogas production from cattle dung. Cattle dung was also found to contain 10.54±1.6 mg of cobalt/kg dry weight. They further reported that a cobalt concentration of about 310 mg/kg of dry dung appears to be necessary to obtain 20% increase in biogas production per unit weight of VS added during anaerobic digestion. Addition of 200 ml of urine to 0.5 kg of dung was found to double the gas production. The effect of trace nutrients on the anaerobic process of dairy waste was investigated by Kelly and Switzenbaum, [71]. Trace nutrients were found to significantly affect the reactor performance. Whey powder supplemented with nitrogen and phosphorous was fuond to be limited by the presence of such micro-nutrients as either nickel, iron or cobalt or some combination of these elements. On the addition of these elements to the reactor feed, COD removal efficiencies increased and volatile organic acids decreased.

The effect of phosphoric acid addition on nitrogen losses from fresh manure and effluent from a dairy cattle manure were evaluated over a 60 days period by Lanyon et al., [76]. Results show that the presence of phosphoric acid at 2.24 g/kg of slurry, which lowered the slurry pH $\leq$ 6.0 throughout the storage period, was most effective in reducing nutrient transformations and losses and exhibited potential for conserving biologically available nitrogen in these animal wastes. Geeta [44] observed an increase in biogas production from cattle manure by 15-30% by the addition of vermiculite, charcoal and lignite to the digester. Pebbles, glass marbles and plastic mesh suspended in the digester having manure slurry increased the gas production by 10-12%. The effect of incorporation of castor oil cake and other wastes to cattle dung was studied by Lingaiah and Rajeshkaran [83]. A maximum output of 18.3 litres over a period of 6 weeks with maximum reduction of 75.4% of TS, 71.8% of VS and 2620 mg/l of TVFA was observed.

2.3.7 Temperature:

The effect of temperature on waste water sludge digestion in the range of 4° to 60°C, indicated by the vitality of bacteria involved in the process has been studied by many authors.

Fair and Moore [37-39] reported that raising the temperature from 25° to 30°C results in higher sludge gas production and this tendency continues upto thermophilic digestion, whereas at 60°C the production was 25% greater than at 25°C. This is contrary to the findings of Viel (1941) and Hatfield [53], who reported no effect at temperatures above 25°C. In the same way Heukelekian [56] reported almost constant gas production at 28°, 33°, 37° and 42°C. Comparatively low amount of sludge gas reported by Rudolfs [107], could be explained on the basis of a short sludge fermentation period and the absence of inoculation in his experiments. Table-2.1 compares the results of these investigators.

TABLE 2.1 Literature reference on effect of temperature on sludge gas production (SGP)

Fair and Moore		Hatfield		Rudolfs		Viel	
Temp. °C	SGP mg/l	Temp. °C	SGP mg/l	Temp. °C	SGP mg/l	Temp. °C	SGP mg/l
10	450	11.5	400	10.0	130	16.1	417
15	530	18.7	500	18.0	250	25.0	512
20	610	25.3	552	24.0	320	38.0	508
25	710	31.4	572	29.5	400	57.1	534
30	710	35.2	566	35.0	400	---	---

Speece and Kem [134] have reported that methane production rate was directly proportional to the temperature above 20°C whereas below a temperature of 20°C, gas production was almost nil. They also reported that the pre-mixing of digested sludge with raw sludge before pumping the mixture into the digester would stop methane production if the temperature of the mixture was lowered to less than 20°C. However, gas production would attain normal rate as soon as the temperature inside the digester was restored to normal. The effect of temperature on buffalo dung on biogas kinetics has also been investigated by Rastogi et al. [104]. They observed an increase in gas production rate with the temperature.

Hashimoto et al., [52] has conducted experiments to study the effect of temperature on the ultimate methane yield from beef cattle manure in the range of 30-65°C. The beef cattle were fed with a ration containing varying amounts of corn silage. They found that the ultimate amount of methane yield per unit mass of VS consumed remains constant at all temperatures. The steady-state and batch values for the ultimate methane yield per kg of VS fed were found to be around 0.32 m^3 methane/kg VS. and the average value of methane production per kg VS consumed was 0.445 m^3. It was also found that temperature affects the rate at which methane is produced with higher production rate at higher temperatures. Kelly and Switzenbaum [71] carried out experiment in an anaerobic film expanded bed reactor to investigate the effect of temperature on biomethanation of whey in the mesophilic temperature range. They reported that the temperature had relatively little impact on reactor performance as compared to the effect of trace nutrients. They also concluded that anaerobic film expanded bed reacter is found to be less temperature sensitive as compared to conventional slurry reactor and activated sludge reactors.

Erdman [36] studied methane fermentation of low solids dairy waste in horizontal, unagitated, isothermally maintained tubular fermenters. Results show that 0.22, 0.31 and 0.32 m^3 of methane/m^3 of fermentor volume/day is produced at 20°, 30° and 40°C, respectively.

2.3.8 <u>Toxic Substances:</u>

Major toxic substances, which affect the gas production are ammonia, ammonium ion, soluble sulphides, and metallic salts. Sonoda and Seiko [132] showed that the presence of hexyl, heptyl, octyl, allyl, crotonyl and propargyl alcohol in concentrations of 1000, 500, 200, 100, 500, and 50 mg/l, respectively, inihibited thermophilic digestion of acids produced from glucose substrate. Ingols [65] reported toxic synergistic effect of high concentrations of NaCl and Na_2SO_4 on sludge digestion. Stickley [137] showed that in continuous digestion, shock doses of 1 mg/l of chloroform caused decrease in gas yield, whereas a continuous dose of 10-11 mg/l produced a noticeable effect. He further reported that a continuous dose of 16 mg/l caused complete inhibition. Lewin [80] gave the following toxicant concentrations for full scale digesters.

Chloroform	1.7 mg/kg dry solids
Tetrachloro ethylene	3.6 mg/kg dry solids
Trichloro ethylene	4.0 mg/kg dry solids

Melbinger and Donnellon [88] showed that ammonia nitrogen became inhibitory when its rate of formation above a threshold limit of 1700 to 1800 mg/l increased more rapidly than the acclimazation of methane formers. Normal it was possible to have the rate of ammonia nitrogen upto 2700 mg/l without inhibitory affect provided volatile fatty acids and alkalinity is controlled. Rastogi et al., [104] reported that α - naphthylamine does not affect the gas evolution in anaerobic digestion of buffalo dung. However, diphenylamine and hydroquinone accelerate gas production, whereas EDTA inhibits it.

The effect of disinfectants and antibiotics on the anaerobic digestion of piggery waste were investigated by Poels et al., [98]. The disinfectants - Tego 51, dettol, NaOCl and creolin, and the antibiotics - chlorotetracyclin, tylosin, erythromycin, chloramphenical, bacitracin and virginiamycin were tested at different concentrations. At concentrations normally used in practice, no inhibitory effect on methanation process was detected. However, higher concentrations of the antimicrobial agents namely, dettol, creolin, bacitracin and virginiamycin, markedly inhibited biogas production. They further recommended that in order to minimize possible digester failure, normal recommended doses and low toxicity antimicrobial agents should be used. Hashimoto et al., [52] found that chlorotetracycline and monensin did affect the ultimate methane yield, however, monensin delayed the start of active fermentation in batch digesters.

2.3.9 pH Value:

Capri and Marais [2Ø] reported that in the anaerobic process, pH in the range of 6.Ø to 7.5 is controlled by the interaction of the carbonic system and a net strong base. The acid-base state of a digester can be monitored by measuring pH and the carbon dioxide partial pressure. They further stated that shock doses of strong base and carbonates causes undersaturated carbon dioxide conditions temporarily and excessively high pH. The bicarbonate dosing leaves the carbon dioxide solubility equilibrium unchanged. Scharer and Moo-Young [111] reported that in anaerobic digestion, the methanogenic, activity in mixed culture is observed only in the relatively narrow pH range of 6.2 to 8.Ø. At 4ØºC, acetate conversion to methane is optimum between pH 6.5 and 7.1. Outside this range , the reaction rate dropped rapidly at pH 6.2 and 7.3 and the reaction rates were just half of the maximum.

Jain et al., [66] reported the change in pH of the anaerobic fermentation of cattle and sheep wastes. The pH of both the substrates was found to drop in the first week of digestion but began to increase thereafter and remained at 6.65 to 7.75 during the last four weeks of fermentation over a digestion period of eight weeks for cattle and sheep wastes, respectively. Singh et al., [125] reported that in the anaerobic digestion of biomass, the pH was found to decrease to the acidic level during the first few weeks of digestion, after which it showed an upward trend. Anaerobic digestion of 1 to 5 days pre-digested cattle waste was carried out in batch and semi-continuous digesters by Singh et al., [126] and found that during pre-digestion, the pH fall down to 6.5 from 7.25 only after one day and it was 6.25 after fourth day.

Ferguson et al., [40] reported that buffering with the carbonic acid/bicarbonate system is desirable and unavoidable since these have high buffer intensity at pH values from 5.5 to 7.0, since massive quantities of carbon-dioxide are produced in anaerobic degradation. The required amounts of various sodium bases depend strongly on the pH needed for biological treatment, with hydroxide considerably more effective than carbonate or bicarbonate as the pH increases above 6. However, When the chemical cost is considered, sodium carbonate is the prefered neutralization chemical. They further reported that dissolved SO_2

strongly affects the amount of base required to attain neutral pH values.

2.3.10 Effect of Stirring:

Both manual and auto type of stirrers are provided in the biogas plants. Hawkers and Young [54] have reported that stirring had little effect on gas production. Aubart and Bully [7] while carrying out the digestion of rabbit and piggery wastes, stirred the digester content for 2 minute every hour by two propellers on a shaft turning at 50 revolutions per minute. For a digester operating on high solid concentrations, stirring is required to keep the solids under suspension but for such digesters the operation cost of agitators was found to be very high.

2.4 DIFFERENT TYPES OF PRE-TREATMENT

2.4.1 Pre-treatment with Alkali:

In order to increase the biodegradability of corn stover, wheat straw and alfalfa hay, thermochemical pretreatment was resorted to by Pfeffer [96]. For untreated corn stover, the biodegradability of VS was 36% in the thermophilic temperature range but after thermochemical pre-treatment, the biodegradability increased upto 71%. For alfalfa hay the biodegradability of VS was 74% at a temperature of 60ºC. Playne [97] carried out pre-treatment of bagasse with alkali and steam injection in order to develop economical and effective methods of increasing the digestibility of bagasse for use as a substrate for the production of biogas. Caustic soda, aqueous ammoniacal solution, solution of ammonia with caustic soda or mixture of lime and sodium carbonate were examined for use at ambient temperatures and in combination with steam injection at 200°C, 6.9mPa pressure and 5 minute cooking time. Digestibilities of upto 733 gm of organic matter (OM)/kg of bagasse dry matter, were obtained for bagasse treated with NaOH and $Ca(OH)_2$+Na_2CO_3 mixture. Bagasse treated with aqueous ammonia gave less than 430 gm of OM while upto 724 gm of OM was obtained from bagasse treated with $Ca(OH)_2$. This digestibility was obtained by using very high concentrations of lime (180-300 g/kg of bagasse). Steam explosion increased the digestibility of bagasse upto 740 g of OM in the presence of alkali. The digestibility of bagasse without pretreatment was found to be 190 g of OM/kg of bagasse dry matter.

Dhavises et al., [33] fermented rice straw pretreated with 0.3N solution of caustic soda and obtained 560 litres of biogas (67% methane,v/v) per kg of substrate after 5 days of incubation at 55°C as compared to 450 litre (60% methane, v/v) per kg of substrate after 7 days of incubation at 37°C. It has also been reported that the pretreatment of biomass feedstock can double the biogas output and it may prove to be very economical provided the pretreatment requires smaller amounts of chemicals or low cost chemicals are used.

Dhar and Tondon [32] reported that the utilisation of pretreated plant residues along with cattle dung offers wide scope for the identification of an appropriate biomass feed material for biogas plants in those areas where cattle dung supply is found to be limited. The addition of pretreated wheat straw, Lantana residue, apple and peach leaf litter (with 1% NaOH solution for 7 days) to cattle dung was found to improve bio-degradation of the substrate during anaerobic fermentation at ambient temperatures (28-31ºC). Almost two fold increase in biogas and methane production was noticed by them after addition of plant residues. The test proved that the digestion efficiency with pretreated plant residues in terms of biogas released per kg of dry matter increased by 31-42% over that found with cattle dung alone.

2.4.2 Pre-treatment with Water:

Tumlos [140] showed that for an efficient digestion of cellulosic plant wastes, pretreatment of the biomass such as size reduction and initial fermentation must be carried out. The plant wastes that were pretreated by fermentation for 20 days produced about 43% more gas as compared to those pretreated for 10 days. Singh et al., [126] predigested cattle dung from 1 to 5 days and used it for anaerobic digestion. The results showed an increase of 17-19% in biogas production and the methane content was found to be 75-86% instead of 68-75%.

Hee [55] investigated the biogas generation characteristics of cattle, hog, caraboo and chicken manure and that of rice straw, rice hull, corn stalk, azola, ipil-ipil and coconut husk at ambient temperature conditions. Results show that biogas yield of crop residues increased significantly by combining them with animal manure. Pretreatment of coconut husk by aerobic fermentation for at least a week before loading to anaerobic digester increased its biogas yield, while the same pretreatment of rice straw resulted in reduction of biogas yield.

2.5 EFFECT OF ADDITION OF SUPPLEMENTS

It has been fuund by a number of researchers [54, 69, 74, 101, 102, 105] that blending of two or more biomass materials or the addition of some special type of materials to the substrate-enhanced the rate and quantity of biogas production.

Hawkes and Young [54] reported that an immediate rise in gas production rate was obtained on addition of glucose corresponding to the conversion of 60% of the added glucose to carbon-dioxide and methane within two hours. Rahman et al., [101] carried out experiments by blending water hyacinth, rice straw and saw dust with cow dung for biogas production and reported that water hyacinth produces almost 2.5 times more biogas than saw dust, and rice straw produces more than the double the amount of gas, when blended with cow dung. Rajeshkaran [102] supplemented silk worm larval with cow dung and biodigested slurry. His results showed that the gas production was enhanced with improved biological activity.

Kamra et al., [69] digested quail droppings with wheat straw, wheat bran and sugarcane molasses in different combinations at solid concentrations between 34 and 44%. Kumar et al., [74] used commercial charcoal with cow dung to enhance biogas production. The addition of 5% charcoal to cow dung on a dry weight basis resulted in augmentation of gas production by 17 and 34% in batch and semi-continuous fermenters, respectively. The decomposition of VS increased from 30 to 40% on addition of charcoal to semi-continuous digester. It was also found that locally produced wood charcoal gave better performance than the commercial charcoal in batch digestion and that other forms of carbom were not efficient. Reddy and Rao [105] found that the addition of water lettuce in equal proportion to cattle dung enhanced the gas production.

2.6 EFFECT OF PARTICLE SIZE

The effect of the size of biomass feed to the digester on the rate of production and total amount of gas produced in a definite time has also been investigated by very few workers.

Liao et al., [81] screened out the coarse solids from the dairy cattle manure and used only liquid and fine fractions for digestion. It was found that this screening had a significant effect on biogas production. It was also found that total methane production and methane content of biogas from screened manure were consistently higher than that obtained from unscreened manure. Erdman [36] separated, through an inclined gravity separating screen, the agitated dilute mixture of cattle waste in water. The liquid and fine fraction which passed through the screen sieve of size 1x6 mm were transfered, stored and used for feeding the digesters. The methane production was found to be o.49 m^3/kg VS fed at 30°C at a retention time of 10 days.

Summers [138] passed cattle waste through 3 mm screen and used this fraction for biogas production. He reported a gas production of 280 l/kg of TS with retention time of 11 days, where 35% reduction of total solids occured out of 3.7% total solids in the feed (w/v).

Gollakota and Meher [45] studied the effect of particle size (in the range of less than 0.5-2.0 mm were used) on biogas generation from castor oil cake in a 5 litre capacity single stage fermentor at 30-37°C. They reported that both the rate and yield of biogas production was higher with feed particle size of 2.0-1.4 mm and 0.5 mm, and less with the particles of 1.4-1.0 mm to 1.0-0.5 mm.

2.7 KINETICS OF BIOGASIFICATION

Clausen et al., [28] studied the feasibility of producing methane by anaerobic digestion of crop materials such as grass and corn stalks. Results show that about 0.37 m^3 of methane is produced/kg of crop material digested. Studies on the design and economics of a large methane plant show that the reactor accounted for the largest cost item and hence efforts should be concentrated on investigating reaction kinetics for high performing design. The microbial rection kinetics of this process can be approximated by a first order reaction, based on carbon concentration. A specific rate constant of 0.086/day has been determined for various agricultural residues.

Doyle et al., [35] stated that the improvements in the kinetics are possible by using enhanced cultures and by increasing the micro-organism concentration through effluent recycling. Significant reductions in the reactor volume can be achieved by feeding concentrated feed material upto 3Ø%. The cell recycle studies have projected an increase in the rate constant to Ø.72/day but to obtain this increase, cell separation equipment must be added to allow the return of organism to the reactor. The culture advancement studies have projected a rate constant increase by Ø.Ø53/day, with essentially no additional capital or operating expences. Once steady-state has been obtained and the culture has been established, no further culture addition are necessary.

The effect of temperature, dilution and incubation period of the cattle dung slurry on biogas kinetics has been investigated by Rastogi et al., [1Ø4]. The experimental data gave the following best fit equation:

$$1/v = m/t + c$$

where v is the volume of the gas evolved in time t, and m and c are constants. The values of m and c were found to decrease with increase in temperature and incubation period. When the ratio of water and cattle dung is 1:2, the volume of gas evolved during a particular interval is maximum and values of m and c at this ratio are minimum.

Singh et al., [127] showed that during the process of anaerobic digestion of substrate, degradation rate falls much faster than the substrate concentration itself which reflects a dynamic nature of substrate quality in the course of anaerobic process. This necessitates the incorporation of a correction factor in the kinetics of the complex substrate degradation. Simple Monod kinetics are not applicable to solid substrate without complex modifications. They further showed that gas production rates are not directly proportional to the substrate utilisation rates as is generally assumed. A minimum amount of substrate degradation is necessary before gas evolution can start. Gas evolved is not constant and tends towards a maximum value with increasing retention time due to higher gas production value for the digestion resistant substrate.

The effect of temperature (35 and 55°C) and influent volatile solids (VS) concentration (S_o= 33.5, 43.6, 54.3, 61.8, and 77.1 kg VS/ m^3) on the kinetic parameter, k of swine manure were evaluated using 3-dm^3 laboratory scale fermenters by Hashimoto [52]. The ultimate methane yield (B_o) of the swine manure was 0.48±0.02 m^3 methane/kg VS fed as determined by 109 day batch fermenters. The value of kinetic parameter k increased exponentially with the increase of VS concentration S_o and was described by:

$$k = 0.6 + 0.0206 \exp.(0.051 \times S_o)$$

Temperature had no significant effect on K for S_o values between 33.5 and 61.8 kg VS/m^3. Chen and Hashimoto [21] showed that the rate of methane production can be expressed as a function of the ultimate methane yield (B_o), influent substrate concentration (S_o), retention time (θ) and the kinetic parameter (K) by the following equation:

$$\gamma_v = (B_o S_o/\theta)\ [(1-K)/(\theta \mu_m - 1+K)]$$

Where γ_v = volumetric methane production rate in litre methane/litre fermentor/day.

B_o = ultimate methane yield in litre methane/g VS fed as $\theta \longrightarrow \infty$

S_o = influent VS concentration in g/litre

θ = hydraulic retention time/day

μm = maximum specific growth rate/day

K = kinetic parameter

They reported that μm increases with temperature and that K is a kinetic parameter that increases as the fermentation becomes inhibited.

2.8 OVERVIEW

From the critical review of the literature as discussed above, it is clearly discerned that most of the research work is concentrated on the use of cattle wastes as the main raw material for biogas production. Work on agricultural residues, horticultural wastes and weed plants are meagre and scarce. Most of the cellulosic biomass residues found in abundance in India, have not been investigated. In view of the large availability of agricultural residues (Tables 1.1 and 1.2) and potentially large untapped resources base of weed plants and urgent need of supplementing the feedstock of cattle dung fed biogas plants, it seems essential to investigate systematically and thoroughly the characteristics of biogas generation from different materials of agricultural/horticultural/weed plant origin. The scope, aims and objectives of the present study have been defined taking the above into consideration and have been elaborated in Chapter-I.

CHAPTER III

EXPERIMENTAL PROGRAMME

3.1 INTRODUCTION:

In order to fulfill the objectives of the present study as indicated earlier in chapter-I, a detailed experimental programme was chalked out. It consisted of screening and identification of easily and abundantly available biomass materials from agricultural and forestry resource base, their physico-chemical characteristics and anaerobic digestion in batch and semi-continuous digesters under varying operating and environmental parameters.

3.2 SELECTION AND CHARACTERISTICS OF DIFFERENT BIOMASS MATERIALS

The total availability of some of the agricultural crop residues are presented in Table 1.1 of Chapter-I. Wheat straw and rice straw are generally used as cattle feed. However, rice straw being rich in silica, is not suitable as cattle feed for milching animals. The high silica content of rice straw makes it difficult for digestion in ruminants [142]. Incorporation of rice straw into the soil is not worth while because of slow degradation and excessive cost [16]. In India, a pilot project has been started for direct combustion of rice straw for thermal power generation (10 MW capacity).

Mirabilis plant has become naturalised in many warmer parts of the world. In India, it is found in the plains, low lying areas (Terai region) and warmer valleys of north-west Himalayas upto a height of 2000m. It grows rapidly in summer in dry and sandy areas and is also found in the shallow lakes and ponds and abounds in growth in sewage water stagnating.

Out of 500 species of Ipomoea available in all over the world, 60 are reported to be found in India [9]. Ipomoea fistulosa Mart ex. Choisy is found all over India in the plains, Terai region and hilly areas upto a height of 1400m. It grows in the shallow water lakes, ponds and in sewage water. Due to the presence of polysaccharide ipomose, anthracene glucoside, jalapin and saponins, cattle do not eat its leaves. The height of the plant is around 3m with a diameter of about 6 to 10 cm.

Dhub grass is naturalised all over the world and is generally found along roadsides and in fields. This grass is normally grazed and used to feed the cattle (as green cattle feed).

Banana is grown in large parts of the world as a fruit crop. It also grows wildly and abundantly in the heavily rain fed areas of the world. As per our estimate the total availability of banana plant residue (wet matter) is around 75 to 180 million tonnes/year in the world. Banana crop is harvested only once and after the fruits are taken out, the trunk is cut and is left over in the field or stacked elsewhere for natural degradation. It has very high moisture content and therefore is not used as fuel for burning. It is also not eaten by cattle either.

Cauliflower leaves are thrown as domestic garbage in urban

India. Cabbage wastes/food wastes etc., enhance the capacity of municipal garbage in the gas generation. Therefore, in our study, we have selected the following biomass materials for detailed studies. The photographs of these dried and shredded biomass materials are shown in Figures 3.1 through 3.3.

The botanical name of these material are given in the bracket against their local/English names.

1. Ipomoea fistulosa plant stem (IFPS).	(Ipomoea fistulosa Mart. ex Choisy)
2. Ipomoea fistulosa leaves (IFL)	(Ipomoea fistulosa Mart. ex Choisy)
3. Mirabilis leaves (ML)	(Mirabilis jalapaLinn.)
4. Banana peelings (BP)	(Musa paradisica)
5. Rice straw (RS)	(Oryza sativa)
6. Wheat straw (WS)	(Triticum aestivum)
7. Dhub grass (DG)	(Cynodon dactylon)
8. Cauliflower leaves (CFL)	(Brassica oleraea; variety Brotritis)

These materials were collected in wet form from the University campus. These were dried first in open sun, reduced in size and then kept in an oven at 90°C for further drying. About 20 kg of each biomass was stored in polyethylene bags and sealed so that it may be sufficient for all of the experimental runs and there should be no change in the characteristics of the biomass. The physico-chemical characteristics of the biomass materials are given in Table 3.1.

FIG. 3.1 PHOTOGRAPHS OF BIOMASS MATERIALS USED FOR EXPERIMENTS

FIG. 3.2 PHOTOGRAPHS OF BIOMASS MATERIALS USED FOR EXPERIMENTS

FIG. 3.3 PHOTOGRAPHS OF BIOMASS MATERIALS USED FOR EXPERIMENTS

TABLE 3.1 CHARACTERISTICS OF DIFFERENT RAW MATERIALS

PARAMETER		IFPS	IFL	ML	BP	RS	WS	DG	CFL	CD	ES
Moisture content,	%	13.3	68.8	68.8	77.6	--	--	68.8	78.8	85.2	94.9
Volatile solids*	%	92.6	87.7	87.8	83.7	79.4	89.9	89.3	84.3	79.2	79.8
Carbon*	%	51.4	48.7	48.8	46.5	44.1	49.9	49.6	46.8	44.0	44.3
Protein*	%	2.1	14.8	14.7	5.3	3.8	3.6	9.3	24.7	5.7	6.7
Cellulose*	%	54.6	56.8	52.3	61.4	38.4	36.4	40.1	47.8	39.9	22.8
Lignin*	%	13.0	25.5	20.4	13.3	11.1	10.3	13.2	6.7	23.8	15.0
Lignin/cellulose ratio*		0.24	0.45	0.39	0.22	0.29	0.28	0.33	0.14	0.6	0.65
Carbon/nitrogen ratio*		155.7	20.9	21.2	55.4	73.5	87.5	34.0	12.1	48.8	42.2
Ethanol-benzene and hot water solubility*		7.6	34.0	24.9	16.7	6.1	7.6	6.7	21.5	5.2	6.1

* Dry weight basis.

3.3 EXPERIMENTAL SETUP

Glass aspirator bottles of 5 litre capacity each with 4 litre working volume were used as digesters. The aspirator bottles were so designed as to have provision for pH electrode, stirring device, gas outlet and biomass feeding and sample withdrawal connecting tubings with accessories. A typical aspirator bottle with the above provisions is shown in Figure 3.4.

The gas outlet tubing was maintained at room temperature by a cold water jacket around it. The gas was passed through a column of anhydrous calcium chloride for the removal of the entrained moisture and then collected over water at atmospheric pressure. For an estimate of methane, a part of the gas was passed through a bubbler tube filled with potassium hydroxide solution (for removal of carbon-dioxide), through a 3-way stop cock arrangement, as shown in Figure 3.5. A thermostatic chamber was used for maintaining a prefixed temperature in the digester.

3.4 EXPERIMENTAL PROGRAMME

In all the experiments, excepting those run for estimating the effect of particle size, the dried biomass material was ground in a portable grinder and sieved through a sieve of 0.40 mm size. The under sized particles were then mixed with distilled water in such a proportion as to give 8% (w/v) total solids concentration in the slurry. Effluent slurry from a Janata type domestic biogas plant with retention time of 55 days, operating

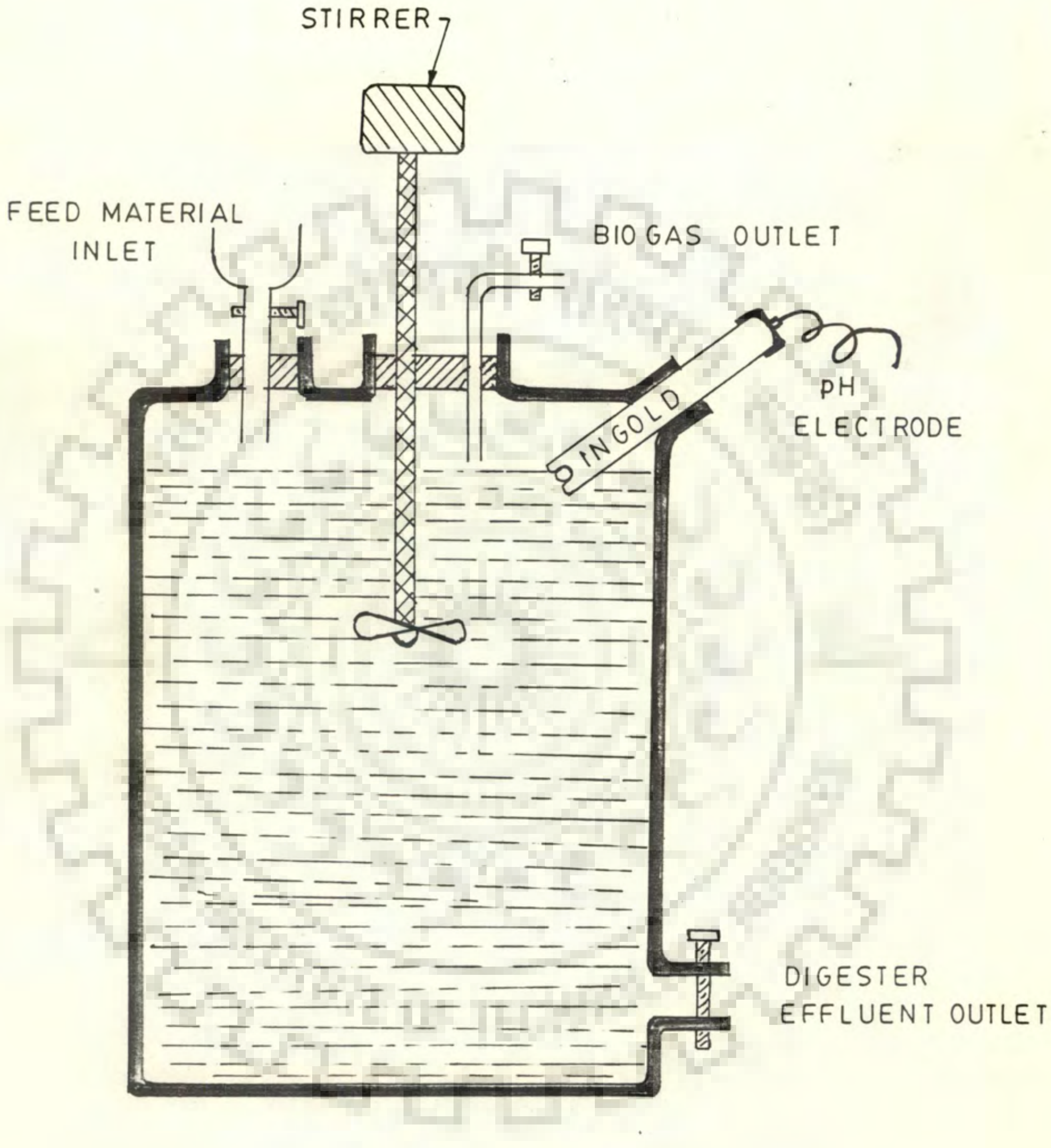


FIG. 3.4- MODIFIED ASPIRATOR BOTTLE USED AS DIGESTER

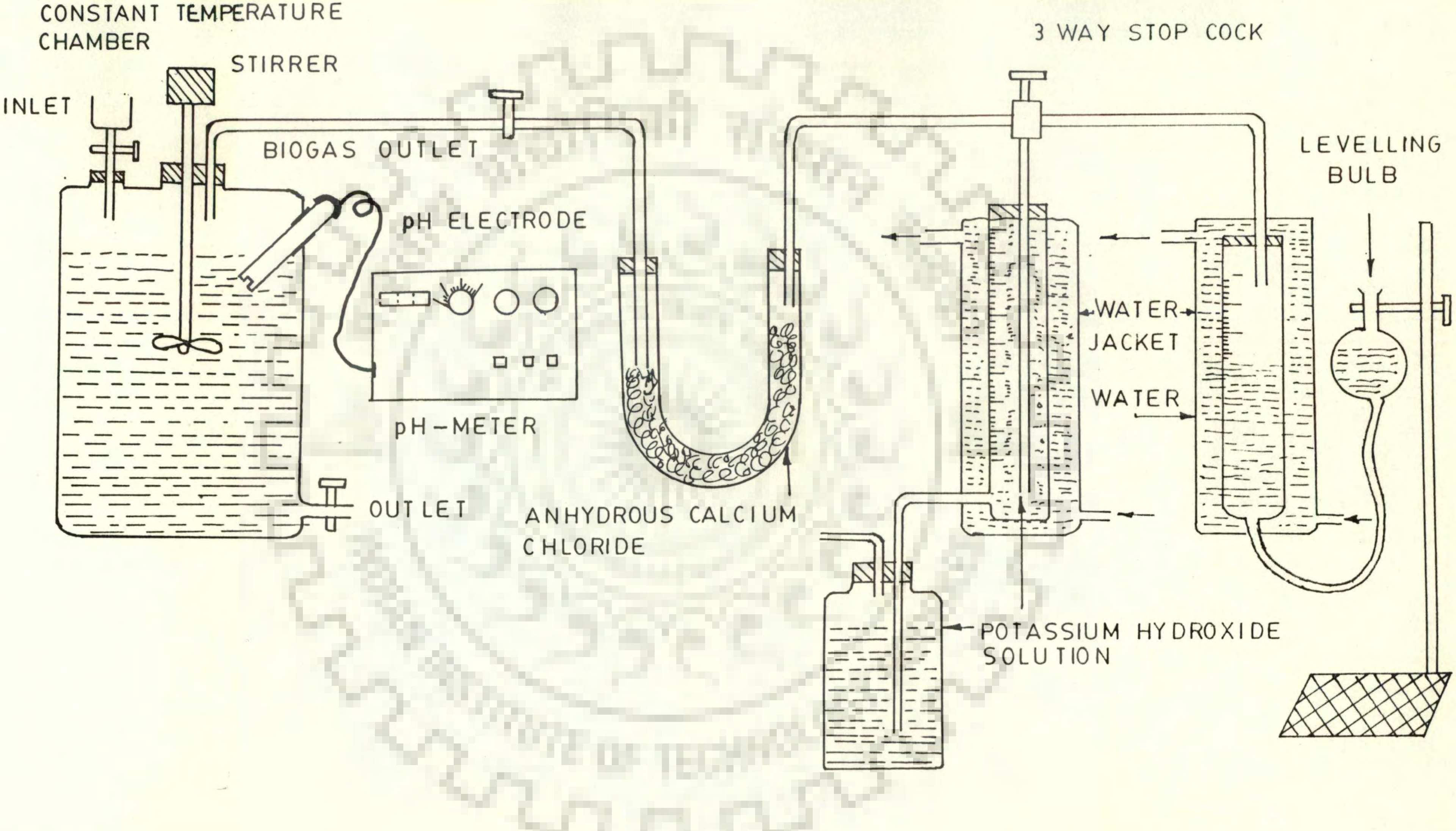


FIG. 3·5 SCHEMATIC DIAGRAM OF EXPERIMENTAL SETUP FOR BIOGAS GENERATION on cattle dung was used for seeding the raw slurry. Seeding was done in 1:1 ratio (v/v). Four litre of the seeded slurry was filled in each of the aspirator bottle digester. All the experiments were conducted in batch type digesters except one experiment which was conducted to determined the kinetics of biogasification. Semi-continuous digesters were fed once a day at fixed interval of time. The prepared slurry was stored in glass bottles at a temperature of 4°C for subsequent use. For daily feeding the required quantity of slurry was taken out, brought to room temperature (22-26°C) by indirect heating in water bath and 450, 300, 225, 180, 150, 128 and 112 ml of the above slurry was once fed daily in between 0900 and 1000 hours to the different digesters operating for the retention time of 10, 15, 20, 25, 30, 35 and 40 days, respectively. The same volume of digester slurry was withdrawn from the bottom of the digester in order to maintain constant volume of digester content. In both batch and semi-continuous digesters the substrate was stirred for a period of 2 minutes after every 3 hours by using a 3 bladed-propeller-stirrer run at 100 revolution per minute.

