BIODIESEL PRODUCTION FROM SEED OILS AND BIODIGESTION OF OIL CAKES FOR ENERGY GENERATION

A PROJECT REPORT

Submitted by

SELVAKUMAR. T

SIVARAMAN. G

in partial fulfillment for the award of the degree

of

BACHELOR OF TECHNOLOGY

in

BIOTECHNOLOGY

KUMARAGURU COLLEGE OF TECHNOLOGY, COIMBATORE

ANNA UNIVERSITY:: CHENNAI 600 025

APRIL 2008

ANNA UNIVERSITY : CHENNAI 600 025

BONAFIDE CERTIFICATE

Certified that this project report "**BIODIESEL PRODUCTION FROM SEED OILS AND BIODIGESTION OF OIL CAKES FOR ENERGY GENERATION**" is the bonafide work of **SELVAKUMAR.T** and **SIVARAMAN.G** who carried out the project work under my supervision.

SIGNATURE

Dr.P.Rajasekaran 19/4/08

PROFESSOR AND HEAD

Department of Biotechnology,
Kumaraguru College of Technology,
Coimbatore – 641006.

SIGNATURE

Dr.P.Rajasekaran 19/4/08

SUPERVISOR

PROFESSOR AND HEAD

Department of Biotechnology,
Kumaraguru College of Technology,
Coimbatore – 641006.

CERTIFICATE OF EVALUATION

COLLEGE : Kumaraguru College of Technology

BRANCH : Biotechnology

SEMESTER : Eighth Semester

NAME OF THE STUDENTS	TITLE OF PROJECT	NAME OF THE SUPERVISOR WITH DESIGNATION
SELVAKUMAR. T Reg No: 71204214027	**BIODIESEL PRODUCTION FROM SEED OILS AND BIODIGESTION OF OIL CAKES FOR ENERGY GENERATION**	**Dr.P.RAJASEKARAN** Professor and Head, Department of Biotechnology.
SIVARAMAN. G Reg No: 71204214028		

The report of the project work submitted by the above students in partial fulfillment for the award of Bachelor of Technology degree in Biotechnology of Anna University was confirmed to be the report of the work done by the above students and then evaluated.

(INTERNAL EXAMINER) **(EXTERNAL EXAMINER)**

ACKNOWLEDGEMENT

We extend our sincere thanks to our principal **Dr.Joseph.V.Thanikkal**, Kumaraguru College of Technology, Coimbatore for his support and encouragement.

We articulate our thankfulness and deep gratitude towards our Head of the Department and our project guide **Dr.P.Rajasekaran**, **Ph.D**, Department of Biotechnology, for his profound ideas, able guidance and continuous motivation. His kindness and invaluable guidance have been integral in the completion of this work. We consider this as an honor to have an opportunity to work under his guidance in this project.

We are grateful to **Dr.N.O.Gopal**, Associate Professor, Department of Bioenergy, TNAU, for lending a hand throughout the project.

We thank **Mr.G.L.Satyamoorthy**, Lecturer, Department of Civil Engineering, for providing all the facilities in the Environmental Engineering Laboratory of our college and timely help for the successful completion of the project.

We thank all the **Teaching** and **Non Teaching Staffs** of our Department for providing us the technical support for the project.

We also thank all our **friends** and **family members** who physically and emotionally helped us to bring out the project successfully.

19/4/08
[Selvakumar. T]

19/4/08
[Sivaraman. G]

ABSTRACT

The increasing industrialization and motorization of the world has led to a steep rise for the demand of petroleum products.Petroleum based fuels are obtained from limited reserves. Hence, it is necessary to look for alternative fuels, which can be produced from the resources that are available within the country. Our project work dealt with the production of biodiesel from *Jatropha curcas*, *Pongamia pinnata* and *Arachis hypogaea* seed oils and then biodiesel thus obtained was tested for various properties like viscosity, acid value, flash point and cetane number .

Biogas technology that provides an alternate source of energy in rural india and is considered as an archetypal appropriate technology that meets the basic need for cooking fuel in rural areas. Cattle dung has been hitherto employed as a feedstock for biogenesis of methane. However its availability in sufficient quantity limits its continuous application. Hence a study was carried out ulitizing the locally available non-edible oil cakes of *Jatropha curcas*, *Pongamia pinnata* and *Arachis hypogaea* along with cattle dung and optimizing these feedstocks at different ratios for maximum gas generation. The gas output of various treatments were recorded over a period of 6 weeks. The maximum gas output of 22815 ml was recorded in the *Arachis hypogaea* cake incorporated treatments. The physical and chemical properties of the raw materials and biodigested slurry were analyzed.The methane content was highest in *Arachis hypogaea* cake incorporated treatment (68%). The biodigested slurry were found to have high manurial values. Thus, this study reveals that these oil cakes can be used as a supplement with cattle dung for augmenting the gas output. In addition, the biodigested slurry can also be utilized as a richer source of organic manure for fertilization of crops.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES

LIST OF ABBREVIATIONS

CD - Cattle dung

JC - *Jatropha curcas*

PP - *Pongamia pinnata*

AH - *Arachis hypogaea*

TS - Total solids

VS - Volatile solids

TOC - Total organic carbon

N - Nitrogen

K - Potassium

P - Phosphorous

ASTM – American Society of Testing and Materials

Introduction

1. INTRODUCTION

1.1 BIODIESEL

1.1.1 BIODIESEL TECHNOLOGY

For the past few decades, a lot of effort has been made to reduce the dependency on petroleum fuels for power generation and transportation all over the world. Among the proposed alternative fuels, biodiesel have received much attention in recent years for diesel engines and could be one remedy in many countries to reduce their oil imports. Biodiesel have many advantages over regular diesel as renewable and domestically produced energy resources. Moreover, they are recognized as environmentally friendly alternative fuels because studies have shown that there is a substantial reduction of co, unburned hydrocarbons and particulate matter emission, when they are used in conventional diesel engines. Biodiesel is an alkyl (e.g.methyl, ethyl) ester of fatty acids made from a wide range of vegetable oils, animal fats and used cooking oil via anyone of the following process like Blending, Micro-emulsification, Cracking and transesterification process.

Chemically, biodiesel is referred to as the mono-alkyl-esters of long chain fatty acids derived from renewable lipid sources. Biodiesel is the name for a variety of ester based oxygenated fuel from renewable biological sources. It can be used in compression ignition engines with little or no modifications.

One hundred years ago, Rudolf Diesel first tested vegetable oil fuel for his engine. With the advent of cheap petroleum, appropriate crude

oil fractions were refined to serve as fuel and diesel fuels and diesel engines started evolving together. Later in the 1940's, vegetable oils were used again as fuel an emergency situations, during the period of World War II. Because of the increase in crude oil prices, limited resources of fossil fuels and the environmental concern, there has been renewed focus on vegetable oils and animal fats for the production of biodiesel fuel. Biodiesel has the potential to reduce the level of pollution and the level global warming.

1.1.2 TRANSESTERIFICATION PROCESS

Transesterification is otherwise known an alcoholysis. It is the reaction of fat or oil with an alcohol to yield esters and glycerin. A catalyat is used to improve the reaction rate and yield. Transesterification of triglyceride using alcohol is shown in Fig 1.1.

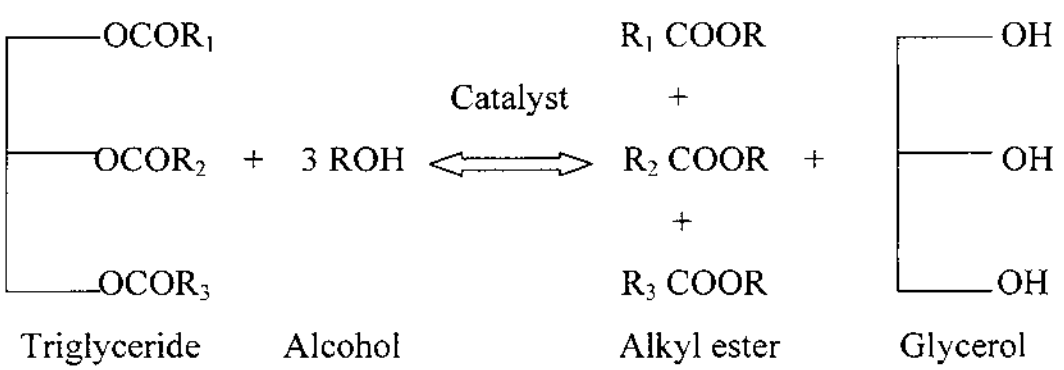


Fig 1.1 Transesterification of triglyceride with alcohol

This transesterification process is widely used since it is used to reduce the viscosity of the triglycerides. Among the alcohols, methanol and ethanol are used commercially because of their low cost and their physical and chemical advantages. They quickly react with triglycerides and NaOH

and are easily dissolved in them. Enzymes, alkalis or acids can catalyse the reaction, i.e. lipases, NaOH, sulphuric acid, respectively. Among these, alkali transesterification is faster and hence it is used commerically

1.2 BIOGAS

1.2.1 BIOGAS TECHNOLOGY

Biogas technology provides an alternate source of energy in rural India, and is hailed as an archetypal appropriate technology that meets the basic need for cooking fuel in rural areas. Using local resources, viz. cattle waste and other organic wastes, energy and manure are derived. Realization of this potential and the fact that India supports the largest cattle wealth led to the promotion of National Biogas Programme in a major way in the late 1970s as an answer to the growing fuel crisis. Biogas is produced from organic wastes by concerted action of various groups of anaerobic bacteria. Methane fermentation is a process which is capable of converting almost all types of organic polymeric materials into methane and carbon dioxide. Some of the natural sources of methane emissions are wetland soils, oceans, rumen of ruminant animals, the lower intestinal tracts of humans, land fills, and sewage digesters.

Microbial conversion of organic matter to methane has become attractive as a method of waste treatment and resource recovery. This process is anaerobic and is carried out by action of various groups of anaerobic bacteria.

Three basic points about this process are:

(i) That most of the important bacteria involved in biogas production process are anaerobes and slow growing;

(ii) That a greater degree of metabolic specialization is observed in these anaerobic microorganisms; and

(iii) That most of the free energy present in the substrate is found in the terminal product methane. Since less energy is available for the growth of organism, less microbial biomass is produced and, consequently, disposal of sludge after the digestion may not be a major problem.

The methanogenic decomposition of organic matter requires microbial consortia composed of at least three interacting metabolic groups of anaerobes. Anaerobes play important roles in establishing a stable environment at various stages of methanogenesis. A variety of microorganisms are involved in the methane fermentation which include the fermentative bacteria, which ferment complex polymers to H_2, CO_2, and various volatile carboxylic acids. The second group is acetogens, which then oxidize the higher acids to acetate and to either H_2 or formate. The strictly anaerobic methane-producing microorganisms are the final group in the consortium and they utilize H_2, formate and acetate as substrate for growth. Methanogens represent the large and the most diverse group within the Archaea domain.

Methane fermentation offers an effective means of pollution reduction, which is superior to that achieved via conventional aerobic process. Methane produced by anaerobic fermentation of biomass is a clean, renewable fuel. In addition, during anaerobic digestion adequate sanitation of the treated material is guaranteed. Recent studies have shown that the most important agricultural pests and parasites are effectively deactivated during thermophilic anaerobic digestion. Although practiced for several years, interest in anaerobic digestion has recently focused on the economic recovery of fuel gas from cattle, industrial and kitchen wastes and agricultural surpluses.

1.2.2 MICROBES IN CONVERSION

The model of microbial groups involved in the flow of carbon from complex polymers to methane consists of five groups .

Group 1	-	Fermentative bacteria
Group 2	-	Obligate hydrogen producing acetogenic bacteria
Group 3	-	Hydrogen oxidizing acetogenic bacteria
Group 4	-	Carbon dioxide reducing methanogens and
Group 5	-	Aceticlastic Methanogens

During the process of biomethanation (Fig 1.2), complex polymers are broken into soluble products by enzymes produced by fermentative bacteria (Group – 1) which ferment the substrate to short chain fatty acids, hydrogen and carbon dioxide. Fatty acids, longer than acetate are metabolized to acetate by obligate hydrogen producing acetogenic bacteria (Group – 2). The major products after digestion of the substrate by these two

groups are hydrogen, carbon dioxide and acetate. Hydrogen and carbon dioxide can be converted into acetate by hydrogen oxidizing acetogens (Group – 3) or methane by carbon dioxide reducing, hydrogen oxidizing methanogens (Group – 4). Acetate is also converted into methane by aceticlastic methanogens (Group – 5).

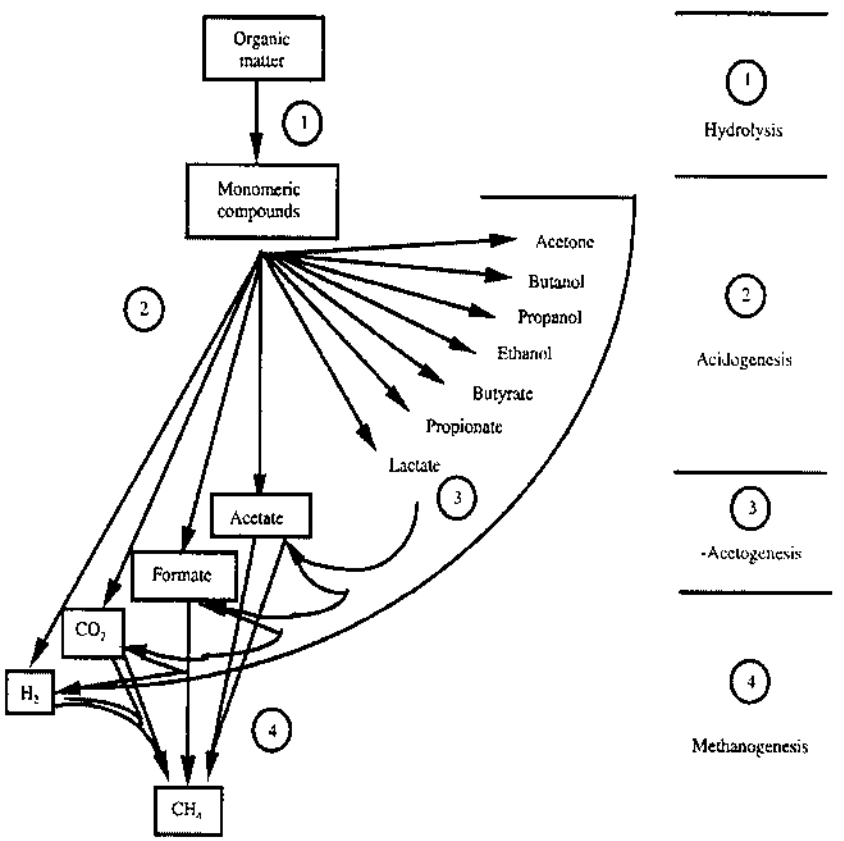


Fig 1.2 Pathway of methane biogenesis

Oil extraction units generates large quantities of wastes in the form of oil cakes which at present is indirectly applied as fertilizers to the plants.

This nitrogen rich waste is a possible supplement to the nitrogen deficient agricultural wastes that are incorporated into the biogas plant for biogas generation. In addition, the spent slurry, after digestion, is of high manorial value than the components incorporated into this plant earlier.

An attempt has been made in the research laboratory of oil extraction units to supplement the oil cakes with cow dung at different proportions for increased biogas generation and also to obtain nutrient rich manure after biodigestion.

1.3 OBJECTIVES

- To crystallize the methodology and processes for the production of biodiesel from various types of seed oil.
- To evaluate the biodiesel on various parameters.
- Recycling of oil cakes through biodigestion for energy generation.
- To estimate the quantity of gas produced from different types of oilcakes codigested with cattle dung.
- To estimate the methane and carbon dioxide content from the gas produced.
- To estimate the manurial values of the biodigested slurry.

Literature Review

2. LITERATURE REVIEW

2.1. BIODIESEL

The Production of biodiesel from various types of oils has been carried out by researchers in various parts of the world. A review of literature concerned with the above is detailed below:

2.1.1. BIODIESEL PROUCTION FROM VARIOUS SOURCES

Hak-Joo Kim *et al.*, (2004) described the Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst. Na/NaOH/-Al_2O_3 heterogeneous base catalyst was adopted for the production of biodiesel. A study for optimizing the reaction conditions such as the reaction time, the stirring speed, the use of co-solvent, the oil to methanol ratio, and the amount of catalyst, was performed.

Mohibbe Azam *et al.*, (2005) studied the prospects and potential of fatty acid methyl esters of some non-traditional seed oils for use as biodiesel. Fatty acid compositions, Iodine value and Cetane Number were used to predict the quality of fatty acid methyl esters of oil for use as biodiesel.

Yong Wang *et al.*, (2007) described the production of biodiesel from waste cooking oil via two-step catalyzed process. The free fatty acids of waste cooking oil were esterified with methanol catalyzed by ferric sulfate in the first step, and the triglycerides were transesterified with methanol catalyzed by potassium hydroxide in the second step. The results showed that ferric sulfate

had high activity to catalyze the esterification of free fatty acids (FFA) with methanol.

Alok Kumar Tiwari *et al.*, (2007) described the Response surface methodology (RSM) based on central composite rotatable design (CCRD) was used to optimize the three important reaction variables—methanol quantity (*M*), acid concentration (*C*) and reaction time (*T*) for reduction of free fatty acid (FFA) content of the oil and for carrying out transesterification of the pretreated oil. This process gave an average yield of biodiesel more than 99%.

Ali keskin *et al.*, (2008) studied the usability of cotton oil soapstock biodiesel–diesel fuel blends as an alternative fuel for diesel engines. Biodiesel was produced by reacting cotton oil soapstock with methyl alcohol at determined optimum condition.

Malaya Naik *et al.*, (2008) discussed the the mechanism of a dual process adopted for the production of biodiesel from Karanja oil containing FFA up to 20%. The first step is acid-catalyzed esterification by using 0.5% H_2SO_4, alcohol 6:1 molar ratio with respect to the high FFA Karanja oil to produce methyl ester by lowering the acid value, and the next step is alkali-catalyzed transesterification.

Srivathsan Vembanur Ranganathan *et al.*, (2008) studied the enzymatic production of biodiesel.

Joelianingsih *et al.*, (2008) studied the kinetic parameters of Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure.

Sharma and Singh (2008) described the development of biodiesel from karanja. NaOH was found to be a better catalyst than KOH in terms of yield.

Maximum yield of 89.5% was achieved at 8:1 molar ratio for acid esterification and 9:1 molar ratio for alkaline esterification, 0.5 wt.% catalyst (NaOH/KOH) using mechanical stirrer.

2.1.2. ENGINE PERFORMANCE USING BIODIESEL

Raheman and Ghadge (2005) investigated the Performance of diesel engine with biodiesel at varying compression ratio and ignition timing.

Avinash Kumar Agarwal (2007) studied the effects of the biodiesel on engine performance and emission, and material compatibility is also considered. This study also focused on performance and emission of biodiesel in compression ignition engines, combustion analysis, wear performance on long-term engine usage, and economic feasibility.

Banapurmath *et al.*, (2007) investigated the Performance and emission characteristics of a DI compression ignition engine operated on Honge, Jatropha and sesame oil methyl esters. Engine performance in terms of higher brake thermal efficiency and lower emissions (HC, CO, NO_X) with sesame oil methyl ester operation was observed compared to methyl esters of Honge and Jatropha oil operation.

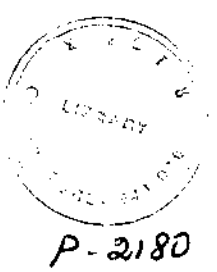
Roskilly *et al.*, (2008) investigated the performance and the gaseous emissions of two marine craft diesel engines fuelled with biodiesel. The CO emissions were found to be lower when the engines operated at higher loads using biodiesel.

Sérgio Machado Corrêa and Graciele Arbilla (2008) reported the Carbonyl emissions in diesel and biodiesel exhaust. Seven carbonyl emissions (formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, butyraldehyde, and benzaldehyde) were evaluated by a heavy-duty diesel engine fueled with pure diesel (D) and biodiesel blends.

Deepak Agarwal *et al.*, (2008) investigated the performance and emission characteristics of linseed oil, mahua oil, rice bran oil and linseed oil methyl ester (LOME), in a stationary single cylinder, four-stroke diesel engine and compare it with mineral diesel. The process of transesterification is found to be an effective method of reducing vegetable oil viscosity and eliminating operational and durability problems.

2.2.BIOGAS

The anaerobic digestion of different types of wastes has attracted the attention of researchers in various parts of the world. A review of literature concerned with the above is detailed below:



2.2.1.DIFFERENT WASTE UTILIZATION AND BIOGAS PRODUCTION

Summers and Bousfield (1980) reported that during piggery waste anaerobic digestion, the gas production was 0.30 m^3 /kg of total solids which contained 69 percent methane.

Rajasekaran and Oblisami (1980) reported the possibility of recycling of sericultural wastes along with cowdung and old slurry for biogas generation.

Maximum quantity of 1524 cc/day was observed on an average over a period of 12 weeks in silkworm larval litter incorporated treatments which also recorded the maximum number of methanogenic bacteria (25.8 x 10^4/g).

Fujita *et al.*, (1980) while studying the effect of cornstorer addition on the anaerobic digestion of swine manure reported that the biogas production was more than 50 percent.

Sharma *et al.*, (1980) while reporting the recycling of waste materials recorded the maximum production of methane (74 liters/kg and 147 liters/kg) from poultry and piggery wastes.

Fischer *et al.*, (1981) designed a biogas plant by using swine wastes as feedstock material.

Hashimoto *et al.*, (1981) stated that the ultimate methane yield obtained from the digestion of cattle manure was 0.210 liter /g of volatile solids.

Singh *et al.*, (1982) reported that 75 percent of the biogas production was obtained during the digestion of cattle waste at the retention time of forty days.

Hills and Roberts (1982) indicated that the gas production were 0.43, 2.45 and 1.5 liters /digester vol/day during the digestion of tomato, peach and honey dew solid wastes respectively.

Varrier *et al.*, (1982) while reporting the French programme on the methane production recorded the maximum production of methane from different animal wastes.

Cenni *et al.*, (1982) made an attempt on the digestion of tannery wastes for biogas production.

Hills(1982) stated that the production of methane were 4.23 litre CH_4/day, 1.36 litre CH_4/day, 0.77 litre CH_4/day and 1.26 litre CH_4/day for beef, swine ,poultry and dairy wastes respectively When the wastes are digested in a comprehensive dynamic model.