3.5 PRETREATMENT OF BIOMASS

In order to assess the effect of pretreatment of the feed biomass on the rate and total gas production capacity, the biomass materials were pretreated in the following manner before being fed to the digesters.

3.5.1 Preincubation with water

All the biomass materials listed in sub-sector 3.2 were preincubated in water for different periods of time to investigate the effect of this pretreatment on total biogas production and rate of production. The known quantities of ground biomass samples of 0.40 mm size were mixed with distilled water to have 8% total solid concentration (w/v). These were then incubated at constant temperature of 37±0.5°C for different periods of time, namely, 5, 10, 20, 30 and 40 days in a sequence so that after preincubation for a definite period of time, inoculation of all the samples could be done simaltaneously. pH and TVFA of all the preincubated materials were determined. VS of some of the materials were also determined. After preincubation, the materials were seeded and fed to the digester for biogasification experiments.

3.5.2 Pretreatment with alkali

In order to investigate the effect of pretreatment of alkali, two biomass materials - rice straw and banana peelings- were selected. Five percent NaOH solution in water was used for incubation. The solid concentration was kept 2% (w/w). The first treatment was carried out at 37°C for 24 hours and another at 100°C for 2 hour. After alkali treatment the incubated mass was filtered and the residue was washed several times with distilled water, until residue was found to be free of alkali. Thereafter, the treated biomass was mixed with water making a slurry of 8%

(w/v). This slurry was seeded with the effluent slurry as detailed earlier and fed to the digester for biogas production.

3.5.3 Particle size reduction:

All the biomass materials mentioned in section 3.2 were used in the experiments to investigate the effect of particle size reduction on biogas generation. The dried materials were first ground in a portable kitchen grinder (Belco make) and then screened through sieves of different sizes, namely, 0.088, 0.40, 1.0 and 6.0 mm. The under sized particles so obtained were not of uniform size, but a mixture of particles in the size (dp) range : $0<dp<0.088$, $0.088<dp<0.40$, $0.40<dp<1.0$ and $1.0<dp<6.0$ mm. However, for convenience, the size of the sieved particles are to be denoted as 0.088, 0.40, 1.0 and 6.0 mm, respectively. The ground material of a known size range was mixed with water, seeded and fed to the digester as explained earlier in section 3.4. The pH of the digester slurry was maintained between 6.75 to 7.25 using calcium hydroxide (Glaxo). Two identical digesters were operated for each particle size of a given feed stock. Details of digesters and raw material particle sizes are given later in Chapter 4.4.

3.6 BLENDING OF RAW MATERIALS

3.6.1 Blending of cattle dung with agricultural and forest residues

All the agricultural and forest residues given in section

3.2 were taken for experiments and were mixed with cattle dung in different ratio in different batch digesters as follows:

Digester No.	Agricultural or forest residues, % (w/w)	cattle dung % (w/w)
D1	00	100
D2	25	75
D3	50	50
D4	75	25
D5	100	00

Digester D1 having 100% cattle dung, was common to all tests. For all raw materials, the notation for digesters was similar.

3.6.2 Blending of two residues:

Dried banana peelings and *Ipomoea fistulosa* leaves were mixed with each other as follows:

Digester No.	Banana peelings % (w/w)	*Ipomoea fistulosa* leaves, % (w/w)
D1	100	00
D2	75	25
D3	50	50
D4	25	75

Further these mixtures were mixed with water and effluent slurry as described earlier.

3.7 ANALYTICAL PROGRAMME

The following parameters were determined in the experimental programme:

3.7.1. **Volume of biogas :** The volume of biogas generated was measured daily at 1000 hours by water displacement method under atmospheric pressure.

3.7.2. **Moisture and solid concentration:** The moisture content of a wet sample was estimated by determining its initial weight, and the final weight after drying in an oven at 90°C until constant weight was obtained. The difference in weight per unit of wet weight gave the moisture content. The remaining solids weight divided by the volume of the initial sample gave the percent solids concentration.

3.7.3. **Volatile solids and ash:** The volatile solids content was taken to be the difference between total solids and the ash which remains on keeping the dry matter in muffle furnace maintained at 550±50°C for 4 hours [22].

3.7.4. **Carbon:** Carbon percentage was calculated by dividing the percentage of volatile solids by 1.8 [140].

3.7.5. **Total nitrogen:** The total nitrogen content was determined by Kjeldahl digestion method [12].

3.7.6. **Protein:** Protein content was calculated by multiplying the percentage of total nitrogen by the factor 6.38 [146].

3.7.7. **Cellulose:** Cellulose was estimated by chlorination method [93].

3.7.8. **Lignin:** Lignin was determined by 72% sulphuric acid method [93].

3.7.9. **Ethanol-benzene and hot water solubility:** Five grams of dry matter was extracted in a soxhlet extraction unit using ethanol-benzene (1:2, v/v) mixture, at 80ºC for 2 hours. It was then transfered to the crucible and washed with distilled water until free from ethanol-benzene solution. Subsequently it now transfered to a beaker having 150 ml of distilled water, stirred for 1 hour at 100ºC, filtered, washed with water and dried until constant weight. The loss in weight was determined as ethanol-benzene & hot water solubility of the material.

3.7.10. **pH:** pH of the substrate was measured using Control Dynamics Digital pH Meter (Model No. APX 175) with gel filled Ingold electrode.

3.7.11. **Total volatile fatty acids:** The digester sample was withdrawl in sufficient quantity and centrifuged at 5000 rpm in a test tube. 25 ml of clear supernanant was pipetted out and buffered to bring down its pH to 3.5 using sulphuric acid (5%, v/v). Total volatile fatty acid were determined by direct titration method [34].

3.7.12. **Analysis of biogas:** Biogas was analysed for methane content on an AIMIL-NUCON gas chromatograph with TCD. Porapak Q column was used at room temperature with nitrogen as a carrier gas.

CHAPTER IV

RESULTS AND DISCUSSION

The results of the experiments carried out to asses the biogas generation characteristics from different biomass materials with and without blending with other biomass materials under different operating operating and environmental conditions are presented in this chapter.

4.1 BLENDING OF BIOMASS WITH CATTLE DUNG

As detailed in section 3.6.1 of chapter III, all the agricultural and forest residues as given in section 3.2, were separately blended with cattle dung in different proportions starting with 100% cattle dung to 100% agricultural residues in 5 batch digesters designated as D1 to D5.

4.1.1 Weekly Biogas Production

The weekly biogas production in litres/kg of total solids (TS), upto eight weeks of digestion are given in Table 4.1.1. In all the digesters, for all the raw materials neither pH nor TVFA were controlled. From the Table 4.1.1, it may be observed that certain residues namely, ML, BP, RS and CFL gave consistently higher amounts of weekly gas production rates with increase in blending percentage of these residues upto 3rd week. In the case of RS, it was observed that the digester D3 with 50%CD and 50%RS gave highest gas production rate from 4th week onwards as compared to other digesters whereas in the case of BP, a slump was observed in digester D4 with 75%BP and 25%CD with recovery in digester D5 fed with 100%BP. It may also be observed that highest production rates were found in the first two weeks of digestion in most of the digesters. The digester fed with different percentage of DG do not show a definite trend of gas production with digestion period nor with the percentage of blending. In the case of WS, digester D3 with 50% blending showed highest gas

TABLE 4.1.1 WEEKLY BIOGAS PRODUCTION RATE

Biomass material	Digester No.	Weekly gas production; l/kg of total solids							
		No of weeks after which gas production is reported							
		1	2	3	4	5	6	7	8
Cattle dung (CD)	D1	37	67	39	20	14	9	8	6
Ipomoea fistulosa plant stem (IFPS)	D2	84	96	56	38	23	27	24	18
	D3	44	64	64	47	43	38	25	20
	D4	26	3	00	00	00	00	00	00
	D5	23	1	00	00	00	00	00	00
Ipomoea fistulosa leaves (IFL)	D2	85	106	62	41	21	18	21	20
	D3	94	110	74	48	26	19	20	14
	D4	35	8	2	00	00	17	15	11
	D5	24	3	00	00	00	00	00	00
Mirabilis leaves (IFL)	D2	40	48	40	32	25	16	18	10
	D3	50	75	60	28	22	20	18	14
	D4	45	110	70	47	24	20	15	9
	D5	58	135	66	50	32	25	22	12
Banana peelings (BP)	D2	55	45	35	33	31	24	10	7
	D3	85	68	55	35	22	18	15	17
	D4	100	85	58	30	20	14	19	14
	D4	110	140	50	35	30	20	18	17

TABLE 4.1.1. CONTD.

Rice straw	D2	52	65	42	33	25	18	15	15
(RS)	D3	72	55	58	59	50	28	20	13
	D4	105	82	70	43	30	24	18	8
	D5	150	115	77	42	28	18	14	11
Wheat straw	D2	43	78	40	28	20	15	9	7
(WS)	D3	68	48	52	38	30	20	10	6
	D4	85	62	45	35	28	25	14	11
	D5	100	68	52	35	25	26	11	8
Dhub grass	D2	30	25	28	34	22	17	10	14
(DG)	D3	28	40	35	25	25	22	20	10
	D4	35	45	32	38	20	20	14	6
	D5	40	23	50	30	37	24	18	13
Cauliflower leaves	D2	77	89	81	34	29	26	24	17
(CFL)	D3	30	47	98	68	73	43	32	17
	D4	30	00	00	00	00	90	89	47
	D5	59	00	00	00	00	00	00	00

production rate from 3rd week onwards in comparison to other digesters.

4.1.2 Failure of Digesters:

During the experiments it was observed that some of the digesters with higher percentage of agricultural residues failed. This was found to be due to low pH and high total volatile fatty acids (TVFA) concentrations. From Table 4.1.1, it may be found that digesters fed with 75% and 100% IFPS, IFL and CFL failed in the second to third weeks. In the case of digesters fed with 75% IFL and CFL i.e. digester D4, the digester showed the symptom of revival after 5th weeks. However, the gas production was found to be very small in the case of IFL as compared to CFL.

4.1.3 Biogas Production Capacity

Table 4.1.2 presents the total biogas production for different materials with different percentage of blending with CD in l/kg of TS. It may be found that all the digesters, excepting those which failed and also the one fed with 25%DG and 75%CD, produced larger biogas amount than that given by CD alone. It may also be noted that digesters fed with 50% of IFL and CFL gave almost the double amount of gas as compared to CD. Total amount of gas produced increased with the increase in percentage of blending in the case of ML, RS, BP, WS, and DG. RS fed digester gave highest quantity of biogas (455 l/kg TS) followed by BP (420 l/kg TS) and ML (400 l/kg TS). Among partially blended digesters, CFL and IFL gave the highest gas production of 408 and 405 l/kg TS,

TABLE 4.1.2 BIOGAS PRODUCTION CAPACITIES OF DIFFERENT MATERIALS

Digester No.	Percentage of blending	Total biogas production; l/kg of TS								
		Biomass materials								
		IFPS	IFL	ML	BP	RS	WS	DG	CFL	CD
D1	00%	--	--	--	--	--	--	--	--	200
D2	25%	366	374	229	240	265	240	180	377	--
D3	50%	345	405	272	315	335	272	205	408	--
D4	75%	29	88	340	340	380	305	210	256	--
D5	100%	24	27	400	420	455	325	235	59	--

respectively for 50% blending with CD. It may be concluded that under un controlledpH conditions, blending of IFPS and IFL upto 50% is only suitable to enhance biogas production while in the case of ML, BP, RS, WS and DG, the gas production increases with increase in percentage of blend.

4.1.4 Methane Concentration in the Biogas

Table 4.1.3 compares in a tabular form the methane content of biogas as obtained from different digesters using different biomass materials. It may be found that BP fed digesters have highest methane content followed by ML and DG. Based on the methane content of the biogas and the total biogas produced as given in Table 4.1.2 it may be observed that BP produces highest methane (302 l/kg TS) followed by ML (280 l/kg TS) and RS (273 l/kg TS). With 50% blending, IFL and CFL produced 275 and 269 l/kg TS of methane.

4.1.5 Performance of Digesters:

The performance of a digester fed with a particular biomass material could be assessed by the degradation behaviour of cellulose or total solids and volatile solids [21]. Table 4.1.4 presents the performance of all the digesters fed with different biomass materials and their blends in terms of reduction in cellulose, TS and VS. From Table 3.1 given in chapter III, it is clear that the cellulose content in various residues were in the following order:

BP > IFL > IFPS > ML > CFL > DG > CD > RS > WS

TABLE 4.1.3 PERCENT OF METHANE IN BIOGAS (V/V)

Digester No.	Biomass materials								
	IFPS	IFL	ML	BP	RS	WS	DG	CFL	CD
D1	--	--	--	--	--	--	--	--	60
D2	66	65	65	65	60	60	66	63	--
D3	66	68	66	70	60	60	66	66	--
D4	60	68	68	71	60	60	68	66	--
D5	60	52	70	72	60	60	68	65	--

TABLE 4.1.4 PERFORMANCE OF DIGESTERS (DRY WEIGHT BASIS)

Biomass materials	Digester No.	Toatl solids Initial g/l	Toatl solids Reduction %	Cellulose Initial % of TS	Cellulose Reduction %	Volatile solids Initial % of TS	Volatile solids Reduction %
Cattle dung (CD)	D1	65.5	24.1	33.21	22.5	79.35	25.8
Ipomoea fistulosa plant stem (IFPS)	D2	65.5	26.2	35.45	28.1	81.4	41.0
	D3	65.5	24.9	37.7	26.8	83.43	37.7
	D4	65.5	23.8	39.92	21.2	85.48	3.0
	D5	65.5	24.5	42.17	22.5	87.52	2.5
Ipomoea fistulosa leaves (IFL)	D2	65.5	28.5	35.8	33.3	80.65	42.0
	D3	65.5	32.1	38.36	37.0	81.94	44.9
	D4	65.5	24.8	40.93	29.1	83.23	9.6
	D5	65.5	27.2	43.52	32.0	84.53	2.9
Mirabilis leaves (ML)	D2	65.5	25.8	35.10	29.7	80.66	25.9
	D3	65.5	30.0	37.00	34.00	81.97	30.5
	D4	65.5	31.8	38.87	35.9	83.28	37.3
	D5	65.5	34.2	40.77	38.8	84.60	43.3
Banana peelings (BP)	D2	65.5	24.1	36.5	29.4	80.05	27.3
	D3	65.5	26.7	39.77	31.9	80.75	35.8
	D4	65.5	33.3	43.02	38.2	81.45	38.1
	D5	65.5	35.0	46.32	38.9	82.16	46.8

TABLE 4.1.4 CONTD.

Rice straw (RS)	D2	65.5	27.5	32.97	32.8	79.33	30.4
	D3	65.5	33.3	32.75	36.8	79.31	38.7
	D4	65.5	36.6	32.52	40.4	79.30	43.6
	D5	65.5	38.1	32.29	42.8	79.29	52.3
Wheat straw (WS)	D2	65.5	25.0	32.67	31.3	80.98	27.0
	D3	65.5	26.3	32.14	31.9	82.61	30.2
	D4	65.5	30.0	31.60	34.9	84.24	33.0
	D5	65.5	30.3	31.07	36.0	85.88	34.7
Dhub grass (DG)	D2	65.5	20.8	33.23	24.0	80.90	20.3
	D3	65.5	25.0	33.27	28.4	82.42	22.8
	D4	65.5	28.0	33.29	31.6	83.97	22.8
	D5	65.5	26.0	33.33	29.6	85.51	25.2
Cauliflower leaves (CFL)	D2	65.5	37.0	34.41	29.4	80.13	42.9
	D3	65.5	39.1	35.62	32.8	80.90	46.0
	D4	65.5	32.0	36.81	28.0	81.68	28.58
	D5	65.5	30.8	38.03	24.4	82.46	6.5

With the cellulose content in the range of 36.4 to 61.4%. In effluent slurry cellulose content was 22.8%. The blending of cow dung with biomass residue and mixing with effluent slurry changed the cellulose content of the mixture. The initial content of cellulose as percentage of TS is given in Table 4.1.4. A careful examination of this table shows that the maximum cellulose reduction takes place in the case of RS seeded with effluent slurry with no cattle dung present in it. In the case of ML, BP, RS, WS and DG, percent reduction of cellulose increases with the increase in residue content in the slurry i.e. digester D5 show the highest cellulose reduction in comparison to that in the other digesters. The only exception to this has been DG fed digester D5. In the case of other residues namely IFPS, IFL and CFL where digesters were found to fail with increased residue content in the feed, the percentage cellulose reduction also decreased. However, it may be noted that in the case of IFL digester D5 showed 32% cellulose reduction as compared to 29.1% in digester D4. The similar trends are found for the reduction of TS also. However, it may be seen that the TS reduction does not directly enhance the gas production in all the cases, e.g., digester D4, D5 for IFPS, IFL and CFL where the TS reduction have been of the order of 24 to 32%, the gas production drastically reduced, indicating the failure of these digesters. This is because of the fact that cellulolytic and acidogenic microbes are at the work, converting the solids into fatty acids, the methane formers almost become non-viable due to very low pH and high TVFA concentrations. This will be discussed in detail later while dealing with the effect of pH and TVFA concentration on gas production.

4.2 BLENDING OF TWO AGRICULTURAL/FOREST RESIDUES

As mentioned earlier in section 3.6.2 of chapter III, dried peelings of banana stem (BP) and Ipomoea fistulosa leaves (IFL) were blended in different proportions and digested in four digesters D1 to D4. Effluent slurry from the Janata type biogas plant of $6 m^3$ capacity was used for seeding the digesters. A fifth digester D5 had only effluent slurry for reference purpose.

4.2.1 Characteristics of the raw materials

The chemical composition of the raw material is presented in Table 4.2.1 The low value of lignin in banana peeling suggests that a greater percentage of cellulose is available for bacterial degradation compared to that of IFL and effluent slurry. The carbon to nitrogen (C/N) ratio is 55.39, 20.92 and 46.60 for banana peeling, IFL and effluent slurry, respectively. IFL have a highest V.S. (87.77 %) and ethanol:benzene and hot water solubility (34.08 percent) among all the three raw materials. Juice obtained from fresh/wet banana peeling and IFL is acidic in nature with their pH value 6.28 and 6.05, respectively.

4.2.2. Change in Composition of Substrate During Anaerobic Digestion

The composition of digester substrate before and after

TABLE 4.2.1 SUMMARY OF FEED COMPONENT CHARACTERISTICS

Sl. No. Test	Banana Peeling	*Ipomoea fistulosa* Leaves	Effluent Slurry
1. Mositure content %	77.65	68.79	94.14
2. Solid concentration %	22.35	31.21	5.86
3.Volatile solids*%	83.75	87.77	81.39
4.Carbon* %	46.53	48.76	45.21
5.Nitrogen*%	Ø.84	2.33	Ø.97
6.Protein* %	5.35	14.86	6.18
7.Carbon/Nitrogen ratio*	55.39	2Ø.92	46.6Ø
8.Cellulose *%	61.42	56.78	42.82
9.Hemicellulose * %	21.98	12.61	23.84
1Ø.Lignin *%	13.3Ø	25.56	28.18
11.Silica ash* %	3.3Ø	5.Ø5	5.16
12.pH	6.28#	6.Ø5#	7.12
13.Total volatile acids (mg litre $^{-1}$ as acetic acid)	N.D.	N.D.	625
14.Ethanol-Benzene and hot water solubility %	16.75	34.Ø8	6.69

* Dry weight basis
\# Juice expressed from fresh material
N.D.Not determined.

digestion is presented in Table 4.2.2 The initial solid concentration in all the digesters except D5, is 7.07 percent which decreased to a value of less than 5.0 percent after anaerobic digestion for eight weeks. The C/N ratio of organic matter undergoing anaerobic digestion is an important factor and its value should be around 30 [1, 46]. However substrate of digester D4 having an initial C/N equal to 30.84, was found to give minimum quantity of gas and the reduction of VS was also found to be the lowest among all digesters except D5. It appears that some organic materials which are resistant to microbial attack would not be digested regardless of its C/N ratio [140].

Table 4.2.3 shows that reduction of cellulose and hemicellulose increases with increase in percentage of IFL in banana peeling and it was found to be highest in digester D4 having 25 percent BP and 75 percent IFL. The cellulose hydrolysis rate is dependent on the substrate and the bacterial concentration (especially cellulolytic bacteria) and also on the operating parameters such as pH and temperature. There was practically no degradation of lignin and the increase in its percentage was due to reduction of other components of feedstock. Cellulose, combined with other organic compounds in a complex waste, is not totally available for bacterial break-down. It has been stated by many investigators that lignin is the major obstacle in the utilisation of cellulosic residues for enzymatic hydrolysis [10, 50, 82, 106].

Lignin is very resistant to degradation by anaerobic digestion [14]. The hydrolysis of lignocelluloses, both native and

TABLE 4.2.2 SUMMARY OF CHANGE IN COMPOSITION OF SUBSTRATE DURING ANAEROBIC DIGESTION (DRY WEIGHT BASIS)

Tests	D1 Initial	D1 Final	D2 Initial	D2 Final	D3 Initial	D3 Final	D4 Initial	D4 Final	D5 Initial	D5 Final
Solid concentration %	7.07	4.75	7.07	4.68	7.07	4.71	7.07	4.82	5.86	4.33
Volatile solids %	82.70	76.85	83.20	74.47	83.82	75.92	84.39	78.08	81.39	78.16
Carbon %	45.94	42.69	46.22	41.37	46.56	42.12	46.88	43.37	45.21	43.42
Protein %	5.67	6.25	7.01	7.71	8.35	9.44	9.69	11.42	6.18	6.89
Cellulose %	53.21	50.15	52.56	49.55	51.91	47.99	51.25	44.62	42.82	41.58
Hemicellulose %	22.77	18.35	21.45	16.10	20.14	11.49	18.83	8.83	23.84	20.15
Lignin %	19.80	23.72	21.52	27.80	23.24	32.40	24.96	36.80	28.18	32.25
Silica ash %	4.22	7.78	4.47	6.55	4.71	8.12	4.96	9.75	5.16	6.02
Carbon/nitrogen ratio	51.61	43.56	42.01	34.19	35.54	28.45	30.84	24.22	46.60	40.20
Ethanol-benzene & hot water solubility %	12.35	19.18	14.87	22.03	17.31	21.45	19.69	26.48	6.69	8.50

TABLE 4.2.3 SUMMARY OF DIGESTER PERFORMANCE (DRY WEIGHT BASIS)

Digester No.	Cellulose Reduction %	Hemicellulose Reduction	Lignin Reduction %	Volatile solids Reduction %	Methane* Production %
D1	36.67	45.85	19.51	46.64	359.36
D2	37.59	50.31	14.48	49.81	378.87
D3	38.41	61.99	7.12	47.88	353.60
D4	40.91	68.03	0.51	44.59	336.99
D5	28.24	37.54	15.43	15.51	103.12

* litres/kg of V.S.

processed, is dependent on the lignin to cellulose ratio [111]. In the anaerobic digestion of banana peeling and its mixture with IFL, the initial lignin to cellulose ratio of the substrate of digester D1, D2, D3 and D4 was Ø.372, Ø.4Ø9, Ø.447 and Ø.487, respectively. It is clear that the rate of cellulose reduction increased and rate of lignin reduction decreased with increase in lignin to cellulose ratio (Table 4.2.3).

The highest (49.81 percent) VS reduction was found to be in digester D2 having 75 percent BP and 25 percent IFL and the lowest reduction of 44.59 percent was in digester D4 having 25 percent BP and 75 percent IFL. During anaerobic digestion, a part of VS is converted into biogas and the conversion efficiency depends upon various operating parameters [114].

The gas generated from all the digesters was analysed daily and the mean values for each week is presented in Table 4.2.4. Digester D2 produced 378.87 litres of methane/kg of VS, the highest quantity out of digesters D1 to D4.

4.2.3 Change in pH and TVFA Concentration During Anaerobic Digestion:

Figures 4.2.1, 4.2.2, 4.2.3, 4.2.4 and 4.2.5 shows the weekly results of pH, TVFA and gas production of digester D1, D2, D3, D4 and D5, respectively. It is clear that with the increase in percentage of IFL in banana peeling samples, there is a sharp decrease in pH in the first week of digestion. In digesters D3 and D4, the pH drops to a value of 5.52 from 6.92

TABLE 4.2.4 QUANTITY OF METHANE (AVERAGE) IN DIGESTER GAS DURING FIRST FOUR WEEKS OF DIGESTION PERIOD

Weeks	Digester No.				
	D1 %	D2 %	D3 %	D4 %	D5 %
First	64.6	62.5	63.0	65.2	58.0
Second	69.5	68.2	68.3	67.4	61.3
Third	73.8	70.8	73.5	76.2	61.8
Fourth	70.5	68.6	71.6	73.0	62.0

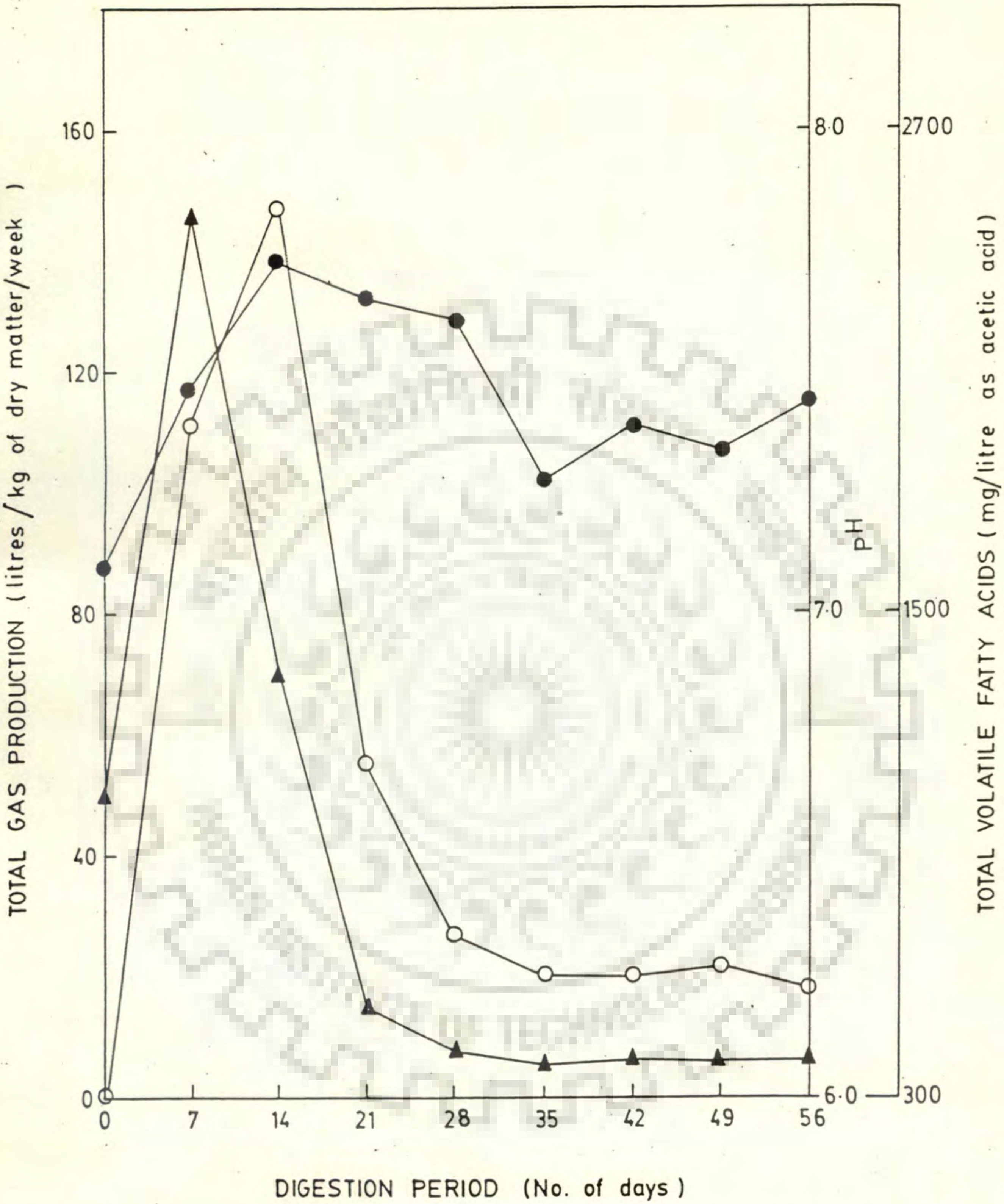


FIG.4.2.1. ANAEROBIC DIGESTION OF BANANA PEELING (100%). o, TOTAL GAS PRODUCTION; ●, pH; ▲, TOTAL VOLATILE FATTY ACIDS (TVFA).

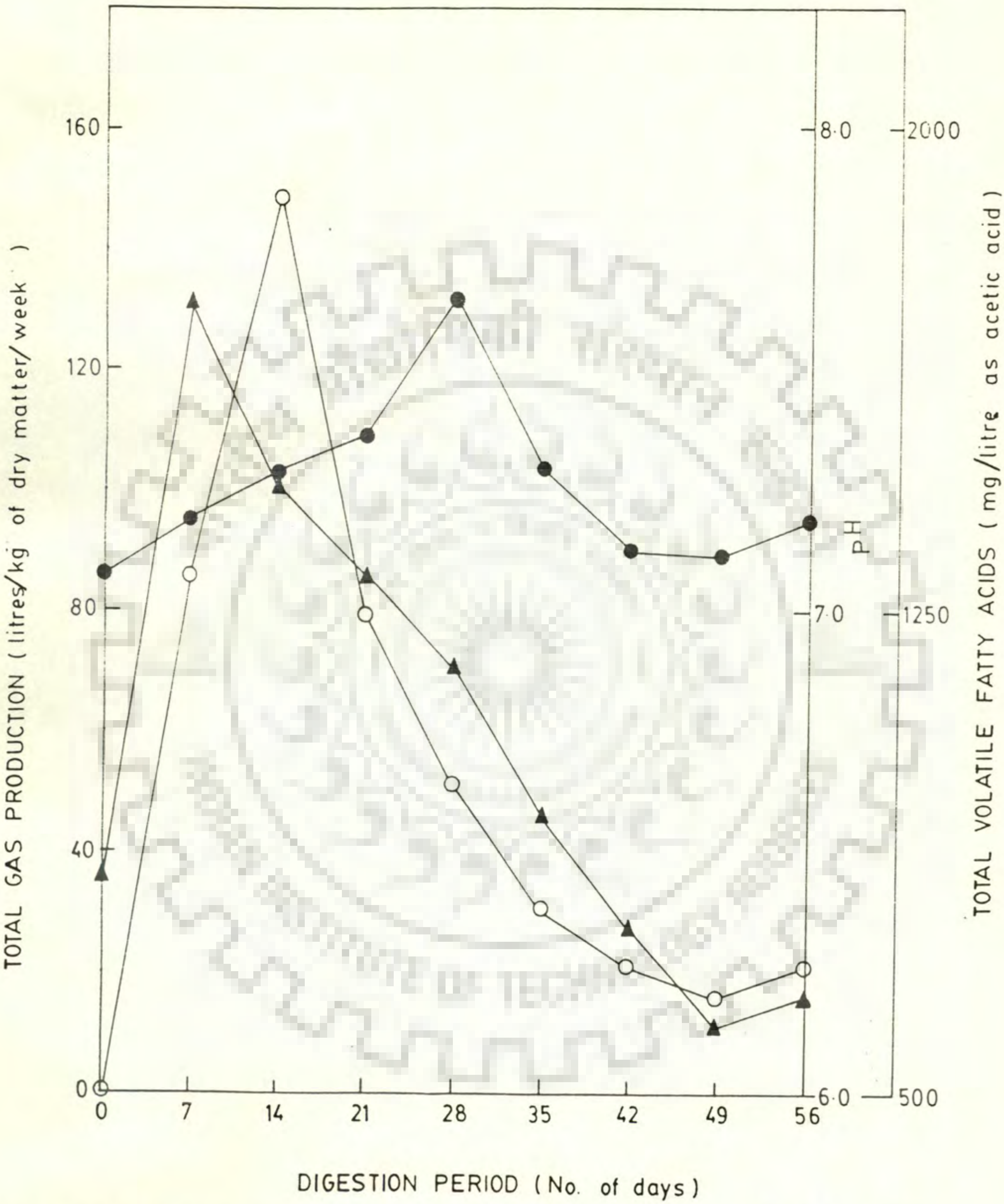


FIG. 4.2.2. ANAEROBIC DIGESTION OF BANANA PEELING (75%) AND I.FISTULASA LEAVES (25%). o, TOTAL GAS PRODUCTION; ●, pH; ▲, TOTAL VOLATILE FATTY ACIDS (TVFA).

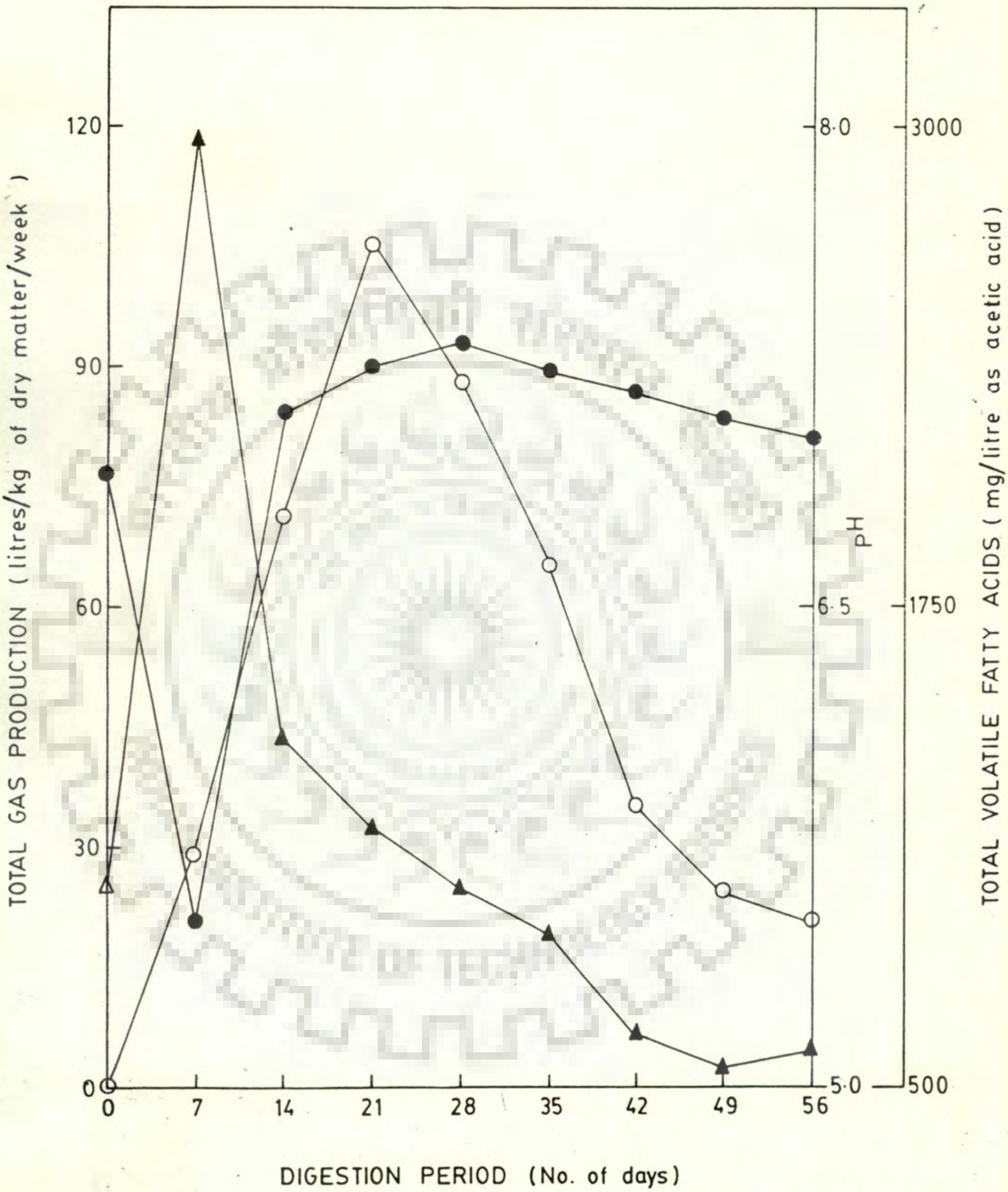


FIG. 4.2.3 ANAEROBIC DIGESTION OF BANANA PEELING (50%) AND I. FISTULASA LEAVES (50%). o, TOTAL GAS PRODUCTION; ●, pH; ▲, TOTAL VOLATILE FATTY ACIDS (TVFA).