Hills and Prince (1983) reported that the methane production was 150 m^3 /day, 69 m^3 /day and 160 m^3 /day for swine, beef and poultry wastes respectively.

Hills (1983) reported that the gas production of 1.72 gas vol/digester vol/day at the 32.3 percent volatile solid was obtained from the intermittently and plug flow digestion of beef feed lot manure.

Roy Holmberg *et al.*, (1983) recorded the flowrates of 75 litres /min in 60 mesh screening size, while reporting the solid liquid separation of swine wastes.

Sleat and Robinson (1984) stated that range of aromatics could be metabolized to methane and carbon dioxide with a greater than 90 percent conversion of substrate in to these gases.

Pathak *et al.*, (1985) obtained a maximum gas production when cattle dung and rice-straw mixture were allowed for bio gasification. The mixture of cattle dung and rice straw was at the ratio of 1:2 and it contained 15.2 percent solids.

Olezzkiewick (1985) while studying the aerated lagoon treatment of piggery wastes, reported that the substrate removal rate was K=0.0014 lt day^{-1} mg^{-1} biomass yield Y=0.5 and decay coefficient K_d =0.02 day^{-1} .a load removal kinetic expression of the type S/S_0 = exp (-K/L) was also proposed.

Zeeman *et al.*, (1985) reported that the ammonia content and volatile solids content were not responsible for the thermophilic process.

Webb and Hawkes (1985) stated that the variation of gas field occurred with reference to ammonia and nitrogen levels, when poultry –manure is allowed for biodigestion.

Vaidyanathan *et al.*, (1985) stated that the gas production may reach 0.16 nm3 kg-1 VS added when water hyacinth was allowed for digestion.

Gunnarson *et al.*, (1985) reported that the utilization of above ground part of Jerusalem articheke (Helianthus tuberosus.L.) for biogas production. The biogas production estimated ranged from 480-680 liters.

Lo and Liao (1986) stated that the maximum methane production of 8.14 liter (CH_4 $litre^{-1}$ day at a loading rate of 7.78 gvs $litre^{-1}$ day^{-1}) from winery wastes.

Lingaiah and Rajasekaran (1986) studied the effects of the incorporation of various wastes with castor cake in relation to biogas generation. The study provides evidence that, with proper C:N ratio adjustments, various types of wastes along with castor cake could profitably be employed for maximum microbiological activity and gas output.

Sushil Kumar *et al.*, (1987), used commercial charcoal with cow dung to enhance biogas production.

Yeole *et al.*, (1987) reported that the bio-gas production is maximum when industrial canteen wastes are subjected to an anaerobic digestion. The left over materials may be used as good manure.

Radhakrishna and Gollakota (1989) designed a pilot plant for biomethanation on non-edible oil cakes. Generation of biogas from agro-industrial wastes has now been successfully demonstrated. In this process, a very stable and efficient microbial consortium was isolated and stabilized to generate biogas from non-edible grade oil cakes.

Shyam and Sharma (1994) described the Solid-state anaerobic digestion of cattle dung and agro-residues in small-capacity field digesters. Anaerobic fermentation of cattle dung alone or with paddy straw, mango leaves or foilage *Parthenium hysterophorus* in uninsulated, small capacity, batch-type out-door digesters of cylindrical and cuboid shapes gave results at initial total solids (TS) concentrations of 16–19%.

Callaghan *et al.*, (1999) studied on batch co-digestion of waste organic solids that reported that the fish offal and brewery solids mixed with cattle slurry produced an enhancement in the methane yield compared with that of control digestion of using cattle slurry alone.

Anthony Mshandete *et al.*, (2004) shown that the Co-digestion of various wastes to improve the digestibility of the materials and biogas yield .

Sumitra Ramachandran *et al.*, (2007) discussed on various applications of oil cakes in fermentation and biotechnological processes, their value addition

by implementation in feed and energy source (for the production of biogas, bio-oil) as well.

Shanta Satyanarayan *et al.*, (2008) found that Biogas production can be enhanced by *Brassica compestries* amendment in cattle dung digesters. This amendment was mustard oil cake (MOC) (*Brassica compestries*) added at different ratios to cattle dung digesters.

Sellami *et al.*, (2008) found that the Co-composting of oil exhausted olive-cake, poultry manure and industrial residues of agro-food activity for soil amendment.

2.2.2. VOLATILE SOLIDS DESTRUCTION, RETENTION TIME AND GAS PRODUCTION

Fischer *et al.*, (1975) stated that during anaerobic digestion of swine manure the biogas production begin at a loading rate of 0.8 g VS litre^{-1} day^{-1}

Varel *et al.*, (1977) recorded the maximum methane production rates of about 0.16, 0.18, 0.2. and 0.22 litre/day per g of VS in the feed from cattle waste. The gas contained 52 to 57 percent methane.

David hills (1979) reported that the total production was 2.1 liter which contained 51.3 percent methane at 11.6 g VS / litre^{-1} day^{-1} on high solid concentration of dairy manure.

Hashimoto *et al.*, (1981) reported that the ultimate methane yield from beef cattle manure was 0.210 litre CH_4 /g of volatile solids.

Fischer *et al.*, (1981) reported that the wheat straw addition reduced the biogas production except for one treatment where alkali treated straw was substituted at 4g VS litre/ day^{-1}

Hills *et al.*, (1982) while reporting on the design of digestion systems recorded the gas production of the digester as 43, 74, 60 and 56 percent and volatile solids reduction was 75, 65, 62 and 30 percent for swine, beef, poultry and dairy wastes respectively.

Fischer *et al.*, (1983) stated that the daily requirement for a mesophilic farm scale anaerobic digester ranging from 16.9 MJ/M^3d.

Walker *et al.*, (1985) while studying the experiment anaerobic digestion on a dairy farm recorded the maximum gas out flow of 400-495 m^3 day.

Lo *et al.*, (1985) stated that the maximum methane production rate of 1.371 CH_4 /day was observed at one day HRT. Highest methane yield of 0.1041 CH_4 per g of volatile solids added occurred at 10 days HRT.

Lo *et al.*, (1985a) attained the maximum methane production at 4.2 percent volatile solids feed. The experimented volatile solids rates were 3.4, 4.2 and 5.2 percent over a HRT from 1.1-15 days.

Liao and Lo (1985) estimated the methane production of 3.531 CH_4 /day at a loading rate of 262 g VS/litre/day.

Vaidyanathan (1985) stated that the specific methane production rate is correlated with volatile solids loading rate.

Lo *et al.*, (1986) the maximum methane production rates of 1.29 and 1.19 litres of CH4 /litre/day at one day HRT were achieved with the volatile solids feeds of 5.2 and 4.2 percent respectively.

Stephenson and Loster (1986) while studying the evaluation of starting and operation of 4 anaerobic processes treating a synthetic meat waste, reported that the proportion of methane in the effluent gases increased as the influent COD concentrations was increased. The two stage reactor which contained to metals cobalt and nickel removed upto85 percent of the influent COD concentration of 5000 mg/l.

2.2.3. EFFECT OF TEMPERATURE IN GAS GENERATION

Converse *et al.*, (1977) made their research on anaerobic degradation of dairy manure under mesophilic and thermophilic temperatures, recorded that the digester operated at 60°C instead of 35°C showed higher rates of gas production.

Varel *et al.*, (1977) stated that thermophilic methane production from cattle waste obtained maximum efficiency at 60°C for 8 days. While an increase from 60 to 65°C lowered the efficiency of gas production.

Van Valsen *et al.*, (1979) stated that at a digestion temperature of 13 °C no methane was produced while in mesophilic range (20 to 40 °C) methane production increased with temperature and under thermophilic condition (55 °C) it decreased by 25 percent.

Jain *et al.*, (1981) while studying the diurnal variations in gas production in a biogas plant reported that the gas production varied in all the seasons at different hours of the day depending upon the variation in the environmental temperatures.

Hills and Roberts (1981) while reporting the continuously expanding anaerobic digestion recorded the production of methane gas averaging 58 to 60 percent at temperature 20 to 30 °C.

Lo *et al* (1985) while studying the mesophilic digestion of screened dairy manure, recorded the maximum biogas production of 1.89 litres of CH_4 /litre day^{-1}

Madamwar and Mittal (1986) expressed that the effect of pectin on anaerobic digestion increases the production of gas with the increased methane content at controlled temperature of 38 °C.

Saraswath and Khanna (1986) while studying a diphasic system with alkali treatment design with an alkali pretreatment step (3.6% Na_2CO_3 + 2.5% $Ca(OH)_2$ (w/w) of water hyacinth, 24 hours duration followed by an open acid phase (2-1 days HRT) and closed methane reactor with sludge recycling (5-7 days HRT,7-7 days MCRT) recorded the gas yield of 501/kg WH /d at 35-37 °C.

2.2.4. MICROORGANISMS INVOLVED DURING BIO DIGESTION

Smith and Hungate (1958) described that methods for the isolation and culturing of methanogenic bacteria from the rumen of cattle and studied the technique of transfer.

Rajasekaran (1980) studied the microbiological changes accompanying degradation of water hyacinth in an anaerobic digester. The cellulytic population of $375x10^3$ /g was recorded in the digester containing cowdung, old slurry and water hyacinth.

Rajasekaran (1980a) stated that the total bacterial population was found to be more in the slurry specimen ranging from $101.3x10^6$ to $367.7x10^6$/g of oven dry samples.

Gollatkota and Jayalakshmi (1983) isolated a mixed culture from cow dung which was responsible for the Biogas production by anaerobic digestion of oil cake.The mixed culture contains organisms hitherto unisolated and unidentified which are capable of synthesizing these hydrocarbons through the mediation of the alkyl derivatives of coenzyme M.

Krishnan Vijayaraghavan *et al.*, (2006) isolated hydrogen generating microflora from cow dung for seeding anaerobic digester. The effectiveness of using cow dung as a source for isolating hydrogen generating microflora was investigated under varying isolating conditions based on viz.: pH adjustment and pH adjustment coupled with heat treatment.

2.2.5. FACTORS AFFECTING BIOGAS GENERATION

Vandenberg *et al.*, (1976) while reporting the conversion of acetic acid into methane gas recorded the maximum gas production was at the acetic acid concentration of 0.2 and 100 mm at the temperature of 40-45 ^{o}C at the pH o 6.5-7.1.

Dennis *et al.*, (1978) reported that the maximum rate of gas production 690ml CH_4 /g occurred at C/N ratio of 19.1.

Hills and Roberts (1979) reported that the effects of C/N ratio on anaerobic digestion of dairy manure screened dairy manure which had a C:N ratio of the feed at 25.

Hills (1983) investigated the parameter for establishing proper mixtures of manure and carbonaceous wastes. He stated that the greatest methane production per unit occurred when the C: N ratio of the feed was25:1.

Gollakota and Meher (1988) studied the effect of particle size, temperature, loading rate and stirring on biogas production from castor cake. The optimal loading rate without stirring was 4 g of Total Solids per liter per day, and with stirring 8 g of Total Solids per liter per day at 37° C.

Nallathambi Gunaseelan (1995) suggested that the C/N ratio is 11 being satisfactory for methanogenic performance using Parthenium, a terrestrial weed, as feedstock for digestion.

2.2.6. MANURIAL VALUES OF THE BIODIGESTED SLURRY

Acharya (1958) stated that the digested slurry contained about 1.8 to 1.9 percent nitrogen on dry basis than farm yard manure.

Fry (1974) reported that the anaerobic digestion of cow dung produced better quality manure rich in humus content.

Barnett *et al.*, (1978) stated that the nitrogen content of cow manure, chicken manure, bagasse, sawdust and poultry litter was 1.7, 6.2, 0.3, 0.1 and 6.7 percent respectively and urine contained about 40 to 70 percent of the fertilizer value of the manure.

Gupta *et al.*, (1986) reported that the losses of plant nutrients by biogas slurry was 36.5, 25.0, 21.5, 14.8, 5.9, 4.9 and 2.7 percent foe K, Zn, N, Cu,Mn,Fe and P respectively.

Dohia and Vasudevan (1986) reported that the biogas plant slurry and it may be used as an alternative to chemical fertilizers.

Beckwith and Parsons (2005) studied that the rate of decomposition wasat a maximum over the first twenty days and was not influenced by the level of nitrogen

Warman and Termeer (2005) stated that compared to the conventional fertilizer, the nutrient availability from the organic amendments (especially N and P) was considerably lower than the 50% assumed at the start of the experiment.

Materials and Methods

3. MATERIALS AND METHODS

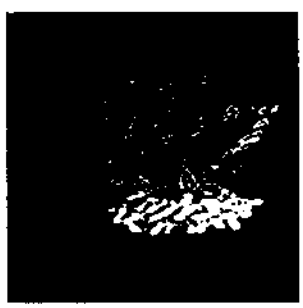
3.1. BIODIESEL

3.1.1.MATERIALS REQUIRED

Oil is the main raw material needed the production of biodiesel. According to Mohibbe Azam *et al.*, (2005), the Fatty acid compositions, iodine value (IV) and cetane number (CN) were used to predict the quality of fatty acid methyl esters of oil for use as biodiesel. Saponification number (SN), iodine value (IV) and cetane number (CN) of fatty acid methyl esters of *Jatropha curcas*, *Pongamia pinnata* and *Arachis hypogaea* were studied from various literatures and they varied from 169.2 to 312.5, 4.8 to 212 and 20.56 to 67.47, respectively. Hence, these three oil bearing plants namely *Jatropha curcas* , *Pongamia pinnata* and *Arachis hypogaea* were selected and their seed oils were used for the production of biodiesel. The three varieties of plants are shown in Fig 3.1. and their seeds used for oil extraction are shown in Fig 3.2. Other materials needed are methanol (99+% pure), catalyst -- either potassium hydroxide (KOH) or sodium hydroxide (NaOH), blender, measuring beakers, half-litre container, funnels to fit the container, Separating funnels for settling, two 2-litre bottles for washing, Thermometer.

(a) *Jatropha curcas*

(b) *Pongamia pinnata*



(c) *Arachis hypogaea*

Fig 3.1. The three varieties of plants used for biodiesel production

(a) *Jatropha curcas*

(b) *Pongamia pinnata*

(c) *Arachis hypogaea*

Fig 3.2. The three varieties of oil seeds used for biodiesel production

3.1.2. METHODOLOGY

a. Catalyst

Catalyst can be either potassium hydroxide (KOH) or sodium hydroxide (NaOH). Use exactly 3.5 grams NaOH if it is at least 97% pure,. If using KOH it depends on the strength. Used exactly 4.9 grams (4.90875) if it is 99% pure (rare). Use 5.3 grams (5.33) if it is 92% pure (more common), Use 5.5 grams (5.454) with 90% pure, Use 5.8 grams (5.775) with 85% pure. Any strength of KOH from 85% or stronger will be good for the production of biodiesel.

b. Mixing the methoxide

About 200 ml of methanol is measured and poured into the half-litre container via the funnel. Methanol also absorbs water from the atmosphere so it is done quickly and the lid of the methanol container is replaced tightly.

Carefully, the catalyst is added to the container via the second funnel. The cap is replaced tightly.

The container is shaked a few times -- swirl it round rather than shaking it up and down. The mixture gets hot from the reaction. Swirling it thoroughly for a minute or so five or six times over a period of time the lye will completely dissolve in the methanol, forming sodium methoxide or potassium methoxide. As soon as the liquid is clear with no undissolved particles, the process can be started. The more we swirl the container ,the faster the lye will dissolve.

c. The process using a blender

Pre-heat 1 litre of oil to 55 deg C (130 deg F) and pour it into the blender.With the blender still switched off, the prepared methoxide is carefully poured from the container into the oil. The blender lid is secured tightly and then the blender is switched on. Lower speeds should be enough. It is mixed for 20-30 minutes.

d. Transfer

As soon as the process is completed, the mixture is poured from the blender into the separating funnels for settling and the lid is screwed tightly.

e. Settling

The mixture is allowed to settle for 12-24 hours. Two layers are obtained which is shown in Fig 3.3.

Fig 3.3. Settling of oil into two layers

Darker-coloured glycerine by-product will get collected in a distinct layer at the bottom of the bottle, with a clear line of separation from the pale liquid above, which is the biodiesel. The biodiesel varies somewhat in colour according to the oil used (and so does the by-product layer at the bottom) but usually it's pale and yellowish . Carefully the top layer of biodiesel is decanted into a clean jar bottle, taking care not to get any of the glycerine layer mixed up with the biodiesel. If gets mixed up, re-settle and try again.

f. Washing

The washing of raw biodiesel fuel is one important step. The purpose is to wash out the remnants of the catalyst and other impurities. There are three main methods:

- Water wash only (a misting of water over the fuel, draining water off the bottom)
- Air bubble wash (slow bubbling of air through the fuel)
- Air/water bubble wash (with water in the bottom of the tank, bubbling air through water and then the fuel)

The method that works the best is dependent on the quality of the fuel. The method used for all fuel is a combination of water washing and air bubble washing. The amount of wash water should equal the amount of oil, and can be drained throughout the washing process.After the water is drained, the air washing process can start. At this point, the biodiesel is usually a pale yellow color. Air should be bubbled through the biodiesel mixture for approximately 8 hours. The bubbling should be just enough to agitate the

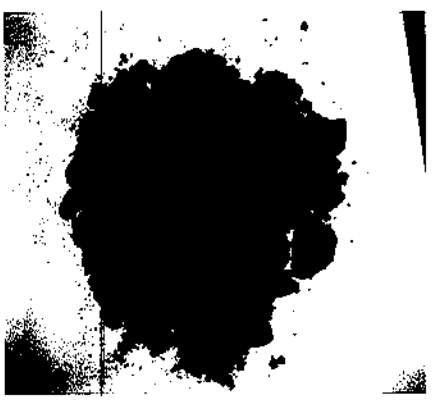
biodiesel surface. A final drain of accumulated contaminants is done immediately after the air bubble wash is finished. After washing the biodiesel, it is tested for various properties.

3.2 BIOGAS

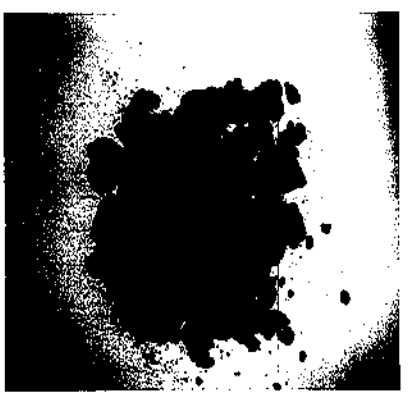
The various waste materials like oil cakes utilized in this study were collected from various places in and Coimbatore. The wastes thus obtained were analyzed for their physical and chemical properties such as moisture, total solids, volatile solids, nitrogen, phosphorous and potassium.

3.2.1. COLLECTION OF RAW MATERIALS

Jatropha curcas oil cake, Pongamia pinnata oil cake and Arachis hypogaea oil cakes was collected from Oil extraction units of Renulakshmi Agro Industries in Ganapathy located 6 km away from Coimbatore. The cattle dung was collected from Saravanamapatty located 2 km away from Coimbatore.. The substrates are shown in Fig 3.4



(a) *Jatropha curcas* cake



(b) *Pongamia pinnata* cake

(c) *Arachis hypogaea* cake

Fig 3.4. Substrates codigested with cattle dung

3.2.2. UTILIZATION OF OIL CAKES AS VARIOUS TREATMENTS FOR BIOGAS GENERATION

There were sixteen treatments . The details of various treatments employed were given as given in table 3.1.

The cattle dung slurry was prepared by mixing the cattle dung with equal amount of tap water (wt/wt basis). The cake slurry was prepared by mixing the oil cakes with thrice the mount of tap water (wt/wt basis). Various combinations of cake codigested with cattle dung were prepared. Thus , sixteen different treatment were prepared in 2.5lt cans which were tightly stoppered. The contents were allowed to undergo anaerobic biodigestion.

SUBSTRATE	NUMBER OF TREATMENTS	LEVEL OF TREATMENTS
Cattle Dung	1 (1:1 DR)	Positive Control
Jatropha curcas cake	5 (3:1 DR)	Control is without mixing of cattle dung and other treatments are with 10, 20, 30 and 40 % Cattle dung addition on w/w basis.
Pongamia pinnata cake	5 (3:1 DR)	Control is without mixing of cattle dung and other treatments are with 10, 20, 30 and 40 % Cattle dung addition on w/w basis.
Arachis hypogaea cake	5 (3:1 DR)	Control is without mixing of cattle dung and other treatments are with 10, 20, 30 and 40 % Cattle dung addition on w/w basis.

Table 3.1. Number and different levels of cake incorporated treatments

DR : Dilution Ratio (water : cake)

3.2.3. GAS COLLECTION

Biogas production in each treatment was measured by liquid displacement method on daily basis as shown in Fig 3.5.