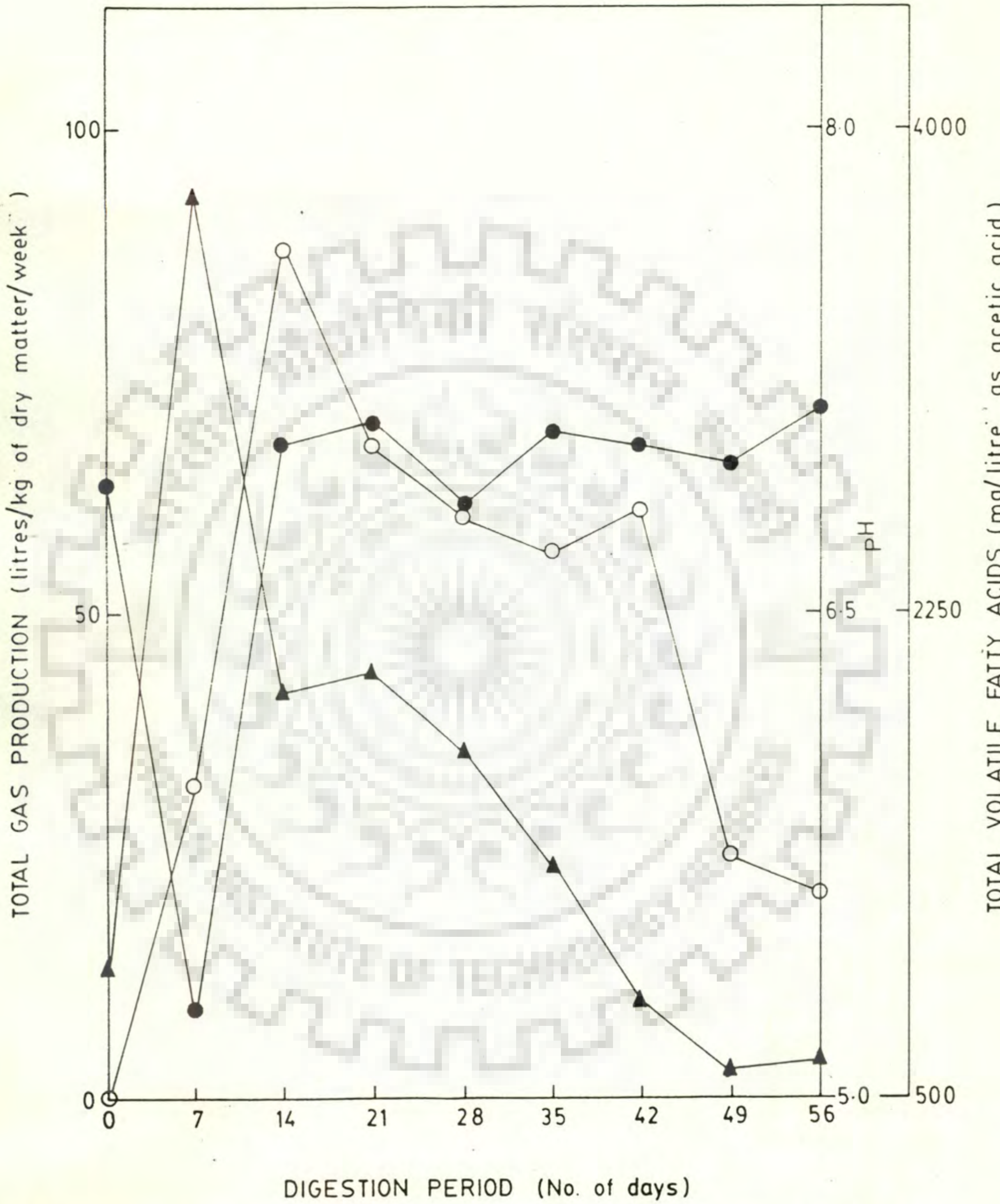


FIG.4.2.4. ANAEROBIC DIGESTION OF BANANA PEELING (25%) AND I.FISTULASA LEAVES (75%). o, TOTAL GAS PRODUCTION; ●, pH; ▲, TOTAL VOLATILE FATTY ACIDS (TVFA).

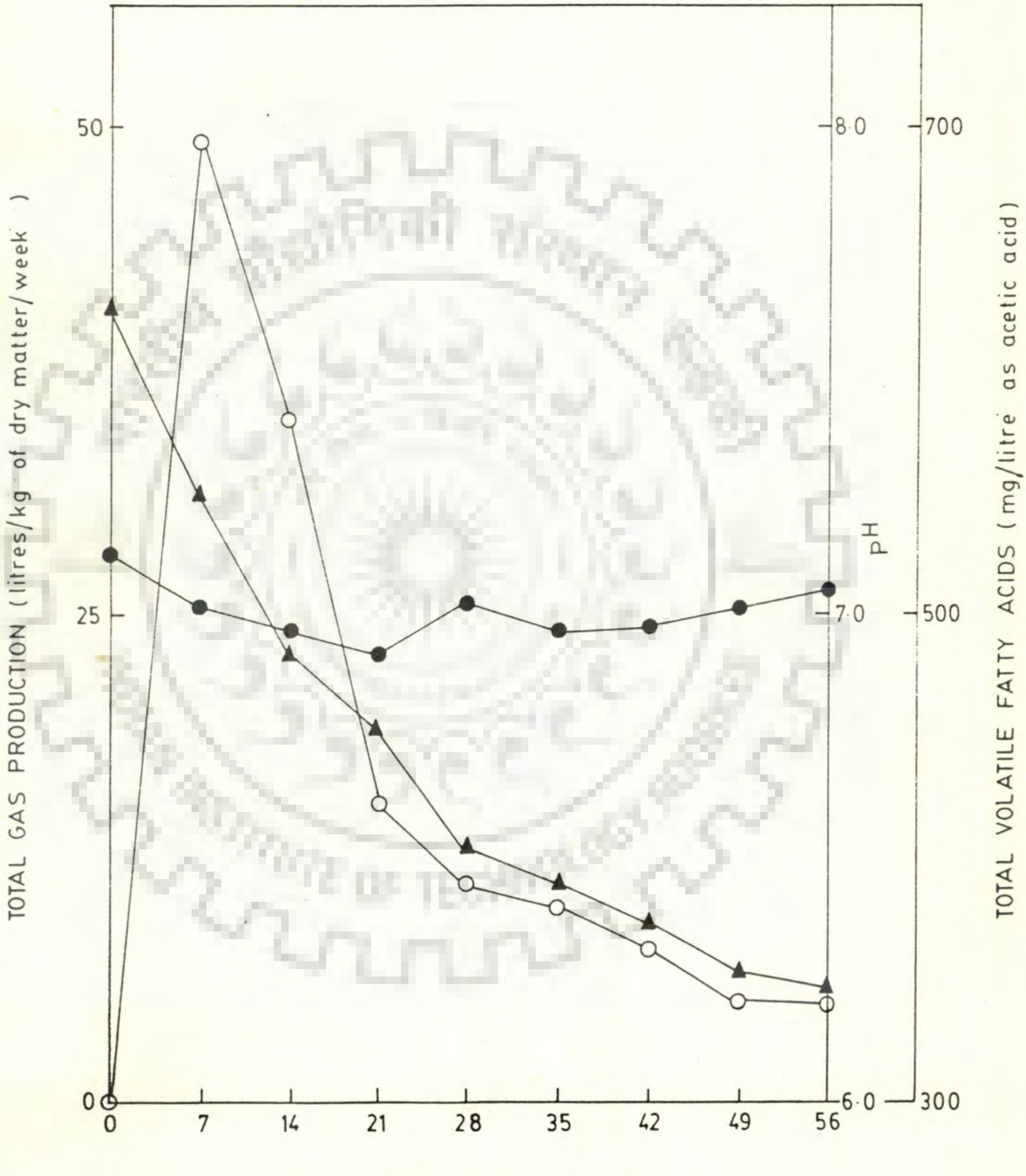


FIG.4.25. ANAEROBIC DIGESTION OF EFFLUENT SLURRY.
○, TOTAL GAS PRODUCTION; ●, pH;
▲, TOTAL VOLATILE FATTY ACIDS (TVFA).

and 5.28 from 6.89, respectively. Subsequently there is increase in pH value and the medium becomes alkaline. In the case of digesters D1 and D2, pH remains above 7.Ø (in alkaline range) throughout the digestion period and it increases upto 7.65. It appears that the fall in pH in the acidic range, in digesters D3 and D4 is due to IFL. Similar is the trend of TVFA. The highest TVFA was formed in the first week of digestion in digesters D1 to D4 but the maximum TVFA (375Ø mg/litre) was formed in digester D4 having 25 percent BP and 75 percent IFL. After first week of digestion period, there is a continuous decrease in TVFA formation upto eighth week. In case of digester D5 having effluent slurry only, TVFA was maximum at the time of start up of the experiment and thereafter it monotonously decreases. TVFA concentration above 2,ØØØ mg/litre causes a decrease in methane producing bacteria regardless of pH maintained. According to Buswell and Hatfield [17] there will be no benefit of increasing the pH and the toxicity of TVFA can only be reduced by dilution or decreasing the organic loading rate if the digester is of continuous or semi-continuous type. Later, it was proved by McCarty and Mckinney [84] that TVFA concentration upto 1Ø,ØØØ mg/litre can be successfully neutralized, with no inhibition effect on methane forming bacteria with the use of calcium or magnesium hydroxide but not by sodium, potassium or ammonium hydroxide.

The gas production rate per week remains higher in digesters D1 and D2 in second week of digestion period compared to other digesters, thereafter, there is a decrease in gas production rate; while in digesters D3 and D4, gas production was maximum in third and second week, respectively. In digesters D3 and D4, the gas production rate does not increases or decreases sharply as in the case of D1 and D2. In the first four weeks of digestion period, the digesters D1, D2, D3, D4 and D5 produced 81.02 percent, 80.30 percent, 66.87 percent, 60.00 percent and 80.40 percent of total gas production capacity, respectively. Hundred percent IFL seeded with effluent slurry and under almost similar experimental conditions gave 405 litres of biogas/kg of dry matter [113].

4.3 pH AND TOTAL VOLATILE FATTY ACIDS

4.3.1 General

In section 4.1 it has been observed that some digesters failed to produce biogas and some digesters showed a sharp decline in gas production. This was found to be due to drop in pH and the presence of very high TVFA concentration. In order to understand the behaviour of different digesters run on blended biomass materials with different percentages, the pH and TVFA concentration of the substrate were monitored every week. These are given in Table 4.3.1 and 4.3.2, respectively.

A glance at Table 4.3.1 shows that for CD fed digester D1 and the digesters having upto 50% blending ratio of residue with CD, pH varied between 5.33 to 7.25. Only in the case of IFPS, IFL and ML fed digesters, the pH fell below 6.0 during the first week of digestion. However, pH value quickly recovered as the acids formed were converted by methane formers to biogas. The digesters fed with other residues showed slight fall in the value of pH in first two weeks and then showed a steady increase. However, in the case of IFPS fed digesters D4 and D5, pH fell sharply to a value less than 5.0 and its recovery was very slow. Even after eight weeks of digestion, pH values recorded were 5.96 and 4.85, respectively for digesters D4 and D5. In the case of IFL fed digester D4, after the sudden slump in pH value (5.45) in the first week, slow recovery in pH was noticed and after six

TABLE 4.3.1 CHANGE IN pH IN DIFFERENT DIGESTERS

Biomass materials	Digester No.	Initial	No. of weeks 1	2	3	4	5	6	7	8
Cattle dung (CD)	D1	6.98	6.91	6.95	7.00	7.03	7.05	7.00	7.03	6.98
<u>Ipomoea fistulosa</u> plant stem (IFPS)	D2	6.97	6.80	6.51	6.37	6.62	6.77	6.88	7.03	7.11
	D3	6.99	5.33	6.40	6.77	6.75	6.82	6.85	6.83	6.88
	D4	6.96	4.90	4.82	4.88	5.06	5.21	5.54	5.88	5.96
	D5	6.95	4.95	4.86	4.85	4.87	4.85	4.88	4.90	4.85
<u>Ipomoea fistulosa</u> leaves (IFL)	D2	6.98	6.59	6.48	6.70	6.77	6.82	6.77	7.05	7.10
	D3	6.99	5.65	6.42	6.80	6.92	6.95	6.85	7.00	7.05
	D4	6.98	5.45	5.48	5.79	6.05	6.25	6.50	6.71	6.83
	D5	7.00	4.86	4.82	4.98	5.02	4.98	5.08	5.12	5.10
<u>Mirabilis</u> leaves (ML)	D2	7.03	5.95	6.95	6.95	7.00	6.98	6.99	7.00	7.03
	D3	7.00	5.85	6.92	6.90	7.03	7.00	7.03	6.97	6.99
	D4	7.00	5.55	6.85	6.83	7.00	7.05	7.08	7.05	7.04
	D5	6.95	5.40	6.70	6.80	7.10	7.10	7.18	7.10	7.06
Banana peelings (BP)	D2	6.98	7.02	7.08	7.12	7.06	7.08	7.03	7.08	7.05
	D3	7.00	7.10	7.25	7.22	7.20	7.10	7.05	7.10	7.08
	D4	7.01	7.15	7.28	7.25	7.15	7.08	7.12	7.17	7.10
	D5	7.05	7.40	7.65	7.60	7.52	7.25	7.30	7.22	7.25

TABLE 4.3.1 CONTD.

Rice straw (RS)	D2	7.00	6.75	6.72	6.85	6.95	7.01	7.08	7.10	7.05
	D3	6.97	6.82	6.85	6.90	6.98	7.03	7.05	7.10	7.10
	D4	7.00	6.90	6.98	7.00	7.10	7.10	7.13	7.15	7.13
	D5	7.07	7.00	7.05	7.10	7.18	7.15	7.22	7.32	7.40
Wheat straw (WS)	D2	7.01	6.68	6.78	6.92	7.00	7.05	7.08	7.10	7.10
	D3	7.02	6.60	6.65	6.88	6.98	7.08	7.15	7.12	7.15
	D4	7.00	6.50	6.45	6.65	6.80	6.95	7.15	7.13	7.18
	D5	7.03	6.40	6.25	6.45	6.80	6.98	7.11	7.17	7.20
Dhub grass (DG)	D2	7.00	6.50	6.45	6.72	6.85	6.95	6.98	6.95	6.95
	D3	7.01	6.18	6.15	6.25	6.45	6.90	6.85	6.92	6.87
	D4	6.98	6.00	6.05	6.10	6.32	6.60	6.70	6.65	6.75
	D5	7.02	5.95	5.75	5.70	5.80	5.90	6.09	6.22	6.35
Cauliflower leaves (CFL)	D2	6.95	7.30	7.21	7.18	7.15	7.20	7.14	7.17	7.19
	D3	6.92	6.13	7.24	7.25	7.21	7.22	7.18	7.15	7.20
	D4	6.90	5.79	5.85	6.71	6.85	7.06	7.13	7.08	7.05
	D5	6.89	5.80	5.81	5.90	6.00	5.95	5.91	6.00	6.03

TABLE 4.3.2 CHANGE IN TVFA CONCENTRATION IN DIFFERENT DIGESTERS (mg/l as acetic acid)

Biomass materials	Digester No.	Initial	1	2	3	4	5	6	7	8
			No. of weeks							
Cattle dung (CD)	D1	300	1300	750	650	500	425	375	400	350
<u>Ipomoea fistulosa</u> plant stem (IFPS)	D2	310	1280	585	515	490	525	540	590	440
	D3	340	2160	815	750	710	650	600	435	445
	D4	335	2410	3280	3500	3580	3600	3565	3590	3625
	D5	400	2600	3450	3700	3700	3750	3600	3680	3760
<u>Ipomoea fistulosa</u> leaves (IFL)	D2	320	1200	810	670	600	550	500	460	435
	D3	320	2500	1100	650	610	600	580	550	510
	D4	325	3150	2800	2100	1340	800	700	650	610
	D5	350	4700	4600	4650	4400	4500	4550	4450	4600
<u>Mirabilis</u> leaves (ML)	D2	410	1765	890	640	515	480	450	435	420
	D3	435	2440	1060	785	680	510	440	450	435
	D4	460	3150	1310	810	670	625	490	455	430
	D5	500	3600	3000	2200	1700	1300	1000	800	610
Banana peelings (BP)	D2	405	1365	618	505	480	465	430	350	315
	D3	412	1550	700	550	510	450	415	360	318
	D4	410	1985	715	565	490	435	410	340	310
	D5	450	2500	1400	800	500	350	400	380	350

TABLE 4.3.2 CONTD.

Rice straw	D2	345	1390	685	490	445	365	330	355	345
(RS)	D3	380	1445	730	515	480	395	350	345	335
	D4	425	1740	1050	775	590	510	460	415	410
	D5	500	2200	1800	1500	1100	800	600	500	450
Wheat straw	D2	315	1440	875	630	560	530	545	490	405
(WS)	D3	355	1850	1350	1090	710	545	530	500	490
	D4	370	2540	1665	1425	1015	570	550	515	465
	D5	400	3200	2700	2200	1400	900	650	535	500
Dhub grass	D2	310	1750	1465	1150	615	625	590	570	575
(DG)	D3	310	1985	1610	1225	885	680	665	630	615
	D4	325	2610	2100	1440	1115	1050	1030	1110	995
	D5	330	2900	3800	3500	3700	2900	1800	1400	1500
Cauliflower leaves	D2	760	1960	785	750	615	550	565	490	415
	D3	775	4500	3650	3465	2840	2115	1340	965	635
(CFL)	D4	795	5730	4365	4490	4240	3360	2550	1710	860
	D5	810	7000	6720	6600	6680	6475	6490	6550	6505

weeks onwards, pH level increased from 6.5 to 6.83. However, for D5, pH level remained between 4.86 to 5.10 during the entire eight week digestion period.

In the case of CFL fed digester D4, there was a sudden fall in pH during the first week to a value of 5.79 and remained almost at the same level during the second week but recovered from third week onwards from 6.71 to 7.05, after eight weeks. Digester D5, however, remained at low pH between 5.8 and 6.0 through the digestion period. In the case of ML, pH dropped to a value below 6.0 during the first week but recovered from second week onwards. In the case of BP, pH never fell below 7.0 and remained at around the same level throughout the digestion. However, it was further noticed that with increase in BP content in digester D2 to D5, pH increased continously, e.g., after the second week, pH values recorded were 7.08 for digester D2, 7.25 for D3, 7.28 for D4 and 7.65 for D5. Similar trends were observed for other weeks as well.

In the RS fed digesters, pH never fell below 6.75 and maintained the similar trend as observed for BP digesters, whereas for WS, pH showed an increasing trend with the time of digestion after the initial slump in the first week and showed a reverse trend of decreasing pH with increase in WS content in the digesters, e.g., after third week the pH observed in digester D2 and D5 were 6.92 and 6.45, respectively. This is in sharp contrast to the observations made in the case of BP and RS. For DG, the slump in pH values were steeper as compared to WS, however, a similar trend of decreasing pH with increasing DG content was observed.

Table 4.3.2 gives the pattern of change in TVFA concentration in different digesters for different residues blended with CD in varying proportions. A good digester should not have accumulated TVFA concentration beyond 1500 mg/l. As it was seen from Table 4.1.1 of section 4.1, the weekly biogas production was found to be maximum in the first two weeks of digestion. During these two weeks, the active digesters never had more than 2500 mg/l of TVFA (as acetic acid). At these levels pH varied between 5.4 to 6.8, however, as reported earlier, pH level varied for different feed materials as TVFA concentration varied. It may be noted that under these conditions the digesters produced biogas at a very good rate as given in Table 4.1.1 of section 4.1. However, some of the digesters showed recovery after certain period when TVFA concentration decreased to a value below 1000 mg/l. The methane production taking place at low pH and high TVFA may be adduced to methanogenesis taking place in the wall growth region. This generates alkalinity, which adjusts pH with time. It was found that this adjustment of pH makes the recovery of biogas production possible in the digester D4 of IFL and CFL which had failed earlier.

Plots of pH, TVFA concentration and gas production against number of weeks were made in order to have a clearer picture of relationships between TVFA concentration, pH and gas production, for the digesters D3 and D5 for IFPS, D4 and D5 for IFL, D5 for BP and D4 and D5 for CFL. Figure 4.3.1 is for IFPS, 4.3.2 for IFL, 4.3.3 for CFL and 4.3.4 for BP. It may be seen from Figure

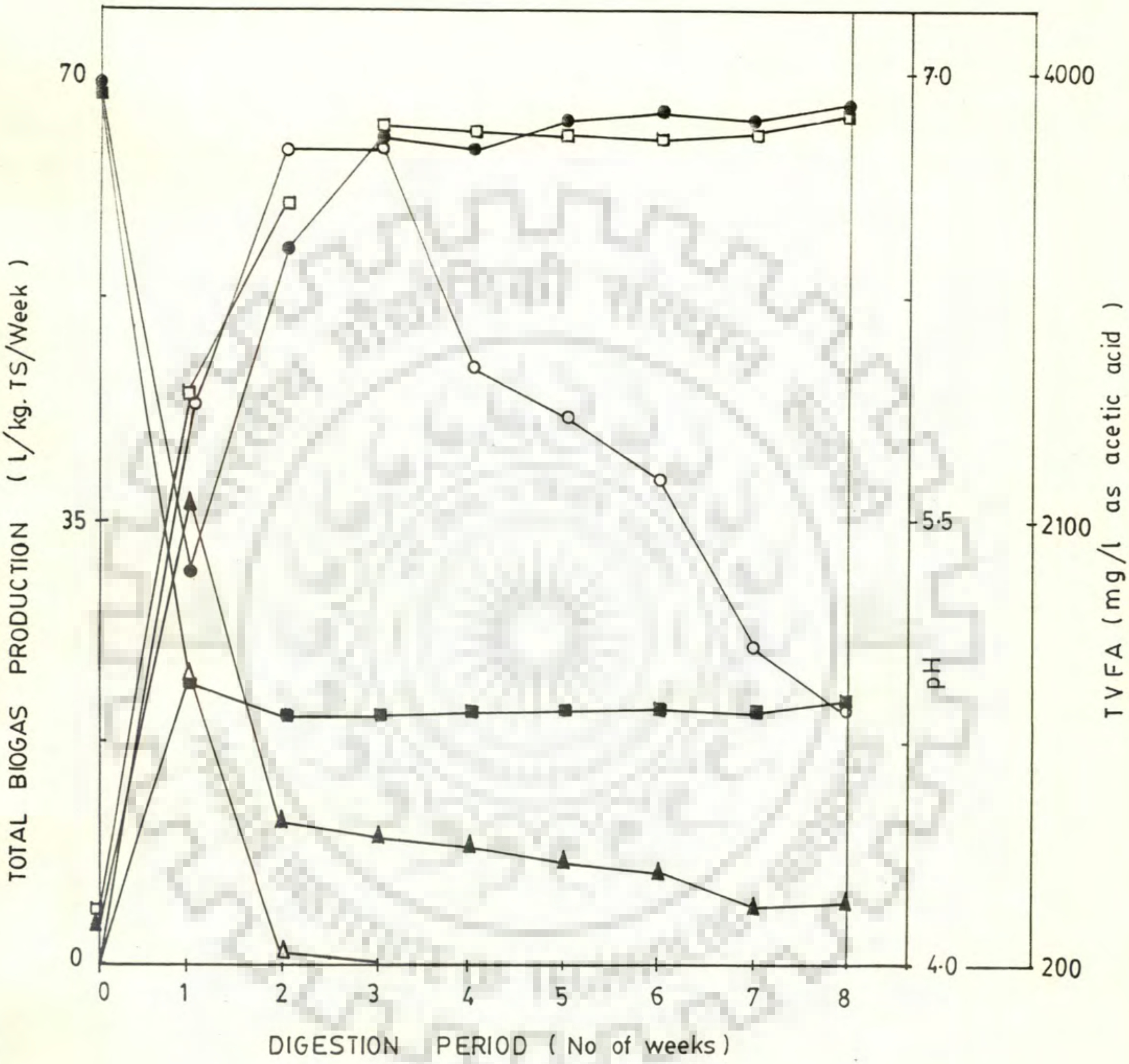


FIG.-4·3·1- ANAEROBIC DIGESTION OF IFPS
DIGESTER, D3 ; ○, TOTAL GAS PRODUCTION ; ●, pH ; ▲, TVFA ; DIGESTER D5; △, TOTAL GAS PRODUCTION ; ■, pH ; □, TVFA .

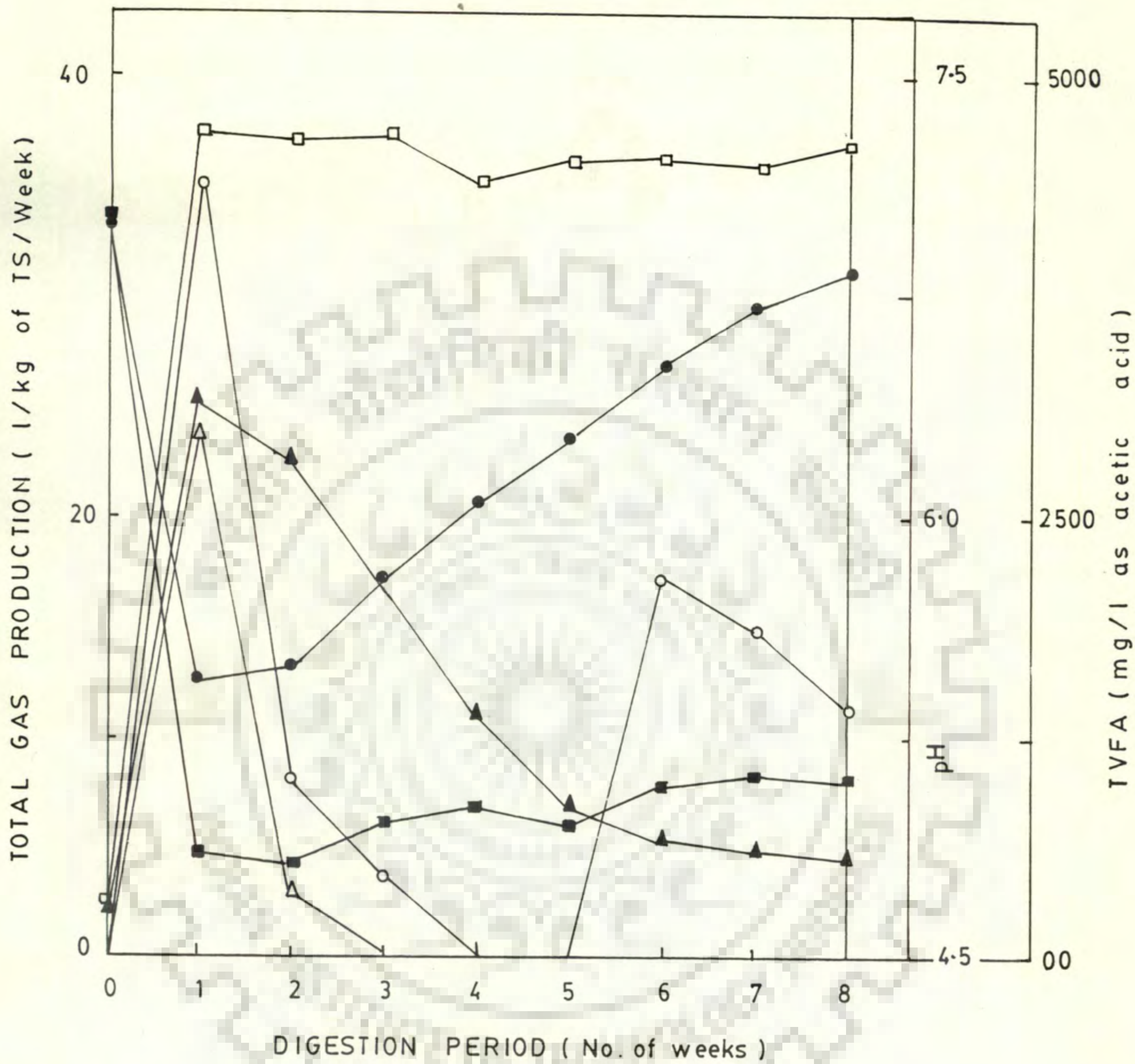


FIG. 4·3·2 ANAEROBIC DIGESTION OF IFL
DIGESTER D4. ○, TOTAL GAS PRODUCTION, ●, pH; ▲, TVFA.
DIGESTER D 5. △, TOTAL GAS PRODUCTION; ■, pH;
□, TVFA.

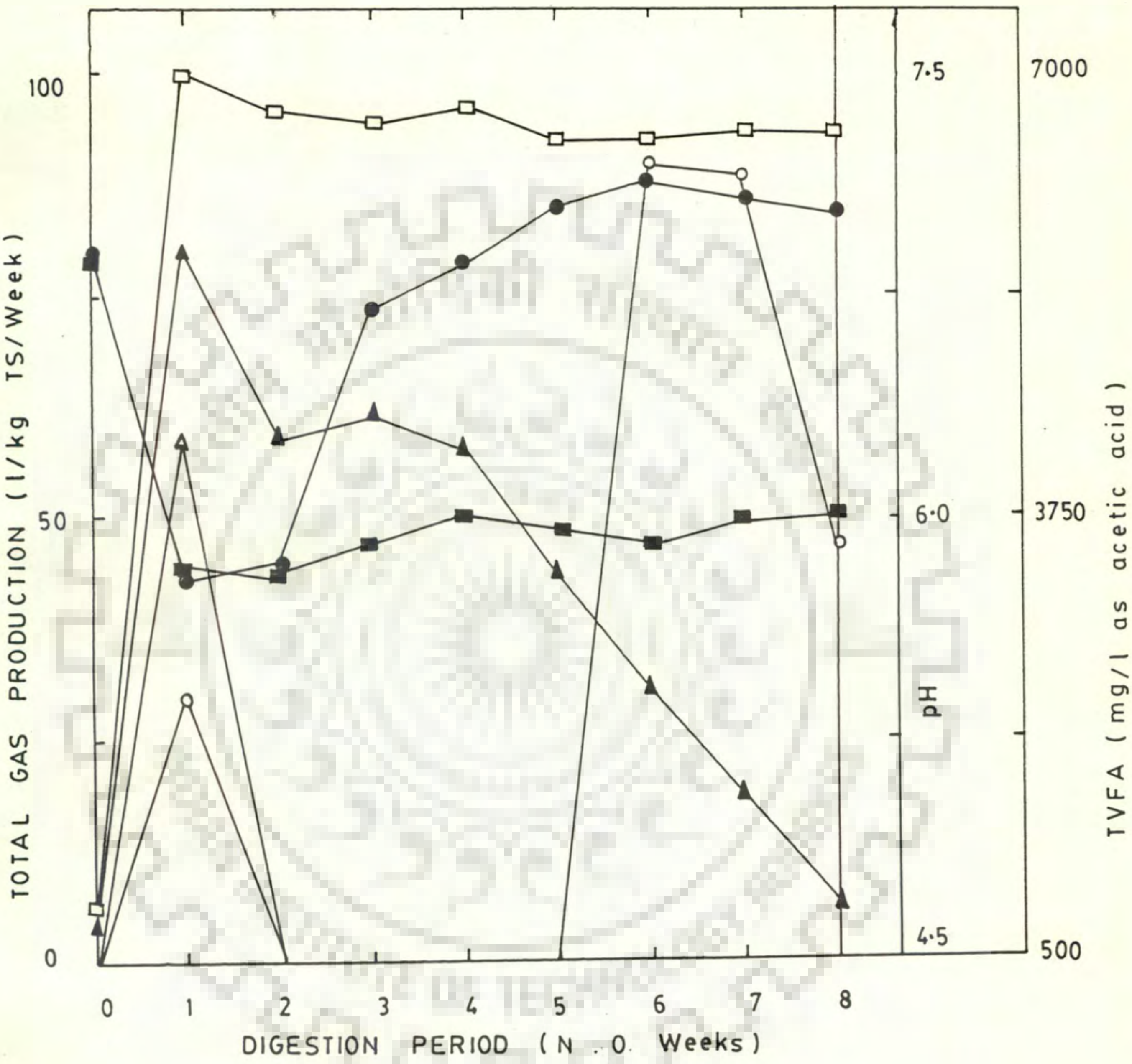


FIG. 4·3·3– ANAEROBIC DIGESTION OF CFL
DIGESTER D4, ○, TOTAL GAS PRODUCTION; ●. pH; ▲, TVFA
DIGESTER D5. △, TOTAL GAS PRODUCTION; ■, pH, □, TVFA

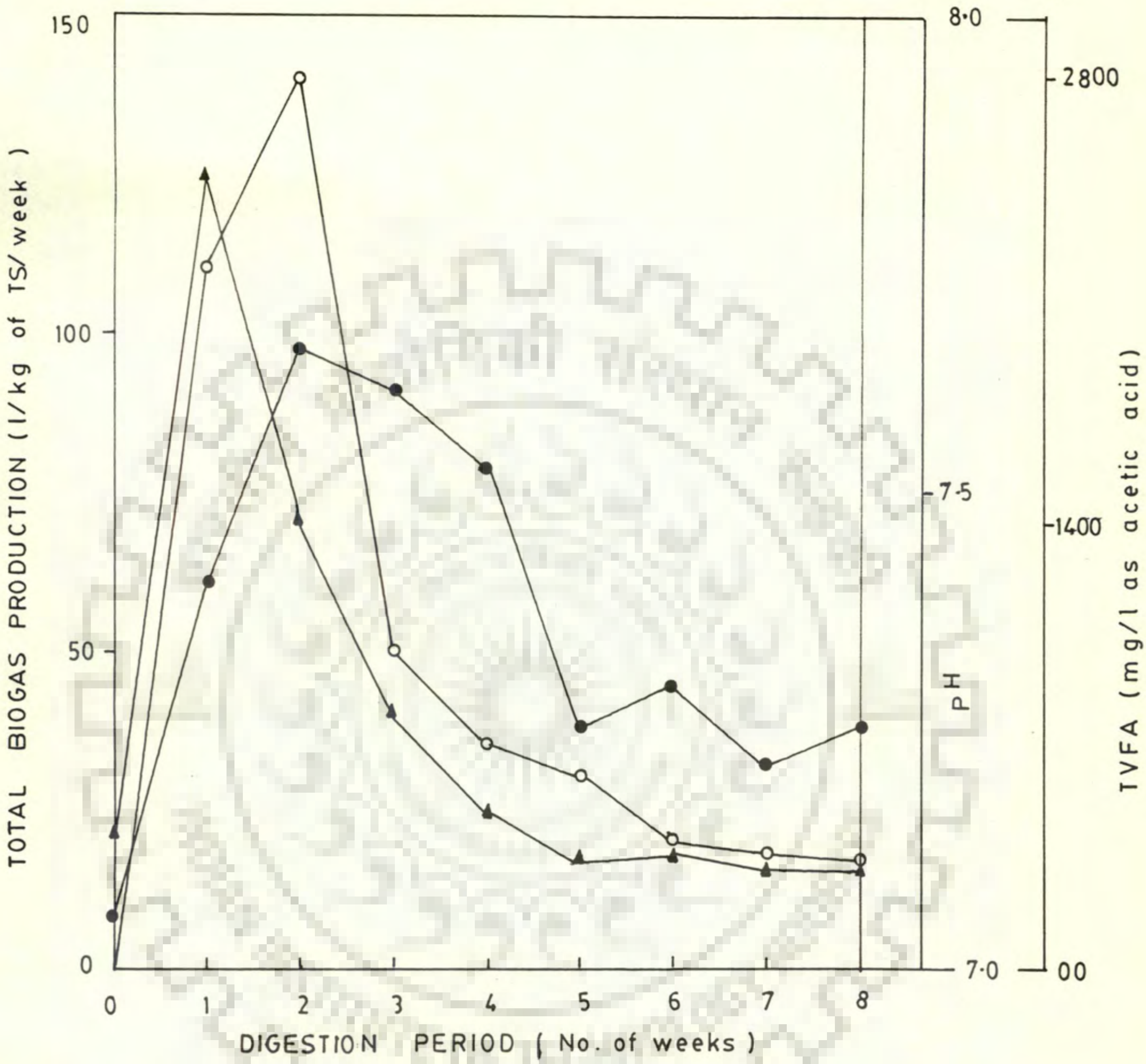


FIG. 4·3·4 - ANAEROBIC DIGESTION OF BANANA PEELINGS DIGESTER D5; ○, TOTAL GAS PRODUCTION; ●, pH, ▲, TVFA.