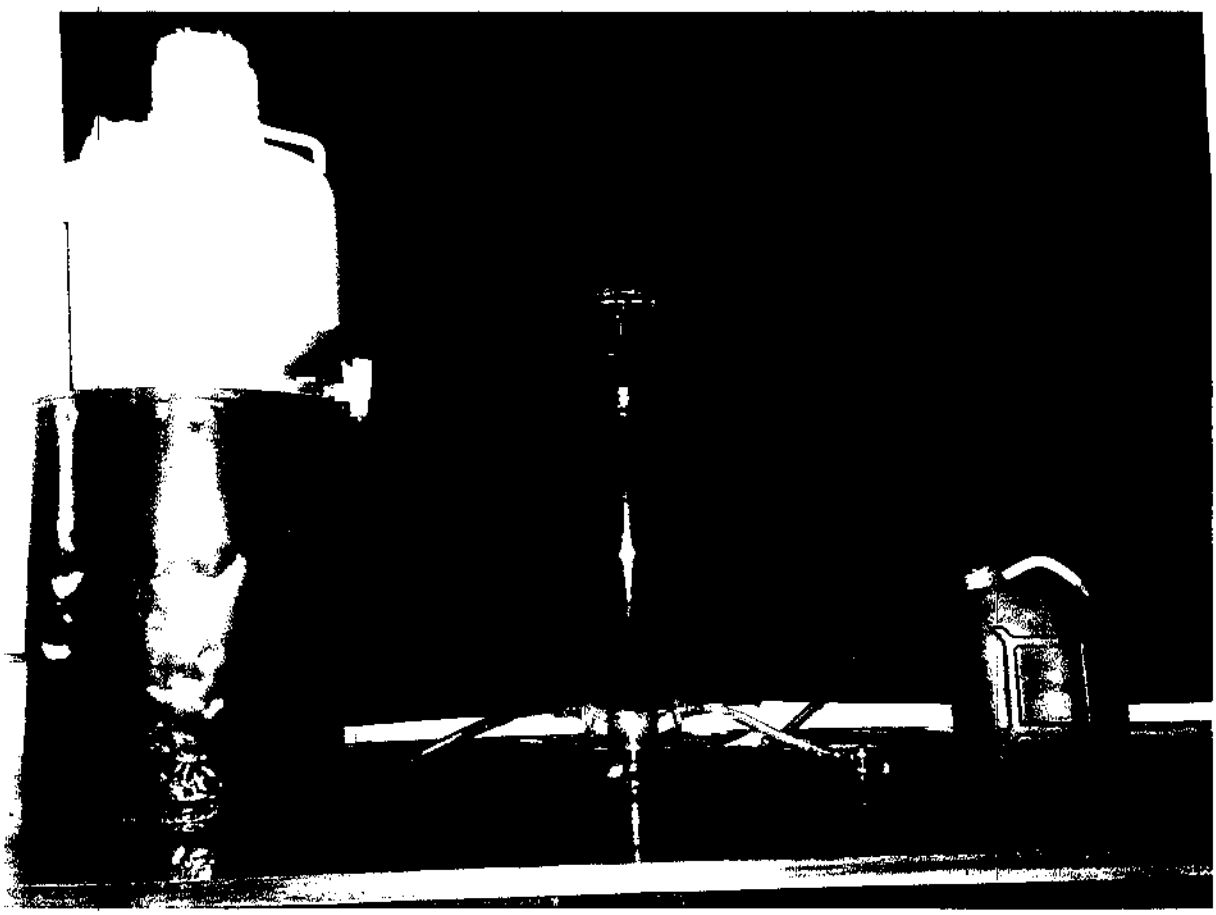


Fig 3.5. Liquid Displacement Assembly

3.2.4 ANALYSIS OF RAW MATERIALS AND SLURRY SPECIMENS OF VARIOUS TREATMENTS

Physical properties like moisture content, total solids and volatile solids, chemical properties like total organic carbon, total nitrogen,

phosphorus and potassium contents of raw materials as well as slurry samples of various wastes incorporated treatments were initially determined.

The biodigested slurry samples of various wastes incorporated treatments were also obtained after the completion of the experiments and analyzed for the moisture, total solids, volatile solids, total organic carbon, total nitrogen, phosphorous and potassium contents.

3.2.4.1. Physical properties

3.2.4.1.1. Moisture content

The moisture content of the various materials used in this study were estimated following the method described by Johnson and Ulrich (1960).

About 10 g of freshly collected samples were placed in weighing bottles and dried in hot air oven at 105° C for 12-16 hours. The bottles were cooled in a desiccator and weighed in a "Melter chemical balance". This procedure was repeated until the concordant values were obtained. The difference in weight was expressed as percentage of moisture on oven dry basis.

Weight of samples before drying in hot air oven	=	A
Weight of samples after drying in hot air oven	=	B
Loss in weight of samples	=	A-B
Moisture percentage	=	$\frac{A-B}{A} \times 100$

3.2.4.1.2. Total Solids

Total solids of the waste materials were determined by deducing the moisture content from 100. Total solids (T.S.) =100-moisture content.

3.2.4.1.3. Volatile Solids

After determining the moisture content and total solids, the contents in the moisture bottles were completely transferred to already weighted silica crucides. The silica crucibles were kept at 645 C for 2-3 hours in a muffle furnace. Weights were taken in a matter chemical balance after cooling to room temperature.

Weight of the moisture bottle = A g

Weight of moisture bottle+ sample = B g

Sample weight = B-A g

Weight of sample after heating in hot air oven = C g

Weight of silica crucible = D g

Weight of silica crucible +sample = E g

Weight of the sample after keeping in muffle furnace = E-D g

Volatile solids percentage = $\frac{C-(E-D)}{B-A} \times 100$

3.2.4.2. Chemical Properties

3.2.4.2.1 Total Organic Carbon

The total carbon content of the samples was estimated by the digestion method of walkly and black as described piper (1950).

Reagents

1. Ferrous ammonium sulphate (0.5 N)
2. Potassium dichromate solution (1.0 N)
3. Diphenylamine indicator

1.5 g of diphenylamine was dissolved in 20 ml of distilled water and 100 ml sulphuric acid.

4. Concentrated sulphuric acid 96 percent.
5. Orthophosphoric acid 85 percent.

Procedure

Samples containing not more than 0.1 g of solid material (1g of wet material) weighed and transferred to 500ml conical flask. 20 ml of 1n potassium dichromate and 20 ml of concentrated sulphuric acid were added and gently the contents were mixed. The mixture was allowed to stand for 20-30 minutes at room temperature.

Standardization blank was also run in the same manner. Then the solution was diluted by adding 200ml of distilled water and 10 ml of 85% orthophosphoric acid. Three drop of diphenylamine indicator was then added. After the contents were titrated against 0.5 M ferrous ammonium sulphate solution the change of color from blue to brilliant green was taken as the end point.

Calculation

1 ml of 1N KCr_2O_7 0.003 g of carbon

Volume of potassium dichromate = 20ml

Blank titre value = BTV

Titre value = TV

Moisture content = M

Percent of organic carbon = $\frac{20 \times TV}{BTV} \times \frac{0.003}{WS} \times \frac{100}{10\text{-}M}$

Where WS is the sample weight

3.2.4.2.2. Total Nitrogen

The total nitrogen content of the wastes were estimated as per the method described by Humphries (1956).

Reagents

1. Sulphuric acid + Salicyclic acid mixture
   (5 g of salicylic acid in 100 ml of concentrated sulphuric acid).
2. Sodium thiosulphate
3. Catalyst mixture (1g of cupric sulphate)
   8 g of potassium sulphate and 1 g of selenium dioxide 1:8:1.
4. 49 percent sodium hydroxide.
5. 2 percent boric acid.
6. Double indicator solution (83.3 mg of bromocresal green + 16.6 mg of methyl red dissolved in 100ml of 95% ethanol).

Procedure

About 0.1 g of the dried waste material was taken in microkjeldhal digestion flask. 2ml of sulphuric acid +salicylic acid mixture was added and mixed well. After 20 minutes approximately 0.3 g of sodium thiosulphate was added and heated gently. Then the flask was cooled and 0.06 g of the catalyst mixture was added. The contents were digested vigorously and color

was observed. The flask was cooled and the content of each flask was made up to 100 ml distilled water.

From the stock solution 10 ml was pipetted out into a microkjeldhal flask to which 100 ml of 40% sodium hydroxide was added. The liberated ammonia was collected in 2% boric acid (20ml) containing a drop at the double indicator which was then back titrated against N/50 sulphuric acid. The suitable blank was simultaneously run and the value was deducted from the sample before calculation.

Calculation

1 ml of 0.1 N H_2SO_4 contain 0.00014 g of N, 1 ml of N/50 sulphuric acid contains 0.00028 g of N, xml of N/50 sulphuric acid contains 0.00028 x Xg. This is present in 10 ml of the aliquot. Therefore, 100ml of the aliquot will contain =0.00028 x100/10 x Xg of N.

Therefore, 0.1 of the substance will contain

=0.00028 x 100/0.1 x X g of N.

3.2.4.2.3. Phosphorous

Reagents

1. Ammonium molybdate .
2. Ammonium metavanadate
3. Potassium dihydrogen phosphate

Procedure

To the sample, 1.25 ml of ammonium molybdate and 0.25 percent of ammonium metavanadate were added. The absorbance of the

color thus developed was read in Bausch and Lomb spectronic-20 colorimeter at 540 nm against a reagent blank. The amount of phosphorus was calculated by referring to a calibration curve with potassium dihydrogen phosphate and expressed on percentage basis.

In 100 ml of distilled water 0.043 g of potassium dihydrogen phosphate was dissolved so as to get concentration equivalent to 100 ppm. A standard curve complying 10, 20, 30, 40, 50 upto 100 ppm concentrations was prepared and from this the unknown concentration was calculated.

Calculation

$$\% \text{ of phosphorous} = \frac{X \text{ ppm} \times 50 \times 100 \times 100}{1000000 \times 5 \times 0.5}$$

Where X is the sample reading

3.2.4.2.4 Potassium

The potassium content of the sample was estimated by flame photometry method described by Jackson (1962).

Standard Potassium Solution

The standard potassium solution was prepared by dissolving 1.907 g of potassium chloride in distilled water and making upto 100 ml, 10 ml of the solution was diluted to 1000 ml to get a solution containing 1 mg of potassium per ml.

Procedure

A known quantity of sample was taken in a flask to which the triacid mixture (15ml) was added and the digestion was until a white mixture was obtained. The flask was cooled and the contents made upto 50 ml with distilled water.

Different concentration of the standard potassium chloride of the standard potassium chloride was fed into EEL flame photometer to prepare a standard curve and the transmittance was recorded using potassium filter. The sample was also treated in the same manner and from the calibration curve; the amount of potassium in the unknown was calculated

3.2.5. CO_2 AND METHANE ESTIMATION OF THE GAS GENERATED IN THE OIL CAKES INCORPORATED TREATMENTS

Carbon dioxide content of the biogas produced was estimated during IV, V and VI weeks in the various treatments using Saccharometer instrument (Fig 3.6). This instrument is a 'U' shaped instrument with two stems. The instrument has one stem with an open end and other stem calibrated with markings. Saturated potassium hydroxide is filled into the instrument. The biogas was first drawn in the separately attached syringe by pressing, the gas and was slowly injected into the stem of the Saccharometer instrument.

Carbon dioxide present in the gas gets absorbed by the saturated potassium hydroxide and methane content present in the gas decreases the level of potassium hydroxide in the instrument. The level of potassium hydroxide decreased is reported as the methane content of the gas. The reading on the calibrated scale attached to the stem. The result was

expressed in terms of percent of methane contained on the injected gas mixture. The CO_2 content was estimated by deducing the methane content from 100% and also giving an allowance of 2% for moisture content and other gases.

Fig 3.6. Saccharometer instrument

Results and Discussion

4. RESULTS AND DISCUSSION

4.1.BIODIESEL

4.1.1 PROPERTIES OF BIODIESEL

The various properties of the biodiesel produced from the various oil sources are shown in table 4.1 and these values are compared with the values quoted by ASTM standards for biodiesel.

PROPERTIES	BIODIESEL			ASTM standards for Biodiesel
	Jatropha curcas	*Pongamia pinnata*	*Arachis hypogaea*	
VISCOSITY at 40°C (10^{-6} m^2s^{-1})	3.5	4.6	6.5	1.8 to 6.0
ACID VALUE (mgKOH/g)	0.38	0.47	0.64	Max 0.8
FLASH POINT (°C)	120	115	96	Max 130
CETANE NUMBER	43	41	52	40 - 55

Table 4.1 Properties of Biodiesel produced from various oils

4.1.2 DISCUSSION ON PROPERTIES OF BIODIESEL

4.1.2.1 Viscosity Measurements

The viscosity of the produced biodiesel is important when considering the fuel within the engine, since the change in spray can gently alter the combustion properties. The esterification of oils reduce the viscosity levels. All the biodiesel samples have viscosity values within the

limit quoted by ASTM expect biodiesel from *Arachis hypogaea*.However, the viscosity of biodiesel from *Arachis hypogaea* can be reduced by blending it with petroleum diesel (Alok Kumar Tiwari *et al.*, 2007)

4.1.2.2 Acid Value

The acid value of the esters gives indication of the quatity of fatty acid in the biodiesel. The Acid values of biodiesel from *Arachis hypogaea* is exceeding those values given by ASTM , apart from other two biodeisel samples. Acid value is the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound such as a fatty acid.

4.1.2.3 Cetane Number

Cetane number or CN is a measurement of the combustion quality of diesel fuel during compression ignition. It is a significant expression of diesel fuel quality among a number of other measurements that determine overall diesel fuel quality. Cetane number of a fuel is defined as the percentage by volume of normal cetane in a mixture of normal cetane and alpha-methyl naphthalene which has the same ignition characteristics (ignition delay) as the test fuel when combustion is carried out in a standard engine under specified operating conditions.

Cetane number is actually a measure of a fuel's ignition delay; the time period between the start of injection and start of combustion (ignition) of the fuel. In a particular diesel engine, higher cetane fuels will have shorter ignition delay periods than lower cetane fuels. Generally, diesel engines run

well with a CN from 40 to 55. Fuels with higher cetane number which have shorter ignition delays provide more time for the fuel combustion process to be completed. Hence, higher speed diesels operate more effectively with higher cetane number fuels. From the Table 4.1 ,biodiesel from all three oils have cetane number within limits 40 to 55.

4.1.2.4 Flash point

The flash point of a flammable liquid is the lowest temperature at which it can form an ignitable mixture in air. At this temperature the vapor may cease to burn when the source of ignition is removed. A slightly higher temperature, the fire point, is defined as the temperature at which the vapor continues to burn after being ignited. Neither of these parameters are related to the temperatures of the ignition source or of the burning liquid, which are much higher. The flash point is often used as one descriptive characteristic of liquid fuel, but it is also used to describe liquids that are not used intentionally as fuels. As per ASTM, the flash point should be Min 130 deg C. The results indicated that biodiesel from all three oils have flash point within the prescribed limits.

4.2 BIOGAS

The results obtained from the experiments carried out are detailed below:

Effect of incorporation of *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake along with cattle dung in relation to biogas generation.

The various types of cakes used were *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake along with cattle dung. These organic wastes were analyzed for their physical and chemical properties such as moisture, total solids, volatile solids, percentage of volatile solids to total solids, total organic carbon, total nitrogen, C: N ratio, phosphorus and potassium.

4.2.1. PHYSICAL PROPERTIES

The results of physical properties of various cakes are presented in Table 4.2.

4.2.1.1. Moisture content

The moisture percentage of various cakes materials ranged from 13.8 (*Arachis hypogaea* cake) to 86.14 (cattle dung).The estimated moisture contents were 86.14, 14, 15.1 and 13.8 percent for cattle dung(CD), *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake respectively.

4.2.1.2. Total solids

The total solids varied with different cakes materials examined. The total solids estimated were 13.88(CD), 86(JC), 84.9(PP) and 86.2(AH) percent respectively.

4.2.1.3. Volatile solids

The volatile solids estimated were 12.12, 78.32, 78.4 and 79.6 percent for cattle dung (CD), *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake respectively.

4.2.1.4. Percentage of volatile solids to total solids

The percentage of volatile solids to total solids for cattle dung (CD), *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake were 87.31, 91.06, 92.34 and 92.34 percent respectively.

Raw Materials	Moisture Content (%)	Total Solids (%)	Volatile Solids (%)	% VS/TS
Cattle dung	86.14	13.88	12.12	87.31
Jatropha curcas oil cake	14	86	78.32	91.06
Pongamia pinnata oil cake	15.1	84.9	78.4	92.34
Arachis hypogaea oil cake	13.8	86.2	79.6	92.34

Table 4.2. Physical properties of raw materials

4.2.2. CHEMICAL PROPERTIES

Various chemical properties analyzed in the different cakes used are presented in Table 4.3

4.2.2.1. Total nitrogen

The total nitrogen content of various cakes was different and the percentage value for cattle dung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake were 1.53, 5.12, 2.03 and 4.00 respectively.

4.2.2.2. Organic carbon

The organic carbon content of the various cakes analyzed ranged from 31.88(AH) to 47.43(PP) percent. The organic carbon content of the cattle dung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake were 33.18, 42.39, 47.43 and 31.88 respectively.

4.2.2.3. C: N Ratio

C: N ratio estimated were 21.68, 8.28, 23.36 and 7.97 percentage for cattle dung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake respectively.

4.2.2.4. Potassium

The potassium content was 0.79, 0.32, 0.30 and 1.31 percent for cattle dung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake respectively.

4.2.2.5. Phosphorous

The phosphorous content was 0.70, 0.50, 0.20 and 0.18 percent for cattle dung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake respectively.

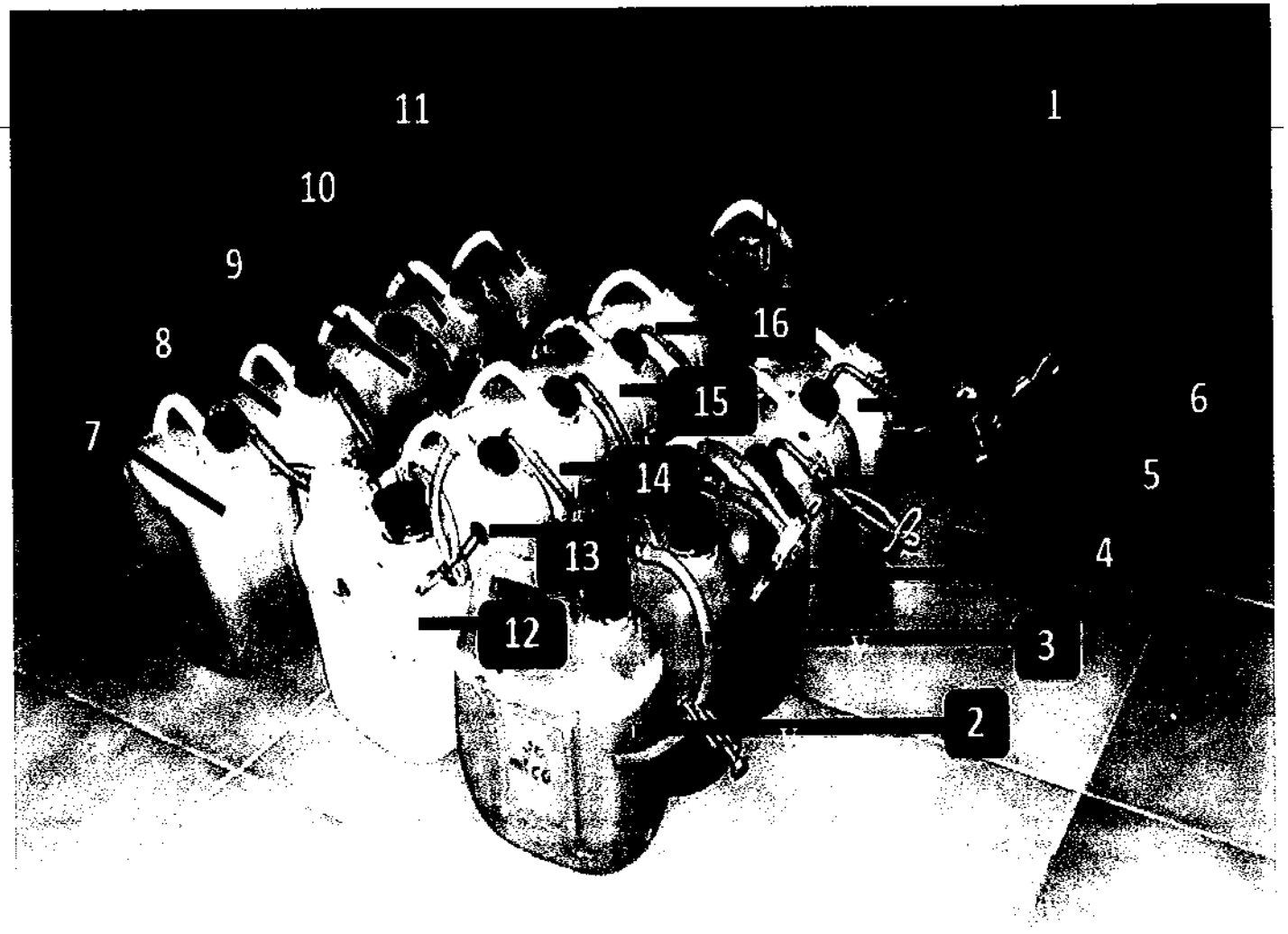
Raw Materials	Nitrogen (%)	Carbon (%)	C/N Ratio	Phosphorus (%)	Potassium (%)
Cattle dung	1.53	33.18	21.68	0.70	0.79
Jatropha curcas oil cake	5.12	42.39	8.28	0.50	0.32
Pongamia pinnata oil cake	2.03	47.43	23.36	0.20	0.30
Arachis hypogaea oil cake	4.00	31.88	7.97	0.18	1.31

Table 4.3. Chemical properties of raw materials

4.2.3. GAS PRODUCTION

The various cake incorporated treatments were allowed to undergo batch digestion in 2.5 litre capacity cans as depicted in Fig.4.1.The maximum gas output recorded from the various sixteen treatments is given in Table 4.4 ,4.5 and 4.6

The maximum gas output of 22815 ml was recorded in the *Arachis hypogaea* cake and cattle dung incorporated treatments (T16). Among the other treatments, *Pongamia pinnata* cake and cattle dung incorporated treatment (T11) recorded 20025 ml. The control cattle dung alone treatment (CD) however recorded 9680 ml over six weeks period. An increase in gas production over the cattle dung control was observed in all the *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake incorporated treatments.