4.3.1, that while for digester D3 with 50% IFPS there is a sudden slump in pH, TVFA rose to 2160 mg/l and then pH showed an increase while TVFA declined. During this period it was found that gas production increased upto second week, remained almost constant in third week and started decreasing with increase in pH and decrease in TVFA concentration. It may be mentioned here that with the sharp decline in pH from 6.99 to 5.33 and increase in TVFA concentration from 340 to 2160 mg/l, the gas production did not decrease but instead showed steep increase. This may be attributed to the fact that hydrolysis and acid formation is accompanied by methanogenesis even at very low pH for about a week. It seems that if the pH remains at such low level for a period larger than a week, methane formers lose their activity. This could be verified from the plots of performance of digesters D5, where pH decrease was even steeper during the first week (pH=4.95) and TVFA concentration rose to a higher value of 2600 mg/l but still gas formation was observed, though almost at a rate of about 50% in comparison to that of digester D3. However, due to non-recovery of pH which further slumped to a value of 4.86, along with further increase in TVFA to 3450 mg/l, the gas production almost stopped after the second week. Similar trends are observed from Figure 4.3.2 for 75% and 100% IFL fed digesters D4 and D5, respectively. In both the cases the digesters failed to produce gas after first week. However, a remarkable feature of recovery in the case of D4 is observed where the digester remained almost dead for gas production for two weeks but started production during the sixth week with pH recovery to 6.50 and TVFA concentration down to 700 mg/l. From the plot for digester D4, it may also be discerned that no gas was produced below a pH of 6.25 and TVFA concentration greater than 800 mg/l. However, the recovery in gas production is found to be too low (17 l/kg of TS) and after sixth week gas production decreased. When this is compared with plot for CFL in Figure 4.3.3, it is found that digester D4 shows a phenomenal recovery in gas production in sixth week giving as high as 90 l/kg TS/week at a pH of 7.13 and TVFA concentration of 2550 mg/l. However, after seventh week the gas production falls down though pH remains in the vicinity of 7.05 and TVFA decreases to a level less that 1000 mg/l. However, digester D5 does not register a recovery. Figure 4.3.4 presents the plot for digester D5 for BP. Here this case shows a peculiar behaviour where TVFA decreases after the first week from 2500 to 1400 mg/l, pH increases from 7.40 to 7.65, but gas production increases from 110 to 140 l/kg TS/week. Thereafter pH shows a decreasing trend with decrease in TVFA concentration and gas production slumps sharply during the third week to a level of 50 l/kg TS. This seems to be strange for the pH and TVFA concentrations are within the range of optimum gas production.

4.3.2 Controlled Experiments:

In view of the above, it was decided to carry out some experiments on biogas production with 100% residues under controlled pH conditions. Calcium hydroxide slurry was used to control pH in the range of 6.75 to 7.25. The results of weekly biogas production rate for digester D5 operated for all the feed materials is given in Table 4.3.3. When compared with results of Table 4.1.1 of section 4.1, it is found that pH control has profound effect on biogas production; whereas IFPS, IFL and CFL fed digesters (D5) had failed under uncontrolled conditions, these produced 484, 507, and 520 l/kg TS of biogas, respectively, under controlled conditions. However, in the case of ML, BP, RS, WS and DG fed digesters, the increase in total biogas production under controlled conditions was found to be unattractive.

It was noticed that in all the cases, pH fell within the first two days of digestion. The pH of the digester was checked every day at 8.00 A.M. in the morning and 6.00 P.M. in the evening and whenever pH was found to be less than 6.75, calcium hydroxide slurry was added in order to mantain pH between 6.75 to 7.25. The quantity of $Ca(OH)_2$ varied for the different digesters.

Figure 4.3.5 presents the comparison of weekly gas production rates with and without pH control for 100% IFPS, IFL and CFL fed digesters, D5. These digesters had failed in the uncontrolled experimentation. However, pH control during the first four days of digestion drastically enhanced the gas production pattern of these digesters. It was found that the digesters produced more than 67% of gas only in the first four weeks. Figure 4.3.6 shows the weekly gas production pattern for controlled and uncontrolled digesters of BP. In this case pH fell sharply during the first two days, thereafter, registering pH values more than 7.0. Therefore, $Ca(OH)_2$ slurry was added on the

TABLE 4.3.3 WEEKLY BIOGAS PRODUCTION RATE (l/kg TS)

Feedstocks 100%	No. of weeks 1	2	3	4	5	6	7	8	Total gas production Controlled digesters	Uncontrolled digesters
CD	35	62	45	22	16	13	8	9	210	200
IFPS	109	100	98	42	35	33	33	34	484	24
IFL	135	125	105	75	28	20	11	8	507	27
ML	120	108	82	47	28	15	10	10	420	400
BP	125	141	82	45	38	13	9	7	460	420
RS	138	121	96	51	25	29	13	12	485	455
WS	130	80	54	35	22	16	13	10	360	325
DG	63	48	40	36	32	28	19	14	280	235
CFL	95	123	122	90	48	20	14	8	520	50

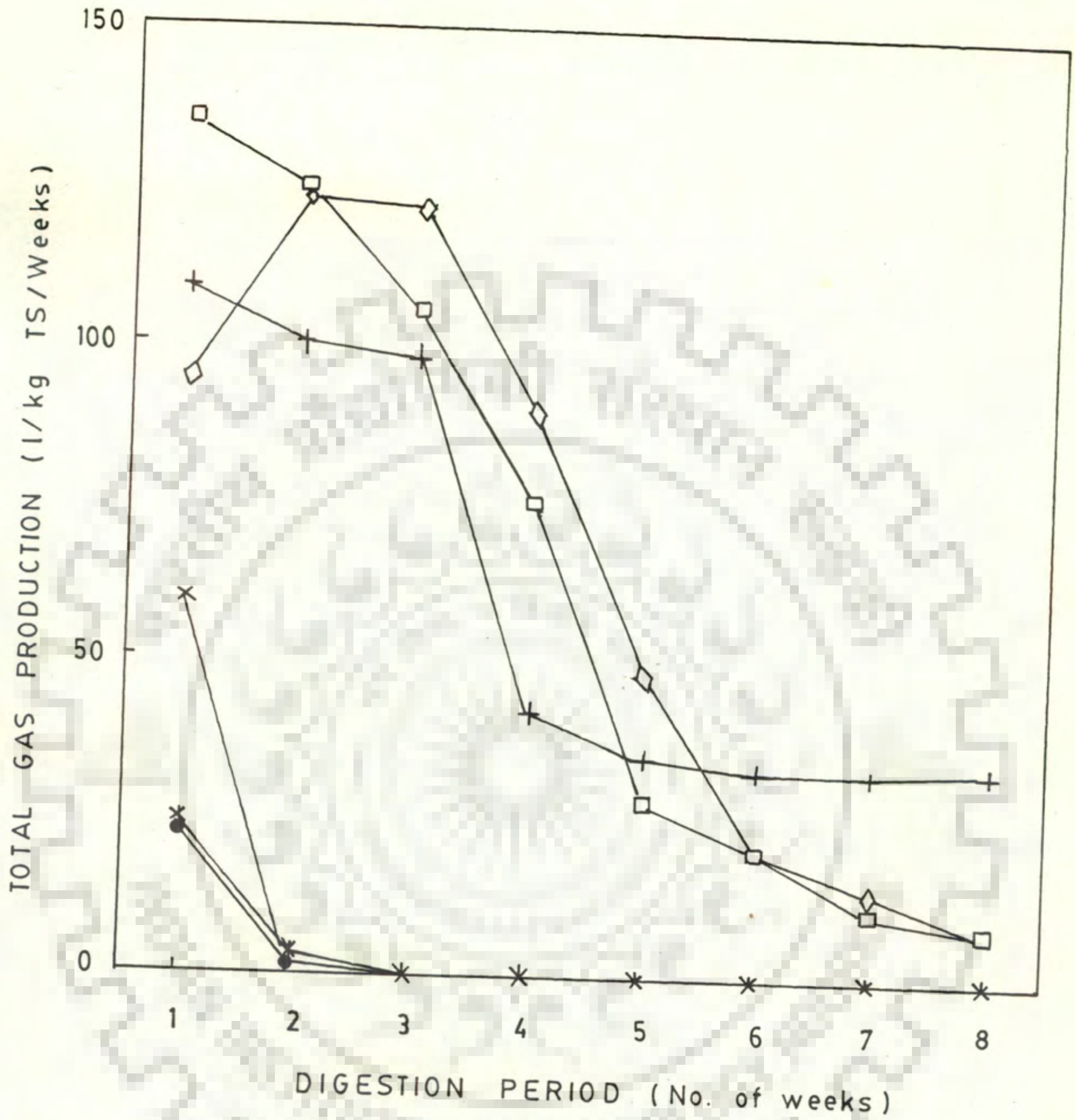


FIG. 4·3·5 ANAEROBIC DIGESTION OF DIFFERENT MATERIALS

pH, UNCONTROLLED •, IFPS; ⁎, IFL; X, CFL.

pH, CONTROLLED +, IFPS, □, IFL, ◊ CFL.

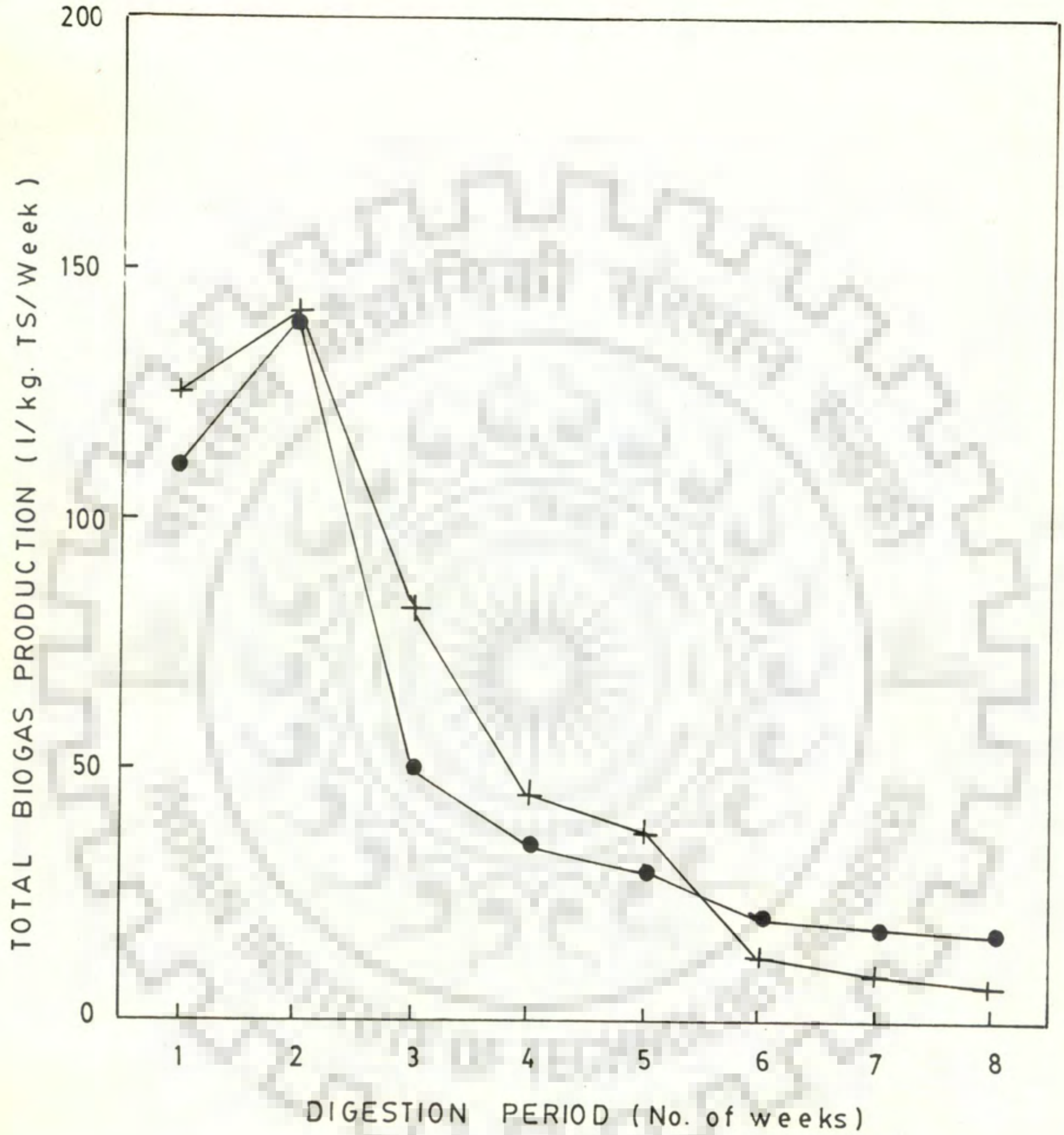


FIG. 4·3·6 – ANAEROBIC DIGESTION OF BP
●, pH UNCONTROLLED; +, pH CONTROLLED

first and second day of the digestion to maintain its pH at 7.0. This increased the gas production rate from 110 to 125 l/kg TS during the first week but reached the same level of 140 l/kg TS during the second week as in the case where pH was not controlled. However, during third to fifth week, digester with controlled conditions produced higher volume of gas as compared to the one which is uncontrolled. After the fifth week, the controlled digester showed decreasing gas production in comparison to uncontrolled digester. However, it may be seen from Table 4.1.1 of section 4.1 that in five weeks the total gas produced in the controlled digester is 431 l/kg TS as compared to 365 l/kg TS for uncontrolled digester. It was also found that in the five weeks gas production of controlled digester is 11 litre more as compared to total eight weeks production of 420 l/kg TS of biogas in uncontrolled digester. This means that with reduced HRT under controlled conditions BP gives higher gas production as compared to that given by uncontrolled digester with higher HRT. This means reduction in volume of digester and consequent cost of construction.

Table 4.3.3 gives the weekly biogas production rate under controlled conditions for 100% residue fed digesters D5. It also compares the total gas production for the controlled digesters with the uncontrolled digesters. It is apparent from this table that under controlled conditions weekly gas production decreases with the digestion period. The last column of this table shows that under controlled conditions 100% CFL produces the highest amount of gas (520 l/kg TS) whereas under uncontrolled conditions the digester had produced only 59 litre of gas and had failed. In the decreasing order of gas production it is found that CFL is followed by IFL, RS, IFPS, BP, ML, WS, DG & CD. Table 4.3.4 presents the percentage reduction of cellulose total solids and volatile solids for all of the digesters D5 with all the feed stocks. It may be seen that CFL has highest cellulose, total solids and volatile solids reduction followed by IFL and RS. Minimum cellulose reduction takes place in the case of DG followed by CD, IFPS, WS & ML. Similar trend is obtained in the case of total solids reduction. The analysis of gas produced from different feed stock showed that BP had highest methane content followed by ML, DG, CFL, IFPS, RS and CD. Gas from WS had minimum methane. In terms of total methane production, IFL produces highest quantity of methane (360 l/kg TS) followed by CFL, BP, IFPS, ML, RS, WS, DG and CD. In comparison to CD, IFL produced 285.7% more methane.

For smooth functioning of anaerobic digester the pH of the substrate should be almost neutral [28, 40]. At low pH, methanogenic bacteria remain viable, thereby, increasing the concentration of TVFA in the substrate. This is the situation witnessed in digesters D4 and D5. In uncontrolled digesters, TVFA concentrations increase and thus the bicarbonate alkalinity decreases according to the following equation.

$$HCO_3^- + CH_3COOH = H_2O + CO_2 + CH_3COO^-$$

Release of ammonia from nitrogeneous compounds during anaerobic digestion, also causes decrease in pH. Due to low pH and high TVFA concentrations and subsequent inhibition of

TABLE 4.3.4 PERFORMANCE OF DIGESTERS (DRY WEIGHT BASIS)

Feedstocks 100%	Cellulose reduction %	Total solids reduction %	Volatile solids reduction %	Methane percentage	Total methane production (l/kg TS)
CD	28.0	21.3	24.2	60	126
IFPS	34.2	36.3	50.5	66	319
IFL	46.1	39.5	55.0	71	360
ML	38.1	33.3	45.5	69	290
BP	40.8	36.1	51.3	73	336
RS	44.9	40.0	55.8	60	291
WS	36.1	30.0	38.4	59	212
DG	25.3	21.0	30.0	69	193
CFL	46.6	40.8	57.5	67	348

methanogenesis, digesters D4 and D5 failed. Thus control of pH and TVFA is very essential for efficient operation of the biogas plant.

TVFA concentrations upto 10.0 g/litre can be successfully neutralized by use of calcium or magnesium hydroxide without any evidence of inhibitory effect on methanogenesis [84]. The cellulose hydrolysis rate depends on substrate and bacterial concentration and also on operating parameters such as temperature, pH, etc. Lignin is the main constituent which protects cellulose from enzymatic hydrolysis [10, 50, 82]. In mixed cultures of sewage sludge, the maximum rate of cellulose hydrolysis is found at a pH value of 7.5, while rumen microflora usually have maxima in more acidic conditions [111].

4.4 EFFECT OF PARTICLE SIZE ON BIOGAS GENERATION FROM BIOMASS RESIDUES

4.4.1 General

One of the major problems in utilizing biomass materials for biogas generation is their low digestibility. Biodegradability or digestibility can be increased by physical, chemical and high temperature pretreatment. In physical treatment, size reduction and preincubation with water have been found to be attractive [119]. The beneficial effect of size reduction on digestion has been reported by Datta [30] and Jerger et al., [67].

In the present work several digesters were used with different sizes of different biomass materials to estimate the effect of particle size on the digestibility and biogas production rate. Details of digesters, raw material and particle sizes are given below:

Set I. Digester A1, A2, A3 and A4 were fed with WS of particle size 0.088, 0.40, 1.0 and 6.0 mm, respectively, whereas digester A5 received WS of size approximately 30 x 5 mm (length x diameter).

Set II. Digesters B1, B2, B3, B4 and B5 were similar to set I but the material was RS instead of WS.

Set III. ML of particle size 0.088, 0.40, 1.0 and 6.0 mm were fed to digesters C1, C2, C3 and C4, respectively. Digester C5 received unshredded leaves of size approximately

80 x 50 mm (length x width).

Set IV. Digesters D1, D2, D3 and D4 were fed with CFL of particle size 0.088, 0.40, 1.0 and 6.0 mm while unshredded leaves of approximately 150 x 100 mm (length x width) were fed to the fifth digester D5.

Set V. Digesters E1, E2, E3, E4 and E5 were fed with IFL of similar particle size as that of set IV digesters.

Set VI. DG of particle size 0.088, 0.40, 1.0 and 6.0 mm were fed to digesters F1, F2, F3 and F4, respectively. Long clippings (30 mm) of DG were anaerobically digested in digester F5.

Set VII. Digesters G1, G2, G3 and G4 received BP of particle size 0.088, 0.40, 1.0 and 6.0 mm, respectively, whereas digester G5 was fed with unshredded BP of 30 x 10 mm (length x width).

4.4.2 Characteristics of Raw Materials:

Characterization of all raw materials as presented in Table 3.1 of chapter III, showed that volatile solids were above 80% in most of the materials. CFL had the highest quantity of protein (24.7%, w/w) whereas BP was the richest in cellulose content with a value of 61.4%, among all the raw materials. Lignin was found to be low in all raw materials excepting ML and IFL. Lignin/cellulose ratio, normally used to represent the degree of digestibility of raw materials, was found to be the highest (0.448) in IFL followed by ML (0.390) whereas rest of the raw materials had the values less than Ø.33Ø. Ethanol-benzene-hot water solubility was found to be the highest for IFL followed by ML, CFL and BP, while for other raw materials, the solubility was very low.

4.4.3 Performance of Digesters:

The average rate per week of biogas production (average of duplicate digesters for each particle size and each feedstock) and total biogas production have been shown in (Table 4.4.1 and Fig.4.4.1). It can be seen that for all the biomass materials, the values of these parameters increased with decreasing particle size. As the feedstock used in duplicate digesters for each particle remained the same and similar operating conditions were maintained during the digestion period, the biogas production rates were almost same, giving maximum standard deviation of ± 6.65 %.

For the fifth digester of each feedstock having the largest particle dimensions, the gas production rate was lower in the first two weeks, reached its maximum value in 3rd, 4th or 5th week depending on the feedstock and then decreased thereafter. In case of WS, RS, ML and IFL, the gas production for the digesters with particle sizes of Ø.Ø88, Ø.4Ø, 1.Ø and 6.Ø mm was higher in the first week only; thereafter it decreased. For BP and CFL highest production rate was noticed in the second week. For DG in digesters F4 and F5, there were sudden fluctuations in gas production. Digesters F1, F2 and F3 fed with finely ground

TABLE 4.4.1. RATE OF BIOGAS PRODUCTION (l/kg OF TS)

Feed stock	Particle size (mm)	Digester No.	No. of weeks Ist	IInd	IIIrd	IVth	Vth	VIth	VIIth	VIIIth	Total
Wheat straw	0.088	A1	128	84	48	40	22	14	14	12	362 ± 1.41
	0.40	A2	130	80	54	35	22	16	13	10	360 ± 0.28
	1.0	A3	122	79	45	30	25	18	16	15	350 ± 0.42
	6.0	A4	115	66	35	36	24	20	18	16	330 ± 1.70
	30x5	A5	33	22	38	50	25	20	22	25	235 ± 4.24
Rice straw	0.088	B1	142	118	105	45	30	24	13	6	483 ± 0.70
	0.40	B2	138	121	98	51	25	29	13	12	487 ± 0.14
	1.0	B3	135	115	90	55	28	17	20	15	475 ± 2.82
	6.0	B4	122	110	80	45	40	34	17	12	460 ± 1.98
	30x5	B5	48	20	31	57	62	40	32	30	320 ± 4.95
Mirabilis leaves	0.088	C1	122	113	78	50	25	13	7	7	415 ± 2.54
	0.40	C2	120	108	82	47	28	15	10	8	418 ± 0.70
	1.0	C3	115	105	65	40	25	20	18	15	403 ± 0.84
	6.0	C4	108	95	75	48	28	17	16	13	400 ± 1.83
	80x50	C5	60	45	82	55	48	32	23	10	355 ± 4.24
Cauliflower leaves	0.088	D1	92	135	128	90	45	13	10	7	520 ± 0.42
	0.40	D2	95	123	122	90	48	20	14	8	520 ± 1.13
	1.0	D3	89	120	118	85	40	28	18	18	516 ± 0.70
	6.0	D4	77	125	113	76	57	21	18	13	500 ± 2.83
	150x100	D5	60	52	95	80	75	45	20	13	440 ± 2.82

TABLE 4.4.1 CONTD.

	0.088	E1	135	132	103	79	25	22	9	5	510 ± 1.84
Ipomoea fistulosa leaves	0.40	E2	135	125	105	75	28	20	11	8	507 ± 1.55
	1.0	E3	131	115	90	70	38	26	15	15	500 ± 5.66
	6.0	E4	120	126	82	60	32	34	18	18	490 ± 0.85
	150x100	E5	80	105	112	75	40	28	12	8	460 ±2.12
	0.088	F1	61	55	46	28	39	32	10	9	280 ± 5.37
Dhub grass	0.40	F2	63	48	40	36	32	28	19	16	282 ± 2.12
	1.0	F3	54	43	32	40	28	25	23	20	265 ± 6.64
	6.0	F4	45	20	18	65	20	40	15	30	253 ± 4.24
	30.0	F5	20	15	30	25	38	10	10	22	170 ± 3.67
	0.088	G1	129	152	85	32	25	15	11	9	458 ± 1.0
Banana peeling	0.40	G2	125	141	82	45	38	13	9	7	460 ± 2.69
	1.0	G3	114	130	70	49	45	18	11	8	445 ± 2.55
	6.0	G4	110	128	50	38	28	28	20	18	420 ± 5.23
	30x10	G5	58	48	105	30	18	20	15	11	305 ± 3.40

NOTE Total biogas is given along with ± standard deviation.

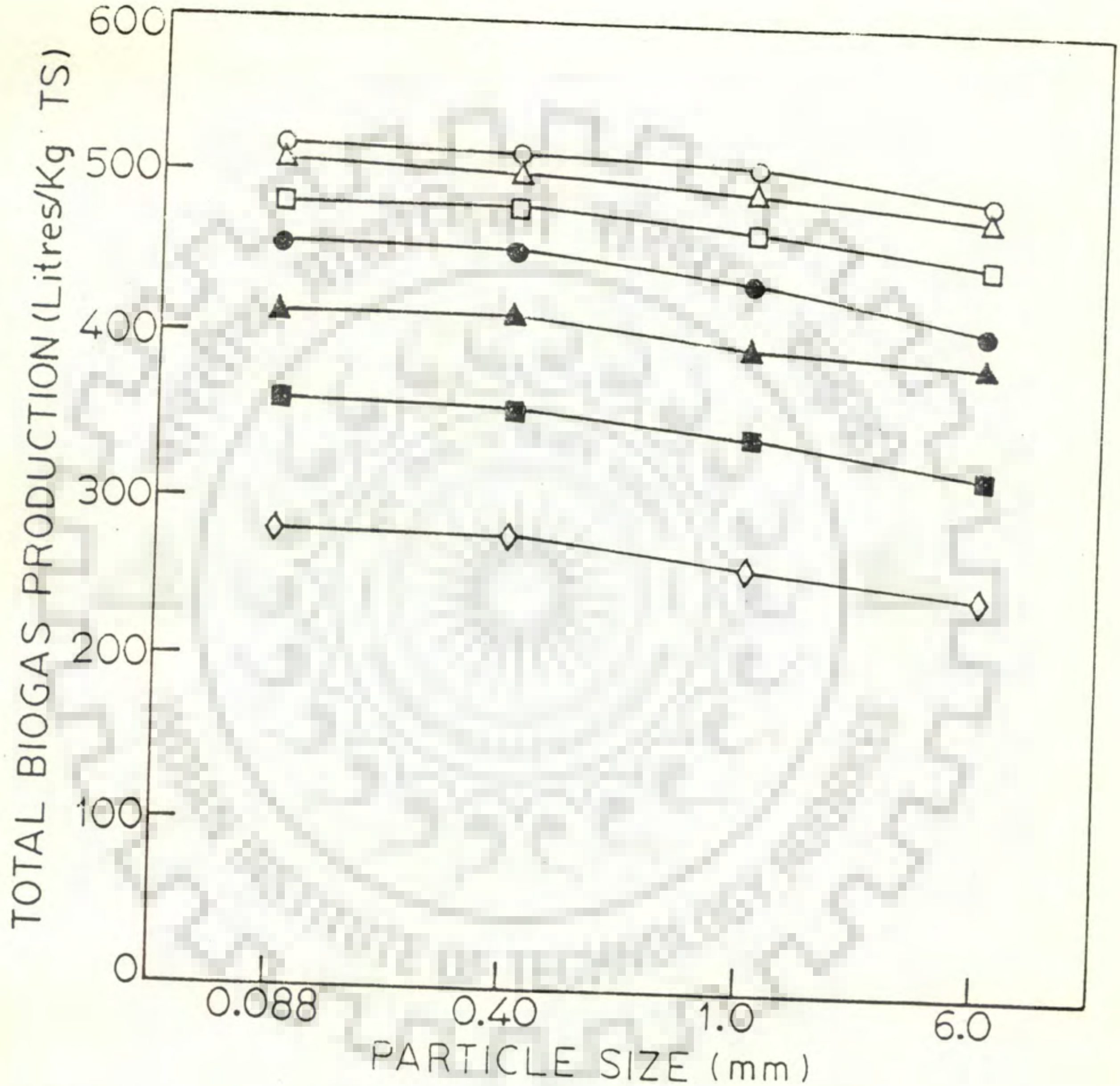


FIG. 4.4.1. TOTAL BIOGAS PRODUCTION VERSUS PARTICLE SIZE. ■, WHEAT STRAW; □, RICE STRAW; ▲, MIRABILIS LEAVES; O, CAULIFLOWER LEAVES; △, IPOMOEA FISTULOSA LEAVES; ◇, DHUB GRASS; ●, BANANA PEELINGS.

grass particles had almost uniform gas production with a difference of 65% in total gas production observed with particle sizes of 0.088 and 30.0 mm. For WS feedstock, digester A1 produced 54% more gas than A5, whereas in case of RS feedstock, digester B1 gave 51% more gas as compared to digester B5.

It may be pointed out that the cellulose in the ligno-cellulosic polymeric form is not totally available for bacterial attack. Lignin surrounds the cellulose crystalline structure forming a 'seal' and protects the cellulose from easy hydrolysis [87]. Lignin itself is very resistant to degradation by anaerobic digestion [14, 108]. Thus grinding, which results in small particle size and consequently high surface area for the cellulosic materials, enhanced the susceptibility of cellulose to bacterial and enzymatic attack, deformed the crystal lattice and reduced the degree of polymerization [51].

In the case of large particle size, especially for WS, RS, DG and BP, the material was solubilized in a longer time and also less surface area was available for bacterial degradation. Consequently there was less gas production. But for ML, CFL and IFL, the gas production was not seriously affected when unshredded leaves were used which may be either due to high protein content and succulent and non-fibrous nature of the feedstock or due to lower C/N ratio (<30). Optimum C/N ratio for methane production is in the vicinity of 30 [46]. The development of the methanogenic microflora is impaired if C/N ratio exceeds

50:1 [111]. Regardless of C/N ratio, many materials are found to be resistant to biodegradation [140]. This situation was observed in case of DG feedstock. The hydrolysis of ligno-celluloses is dependent on lignin to cellulose ratio and the digestibility of grasses is highly correlated with the lignin content [111].

The digesters run on particle size of 0.088 mm for feedstocks ML, CFL, IFL, and BP were found to produce, respectively, 16.9%, 18.2%, 10.9%, and 50.2% more biogas as compared to that with digesters run on largest particles of the respective feedstocks. Comparative analysis of total gas production for each particle size of each feedstock could be made from Fig.4.4.1. Since the fifth digester of each feedstock was run on particles of differing dimensions, these values are not shown in the figure. It is evident that biogas production was highest for CFL followed by IFL, RS, BP, ML, WS and DG, respectively. CFL produced almost 100% more gas than did DG.

Statistical analysis of the gas production rate (ANOVA) was carried out to examine if there was significant difference between the gas produced for each particle size in duplicate digesters as also among the particle sizes for each feedstock. It was found that for all the feedstocks, the calculated values of F at 5% and 1% significance level were very large as compared to tabulated F values. Thus, it can be discerned that the particle size has significant effect on gas production rate for each feedstock.

Reduction of cellulose, total solids and volatile solids was found to be lower for DG among all the seven materials and higher for RS, CFL and IFL (Table 4.4.2). In anaerobic digestion process, cellulolytic bacteria constitute a small fraction of total acidogenic population. Cellulose reduction increased with the decrease in particle size for each feedstock. The maximum increase in cellulose reduction between smallest and largest particle sizes was observed for RS (13.5%), followed by WS (11.6%), BP (8.5%), DG (7.9%), CFL (6.5%), ML (5.6%) and IFL (4.6%). Reduction of higher quantities of cellulose in any feedstock does not imply higher biogas or methane production. This is witnessed in case of RS, CFL, IFL and BP.

No definite conclusions can be drawn for the effect of total solids (TS) and VS reduction on the biogas and methane production, though higher TS and VS reduction should give higher quantity of gas. Percentage of methane in biogas obtained from feedstocks WS, RS, ML, CFL, IFL, DG and BP for all particle sizes, was 59%, 60%, 69%, 67%, 71%, 69% and 73% (v/v), respectively. Total methane production was highest for 0.088 mm particle size of IFL followed by CFL, BP, RS, ML, WS and DG, whereas CFL gave highest biogas quantity followed by IFL, RS and BP. This is only true for particle sizes 0.088, 0.40, 1.0 and 6.0 mm, and not for the feedstocks in the fifth digesters as the particle dimensions were not similar.

TABLE 4.4.2. DIGESTERS PERFORMANCE (DRY WEIGHT BASIS)

Feed stock	Particle size (mm)	Digester No.	Cellulose reduction %	Total solids reduction %	Volatile solids reduction %	Total methane production Litres/kg VS	Litres/kg TS
Wheat straw	0.088	A1	37.6	30.3	38.7	249 ± 0.97	213 ± 0.83
	0.40	A2	36.8	30.0	38.5	248 ± 0.19	212 ± 0.16
	1.0	A3	35.2	29.2	37.4	241 ± 0.29	206 ± 0.25
	6.0	A4	31.4	26.7	35.2	227 ± 1.17	195 ± 1.0
	30x5	A5	26.0	22.5	25.0	162 ± 2.92	138 ± 2.5
Rice straw	0.088	B1	47.7	41.7	55.6	365 ± 0.53	290 ± 0.42
	0.40	B2	46.2	40.8	56.0	367 ± 0.10	292 ± 0.08
	1.0	B3	44.9	40.0	54.6	358 ± 2.12	285 ± 1.70
	6.0	B4	42.0	38.3	52.9	347 ± 1.49	276 ± 1.19
	30x5	B5	34.2	31.7	36.8	241 ± 3.72	192 ± 2.97
<u>Mirabilis</u> leaves	0.088	C1	39.4	33.8	45.0	339 ± 2.07	286 ± 1.75
	0.40	C2	38.8	33.7	45.3	341 ± 0.57	288 ± 0.48
	1.0	C3	38.0	33.3	43.7	329 ± 0.68	278 ± 0.58
	6.0	C4	36.6	32.3	43.3	327 ± 1.49	276 ± 1.26
	80x50	C5	33.8	30.0	38.5	290 ± 3.46	245 ± 2.92
Cauli-flower leaves	0.088	D1	46.7	41.5	57.8	423 ± 0.34	348 ± 0.28
	0.40	D2	46.6	40.8	57.8	423 ± 0.92	348 ± 0.75
	1.0	D3	44.8	40.0	57.3	420 ± 0.57	346 ± 0.46
	6.0	D4	43.4	39.1	55.5	407 ± 2.30	335 ± 1.89
	150x100	D5	40.2	36.7	48.9	358 ± 2.29	295 ± 1.88

TABLE 4.4.2 CONTD.

Ipomoea fistulosa leaves	0.088	E1	46.6	39.5	55.3	429 ±1.54	362 ± 1.30
	0.40	E2	46.1	39.1	55.0	427 ± 1.3	360 ± 1.10
	1.0	E3	45.3	38.7	54.2	421 ± 4.76	355 ± 4.01
	6.0	E4	44.4	38.3	53.1	413 ± 0.71	348 ± 0.60
	150x100	E5	42.0	36.7	49.9	387 ± 1.78	327 ± 1.50
Dhub grass	0.088	F1	27.4	21.7	30.0	226 ± 4.33	193 ± 3.70
	0.40	F2	26.5	21.5	30.2	228 ± 1.71	194 ± 1.46
	1.0	F3	25.3	21.0	28.4	214 ± 5.36	183 ± 4.58
	6.0	F4	23.7	20.0	27.1	205 ± 3.43	174 ± 2.92
	30.0	F5	19.5	17.5	18.2	137 ± 2.95	117 ± 2.53
Banana peeling	0.088	G1	42.9	37.3	51.0	408 ± 0.89	334 ± 0.72
	0.40	G2	42.0	36.7	51.2	409 ± 2.39	336 ± 1.96
	1.0	G3	40.8	36.1	49.6	396 ± 2.26	325 ± 1.86
	6.0	G4	39.1	34.8	46.8	374 ± 4.65	307 ± 3.81
	30x10	G5	34.4	31.7	34.0	271 ± 3.02	223 ± 2.48

Note: Total methane production is given along with ± standard deviation.

4.5 EFFECT OF PRETREATMENT OF BIOMASS ON BIOGAS GENERATION

4.5.1 General

Preincubation of biomass with water and pretreatment with alkali before feeding these materials into digesters has been found to have pronounced effect on digestibility, rate of gas generation and total gas production [32, 33, 97, 126]. The results of pretreatment of all the biomass materials as listed in section 3.2 are presented and discussed in this section.

4.5.2. Preincubation with Water:

Preincubation has been found to affect pH of the slurry because of the formation and increased concentration of TVFA. In all the biomass - water slurry materials, pH was found to decrease with increase in incubation period and is showing acidic nature. The change in pH and TVFA concentration for all the biomass materials have been given in Figs. 4.5.1 to 4.5.3. It is found that the rate of change in pH which is linked with the rate of formation of TVFA, is more during the first five days of incubation as compared to later periods of incubations. For BP and CD, the pH falls slowly with pH falling from 6.8 to 5.9 for BP and 6.6 to 5.8 for CD from the 2nd to 40th day of incubation. For other materials pH fall is steep within the first day of incubation with pH falling to values in the range of 5.5 to 5.9. It may be recalled that the pH of the feedstock slurry for all the biomass materials was found to be initially around 7.0 with

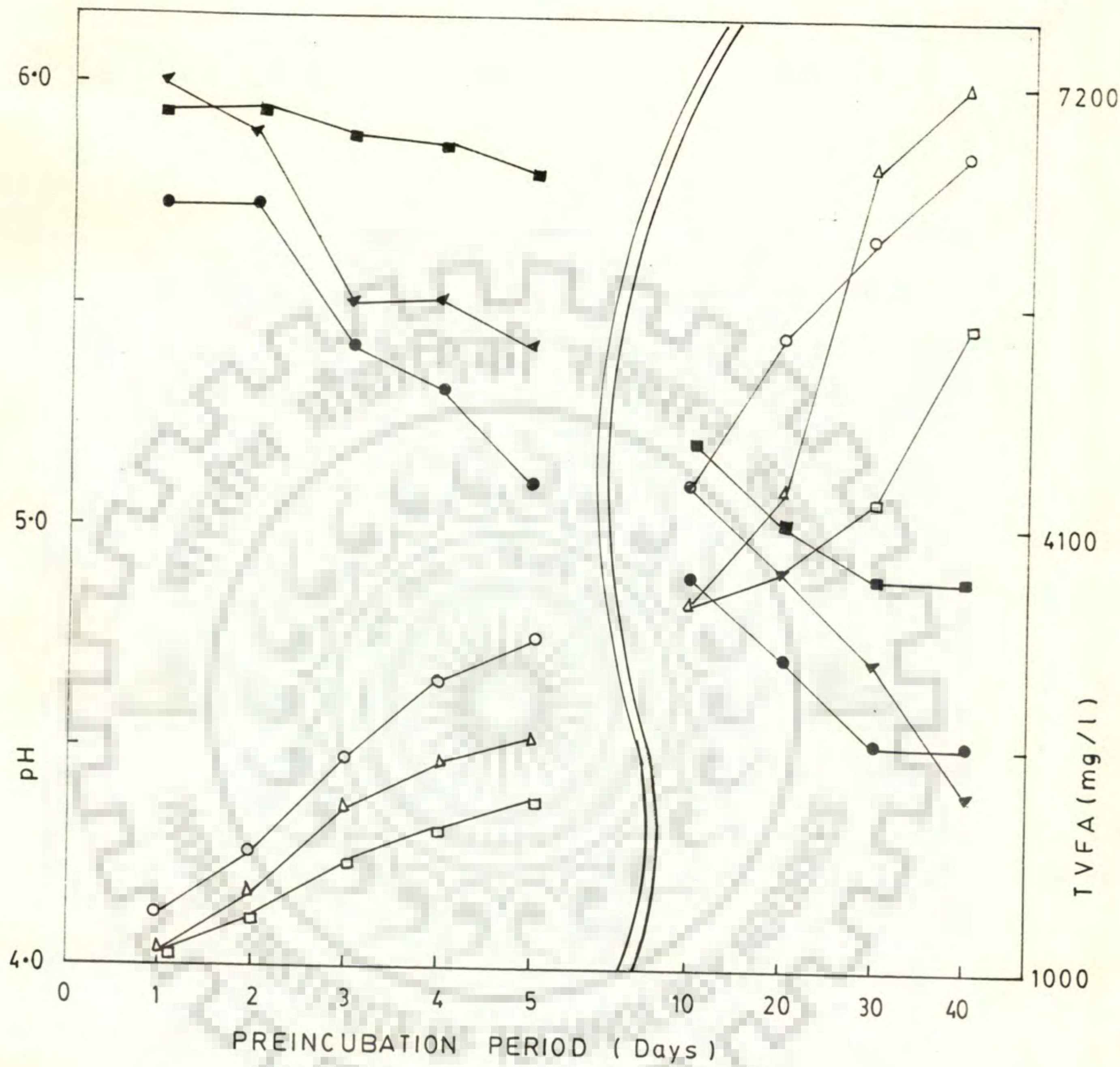


FIG. 4·5·1 pH AND TVFA CONCENTRATION IN IFPS, IFL, RS.

IFPS: ●, pH; ○, TVFA

IFL : ▲ pH; △, TVFA

RS : ■ pH; □, TVFA

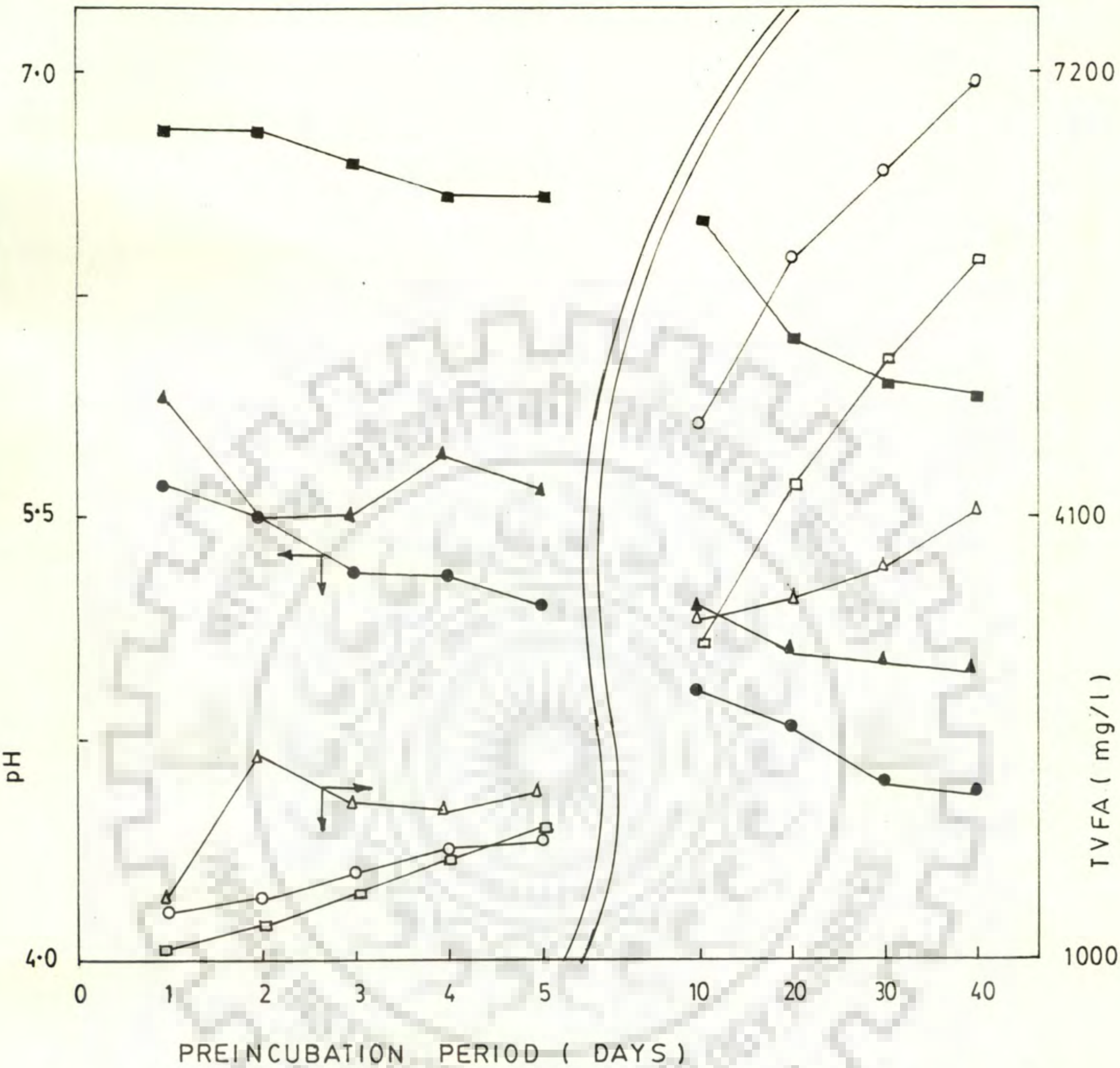


FIG. 4·5·2 pH AND TVFA CONCENTRATION IN CFL, ML, BP.

CFL : ●, pH ; ○, TVFA

ML : ▲, pH ; △, TVFA

BP : ■, pH ; □, TVFA

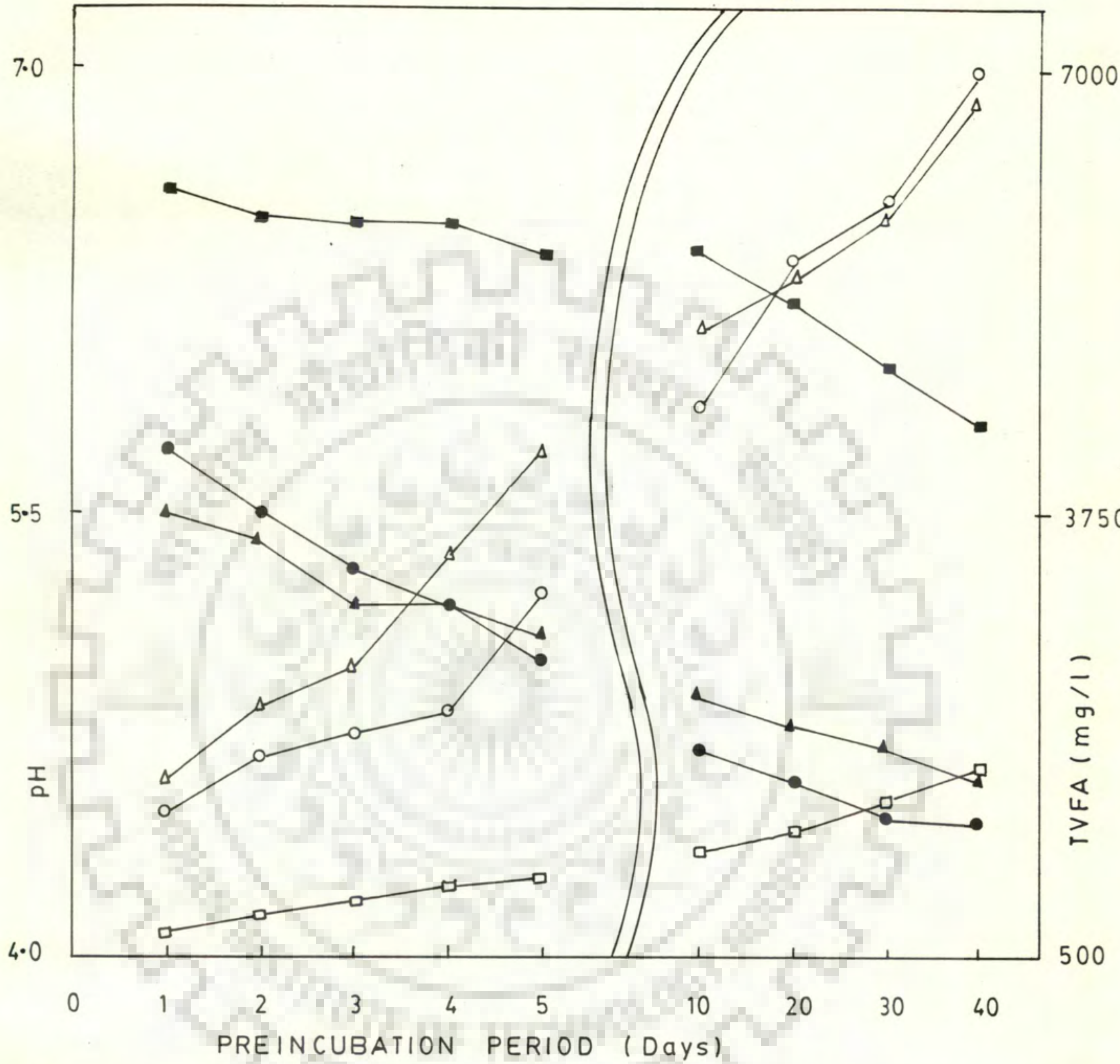


FIG. 4·5·3 pH AND TVFA CONCENTRATION IN WS, DG, CD

WS: ●, pH; ○, TVFA

DG: ▲, pH; △, TVFA

CD: ■, pH; □, TVFA

IFPS, CFL, ML showing values slightly higher than 7.Ø and those with IFL, RS, BP, WS, DG and CD showing slightly higher than 7.Ø, with the pH in the overall range of 6.92 to 7.Ø7.

Within a day of preincubation with water, the pH of the digester slurry for most of the biomass materials fell down and TVFA concentration rose sharply. The comparative values of pH and TVFA for the initial slurry and after one day preincubation is given in Table 4.5.1. Excepting IFL, BP and CD, the pH fall was to a value below 6.Ø for the rest of the materials. In the case of DG, the fall was maximum reaching a value of 5.5. In the case of CD, the pH reduction was minimum, from 7.Ø6 to 6.6. Similarly, for TVFA, maximum increase was found in the case of DG rising from 33Ø to 18ØØ mg/l. In the case of IFL and CD, the increase was found to be minimum (35Ø to 11ØØ and 3ØØ to 69Ø mg/l, respectively). It appears that the close and orderly arrangement of cellulose and hemicellulose in the molecular structure of lignin is loosened and the cellulose lignin bonds are softened.

Similar results were also obtained by Singh et al., 1983, who predigested cattle waste before anaerobic digestion. They reported a sharp decrease in pH (from 7.4 to 6.5) with a simultaneous increase in the level of TVFA (from 68Ø to 1Ø42 mg/l) after one day of preincubation. However, during prolonged incubation (4 to 5 days), slight increase in pH (from 6.4 to 6.6) with a simultaneous depletion in TVFA (from 1Ø42 to 666 mg/l) was reported. Since these workers used fresh cattle dung (with viable microbial population), methane formers grew as was confirmed by the appreciable methane content of predigested digesters. In

TABLE 4.5.1. **pH AND TVFA VALUES OF PREINCUBATED RAW MATERIALS**

	Days			
	Initial		After one day	
Biomass	pH	TVFA (mg/l)	pH	TVFA (mg/l)
IFPS	6.95	400	5.7	1350
IFL	7.00	350	6.0	1100
CFL	6.92	810	5.6	1300
RS	7.07	500	5.94	1100
ML	6.95	500	5.9	1500
BP	7.05	450	6.8	1025
WS	7.03	400	5.7	1525
DG	7.02	330	5.5	1800
CD	7.03	300	6.6	690

the present study, dried CD was used and neither such a drastic fall in pH nor increase in TVFA concentration (as was observed by Singh et al., [126] after the first day of incubation) was observed. Similarly, there was no increase in pH nor decrease in TVFA concentration upto 5 days of incubation as was observed by these workers. As can be seen from Figs. 4.5.1 to 4.5.3, pH showed a decreasing trend and TVFA showed an increasing trend during the full 40 days of preincubation period.

It is found that with an increase in incubation period there is decrease in VS and increase in TS reduction, e.g., in the case of preincubated IFPS and RS, the VS reduction was from 92.6% to 88.1% and from 79.38% to 74.99%, respectively, during 40 days of preincubation. Similarly TS reduction was found to be 23.1% in the case of IFPS and 20.25% in the case of RS during the same period of incubation.

4.5.3. Effect of Preincubation on Biomethanation:

Biomass materials preincubated for 10, 20, 30 and 40 days were inoculated with biogas plant effluent slurry and fed to different digesters. It was found that all digesters excepting those run on CD, failed to produce biogas (very insignificantly small amount of biogas was found to be produced, e.g. for IFPS only 8.8 litres of biogas/kg of VS). The failure of digesters could be attributed to low pH and high TVFA concentration which induced toxicity to methanogens. Methanogenic bacteria are inhibited in high TVFA concentration due to cation present in the slurry. McCarty and McKinney, [84] suggested that TVFA concentration should not go beyond 2000-3000 mg/l under optimum conditions. The pH of the substrate is controlled by ammonia nitrogen concentration as follows:

$$NH_4^+ \longrightarrow NH_3 + H^+$$

Ammonia nitrogen concentration of 1250 mg/l has been indicated as limiting value.

In the case of cattle dung, the digesters did not fail and continued to produce biogas for all the four preincubated CD samples for the entire period of 8 weeks of digestion.

Weekly biogas production rate for CD is given in Table 4.5.2. For unincubated CD fed digesters with or without pH control and preincubated CD fed digesters without pH control, gas production increases during the second week and starts decreasing upto 8th week. However, for digesters fed with preincubated CD and with pH control, gas production is the highest during the first week itself and then starts decreasing. Without pH control, the preincubation for 10, 20, 30 and 40 days does not increase the total gas production appreciably. However, with the pH control, gas production picks-up and with 10 days of preincubated feed shows an enhancement of 18 l/kg TS. It is found that during the first three weeks, more than 60% of the total gas is produced. The above findings support the results of Singh et al., 1983, who had shown that predigestion of cattle waste for 1-2 days helped in effecting 17-19% increase in the gas production.

4.5.4. Biogas Production from Preincubated Material with pH Control:

TABLE 4.5.2. WEEKLY BIOGAS PRODUCTION FROM CATTLE DUNG (1/kg TS)

No of weeks	Unincubated pH uncontrol	Unincubated pH control	Preincubated pH control, No of days: 10	20	30	40	Preincubated pH uncontrol, No of days: 10	20	30	40
1	30	35	34	35	31	26	60	66	68	73
2	65	62	64	68	70	66	43	48	53	57
3	38	45	40	43	45	38	36	31	40	41
4	20	22	19	20	22	23	30	28	27	31
5	17	16	18	16	16	18	19	23	21	18
6	12	13	10	10	17	15	17	18	14	12
7	10	8	10	11	17	11	12	10	9	7
8	8	9	11	8	10	7	7	8	5	7
Total	200	210	206	211	228	204	224	232	237	243

Weekly biogas production for all the preincubated biomass materials showed an enhancement in the gas production rate for the first week of digestion. In the case of CFL, it was found that with feed of upto 30 days preincubation period, the gas production rate in the 2nd week was more as compared to 1st week of digestion. In the case of CFL the gas production in the 2nd week was found to be more with 20 and 30 days incubation periods. For the rest of the materials, the gas production during the 1st week was found to be maximum with a decreasing trend thereafter.

Table 4.5.3 presents the data for weekly biogas production for 10 days-preincubated biomass materials. Similar trends were obtained with 20, 30 and 40 days of preincubation. It may be seen from the Table that during first 3 weeks, IFL, RS, ML, BP and WS produced more than 73% of the total biogas while IFPS, CFL and DG produced, respectively, 60%, 65% and 57% of the total production.

Table 4.5.4 compares in a summary form the total biogas produced during 8 weeks of digestion for all the biomass materials preincubated for different periods. It may be seen that significant enhancement in gas production is obtained only with 40 days of preincubation in the case of IFPS, RS, WS, DG and CD. In terms of total gas produced, IFPS, IFL, CFL and RS compare well with each other.

It is found that preincubation of the biomass materials does not affect the methane content of the biogas produced in the digesters, and almost same methane concentration is found for a

TABLE 4.5.3. WEEKLY BIOGAS PRODUCTION RATE (L/KG TS)
pH CONTROLLED

Raw materials	Preincubation period - 10 days No of weeks 1	2	3	4	5	6	7	8	Total
IFPS	116	104	77	56	44	34	30	29	490
IFL	138	132	110	73	28	17	10	7	515
CFL	107	127	108	96	49	16	11	10	524
RS	144	125	94	50	31	22	17	10	493
ML	122	113	80	43	31	17	12	11	429
BP	138	129	94	51	27	14	10	8	471
WS	134	89	60	34	22	15	10	9	373
DG	69	53	42	35	30	27	20	12	288

TABLE 4.5.4 TOTAL BIOGAS PRODUCTION CAPACITY OF PREINCUBATED RAW MATERIALS (L/KG TS) pH CONTROLLED

Raw materials	Incubation period (Days) 00	10	20	30	40	Average methane content % (v/v)	Enhancement in gas production in 40 days over unincubated samples (%)
IFPS	485	490	515	548	565	66	16.5
IFL	507	515	523	528	541	71	6.7
CFL	520	524	537	553	565	67	8.65
RS	485	493	513	530	547	60	12.78
ML	420	429	440	453	460	69	9.52
BP	460	471	478	484	496	73	7.82
WS	360	373	390	408	419	60	16.38
DG	280	288	298	311	320	69	14.28
CD	210	224	232	237	243	60	15.71

particular biomass incubated for different periods of time. From the average methane content given in Table 4.5.4, it is found that BP gives the highest methane content followed by IFL. However, the total methane production (l/kg TS) is found to be maximum for IFL followed by CFL, IFPS and BP in the descending order.

Table 4.5.5 presents cellulose reduction for different biomass materials preincubated for different periods. It is found that preincubation does not help appreciably in the cellulose reduction during anaerobic digestion, with the exception of IFPS. For Ipomoea fistulosa plant stem, incubation period has pronounced effect as could be seen from the table. This shows that solubilization of cellulose and subsequent hydrolysis increases the biogas production in this case , which however may not be true for other raw materials. Preincubation helps in physical swelling of raw materials, although water may not penetrate the crystaline structure of cellulose and swelling is only possible in the amorphous region. Some salts or alkaline solutions may aid the swelling of intercrystaline structure of cellulose. For loosening plant cellulose structure, swelling is the best method. In the case of IFPS, it was found that if the incubated and swollen material was dried and then utilised for biogasification, there is a fall in the gas production, possibly due to collapse of the structure. IFPS preincubated for 40 days was dried and then used for anaerobic digestion under controlled pH conditions. Biogas generation was found to be 460 litres of biogas/kg of TS or 304 litres of methane/kg of TS, which is about

TABLE 4.5.5. PERFORMANCE OF DIGESTERS pH CONTROLLED

Raw materials	Cellulose reduction % Preincubation period (No of days) ØØ	1Ø	2Ø	3Ø	4Ø
IFPS	34.7	35.5	38.6	44.6	47.4
IFL	43.8	44.2	44.8	45.5	46.7
CFL	46.6	46.9	47.9	49.Ø	49.8
RS	46.2	46.7	47.3	48.2	49.Ø
ML	38.8	39.3	39.9	4Ø.Ø	4Ø.2
BP	42.2	42.7	44.Ø	44.8	45.9
WS	36.8	37.Ø	37.2	37.3	37.6
DG	26.5	26.8	27.Ø	27.1	27.1
CD	28.Ø	28.4	28.9	29.1	29.5

5.4% less than that obtained from unincubated IFPS. This is due to reduction of VS and evaporation of TVFA formed during incubation. The highest quantity of total methane in incubated and unincubated materials was produced by IFL followed by CFL.

From Tables 4.5.4 and 4.5.5, it is found that 40 days - preincubation of RS and BP with water enhances gas production but the total reduction in cellulose, TS and VS is only marginal and the enhancement in gas production is not substantial as to necessitate preincubation with water for 40 days. In the case of IFPS, cellulose reduction plays an important role in the enhancement of gas production.

Thus it may be concluded that preincubation for 40 days enhances gas production (and therefore methane generation) in the case of IFPS, RS, BP, WS and DG.

4.5.5. **Pretreatment with Alkali:**

Since thermo-chemical treatment has been found to increase the biodegradability of cellulose and VS [32, 33, 96, 97], two materials, namely, RS and BP were chosen for alkali pretreatment at two temperatures, 37°C and 100°C for 2 hours, respectively. These materials are agricultural/horticultural residues and are available in large amounts at several places.

Weekly biogas production from these two alkali (caustic soda) treated residues under controlled pH conditions are presented in Table 4.5.6 and Fig. 4.5.4. The table also compares the data for raw materials preincubated for 10 days and 40 days

TABLE 4.5.6. COMPARISON OF WEEKLY BIOGAS PRODUCTION FOR WATER/ALKALI TREATED RESIDUES UNDER CONTROLLED pH CONDITIONS

Raw materials	Alkali/water treatment	Period of treatment	No. of weeks 1	2	3	4	5	6	7	8	Total
RS	Water	40 days	156	137	110	73	38	16	11	6	547
	Alkali	1 day at 37°C	152	144	106	81	29	15	11	7	545
	Alkali	2 hours at 100°C	161	145	113	77	35	18	13	6	568
BP	Water	40 days	149	136	101	49	33	14	8	6	496
	Alkali	1 day at 37°C	146	138	110	53	31	21	12	11	522
	Alkali	2 hours at 100°C	148	136	109	57	37	23	12	9	531

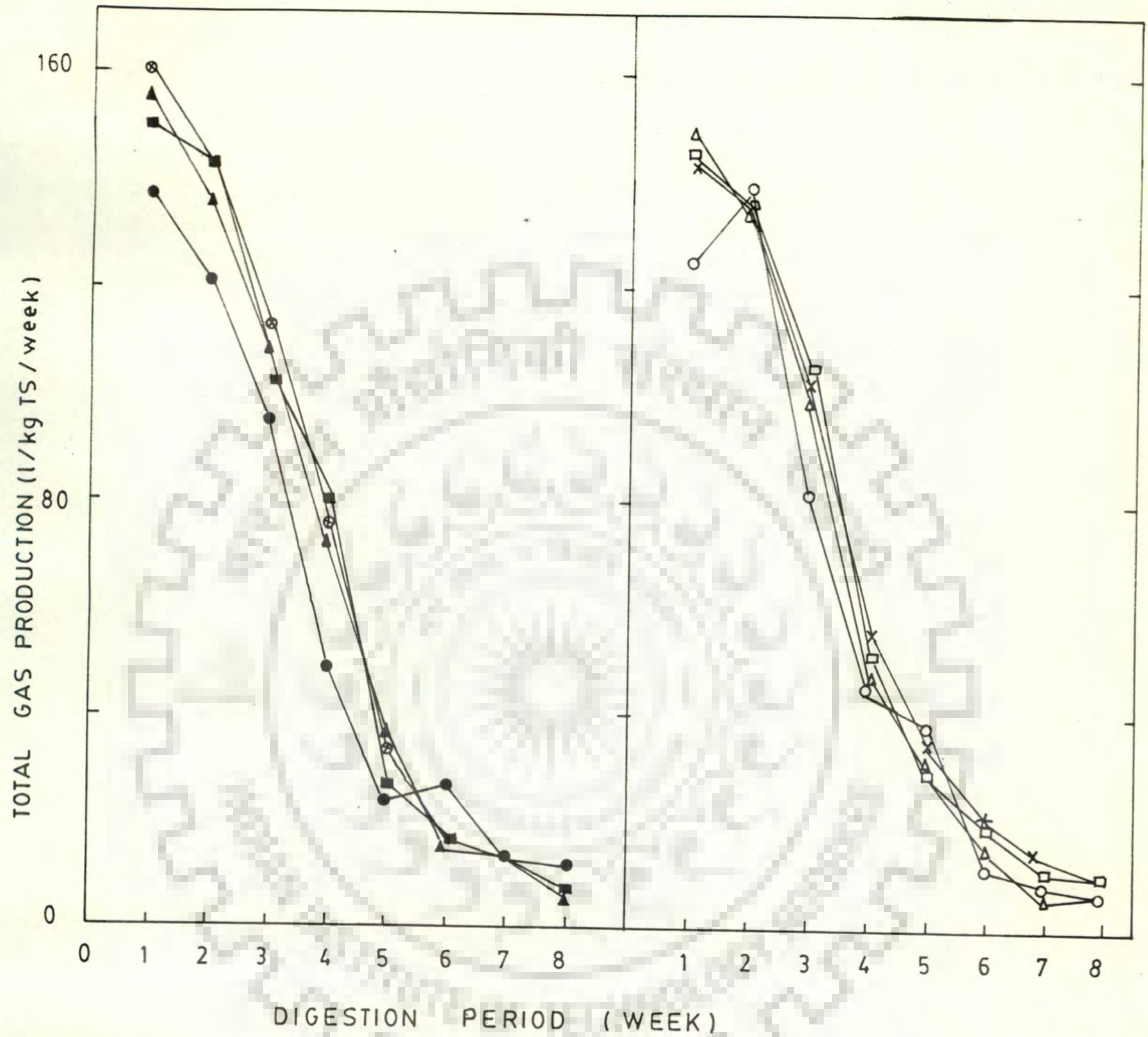


FIG 4.5.4 ANAEROBIC DIGESTION OF RS AND BP

RS : ●, Unincubated; ▲, 40 Days incubated; ■, Alkali treated (37°C); ⊗, Alkali treated (100°C).

BP : ○, Unincubated; △, 40 Days incubated; □, Alkali treated (37°C) ×, Alkali treated (100°C) in water. It is found from this table that one day alkali treated RS at 37°C produces almost the same amount of biogas as that obtained from RS preincubated in water for 40 days. In the case of BP, alkali trteatment for one day increases the gas production rate by more than 5% over that from 40 days water preincubation. When the wastes were cooked in 5% alkali solution at 100°C for 2 hours, the improvement in gas production over that from 24 hour treatment at 37°C is less than 4% in the case of RS and less than 2% in the case of BP. The above data indicate that alkali treatment for one day at normal temperature will improve the biodegradability of residues.

Table 4.5.7 shows the performance of digesters fed with RS and BP treated with alkali under controlled pH conditions. It is seen that alkali treatment for one day at 37°C increases cellulose reduction by about 2% in the case of RS and by about 1.4% in the case of BP with corresponding increase of methane content by 6% methane in the case of RS and 8% in the case of BP. Further treatment at 100°C for 2 hours with alkali solution makes little change in the over all TS reduction; though the reduction in VS is more than 2.7% in the case of RS and 1% in the case of BP. Comparing the data of Dhavises et al., 1985 for fermentation of RS pretreated with 0.3N solution of NaOH, after 7 days of incubation at 37°C, it was found that the Dhavises [33] data gives high biogas production rate [450 litre of biogas/kg of material; 60% methane (v/v)] as against 152 litre of biogas /kg of TS with 64% methane (v/v).

Comparing the results for biogas production under

TABLE 4.5.7. DIGESTERS PERFORMANCE FED ON WATER/ALKALI TREATED RS AND BP UNDER CONTROLLED CONDITIONS

Raw materials	Water/alkali treatment	Period of treatment	Cellulose reduction %	TS reduction %	VS reduction %	Methane Production (l/kg TS)
RS	Water	40 days	49.0	45.2	63.1	328
	Alkali	1 day at 37°C	51.2	48.1	62.9	349
	Alkali	2 hours at 100°C	52.0	49.3	65.6	363
BP	Water	40 days	45.9	39.6	55.2	362
	Alkali	1 day at 37°C	47.3	42.2	58.1	391
	Alkali	2 hours at 100°C	47.4	43.0	59.1	398

controlled pH conditions from preincubated biomass residues in water for different periods at 37°C and alkali treatment at 37°C and 100°C, it is clear that the pretreatment enhances the biogas production over that from biomass without treatment or preincubation. Alkali treatment for 1 day at normal temperature of 37°C gives the amount of biogas comparable with that obtained with 2 hour alkali treatment at 100°C. This supports the claim of Han, 1984 that alkali treatment is quite useful improving the digestibility of biomass due to the extensive swelling of lignocellulosic biomass and separation of structural elements and fibres.

By using the equation described by Chynoweth et al., [24]

$$C_{3.67}\,H_{4.99}\,O_{1.84} + 1.5\,H_2O \longrightarrow 1.99CH_4 + 1.67\,CO_2$$

the maximum theoritical yield of methane will be 0.633 m^3/kg VS for RS. As a fraction of organic matter in all microbial fermentations is usedup for the growth of micro-organisms, the above yield of methane is corrected for microbial cell (Appendix-I). The net theoretical yield after correction will be 0.510 m^3/kg VS, whereas present results show a total yield of 0.369 m^3/kg VS for unincubated RS and 0.414 m^3/kg VS for 40 days incubated RS. After alkali treatment the maximum methane yield is found to be 0.431 m^3/kg VS. There are a number of parameters which are responsible for difficult digestion of lignocellulosic plant materials:

1) crystallinity of cellulose.
2) cellulose - lignin association.