CAN 1 : CD

CAN 2 : JC

CAN 3 : JC + 10%CD

CAN 4 : JC + 20%CD

CAN 5 : JC + 30%CD

CAN 6 : JC + 40%CD

CAN 7 : PP

CAN 8 : PP + 10%CD

CAN 9 : PP+ 20%CD

CAN 10 : PP + 30%CD

CAN 11 : PP + 40%CD

CAN 12 : AH

CAN 13 : AH + 10%CD

CAN 14 : AH + 20%CD

CAN 15 : AH + 30% CD

CAN 16 : AH + 40 % CD

Fig 4.1. Sixteen different sets of various cake incorporated treatments

[CD-*Cattle dung* ; JC-*Jatropha curcas* ; PP-*Pongamia pinnata* ; AH-*Arachis hypogaea*]

Treatments	Weekly total gas output (in ml)						Total gas output over 6 weeks (ml)	Weekly average gas output (ml)	Percentage increase over control
	I	II	III	IV	V	VI			
T1 : CD	1250	`1450	1670	1950	1740	1620	9680	1613..33	--
T2 : JC	1880	2225	2450	2670	2520	2410	14155	2359.16	44.75
T3 : JC+ 10%CD	2000	2370	2700	2950	2790	2640	15450	2575	57.70
T4 : JC+ 20%CD	2100	2475	2800	3150	3020	2910	16455	2742.5	67.75
T5: JC+ 30%CD	2060	2630	2900	3240	3130	3020	16980	2830	73.00
T6: JC+ 40%CD	2475	2795	3150	3450	3310	3190	18370	3061.66	86.90

Table 4.4. Amount of Biogas produced from *Jatropha curcas* cake incorporated treatments

CD = Cattle dung
JC = *Jatropha curcas*

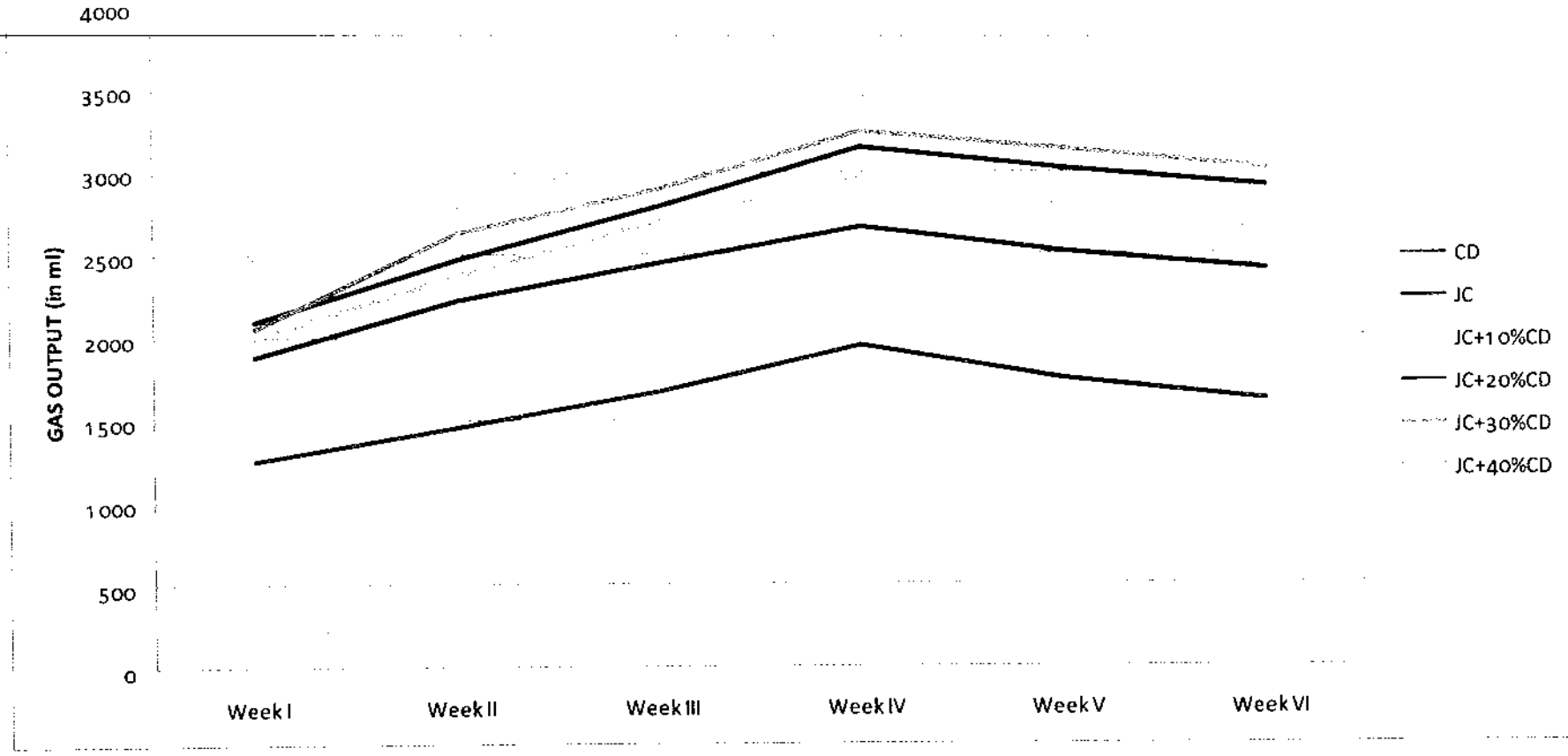


Fig 4.2. Weekly gas output (in ml) of *Jatropha curcas* cake incorporated treatments

CD = Cattle dung ; JC = *Jatropha curcas*

Treatments	Weekly total gas output (in ml)						Total gas output over 6 weeks (ml)	Weekly average gas output (ml)	Percentage increase over control
	I	II	III	IV	V	VI			
T1 : CD	1250	1450	1670	1950	1740	1620	9680	1613.33	--
T7 : PP	1975	2375	2650	2940	2730	2620	15290	2548.33	56.10
T8 : PP+ 10%CD	1925	2475	2750	3040	2970	2760	15920	2653.33	62.40
T9 : PP+ 20%CD	2125	2660	3050	3270	3120	3010	17285	2872.5	75.55
T10: PP+ 30%CD	2460	2980	3250	3540	3330	3120	18680	3113.33	90.00
T11: PP+ 40%CD	2700	3185	3450	3730	3570	3390	20025	3337.5	103.45

Table 4.5. Amount of Biogas produced from *Pongamia pinnata* cake incorporated treatments

CD = Cattle dung
PP = *Pongamia pinnata*

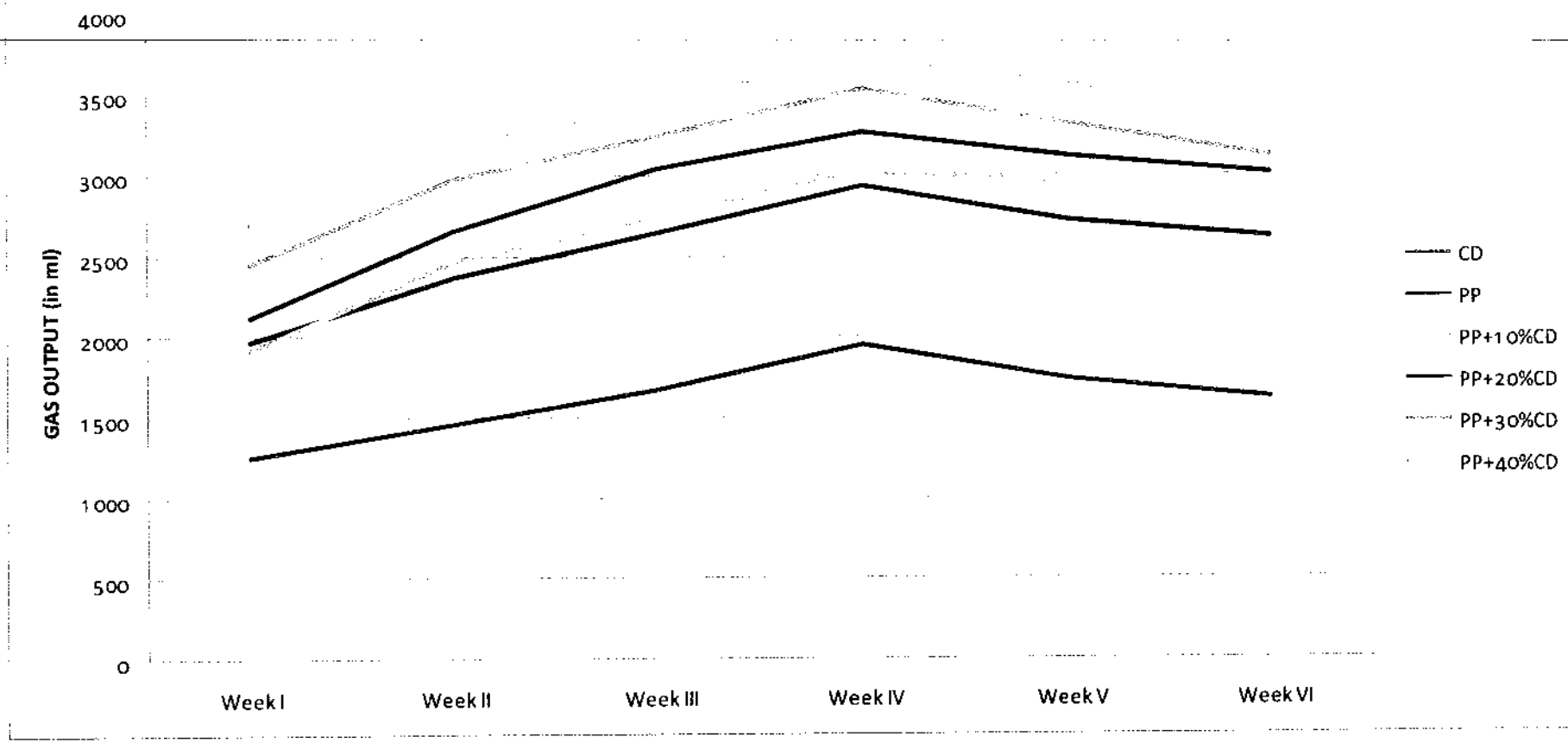


Fig 4.3. Weekly gas output (in ml) of *Pongamia pinnata* cake incorporated treatments

CD = Cattle dung ; PP = *Pongamia pinnata*

Treatments	Weekly total gas output (in ml)						Total gas output over 6 weeks (ml)	Weekly average gas output (ml)	Percentage increase over control
	I	II	III	IV	V	VI			
T1 : CD	1250	1450	1670	1950	1740	1620	9680	1613.33	--
T12 : AH	2425	2750	3050	3250	3470	3290	18235	3039.16	85.55
T13 : AH+ 10%CD	2540	2995	3250	3500	3720	3590	19595	3265.83	99.15
T14 : AH+ 20%CD	2610	3250	3475	3550	3910	3790	20585	3430.83	109.05
T15: AH+ 30%CD	2775	3375	3550	3750	4110	3980	21540	3590	118.60
T16: AH+ 40%CD	3200	3475	3750	4070	4230	4090	22815	3802.5	131.35

Table 4.6. Amount of Biogas produced from *Arachis hypogaea* cake incorporated treatments