3) molecular arrangement, which includes degree of polymerization.

4) degree of substitution and hydrogen bonding.

5) moisture content and maturity.

6) association with other substances.

Thus pretreatment is an essential prerequisite to enhance the susceptibility of ligno-cellulosic materials to enzymatic and microbial attack.

4.6 EFFECT OF TEMPERATURE ON BIOGAS GENERATION

4.6.1 General:

Four biomass materials, namely cattle dung, *Ipomoea fistulosa* plant stem, *Ipomoea fistulosa* leaves and *Mirabilis* leaves were selected to carry out experiments for the investigation of the effect of temperature on biogasification. The experiments were carried out at temperatures of 20°C, 25°C, 30°C, 37.5°C, 40°C and 45°C. One set of experiments was conducted without controlling the pH of the digesters substrate while the other sets were conducted under controlled pH conditions by adding calcium hydroxide slurry in the digester.

4.6.2. Biogas Production Capacity Under uncontrolled pH Conditions:

Fig. 4.6.1 shows the plot of total biogas production (in eight weeks of digestion) against temperature for all the materials, without pH control of the digester slurry. It is seen that all the digesters failed at 45°C. Digester run on CD and ML showed increasing biogas production with increase in temperature until 37.5°C and thereafter, drastic reduction in gas generation was observed, with total failure at 45°C. However, digesters run on IFPS and IFL failed at 30°C only with negligible recovery at 37.5°C and 40°C. The main reason for the failure of these digesters seems to be the drastic fall in pH at lower temperatures and death of acidogenic and methanogenic

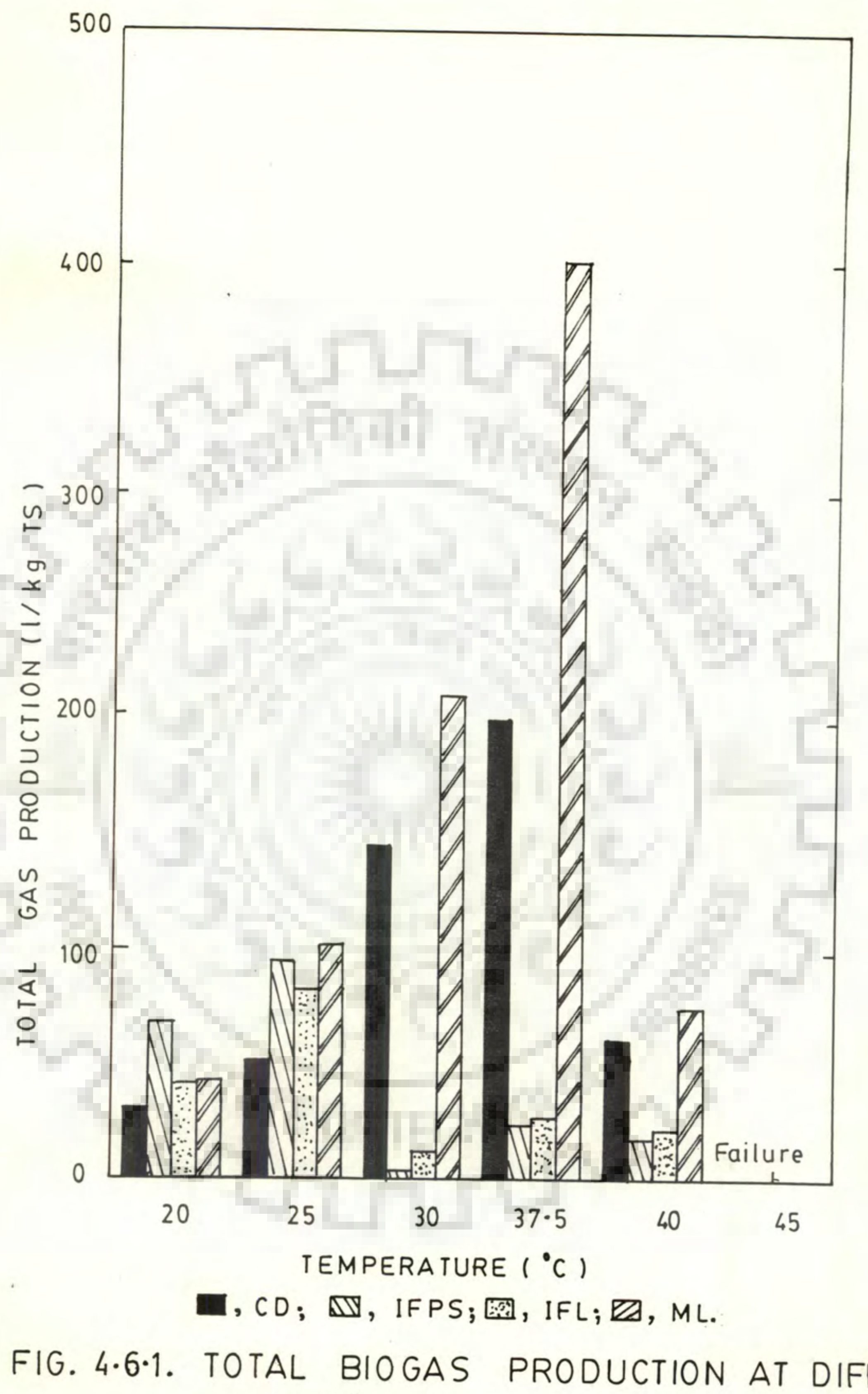


FIG. 4·6·1. TOTAL BIOGAS PRODUCTION AT DIFFERENT TEMPERATURE WITH pH UNCONTROL micro-organisms at higher temperatures..

4.6.3. pH and TVFA concentration:

Table 4.6.1 shows the pH and TVFA concentration for the digesters run on IFPS and IFL. The variation of pH and TVFA concentration with temperature for CD and ML are given in APPENDIX-II. .In the case of CD and ML, the pH always remains high more than 6.5 for CD and 5.9 for ML.

From Table 4.6.1 it is found that in the digesters run on IFPS and IFL, pH droped and remained at around 5.0 and TVFA concentration remained around 2150 mg/l at 30°C. For IFPS digesters, at 25°C, pH dropped after first week of digestion from 5.62 to 5.22 and picked up slowly but steadily through the period of digestion. During eighth week pH rose to 5.72, however, at 30°C, digesters run on IFPS and IFL did not recover and pH remained almost at the same level at around 5.0. TVFA cocentration in the case of IFL, rose from 2650 mg/l during the first week to 3260 mg/l during the eighth week of digestion at 30°C. Table 4.6.1 also shows a very peculiar trend concerning variation of pH for IFPS. In the IFPS digesters pH decreased consistently from 25°C to 37.5°C with slight increase at 40°C and sudden rise at 45°C, e.g. during the first week pH rose from 4.95 to 6.73 and during the eighth week it rose from 5.05 to 6.75 with temperature varying from 40°C to 45°C. This is due to the fact that the TVFA concentration went down as the temperature increased from 37.5°C to 45°C, e.g. during the third week of digestion, TVFA concentration decreased from 3500 mg/l at 37.5°C

TABLE 4.6.1. pH VALUES AND TVFA CONCENTRATION (mg/l)

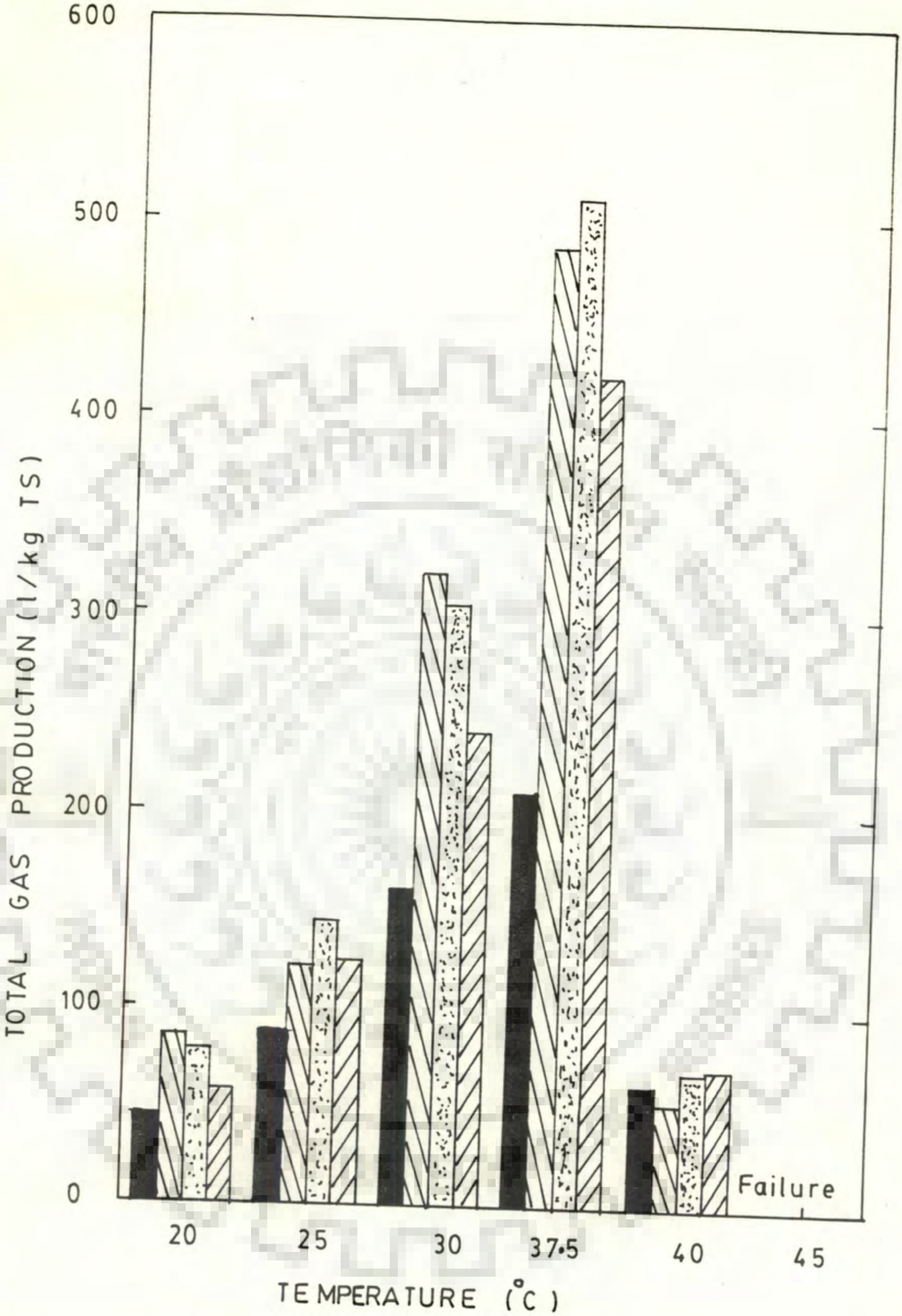
Raw materials	Temp. °C	No of weeks I		II		III		IV		V		VI		VI		VIII	
		TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH
IFPS	20	1315	5.60	1390	5.35	1410	5.29	1450	5.25	1485	5.31	1525	5.43	1510	5.45	1520	5.49
IFL	20	1500	5.95	1635	5.93	1660	6.06	1650	6.13	1690	6.15	1665	6.10	1640	6.12	1600	6.17
IFPS	25	1340	5.62	1465	5.22	1495	5.36	1580	5.42	1645	5.65	1735	5.76	1740	5.75	1750	5.72
IFL	25	1640	5.80	1655	6.03	1700	6.01	1735	6.09	1750	6.12	1725	6.06	1740	6.10	1750	6.10
IFPS	30	1825	5.06	1950	4.92	2095	4.95	2135	4.98	2150	5.03	2140	5.10	2150	5.05	2165	5.08
IFL	30	2650	4.91	2910	4.83	3140	4.80	3190	4.83	3155	4.93	3185	4.95	3235	4.92	3260	4.98
IFPS	37.5	2400	4.89	3200	4.80	3500	4.83	3700	4.87	3765	4.90	3750	4.92	3760	4.95	3775	4.95
IFL	37.5	4475	4.80	4660	4.79	4600	4.83	4580	4.88	4550	5.05	4550	5.11	4489	5.17	4400	5.15
IFPS	40	2240	4.95	2100	4.99	2140	5.08	2130	5.10	2150	5.05	2175	5.02	2170	5.00	2190	5.05
IFL	40	1950	5.26	1985	5.09	1950	5.10	1928	5.13	1940	5.08	1915	5.15	1900	5.19	1910	5.20
IFPS	45	650	6.73	660	6.75	660	6.75	650	6.77	630	6.75	610	6.78	610	6.77	620	6.74
IFL	45	845	6.22	850	6.18	840	6.20	825	6.20	835	6.25	820	6.27	810	6.25	815	6.28

to 2140 mg/l at 40°C and then suddenly dropped to 660 mg/l at 45°C. One possible reason for the above may be the destruction (loss of viability) of acidogeneic and methanogenic micro-organism as the temperature rises above 37.5°C. It seemed that the population of acidogens may remain viable while methanogens shows greater viability at higher temperatures.

4.6.4. Biogas Production Capacity Under Controlled pH Conditions:

Fig. 4.6.2 shows the plot of total biogas production against temperature under controlled pH conditions. On comparing Figs. 4.6.1 and 4.6.2, it is found that pH control has no significant effect on the total biogas production for CD and ML at temperatures 30°C and 37.5°C. At 20°C and 25°C the increase in biogas production in controlled digesters over uncontrolled ones is substantial for CD. At 40°C even under controlled conditions, biogas production is very small as compared to that obtained at 37.5°C, and at 45°C the digesters failed. In the case of IFPS and IFL, pH control appears to have a miraculous effect and gas production rose quickly at 30°C and 37.5°C. However, again at 40°C, gas production slumped drastically and at 45°C digesters failed. Thus, pH control does not enhance the gas production beyond 37.5°C and the near absence of viable microbial cells of acidogens and methanogens, cripples the digester.

A comparative study of total gas production capacity shows a major difference at 30° C and 37.5°C for IFPS and IFL. Out of all the four materials, IFL produced 510 l/kg TS of biogas which is the highest quantity. At 37.5°C, CD, IFPS, IFL and ML



■, CD; ▧, IFPS; ▩, IFL, ▨, ML;

FIG. 4·6·2. TOTAL BIOGAS PRODUCTION AT DIFFERENT TEMPERATURES WITH pH CONTROL produced biogas which is respectively 4.66, 5.70, 6.53 and 7.11 times more in comparison to that produced when temperature was 20°C.

Total biogas production during eight weeks of digestion seems to follow **Arrhenius** type of relationship with temperature,

i.e. $$Q = Q_o \exp(-A/T) \qquad \text{---------------(1)}$$

The plot of Q versus 1/T on semilog scale (log of ordinate and normal for abscissa) for CD, IFPS, IFL and ML are given in Figure 4.6.3, 4.6.4, 4.6.5 and 4.6.6, respectively. The various values of Q_o and (-A) for the four biomass materials are given in Table 4.6.2.

4.6.5. <u>Methane Content in Biogas:</u>

Tables 4.6.3 and 4.6.4 present the methane and carbon-dioxide content of biogas generated at different temperatures using different biomass materials, respectively, for uncontrolled and controlled pH conditions.

From Table 4.6.3, it is observed that as the temperature of the digester increased beyond 25°C, methane content went down slowly and at 45°C methane content went down drastically to around 50%. It is also seen that ML had highest methane content in the gas generated. From Table 4.6.4, a peculiar trend in the methane content of the gas is obtained. While for CD, there seems to be no difference in methane content in the gas obtained from uncontrolled and controlled digesters, the methane content remains almost constant while for ML highest methane content is

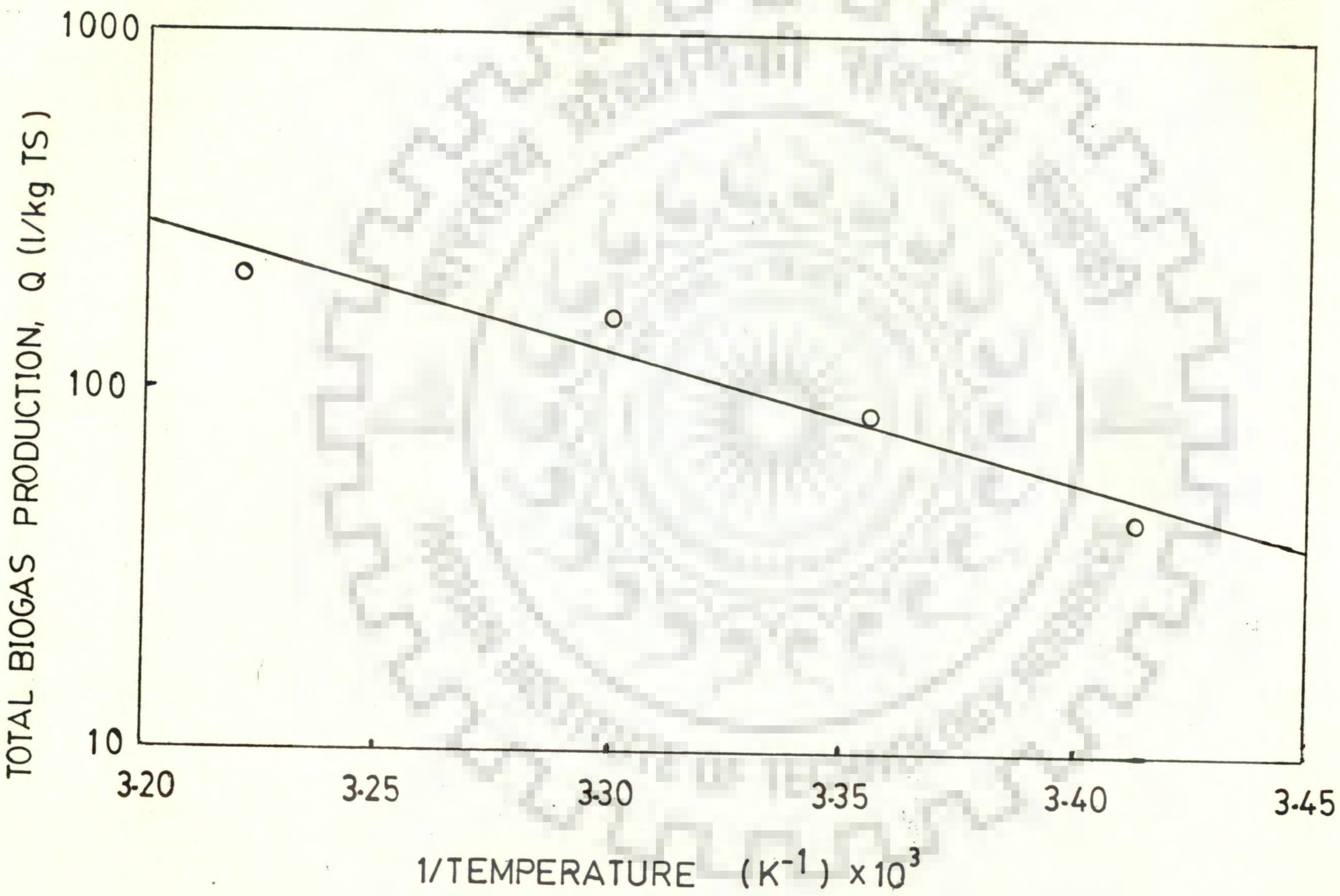


FIG. 4.6.3. ARRHENIUS PLOT FOR BIOGAS PRODUCTION AGAINST 1/T FOR CD.

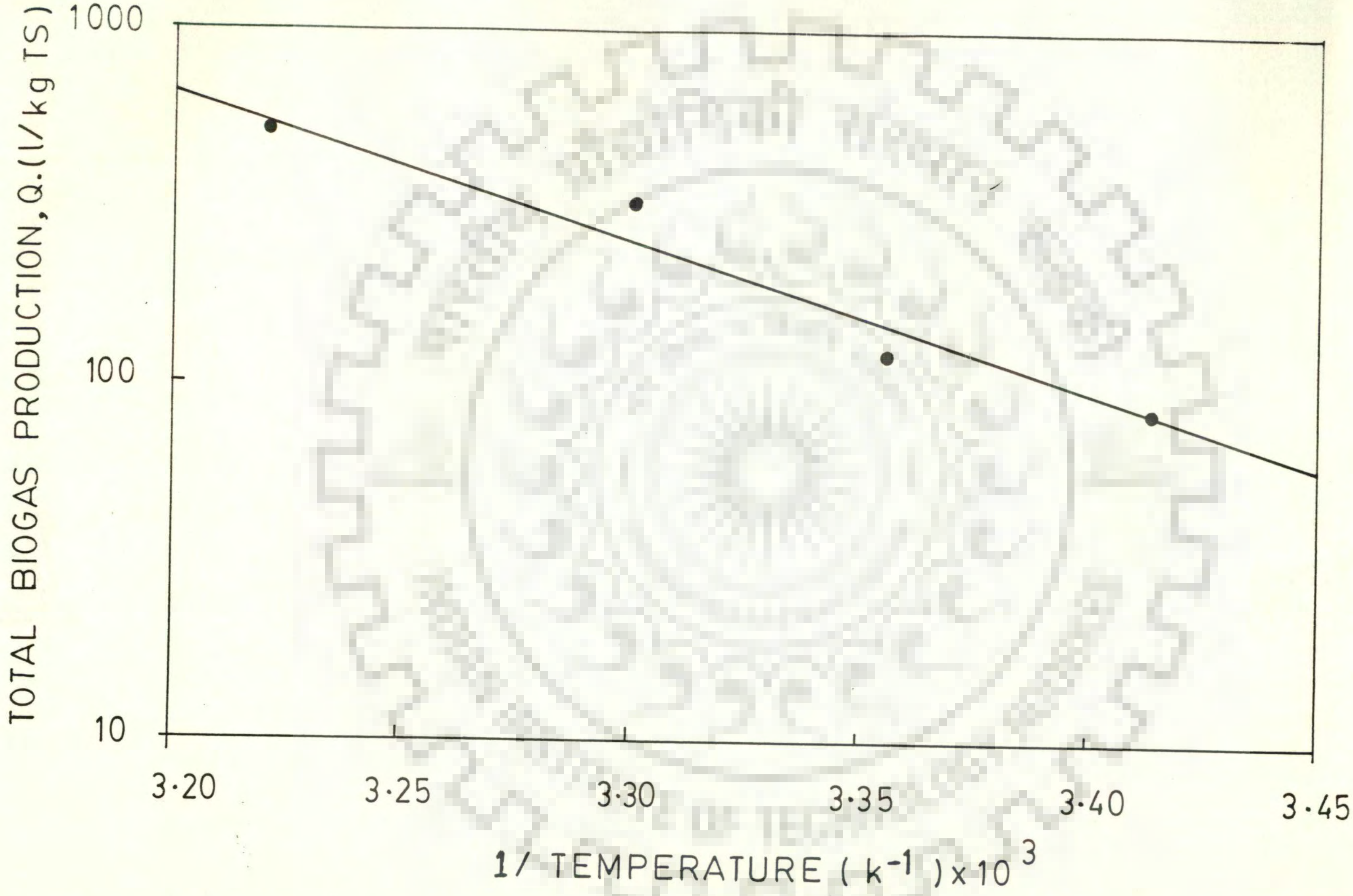


FIG. 4·6·4 ARRHENIUS PLOT FOR BIOGAS PRODUCTION AGAINST 1/T FOR IFPS

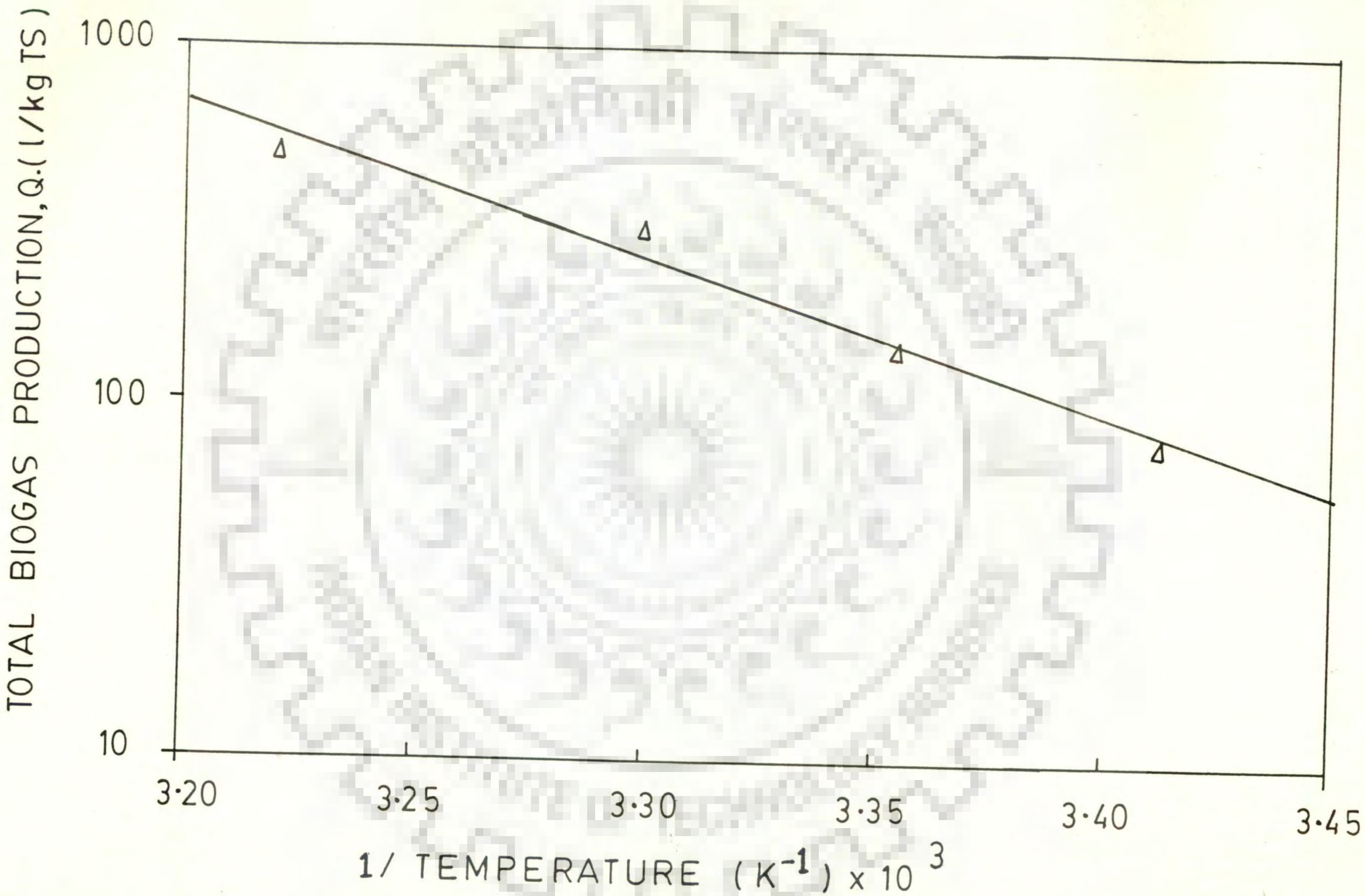


FIG. 4·6·5 ARRHENIUS PLOT FOR BIOGAS PRODUCTION AGAINST 1/T FOR IFL

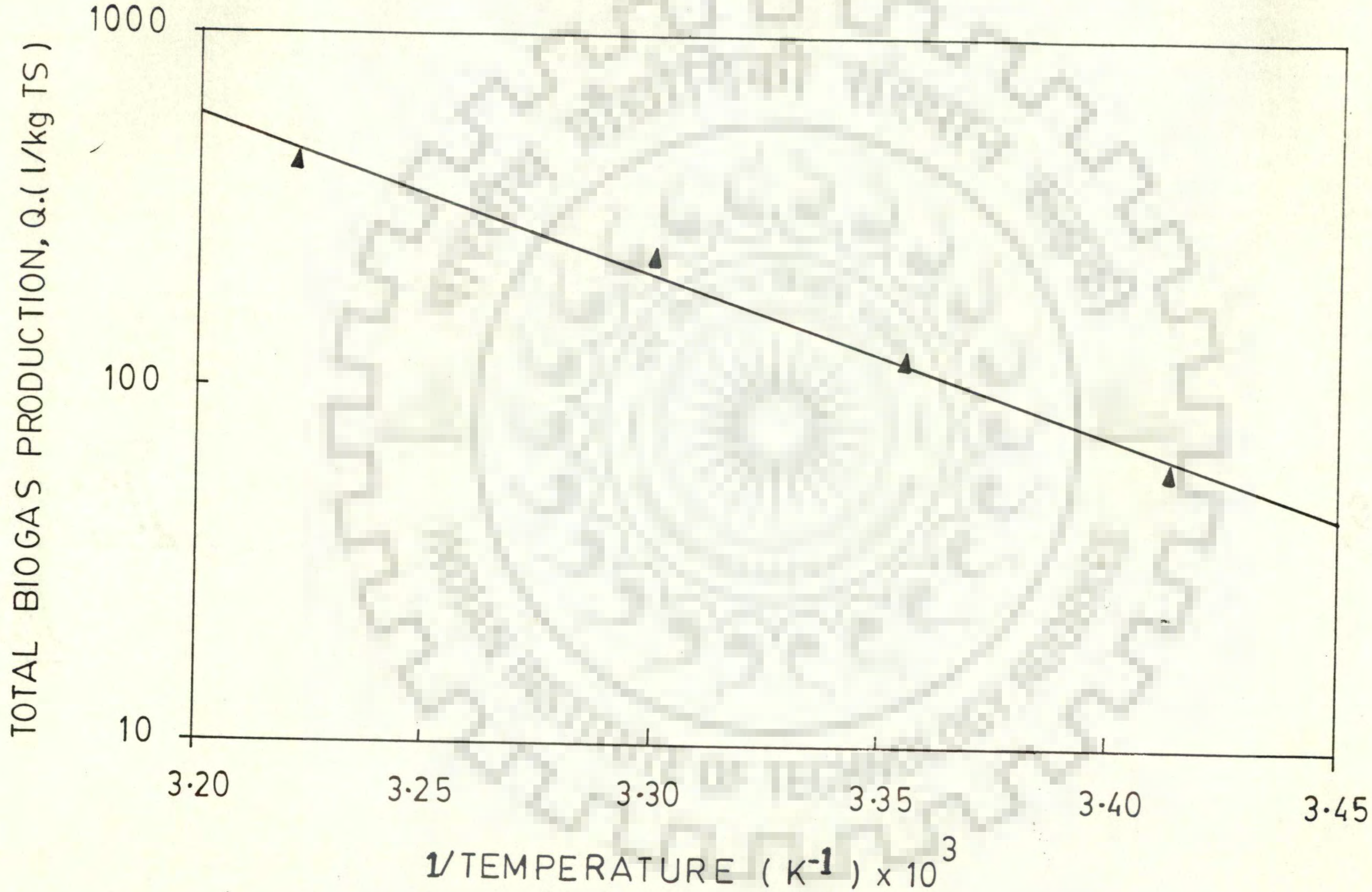


FIG 4·6·6 ARRHENIUS PLOT FOR BIOGAS PRODUCTION AGAINST 1/T FOR ML

TABLE 4.6.2. PARAMETER VALUES FOR ARRHENIUS TYPE PLOTS OF FIGURES 4.6.3 TO 4.6.6

Biomass	Figure No.	Q_o l/kg TS	$-A \times 10^3$ K^{-1}	Correlation coefficient
CD	4.6.3	13.65	3.497	0.9653
IFPS	4.6.4	16.22	4.180	0.9733
IFL	4.6.5	16.65	4.320	0.9886
ML	4.6.6	16.93	4.430	0.9887

TABLE 4.6.3. QUANTITY OF METHANE AND CARBONDIOXIDE IN BIOGAS Percent, (v/v). Without pH control.

Temperature °C	CD		IFPS		IFL		ML	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
20	62.5	37.5	58.5	41.5	63	37	70	30
25	63.2	36.8	58.0	42.0	63.5	36.5	68.2	31.8
30	61.7	38.3	52	48	55	45	67.8	32.2
37.5	60	40	57	43	52	48	67	33
40	59.8	40.2	57	43	53	47	65	35
45	50	50	54	46	48.5	51.5	51	49

TABLE 4.6.4. QUANTITY OF METHANE AND CARBONDIOXIDE IN BIOGAS
With pH control.

Temperature °C	Methane % (v/v) in biogas							
	CD		IFPS		IFL		ML	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
20	62	38	65.4	34.6	69	31	68	32
25	63.3	36.7	64.5	35.5	67.8	32.2	68.5	31.5
30	60.9	39.1	65	35	69.4	30.6	69.7	30.3
37.5	59.4	40.6	65	35	68.5	31.5	70	30
40	59.5	40.5	61	39	68	32	68.8	31.2
45	50	50	45.6	54.4	42	58	45	55

obtained at 37.5°C.

Thus it can be concluded that for mesophilic digestion the temperature of digester should never rise above 37.5°C. Above this temperature pH control has no effect on the augmentation of gas production. For CD and ML, pH control is not significantly benefecial.

4.7 EFFECT OF C/N RATIO ON BIOGAS GENERATION

4.7.1. GENERAL:

C/N ratio is one of the important parameters responsible for the decomposition of ligno-cellulosic materials during anaerobic digestion and consequently methane production. The experiments were carried out to determine the optimum C/N ratio for biogas generation by using rice straw, wheat straw and dhub grass.

4.7.2. Adjustment of C/N ratio:

The C/N ratio of the raw RS, WS and DG were found to be 73.5, 87.5 and 34.Ø, respectively, (Table 3.1). In order to adjust C/N ratio at 25, urea with a nitrogen content of 46% was added to each of the biomass material in the following proportions:

Biomass	Urea added, % (w/w)
Rice straw	2.52
Wheat straw	3.Ø86
Dhub grass	1.13

These materials were also digested anaerobically without addition of urea under similar experimental conditions. As the C/N ratio of ML, CFL and IFL were 21.2, 12.1 and 21.2, respectively, these were also used for biogas generation for comparison. The pH of substrates of all the digesters was controlled within the range of 6.75 to 7.25.

4.7.3. Digester Performance:

Fig. 4.7.1 shows the weekly biogas production rate for nitrogen supplemented RS, WS and DG. The gas production rate was found to be higher during the first week of digestion as expected and thereafter it decreased. RS, WS and DG produced 83.6%, 83.1% and 67.5% of biogas, respectively, of their total biogas production capacity, within the first four weeks only. Similar trend of biogas production from other biomass materials excepting CFL (Fig. 4.7.2) was observed. From the comparison of the Fig. 4.7.3 with Fig. 4.7.4, which show the total biogas production capacity obtained from nitrogen supplemented and unsupplemented materials, it is found that there was about 3.5%, 5.5% and 1.07% enhancement in biogas production capacity, for RS, WS and DG, respectively. Urea was not added to the digesters fed with ML, CFL and IFL, as the C/N ratio of these materials was found to be less than 25. However, the digesters run on ML, CFL and IFL gave better performance as compared to digester run on nitrogen supplemented RS, WS and DG. The highest quantity of biogas was produced by CFL followed by IFL.

Performance of digesters in terms of cellulose, total solids and volatile solids reduction and methane production is presented in the Tables 4.7.1 and 4.7.2. The reduction of cellulose and TS in nitrogen supplemented and unsupplemented RS, WS and DG were almost equal but the VS reductions were 61.4%, 40.6% and 30.5% in the nitrogen supplemented RS, WS and DG compared to 56%, 38.5% and 30.2% in the unsupplemented RS, WS and DG, respectively. Also in the C/N ratio controlled RS, WS and

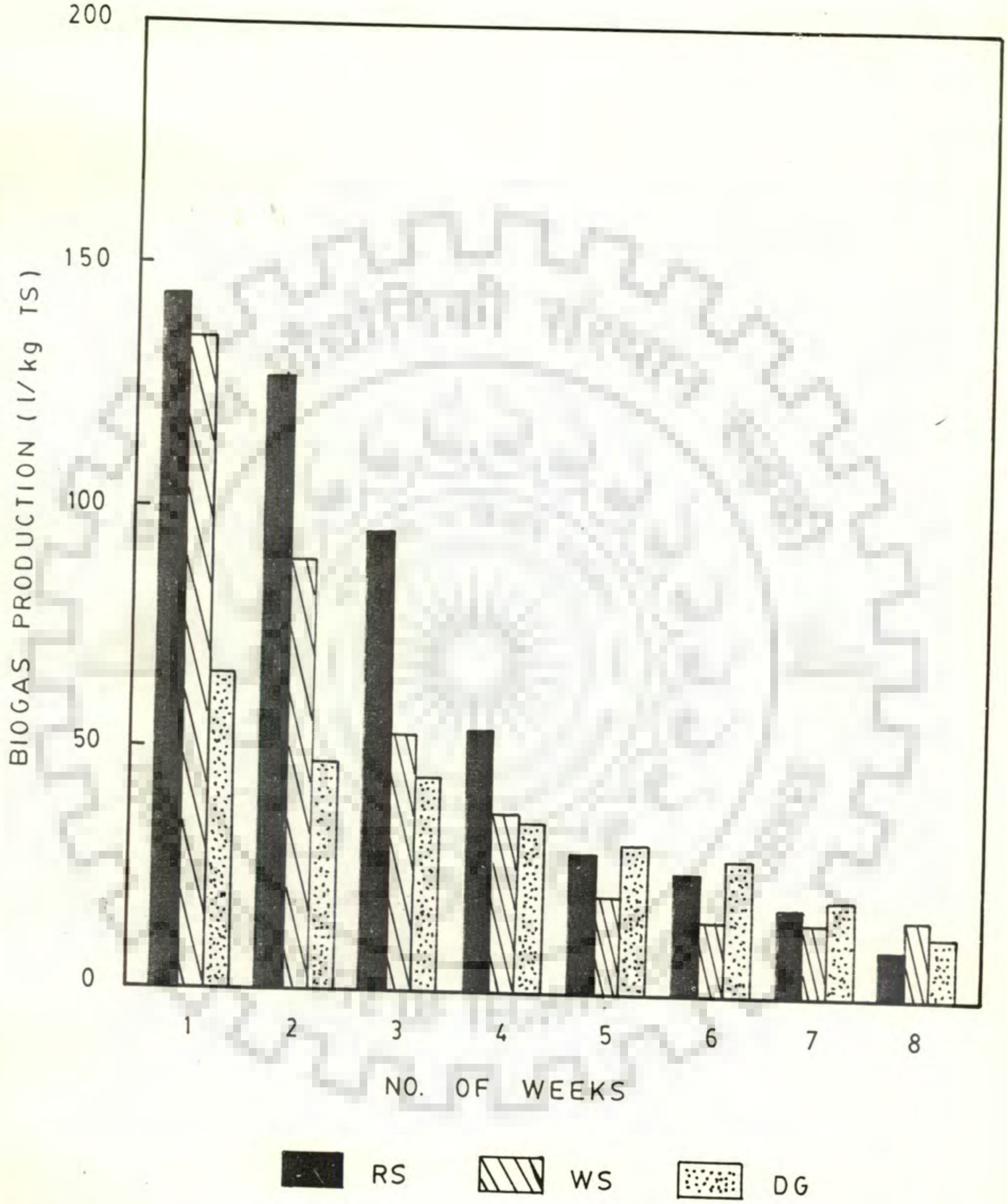


FIG.4.71. WEEKLY BIOGAS PRODUCTION RATE OF NITROGEN SUPPLEMENTED RAW MATERIALS

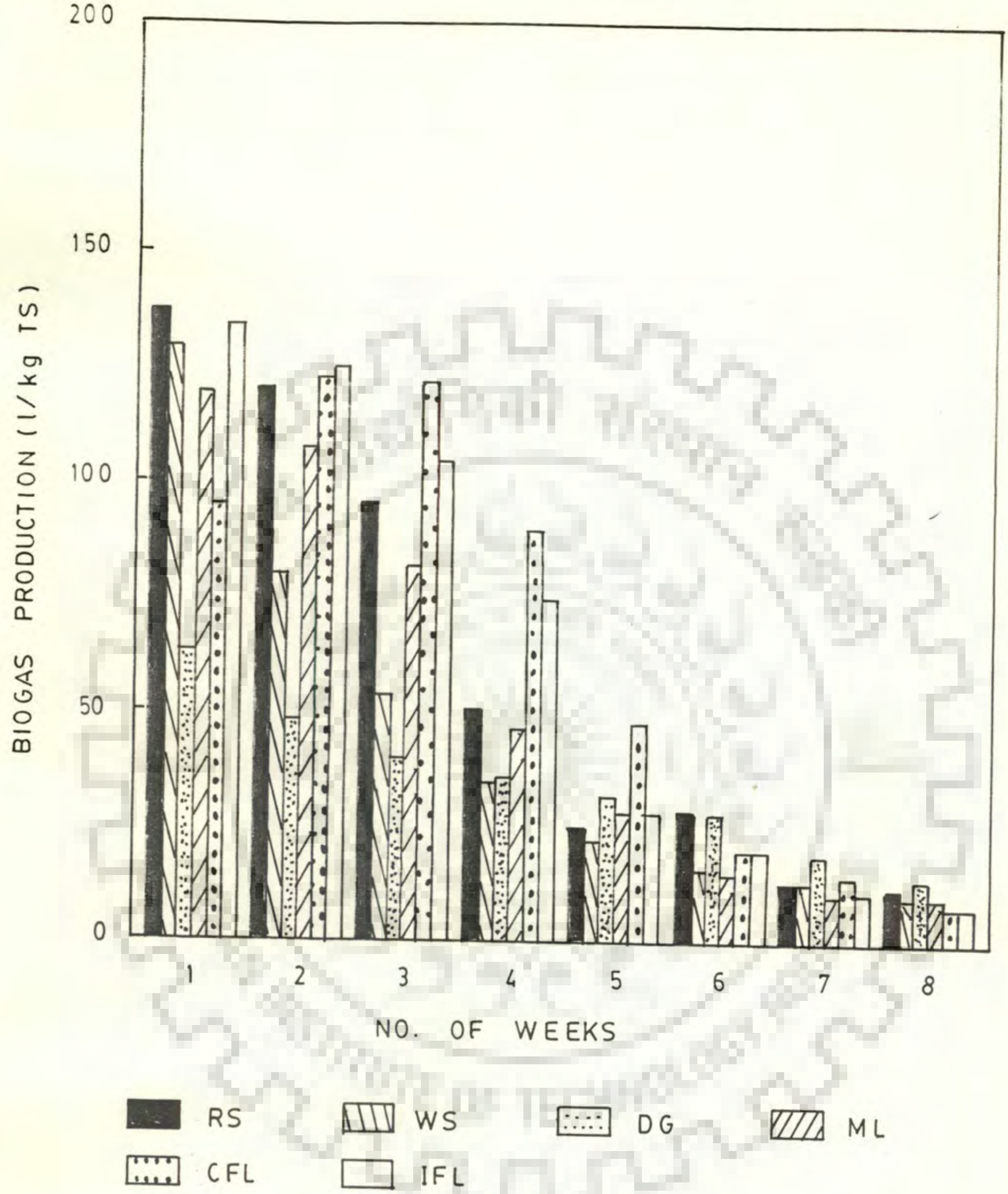


FIG.4.7.2. WEEKLY BIOGAS PRODUCTION RATE OF DIFFERENT RAW MATERIALS WITHOUT NITROGEN SUPPLEMENTATION

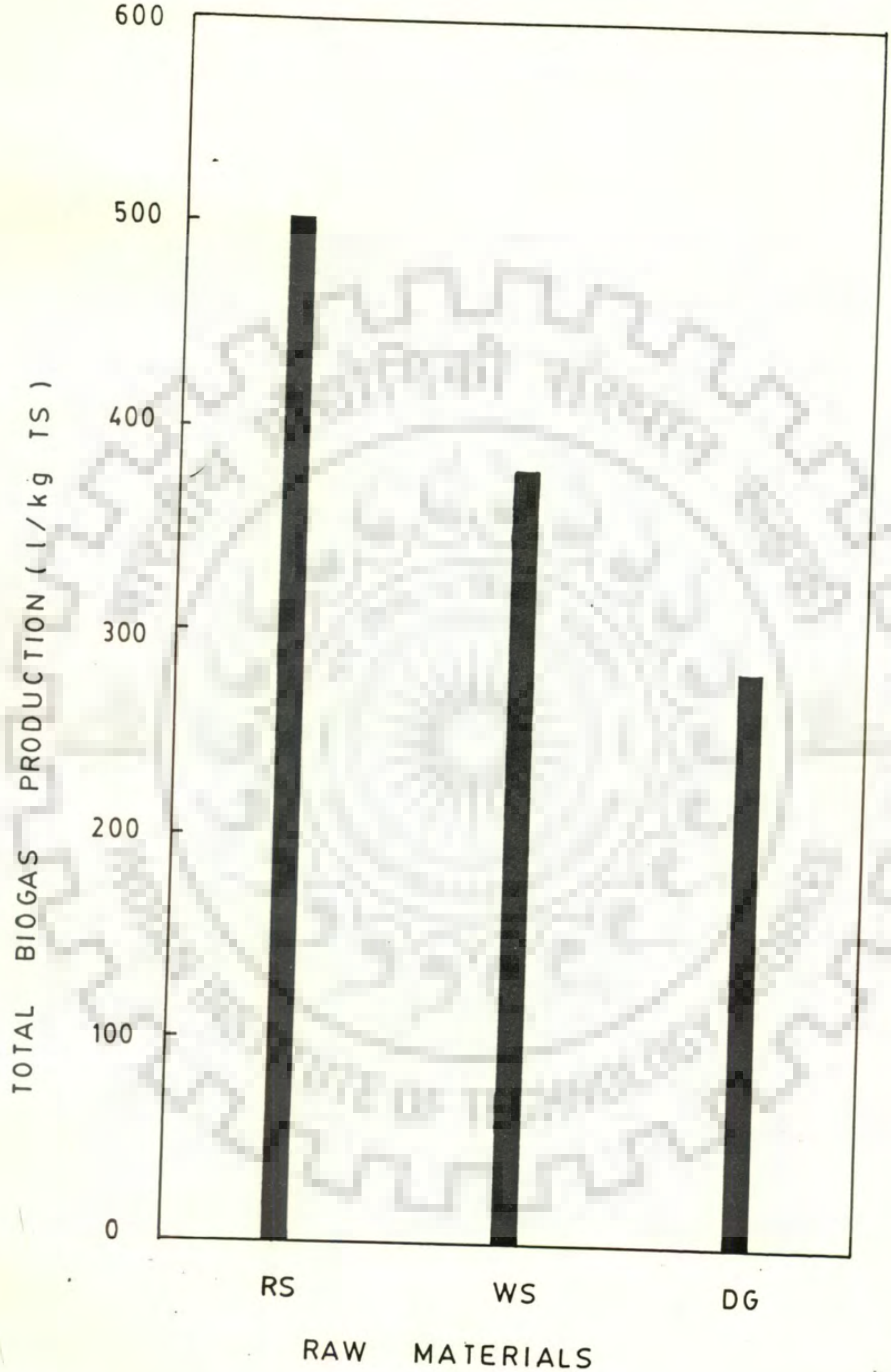


FIG.4.7.3. TOTAL BIOGAS PRODUCTION CAPACITY OF NITROGEN SUPPLEMENTED RAW MATERIALS

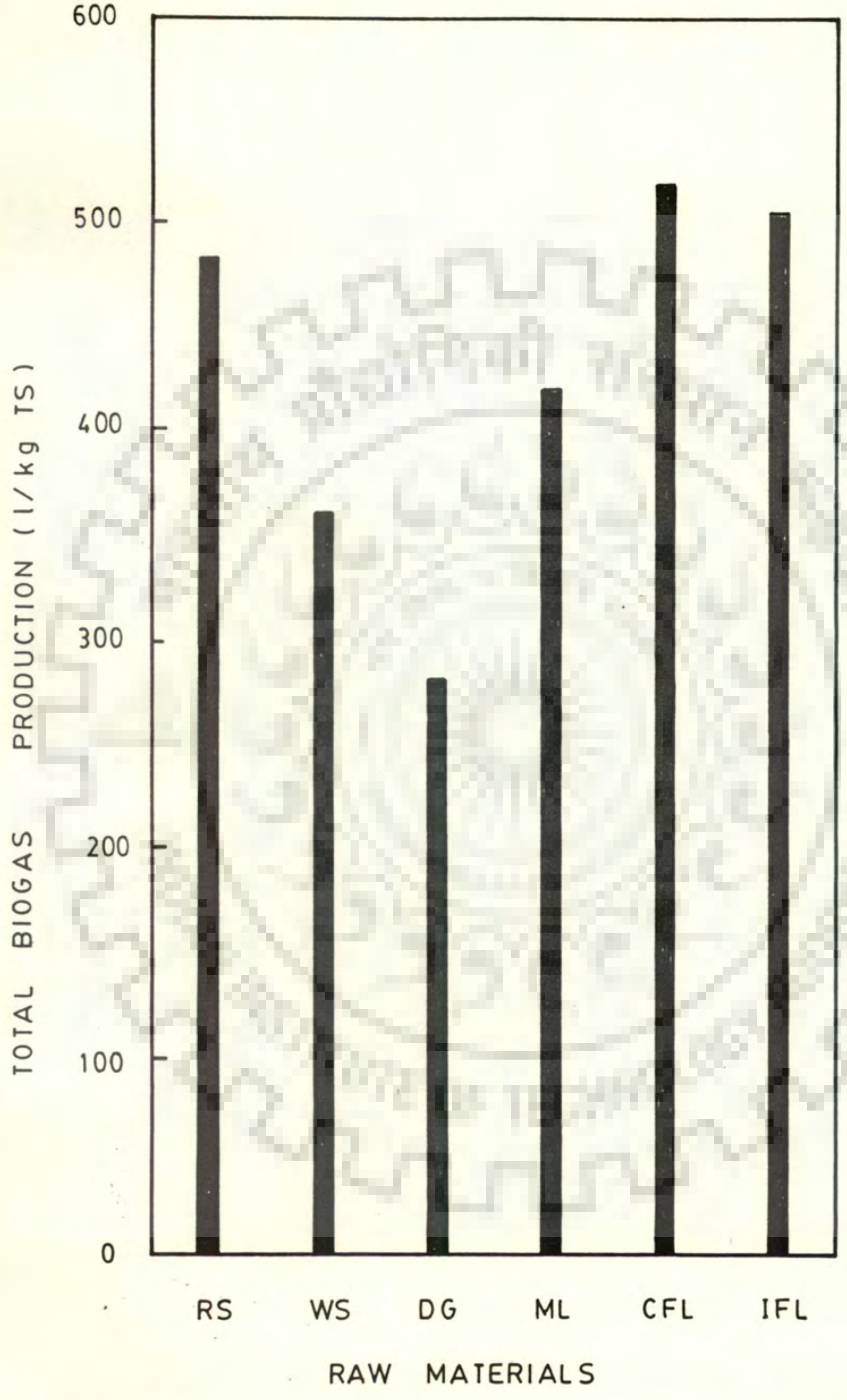


FIG.4.7.4. TOTAL BIOGAS PRODUCTION CAPACITY OF DIFFERENT RAW MATERIALS WITHOUT NITROGEN SUPPLEMENTATION

TABLE 4.7.1. PERFORMANCE OF DIGESTERS
(C/N RATIO ADJUSTED TO 25)

Biomass materials	Cellulose reduction %	Total solids reduction %	Volatile solids reduction %	Methane production (l/kg TS)
RS	46.8	41.6	61.4	300
WS	37.0	30.8	40.6	223
DG	26.4	21.5	30.5	196

TABLE 4.7.2. PERFORMANCE OF DIGESTERS
(C/N RATIO NOT ADJUSTED TO 25)

Biomass materials	Cellulose reduction %	Total solids reduction %	Volatile solids reduction %	Methane production (l/kg TS)
RS	46.5	41.Ø	56.Ø	29Ø
WS	36.8	3Ø.3	38.5	212
DG	26.5	21.5	3Ø.2	194
ML	38.8	33.7	45.3	288
CFL	46.6	4Ø.8	57.8	348
IFL	46.1	39.1	55.Ø	36Ø

DG fed digesters, the methane production was found to be 10, 11 and 2 litre (per kg TS) higher in comparison to those in uncontrolled digesters.

The overall results of the experiment show that the materials resistant to microbial attack are not digested properly even after the supplementation of nitrogen to bring their C/N ratio around 25. The addition of nitrogen in the form of urea does not appear to be so effective as that of nitrogen present in-situ in the materials.

4.8 EFFECT OF MIXING EFFLUENT SLURRY WITH FRESH CATTLE DUNG ON BIOGAS GENERATION

4.8.1. General:

It has been observed that in the existing biogas plants the effluent slurry is not fully digested due to a number of problems. In order to extract and to determine the residual energy from this effluent slurry and thus to improve the economics of the existing biogas plants, it is worth considering the recycling of a part of effluent slurry by mixing it with fresh cattle dung. Laboratory studies have been conducted to study the effect of mixing of effluent slurry with fresh cattle dung in different proportions.

4.8.2. Experimental Work:

Seven Erlenmeyer flasks of four litre capacity each, were used as batch digesters. These were fed with cattle dung, water and effluent slurry. The first six digesters designated as S1, S2, S3, S4, S5 and S6, had cattle dung and water mixed in 1:1 ratio (w/v) to make slurry. These digesters were then fed with different quantities of effluent slurry from zero to fifty percent. This effluent slurry was taken from a Janata type domestic biogas plant operating on cattle dung as feed material. For reference purpose, one litre of this effluent slurry was also kept in the seventh digester designated as S7. The details of all the samples are given in Table - 4.8.1.

TABLE 4.8.1. DETAIL OF SAMPLES

Digester No.	Quantity of wet cattle dung, gm.	Quantity of water, ml.	Quantity of effluent slurry, ml.
S1	1000	1000	00
S2	1000	1000	200
S3	1000	1000	400
S4	1000	1000	600
S5	1000	1000	800
S6	1000	1000	1000
S7	00	00	1000

4.8.3. Characteristics of Feed Materials:

Analysis of fresh cattle dung and effluent slurry is given in Table - 4.8.2. Cattle dung has 79.38% of volatile solids whereas effluent slurry contains 76.48% of VS. TVFA concentrations, respectively, are 1496 mg/l and 932 mg/l, in CD and effluent slurry. pH of the CD and effluent slurry is around neutral. The C/N ratio is 38, and this should be a limiting factor in anaerobic digestion. Low lignin to cellulose ratio of Ø.75 shows the high degree of digestibility of this biomass material. In anaerobic digestion process, cellulolytic bacteria constitute a small fraction of total acidogenic population and due to the presence of cellulolytic bacteria, the cellulose fraction is also digested during anaerobic digestion.

4.8.4. Biogas Production Capacity:

Weekly gas production rates from all the seven digesters are given in Table - 4.8.3. From this table it is found that during the the first week of digestion, digester S6 produced 25.77 times more gas as compared to that produced by digester S1.

In the case of digester S1 which was not seeded with the effluent slurry, the gas production rate was higher in the first week followed by a decrease in second week and continuous increase upto fourth week, thereafter the gas production rate decreased. It shows that if the cattle dung is not seeded with effluent slurry, the normal gas production starts in third week. Although methanogenic and non-methanogenic bacteria are present in cattle dung but the usual gas production starts later:

1) due to low population of methanogenic and

TABLE 4.8.2. ANALYSIS OF FEED MATERIALS

Tests	Cattle Dung	Effluent slurry
Moisture content %,	87.70	91.54
Solid concentration %,	12.30	8.46
Volatile solids %,	79.36	76.48
Ash %,	20.64	23.52
Carbon %,	44.08	42.48
Nitrogen %,	1.16	1.24
Protien %,	7.40	7.91
Cellulose %,	28.65	19.84
Lignin %,	21.46	13.68
C/N ratio	38.00	34.26
Lignin/cellulose ratio	0.75	0.69
TVFA (mg/l) (as acetic acid)	1496	932
pH of slurry	7.06	7.05

TABLE 4.8.3. WEEKLY BIOGAS PRODUCTION RATE (l/kg of wet CD)

Digester No.	No. of weeks							
	1	2	3	4	5	6	7	8
S1	0.63	0.14	1.84	2.79	2.32	1.23	0.99	0.76
S2	7.32	7.51	5.98	2.49	3.00	1.30	1.59	0.90
S3	10.75	7.47	6.12	3.50	2.76	2.76	1.56	1.63
S4	11.75	9.49	5.86	3.09	2.73	2.26	1.85	1.79
S5	13.78	9.72	7.52	4.70	3.52	3.09	2.31	1.53
S6	16.24	11.72	6.96	4.92	3.56	3.10	2.24	1.65
S7*	2.19	0.56	0.75	0.57	0.38	0.26	0.22	0.14

* Digester S7 shows the weekly gas production in l/kg of effluent slurry.

non-methanogenic bacteria,

2) due to conversion of the insoluble matter i.e. fat, protein, cellulose, etc., into soluble organic matter by the decomposing organisms, which are then converted into organic acids by non-methanogenic bacteria.

This conversion process of organic matter into biogas takes some time for solubilization which is about 20 days as seen from this experiment. Similar phenomenon takes place in the case of freshly started biogas plant. If the cattle dung is not seeded with effluent slurry, the ususl gas production gets delayed by about two weeks. Therefore, in order to get gas within the first 3-4 days of the start of the biogas plant, cattle dung should be seeded with at least 20-30% of effluent slurry obtained from an operating biogas plant.

In effluent slurry the methanogenic and non-methanogenic bacterial population is sufficient to activate the seeded digesters and the gas production starts within a day of inoculation.

It is clear from Table 4.8.3 that in digesters S2 to S7, the gas production was higher in the first week and then it continued to decrease. The maximum quantity of gas (50.39 litre/kg of wet cattle dung) was produced by digester S6, having highest percentage of effluent slurry as seen from Fig.4.8.1. Digester S2 seeded with minimum quantity of effluent slurry, produced 30.07 litre of biogas per kg of wet cattle dung. Thus it

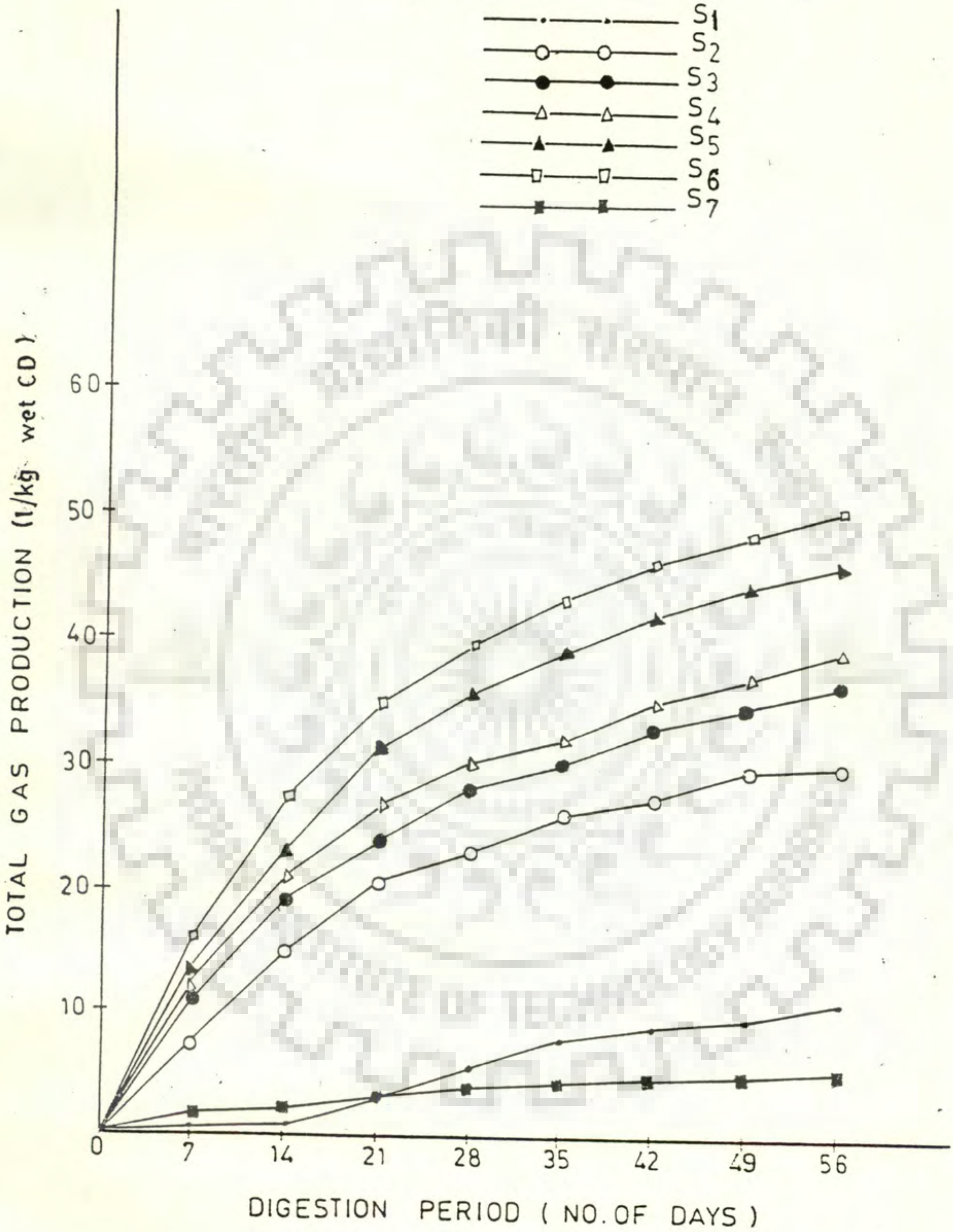


FIG. 4.8.1 TOTAL GAS PRODUCTION VERSUS DIGESTION PERIOD

is clear that by increasing the proportion of effluent slurry in cattle dung the total gas production increased. This may be explained by the fact that by increasing the proportion of effluent slurry, the number of micro-organisms increases and thus there is fast degradation of organic matter with resultant increase in gas formation. The total gas production capacity of all the seven digesters in eight weeks of digestion period is in the following order:

S6 > S5 > S4 > S3 > S2 > S1 > S7

4.8.5. **Performance of Digesters:**

Tables - 4.8.4 and 4.8.5 present the results of analyses of substrate before and after anaerobic digestion. The initial solid concentration of all the digester matter was between 6.25% to 8.46% and the VS concentration was between 79.36% to 76.48%. After anaerobic digestion the VS concentration decreased and was found to be between 74.52% and 65.18%. The maximum reduction was found in the case of digester S6 (65.18%). The initial TVFA concentration were between 1310 mg/l and 1496 mg/l which also reduced and the minimum concentration (549 mg/l) was found in the digester S6. In balanced anaerobic digestion, TVFA concentrations were lower because the quantity of TVFA formed in the digester were subsequently converted into biogas and little accumulation of TVFA in the digester. The initial and final pH values were around neutral except that of effluent slurry (digester S7. In the case of effluent slurry (S7), after

TABLE 4.8.4. ANALYSIS OF SUBSTRATE BEFORE AND AFTER ANAEROBIC DIGESTION

Digester No.	Solid concentration Initial %	Final %	Moisture concentration Initial %	Final %	Volatile solids Initial %	Final %	Ash Initial %	Final %
S1	6.25	--	93.75	--	79.36	74.52	20.64	25.48
S2	6.45	--	93.55	--	79.04	70.94	20.96	29.06
S3	6.70	--	93.30	--	78.67	70.80	21.33	29.92
S4	6.85	--	93.15	--	78.51	68.40	21.49	31.60
S5	6.98	--	93.02	--	78.30	67.35	21.70	32.65
S6	7.12	--	92.88	--	78.17	65.18	21.83	34.82
S7	8.46	--	91.54	--	76.48	74.38	23.52	25.62

TABLE 4.8.5. ANALYSIS OF SUBSTRATE BEFORE AND AFTER ANAEROBIC DIGESTION

Digester No.	TVFA (mg/l) Initial	TVFA (mg/l) Final	Carbon % Initial	Carbon % Final	Total nitrogen% Initial	Total nitrogen% Final	Protein % Initial	Protein % Final	pH Initial	pH Final
S1	1496	1185	44.08	41.40	1.16	1.20	7.40	7.65	7.04	6.92
S2	1448	980	43.91	39.40	1.17	1.21	7.46	7.71	7.04	7.05
S3	1400	755	43.70	38.93	1.18	1.23	7.52	7.84	7.04	6.99
S4	1376	710	43.61	38.00	1.18	1.23	7.52	7.84	7.04	6.96
S5	1342	565	43.50	37.41	1.19	1.22	7.59	7.78	7.05	7.02
S6	1310	540	43.42	36.21	1.18	1.25	7.59	7.97	7.05	7.06
S7	932	477	42.48	41.32	1.24	1.28	7.91	8.16	7.05	7.15

anaerobic digestion of eight weeks, the pH, however, rose to 7.15. It is also found from these tables that after anaerobic digestion there was increase in total nitrogen content.

Analysis of biogas in the third week of digestion shows that the methane content in the gas obtained from all the digesters was between 61% to 63%.

4.9 EFFECT OF STIRRING ON BIOGAS GENERATION

4.9.1 General:

As already indicated, an enhancement in the gas production can be brought about by mechanical, thermal and chemical methods. The mechanical method involves stirring of slurry in the digester. Mixing of the digester slurry (substrate) is an important factor in enhancing the biogas production. Mixing serves to remove stagnant zones and by-passing and allows uniform substrate concentration and retention time. This also allows the uniform and continuous availability of digester substrate to the microbial flocs by surface renewal and also breaks off foams and blanket/scum of floating particles/gas bubbles at the top of the digester slurry level [116].

Mixing of the digester slurry may be affected by mechanical stirring - manual, auto or through diffused bubbling of the biogas generated at the bottom of the digester. Placement of the inlet and outlet pipes at different positions also helps in circulation and mixing, however, this is possible in Khadi & Village Industries Commission (KVIC) model digesters only. Angled iron and flat strips may be attached to the gas holder dome in the KVIC model. Mechanical rotation of this dome may also be used to bring about mixing.

Experiments were conducted to investigate the effect of stirring on biogas generation. The results pertaining to the effect of stirring on biogas production from cattle dung seeded with effluent slurry taken from a cattle dung fed Janata biogas plant, are discussed in this section.

4.9.2. Experimental Procedure:

Fresh wet cattle dung was mixed with tap water in 1:1 ratio (w/v) and then with effluent slurry so as to give a solid concentration of 7.33%. Of the two sets of batch experiments, the one designated as D1 had its stirring after an interval of three hours for five minutes using a magnetic stirrer and the other designated as D2 was kept unstirred throughout the digestion period of 8 weeks. Nine digesters were used in each set of experiments; two for daily gas production measurement and seven for weekly analysis of substrate for pH and total volatile fatty acids (TVFA).

4.9.3 Characteristics of the raw material:

The characteristics of the of the wet cattle dung and the effluent slurry are given in Table 4.9.1. It is seen that the TVFA content is much higher in fresh cattle dung as compared to that in the effluent slurry. Further while the cattle dung is almost neutral, the effluent slurry is acidic.

4.9.4. Change in composition of substrate during anaerobic digestion:

The composition of the substrate in the digesters before and after anaerobic digestion are given in Table 4.9.2. The initial composition of substrates in both the digesters (D1 and

TABLE 4.9.1 CHARACTERISTICS OF CATTLE DUNG AND EFFLUENT SLURRY

Sl. No.	Parameter	Cattle Dung	Effluent Slurry
1.	Moisture content, %	86.75	92.96
2.	Solids concentratons, %	13.25	7.04
3.	Volatile solids*,%	82.07	72.34
4.	Ash *, %	17.92	27.66
5.	Nitrogen*,%	1.20	1.28
6.	Protein*,%	7.65	8.16
7.	Cellulose*, %	27.23	20.24
8.	Hemicellulose*,%	50.73	52.18
9.	Lignin*,%	18.04	16.88
10.	Carbon/nitrogen ratio*	37.99	31.39
11.	TVFA, mg/litre as acetic acid	18.07	6.15
12.	pH	6.98	6.69

* Dry weight basis

TABLE 4.9.2 COMPOSITION OF THE SUBSTRATE IN DIGESTERS (DRY WEIGHT BASIS)

Sl. No.	Parameter	Initial value	Final value (after anaerobic digestion for eight weeks)	
			D1	D2
1.	Solids concentration, %	7.33	4.77	5.28
2.	Volatile solids, %	77.05	68.91	71.57
3.	Ash, %	22.95	31.09	28.43
4.	Nitrogen,%	1.22	1.42	1.40
5.	Protein, %	7.78	9.05	8.93
6.	Cellulose, %	23.96	20.90	22.16
7.	Hemicellulose, %	51.47	40.08	46.26
8.	Lignin, %	17.44	23.65	20.58
9.	Carbon/nitrogen ratio	35.08	26.96	28.40

D2) is same. After anaerobic digestion for 8 weeks, the solid concentration in stirred digester (D1) and unstirred digester (D2) was found to be 4.77% and 5.28% respectively. The volatile solids, cellulose and hemicellulose contents were found to be lower in digester D1 as compared to those in digester D2. This shows that stirring enhances the reduction and solubilization of total solids, volatile solids, cellulose and hemicellulose. Data on percentage reduction of different components are given in Table 4.9.3. Reduction in volatile solids in digester D1 is 43.53% compared to 38.58% in digester D2. The cellulose hydrolysis rate is dependent on substrate composition and bacterial concentration (especially cellulolytic bacteria) and also on the operating parameters, such as pH, temperature, etc.. There was practically no degradation of lignin and the increase in its proportion was due to the reduction of other components. Lignin is the major hindrance to the utilization of cellulosic residues from enzymatic hydrolysis and is very resistant to degradation by anaerobic digestion.

The proportion of methane in biogas obtained from digesters D1 and D2 was in the range of 62-64%. Digester D1 produced 231.82 litres of methane/kg. of VS as compared to 205.44 l/kg VS for digester D2. The higher reduction in the proportions of volatile solids, cellulose and hemicellulose and higher gas production in the stirred digester compared to that in unstirred one may be attributed to the following factors:

(i) Better contact between microbial biomass and the

TABLE 4.9.3. RELATIVE PERFORMANCE OF STIRRED AND UNSTIRRED DIGESTERS

Digester	VS reduction %	Cellulose reduction %	Hemicellulose reduction %	Lignin reduction	Methane Production litre/ kg VS
Stirred (D1)	43.53	43.23	49.32	11.75	231.82
Unstirred (D2)	38.58	33.38	35.25	14.99	205.44

substrate,

(ii) Quick digestion of biomass material,

(iii) Maintenance of uniform temperature in the whole of the digester,

(iv) Dispersion of accumulated total volatile fatty acids.

4.9.5. Change in pH and TVFA during anaerobic digestion:

Weekly values of pH, TVFA and gas production for digesters D1 and D2 are shown in Figs.4.9.1 and 4.9.2, respectively. The initial pH of substrate in both the digesters was 6.83; it decreased to 6.71 in the second week and then started increasing in digester D1. In the anaerobic digestion of CD, pH is self regulated. Due to the formation of TVFA, pH falls. The methanogenic bacteria convert the so formed acids into methane, thus increasing the pH. When the acid forming and methanogenic bacteria are present in proper concentration, the pH of the whole system reaches almost 7.Ø. In digester D2, after the fourth week of digestion pH was above neutral. The highest TVFA values (2835 mg/litre in D1 and 214Ø mg/litre in D2) were obtained in the first week of digestion. Thereafter, TVFA formation showed a decreasing trend. The weekly gas production rate remains higher in D1 compared to that in D2 for the first five weeks. Thereafter, gas production was slightly higher in D2 compared to that in D1.

Clausen and Gaddy [27] conducted an experiment to determine the effect of agitation on reactor performance. A sixty day cycles were conducted with no agitation and with frequent

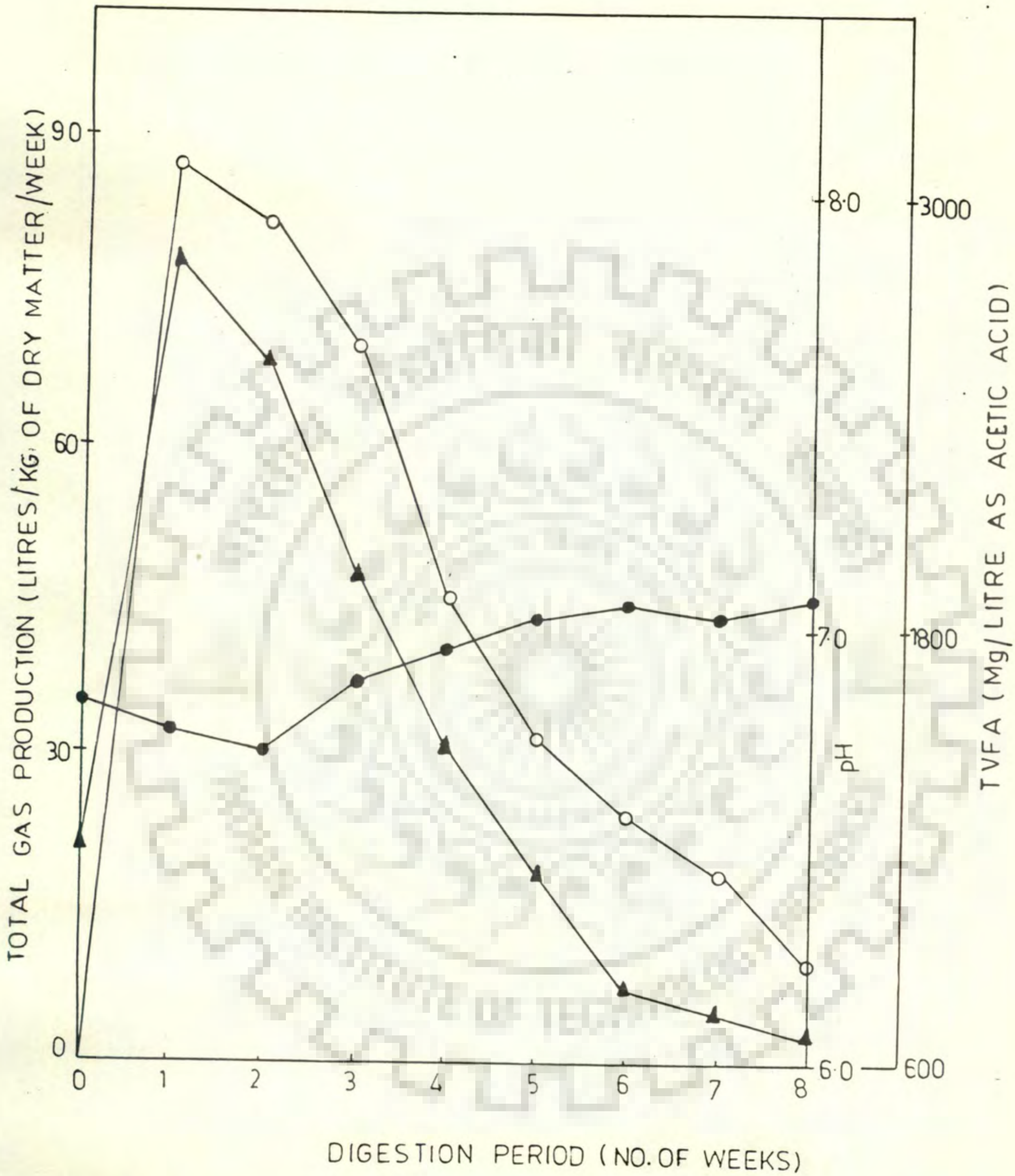


FIG 4.9.1. ANAEROBIC DIGESTION OF STIRRED CATTLE DUNG

o, TOTAL GAS PRODUCTION; ●, pH; ▲, TVFA.

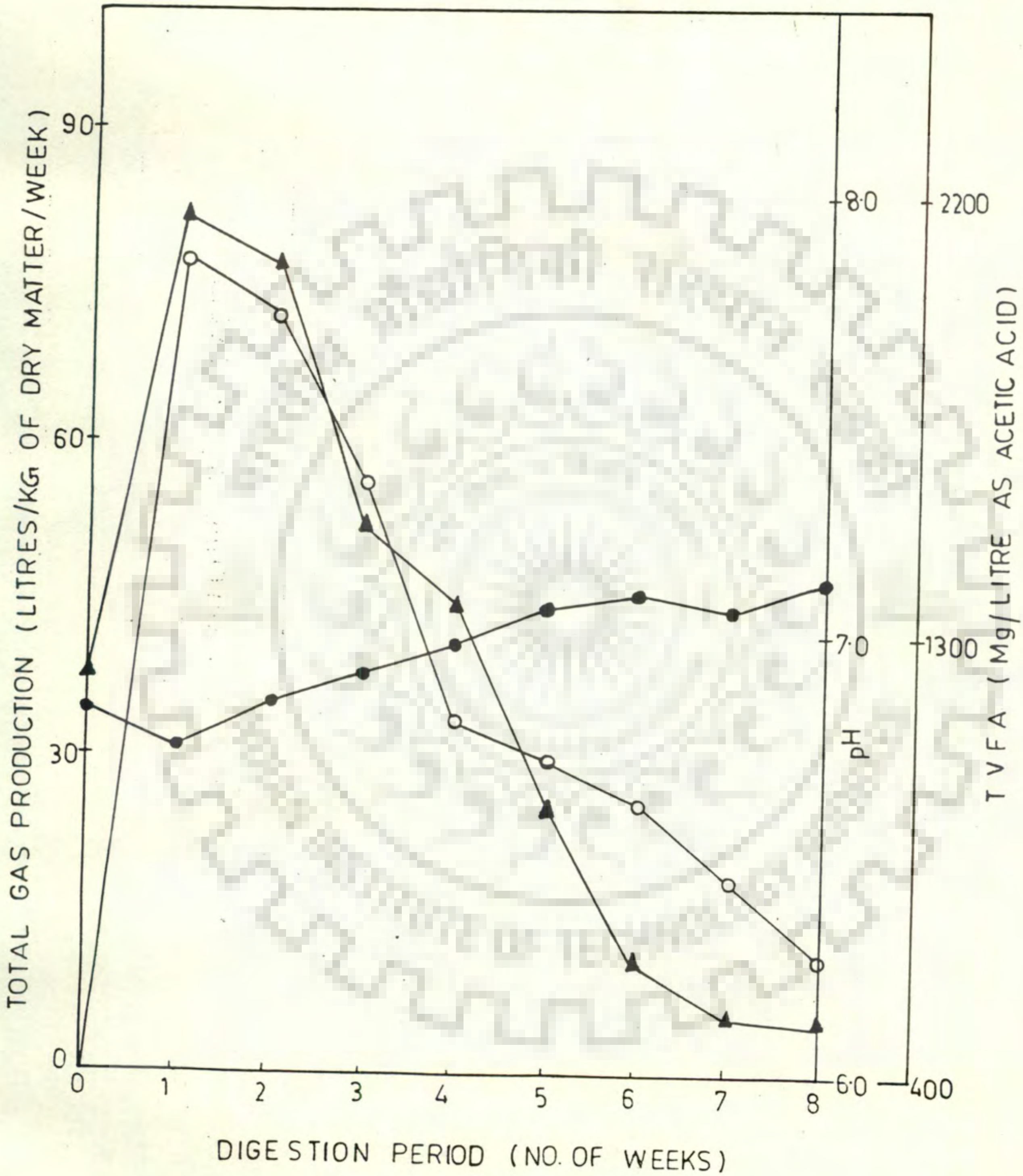


FIG. 4.9.2. ANAEROBIC DIGESTION OF UNSTIRRED CATTLE DUNG

o, TOTAL GAS PRODUCTION; •, pH; ▲, T V F A.

(1.5 hr/day) agitation to compare gas production and conversion with normal agitation cycle and obtained the similar results as that of ours.

4.10. KINETICS OF DEGRADATION OF *IPOMOEA FISTULOSA* LEAVES

Seven semicontinuous digesters with different retention timess were run for studying the kinetics of degradation of IFL to produce biogas. For each digester the steady state values of gas production and carbon concentration in the influent and effluent streams were noted for 5 days. The analysis of gas obtained from these digesters showed a markedly uniform composition with methane content varying from 69 to 71%. The averaged values of biogas production rate, methane production rate and carbon concentration for each digester with different retention time are presented in Table 4.10.1.

Normally Monod kinetics is used to describe the rate of simple anaerobic digestion for mixed cultures,

$$-r_A = \frac{K_1 C_m C_A}{K_M + C_A} \qquad \text{----------- (1)}$$

Where K' and K_M are substrate specific constants and C_m and C_A are micro-organism and substrate concentrations, respectively. However, the accurate determination of micro-organism concentration in the mixed culture slurry substrate is not possible since the soild particles were present in the undigested form in the effluent. Many researchers [25, 35, 90, 127], however, successfully used the first order rate equation (with and without modifications) to express anaerobic digestion kinetics.

For perfectly mixed flow reactor, the reaction rate of the

TABLE 4.10.1. GAS PRODUCTION DATA FOR DIFFERENT DIGESTERS

Retention Time (days)	Biogas Production/ Day (Litre/kg dry matter fed/ day)	Methane Production/ Day (Litrs/kg VS fed/day)	C_{Ao} (mole carbon/ litre)	C_A (mole carbon/ litre)	-Reaction Rate ($-r_A$) (mole carbon/ litre/day)
10	18.5	15.0	3.965	3.789	0.01760
15	16.9	13.7	3.965	3.679	0.01906
20	15.3	12.4	3.965	3.642	0.01615
25	14.0	11.4	3.965	3.596	0.01476
30	13.0	10.6	3.965	3.582	0.01277
35	12.0	9.8	3.965	3.563	0.011486
40	11.6	9.4	3.965	3.550	0.010375

substrate (carbon) can be calculated at various retention times by using the design equation [79].

$$-r_A = \frac{C_{A0} - C_A}{\tau} \qquad \text{---------------(2)}$$

Where C_{A0} and C_A are inlet and outlet substrate concentrations and τ is the retention time.

The digesters used in the experiment were frequently stirred and the gas generation is assumed to keep the reactor vessel contents well mixed and of constant composition. Therefore, equation (2) could be used to determine the rate of digestion. Using carbon concentration of the inlet feed and the reactor effluent, the rate of reaction was determined using equation (2) and is given in Table 4.10.1.

If the anaerobic digestion followed a simple first order kinetics, the plot of reaction rate as a function of effluent carbon concentration should give a linear straight line relationship. Figure 4.10.1 shows such a plot for the present experimental data. It is found that all the data, excepting that for 10 day retention time is fitted by a straight line relationship:

$$-r_A = 0.06417\, C_A - 0.21703 \qquad \text{-------------(3)}$$

Similar linear relationships have been obtained by Clausen and Gaddy [25] and Doyle et al., [35] for the anaerobic digestion of orchard grass and corn stover, respectively.

From equation (3) it is observed that methane production

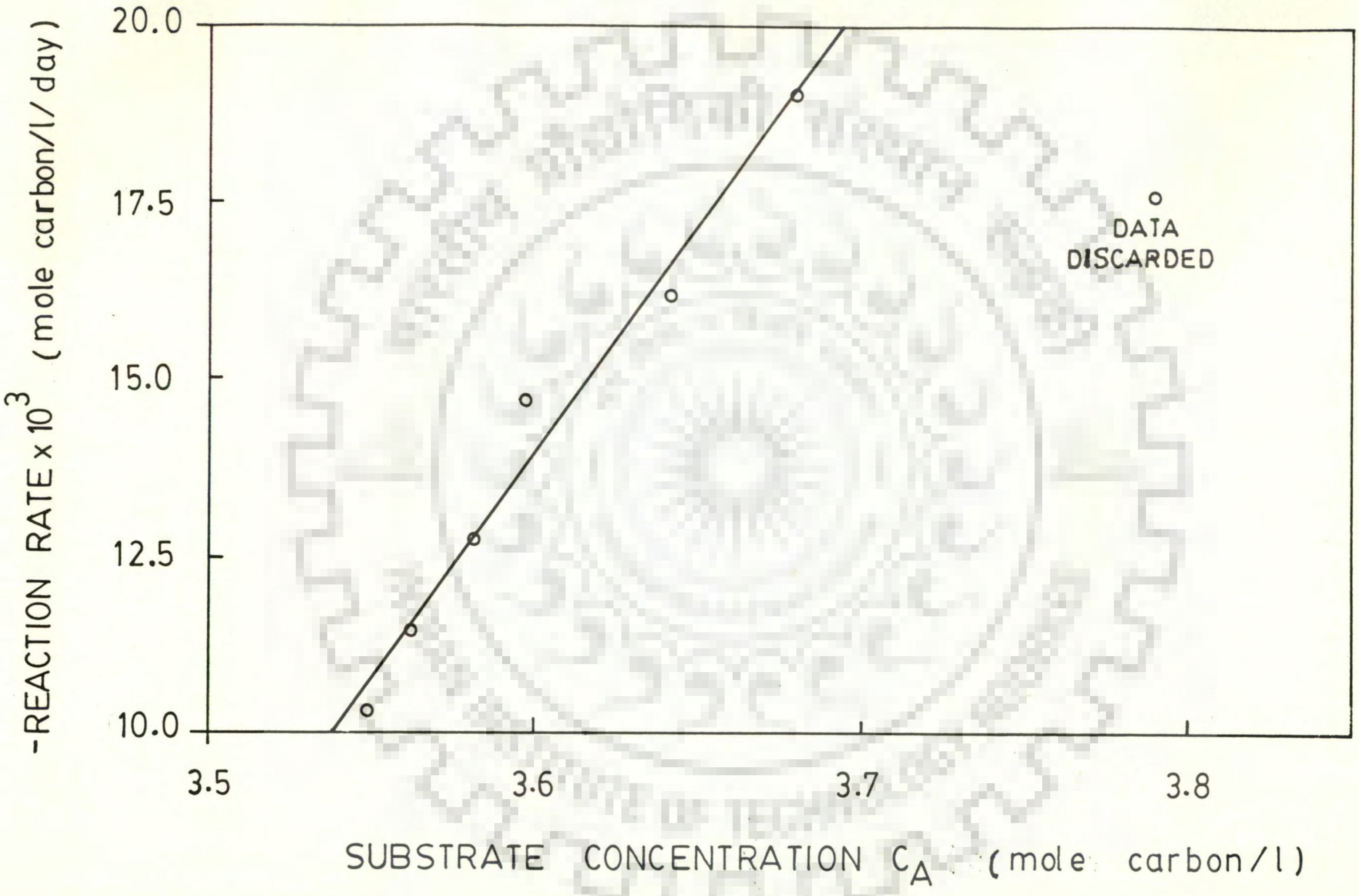


FIG. 4·10·1 DETERMINATION OF A REACTION RATE EQUATION FOR SINGLE STAGE METHANE PRODUCTION stops at a carbon concentration of 3.3822 mole/litre. The inoculum used in the present study has been obtained from a domestic Janata type biogas plant operating on cattle dung as a feed material. It is possible that the necessary microbial species may not be present to further digest complex cellulosic molecules. It is further possible that the straight line to the abscissa extraploting to a value of $-r_A=0$, is an oversimplication and that a minimum carbon concentration exists at a lower value than 3.3822 mole/litre [25]. In this condition, the rate of reaction would be slightly increased and equation (3) would give the minimum rate of carbon utilization for the reaction.

Thus, the first order reaction kinetics may be used to describe anaerobic digestion of IFL. This kinetic expression is independent of microorganism concentration and highly limited by the degradation of cellulosic molecules by the microbes present in the reactor. The digestion can be enhanced by pretreatment like preincubation, alkali treatment and or by addition of microbial culture suitable to attack complex cellulose structure, as it is quite possible that the suitable microorganisms may not be present in the inoculum.

The methane production rate, (l/kg VS/day) is found to be dependent upon retention time and decreases with an increase in retention time. For the digester having a retention time of 10 days, daily methane production was obtained as 15.0 l/kg of VS fed/ day whereas the digester with 40 days retention time gave a daily production of 9.4 l/kg of VS fed/day, under steady state conditions. The data seems to follow an experimental decay relationship:

$$Q_M = Q_{MO}\ e^{-k_d \tau} \qquad \text{----------------(4)}$$

where Q_M is the methane production rate, k_d is the decay coefficient (day-1) and Q_{MO} is the maximum production rate possible at zero retention time.

Figure 4.1Ø.2 is a plot of ln Q against τ. It is found that the data are best fitted by a linear relationship:

$$Q_M = 17.2783\ \exp.(15.9236 \times 1Ø^{-3}\ \tau)$$

The correlation coefficient of data for the above equation is Ø.9948.

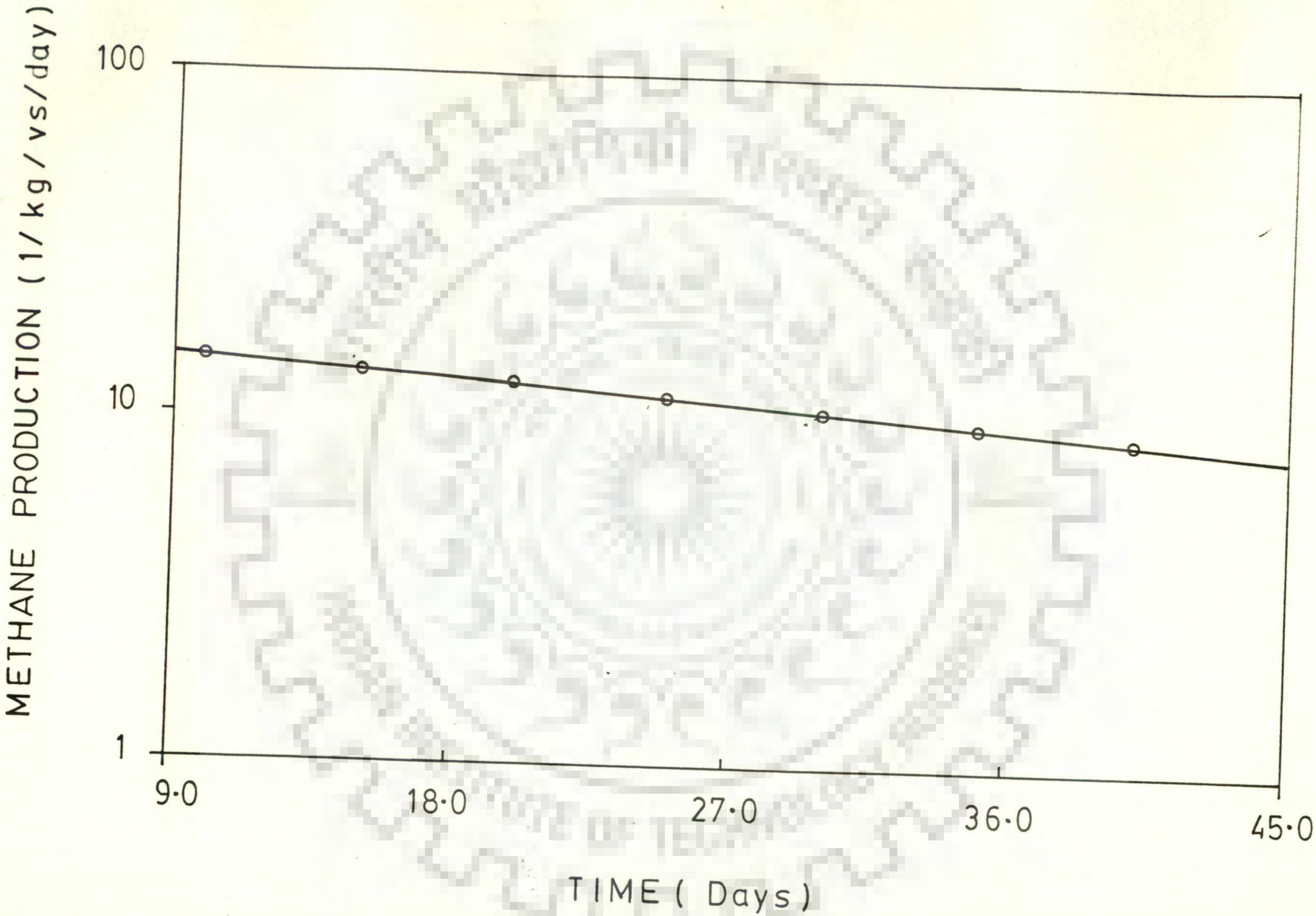


FIG. 4·10·2 EFFECT OF RETENTION TIME ON METHANE PRODUCTION

CHAPTER V

CONCLUSIONS

On the basis of extensive investigations related to biogasification of crop/plant residues and weed plants individually, in blends and as supplement to conventional cattle dung substrate and the effect of various process and operating parameters on the quality, rate of biogas production and the total gas production, the following important conclusions can be drawn:

1. *Ipomoea fistulosa* plant stem (IFPS), *Ipomoea fistulosa* leaves (IFL), Cauliflower leaves (CFL), Rice straw (RS), *Mirabilis* leaves (ML), Banana peelings (BP), Wheat straw (WS) and Dhub grass (DG) are found to be good substitutes for the cattle dung for biogas production. These biomass materials have been found to produce biogas in reasonably good quantities individually as well as in the form of blends with other materials.

2. Blending of biomass with cattle dung is found to enhance the production of biogas. However, some of the digesters fed with 5% and 100% IFPS, IFL and CFL individually failed to produce biogas. In the case of ML, BP, RS, WS and DG the total gas production increases with increase in the percentage of biomass. However, very high percentages of

IFPS, IFL and CFL (75 to 100%) failed to yield biogas successfully indicating that it is essential to blend these biomass materials with cattle dung to have successful operation of the digesters.

3. Banana peelings (BP) supplemented with and without Ipomoea fistulosa leaves (IFL) have good potential for producing biogas. Under uncontrolled conditions of pH and total volatile fatty acids, a blend of 75% BP and 25% IFL produces more biogas (453.23 l/kg of TS) in comparison to 100% BP (421.85 l/kg TS).
During the first four weeks of digestion more than 80% of biogas is produced out of the total production in eight weeks of digestion period, in the case of 100% BP and a blend of 75% IFL and 25% BP. This is a very important conclusion as banana peeling is simply wasted in India with very slow composting property.

4. The pH and TVFA concentration have profound effect on biogas generation. The acidogenic bacteria have been found to be less sensitive in comparison to methanogenic bacteria and may survive in acid medium having pH around 5.25. These bacteria continue to convert organic matter into intermediate acids even at pH around 5.25 while the methanogenic bacteria cease to remain viable. Under such conditions the TVFA concentration increases and the digester fails to produce biogas. However, methanogenic

bacteria have been found to remain active at TVFA concentration levels as high as 3800 mg/l.

5. Calcium hydroxide has been successfully used to neutralise TVFA concentrations in the digesters, and the digesters which failed to produce biogas due to high TVFA concentrations and low pH, were found to operate successfully when the TVFA concentration level was brought down in the range of 1000 to 1500 mg/l and pH between 6.75 to 7.25. In the case of IFPS, IFL and CFL, the control of pH and TVFA concentration in the optimum range is essential for the successful and continuous operation of the digesters.

6. Particle size is found to have profound impact on the digestion capabilities of biomass and therefore on the resultant biogas production. Out of four particle sizes investigated (0.088, 0.40, 1.0, and 6.0 mm), the biomass materials with particle size of 0.088 mm and 0.40 mm produced an almost equal quantity of biogas, thus size reduction below 0.40mm would seem to be uneconomical. In the case of succulent leaves such as ML, CFL, IFL etc., full leaves can also be used without shredding.
The highest quantity of methane (362 l/kg of TS) was produced by 0.088 mm particles of IFL followed by CFL (348 l/kg of TS) and BP (334 l/kg of TS). Except for DG, the digestibility of all the biomass materials were found to

be satisfactory. The methane content of the biogas was found to be 67% (v/v) for all the materials except WS and RS (60%).

7. Preincubation of biomass materials with water as also the pretreatment of biomass with alkali before using these materials as the digester feedstock have been found to have pronounced effect on the digestibility, rate of gas production and total gas production. Increase in preincubation period results in pH depression and an increase in TVFA concentration. This causes the failure of digesters unless the pH of the preincubated feed is brought to around 7.0 (excepting for the cattle dung digester).

8. Preincubation of biomass materials does not effect the methane content of the biogas produced in the digester and almost same methane concentration is found for a particular biomass incubated for different periods of time. Banana peeling gave highest methane content followed by IFL. Preincubation was found to help in higher reduction of cellulose and total solids.

9. Drying of biomass materials after preincubation and subsequent feeding to digester was found to reduce biogas production. However, the preincubation for long periods like 40 days may prove to be counterproductive due to large volume requirement for the preincubation of the

biomass and thus may not be a feasible proposition to be adopted for most of the biomass materials in large community biogas plants.

10. Alkali treatment is found to improve the biogas production considerably. It is found that treatment of RS with 1% NaOH solution for one day at 37°C produces almost the same amount of biogas as that obtained from RS preincubated in water for 40 days. In the case of BP the same treatment increases the gas production by more than 5% over that obtained from 40 days preincubation with water. It is found that cooking with 5% alkali solution at 100°C for 2 hours, gives only a marginal improvement in gas production over that from 24 hours treatment with 1% alkali at 37°C. Thus, it may be found that one day preincubation in 1% alkali solution at normal temperature may be a preferable option for preincubation/pretreatment to enhance biogas production.

11. The biogas production was found to have a linear variation with the logarithm of inverse of temperature upto 37°±0.5° C. For temperature higher than 37° ±0.5°C the gas production decreased and at 45°C the digesters failed completely. It is found that pH control plays an important role upto a temperature of 37° ±0.5°C with an increase in biogas production with increase in temperature. In the case of CD and ML, no pH control is required.

12. The addition of urea as a nitrogen supplement to some of the biomass materials for maintaining C/N ratio of the initial feed to 25 (according to Scharer and Moo-Young, [111], C/N ratio of 25-35 was optimum for gas production) was found to enhance the biogas production only marginally by 1 to 5.5%. Those biomass materials which have C/N ratio less than 25 were found to give better performance than those biomass materials having higher C/N ratio and which were supplemented with urea to adjust their C/N ratio to around 25. Thus it brings out very clearly that the materials resistant to microbial attack (WS and DG) are not digested properly even after supplementation with nitrogen.

13. Though the fresh cattle dung contains microbial population including those of acidogens and methanogens, their population is so small that without inoculation the gas production is delayed by about 20 days. Once the biogas plants are seeded with about 20 to 30% of effluent slurry obtained from another operating biogas plant, the gas production starts within a day of feeding.

14. Stirring of digester slurry is an important factor in enhancing the biogas production. It serves to remove the stagnant zones and allows uniform substrate concentration. It has been found that stirring the digester substrate (cattle dung) at an interval of 3 hours for 5 minute

duration, enhances the total gas production capacity by 11.4%. Reduction of volatile solids and cellulose was 43.5% and 43.2% in stirred digester compared to 38.6% and 33.4% in unstirred digesters, respectively. The methane percentage was also found to be higher in stirred digesters compared to unstirred ones. Therefore a suitable stirring/mixing device should be provided in family size and domestic biogas plants in order to enhance the biogas production.

15. Based on the total quantum of methane produced during the eight weeks of digestion period from unincubated biomass materials under conditions, the materials in the decending order of importance (litre of methane/kg TS) are: IFL (360), CFL (348), BP (336), IFPS (315), RS (292), ML (288), WS (212), DG (194), CD (126).

16. The expression for the rate of degradation of IFL as a function of substrate concentration as determined from semi-continuous steady state experiments could be given by a linear relationship as:

$$-r_A = 0.06417\ C_A - 0.021703$$

where r_A is expressed in mole carbon/l/day and C_A is expressed in mole/l.

To summerise, it can be stated that "a number of crop/plant residues and weed plants could be successfully used as substitutes or as supplements to the cattle dung for biogas production and a considerable amount of quantitative and qualitative improvements in gas production could be brought about by the blending of biomass materials, stirring the digester slurry, preincubation and pretreatment of the substrates and a judicious control of their C/N ratio, pH, TVFA, temperature and particle size".

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APPENDIX-I

The composition of rice straw on dry weight basis is given as follows:

C = 44.1%
H = 4.99%
N = 0.59%
O = 29.4%

Ash = 20.9%
VS = 79.1%
Protein = 3.8%

After neglecting nitrogen, the emperical formula of rice straw (by using equation given by Chynoweth et al., [24] is:

$$C_{3.67}\ H_{4.99}\ O_{1.84}$$

Biomethanation of rice straw (by stoichiometry) could be expressed as follows:

$$C_{3.67}\ H_{4.99}\ O_{1.84} + 1.5H_2O \longrightarrow 1.99CH_4 + 1.67CO_2$$

Maximum theoretical methane yield could be calculated as follows:

1.99 k mole of methane X 25.20 m^3 methane/k mole

= 50.148 m^3 methane

$$1 \text{ kg rice straw VS} \times \frac{1 \text{ k mole}}{79.1 \text{ kg rice straw VS}} \times \frac{50.148 \ m^3\ CH_4}{\text{k mole}}$$

= 0.6339 m^3 CH_4/kg VS

<u>Correction for bacterial cell mass</u>

Estimating that some VS converted to cell and not to gases. Let 20% and 7% of carbohydrate and protein converted to bacterial cell, respectively.

Carbohydrate = 100 - (20.1 + 3.8)

= 76.1%

$$\text{and VS} = \frac{76.1 \times 100}{79.1}$$

= 96.329% (CHO)

Protein = 100 - 96.329

= 3.671%

$$\therefore \begin{array}{r} 20 \times 0.96329 = 19.26 \\ 7 \times 0.03671 = 0.2569 \\ \hline 19.5169 \\ \hline \end{array}$$

Thus theoretical yield of methane corrected for bacterial cell = theoretical yield X (1-0.1951) m^3 CH_4/kg VS

= 0.6339 X 0.8049

= 0.510 m^3 CH_4/kg VS.

APPENDIX-II

APPENDIX II. pH VALUES AND TVFA CONCENTRATION (mg/l)

Raw materials	Temp. °C	I		II		III		IV		V		VI		VII		VIII	
		TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH	TVFA	pH
CD	20	665	6.85	840	6.70	915	6.55	985	6.48	965	6.65	995	6.78	910	6.75	875	6.75
ML	20	1440	5.92	1310	5.90	1400	6.00	1465	5.98	1470	6.00	1450	6.03	1390	6.05	1200	6.03
CD	25	705	6.83	950	6.65	935	6.72	1015	6.77	915	6.70	890	6.75	855	6.80	840	6.78
ML	25	1450	5.90	1250	5.99	1200	6.03	1230	6.05	1180	6.05	1200	6.08	1210	6.05	1185	6.10
CD	30	995	6.73	950	6.75	815	6.82	740	6.85	710	6.83	690	6.95	585	6.95	525	6.93
ML	30	2150	5.65	2050	5.81	1840	5.99	1610	6.13	1200	6.25	1090	6.40	900	6.50	765	6.55
CD	37.5	1300	6.55	1090	6.85	1000	6.89	810	7.00	535	6.98	450	6.98	485	7.00	450	7.00
ML	37.5	3200	5.60	1800	6.70	1300	6.90	950	7.08	610	7.15	540	7.06	485	7.05	350	7.05
CD	40	800	6.78	810	6.82	750	6.88	750	6.85	735	6.85	750	6.90	715	6.90	720	6.93
ML	40	1450	6.05	1390	5.95	1440	5.98	1425	6.00	1400	6.06	1390	6.05	1400	6.03	1385	6.05
CD	45	560	6.92	560	6.95	550	6.97	545	6.95	555	6.96	548	6.97	540	6.95	525	6.96
ML	45	1025	5.90	1150	5.92	1140	5.95	1145	5.95	1130	5.98	1115	6.02	110	6.00	1100	6.03

No of weeks

LIST OF PUBLISHED PAPERS FROM THIS THESIS

PAPERS PUBLISHED IN JOURNALS

1. "Predigestion of rice straw to improve biogas production". **URJA**. 22(3), 1987. pp. 202-209.

2. "Biogas generation: effect of mixing effluent slurry with fresh cattle dung". **ENERGY MANAGEMENT**. 11(3), 1987. PP.197-202.

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5. "Biogasification of banana peeling and Ipomoea fistulosa leaves". **KHADIGRAMODYOG**. 34(7), 1988. pp. 324-332.

6. "Biogasification of woody biomass: Ipomoea fistulosa plant stem". **BIOLOGICAL WASTES**. 28(1), 1989. PP. 25-32.

7. "Effect of particle size on biogas generation from biomass residues". **BIOMASS**. 17(4), 1989. PP. 251-264.

8. "Biogas from biomass". **Indian Journal of Rural Technology**. (In the press).

PAPERS PRESENTED IN SYMPOSIUMS/SEMINARS

9. "Effect of stirring on biogas generation". Paper presented at

4th National Convention and Symposium "Bioenergy for Arid Regions". BESI-IV. Sukhadia University, Udaipur. 3-4 September, 1987.

10. "Microbial production of methane from grass". Paper presented at National Seminar on Alternate Energy Generation and its Community and Industrial Applications. KNIT, Sultanpur (U.P.). 16-17 January.

11. "Biogas generation from agricultural residues for rural development". Paper presented at 4th National Convention of Chemical Engineers, Institution of Engineers, Roorkee Local Centre, Roorkee. 3-4 October, 1988.

12. "Fuel wood: conversion and utilization through thermal and biogasification". Paper presented at 6th annual BESI Convention, Baroda. 30-31 October, 1988.