CD = Cattle dung
AH = *Arachis hypogaea*

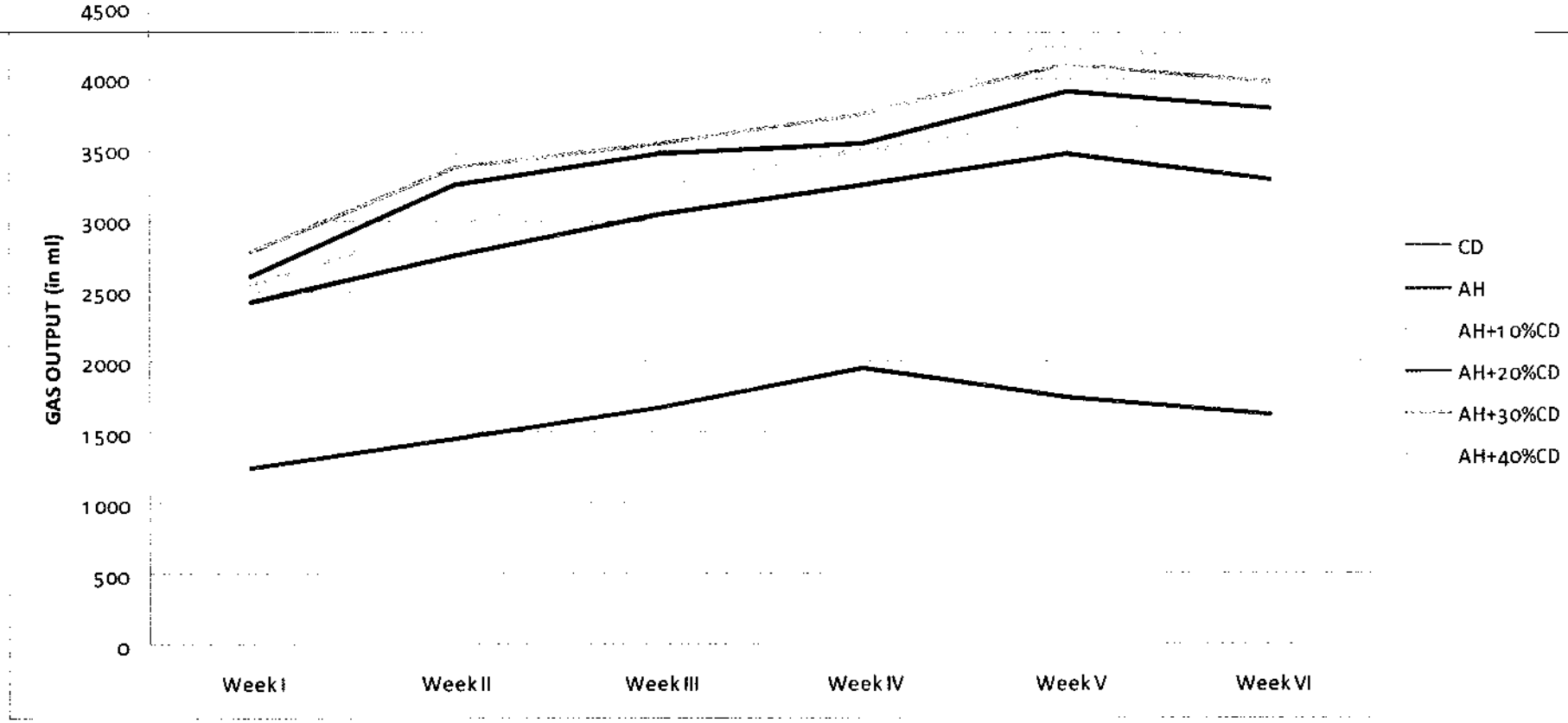


Fig 4.4. Weekly gas output (in ml) of *Arachis hypogaea pinnata* cake incorporated treatments

CD = Cattle dung ; AH = *Arachis hypogaea*

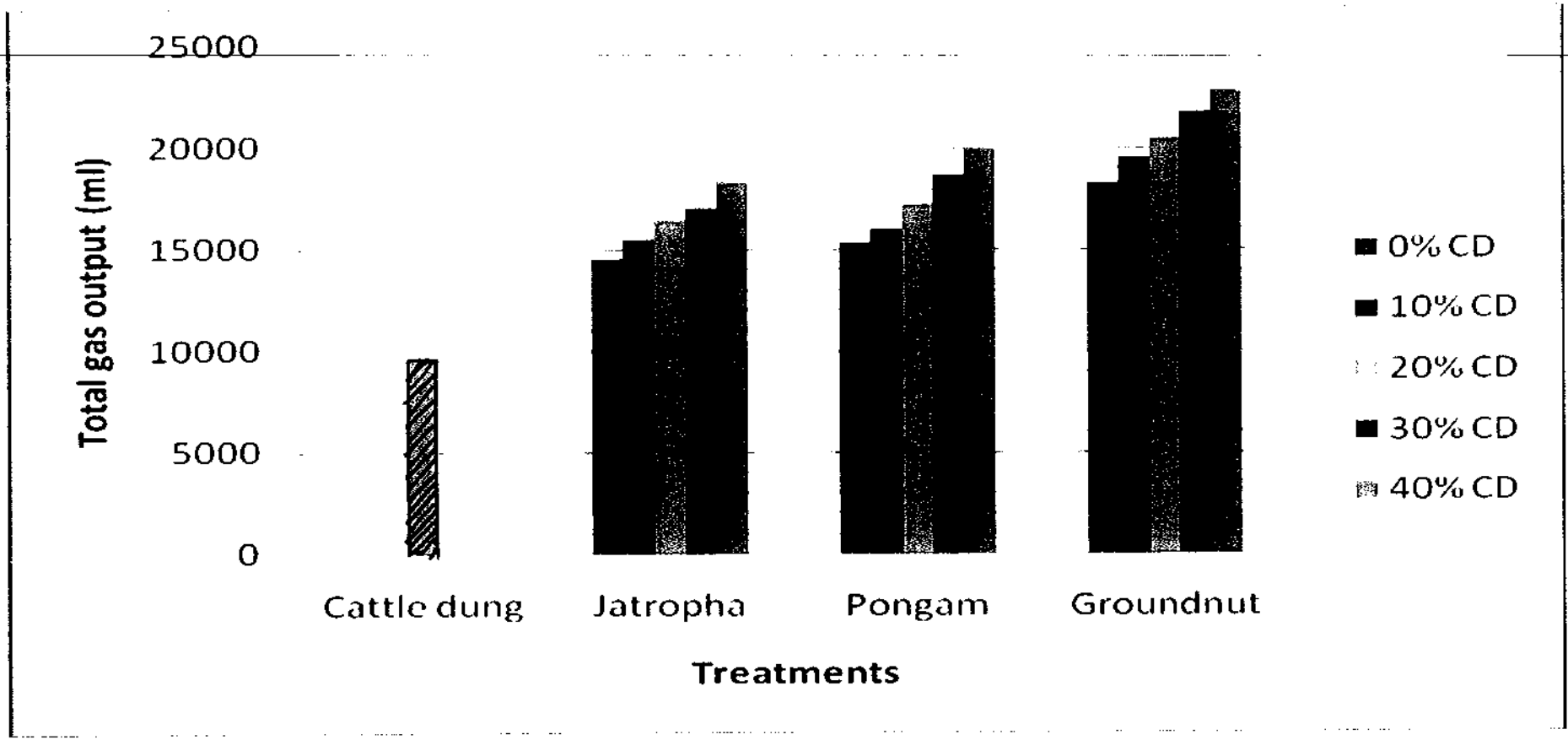


Fig 4.5. Comparison of total gas output over 6 weeks for various cake incorporated treatments

[CD-*Cattle dung* ; JC-*Jatropha curcas* ; PP-*Pongamia pinnata* ; AH-*Arachis hypogaea*]

4.2.4. ANALYSIS OF SLURRY SAMPLES OF VARIOUS CAKES INCORPORATED TREATMENTS

Initial and final analysis of moisture content, total solids and volatile solids of the composite samples of biodigested slurry of the different treatments are presented in Table 4.7, 4.8 and 4.9.

4.2.4.1. Moisture content

The initial moisture content of the various wates incorporated treatments were analyzed and the highest percentage of moisture content, 87.17 percent was observed in cattle dung control and the lowest 18.03 percent in *Pongamia pinnata* cake codigested cattle dung. The final moisture content of the various treatments ranged from

4.2.4.2. Total solids

The initial solids content of the various treatments varied from 12.83(CD) to 81.97 (PP+40%CD) percent. The total solids at the end of the experiment ranged from 9.53(CD) to 38.36 (JC+20%CD) percent.

4.2.4.3. Volatile solids

The initial volatile solid content of the various treatments ranged from 10.89 to 79.06 percent. The highest volatile solids content was observed in AH+40%CD and the lowest in CD. The final volatile solid content ranged from 7.11 to 20.67 percent. The highest was observed in the treatment JC+10%CD and the lowest observed in CD.

4.2.4.4. Percentage degradation of total solids

The percentage degradation of total solids of the various treatments were estimated at the end of the experiment and ranged from 46.79 to 66.01 percent. The percentage degradation of total solids were highest in the treatment (AH+40%CD) and lowest in the treatment (CD). The initial and final total solids of various wastes incorporated treatments are presented in Fig 4.6.

4.2.4.5. Percentage degradation of volatile solids

At the end of the experiment, the percentage degradation of the volatile solids were obtained and the highest being in the treatment AH+40%CD (79.82) and the lowest in the treatment CD (60.85). The initial and final volatile solids estimated in the treatments are presented in Fig 4.7.

Treatments	Moisture Content (%)		Total Solids (TS) %				Volatile Solids (VS) %			
	Initial	Final	Initial	Final	Difference	%Degradation of TS	Initial	Final	Difference	%Degradation of VS
T1: CD	87.17	90.47	12.83	9.53	3.30	46.79	10.89	7.11	3.78	60.85
T2: JC	23.92	61.69	76.08	38.31	37.77	49.65	54.30	19.96	34.34	63.25
T3: JC+ 10%CD	22.15	61.79	77.85	38.21	39.64	50.92	57.65	20.67	36.98	64.15
T4: JC+ 20%CD	21.32	61.64	78.68	38.36	40.32	51.25	59.37	20.22	39.17	65.98
T5: JC+ 30%CD	20.51	62.49	79.49	37.51	41.98	52.82	60.90	20.08	40.82	67.03
T6: JC+ 40%CD	19.98	63.19	80.02	36.81	43.21	54.01	62.03	19.16	42.87	69.12

Table 4.7. Physical properties of *Jatropha curcas* cake incorporated treatments

JC - *Jatropha curcas* : CD – Cattle dung

Treatments	Moisture Content (%)		Total Solids (TS) %				Volatile Solids (VS) %			
	Initial	Final	Initial	Final	Difference	%Degradation of TS	Initial	Final	Difference	%Degradation of VS
T1: CD	87.17	90.47	12.83	9.53	3.30	46.79	10.89	7.11	3.78	60.85
T7: PP	22.57	62.66	77.43	37.34	40.09	51.78	56.43	20.19	36.24	64.23
T8: PP+10%CD	22.16	63.52	77.84	36.48	41.36	53.14	57.95	19.95	38.00	65.58
T9: PP+20%CD	20.89	64.61	79.11	35.39	43.72	55.27	59.89	19.73	40.16	67.07
T10: PP+30%CD	19.37	65.84	80.63	34.16	46.47	57.64	61.23	19.16	42.07	68.72
T11: PP+40%CD	18.03	67.01	81.97	32.99	48.98	59.76	63.74	18.83	44.91	70.46

Table 4.8. Physical properties of *Pongamia pinnata* cake incorporated treatments

PP - ***Pongamia pinnata*** **: CD – Cattle dung**

v **Treatments**	**Moisture Content (%)**		**Total Solids (TS) %**				**Volatile Solids (VS) %**			
	Initial	Final	Initial	Final	Difference	%Degradation of TS	Initial	Final	Difference	%Degradation of VS
T1: CD	87.17	90.47	12.83	9.53	3.30	46.79	10.89	7.11	3.78	60.85
T12: AH	23.87	70.8	76.13	29.2	46.93	61.65	72.18	19.1	53.08	73.54
T13:AH+10%CD	22.91	72.18	77.09	27.82	49.27	63.92	74.26	18.59	55.67	74.97
T14:AH+20%CD	21.88	72.85	78.12	27.15	50.97	65.25	75.98	18.15	57.83	76.12
T15:AH+30%CD	20.77	72.12	79.23	27.88	51.35	64.82	77.13	17.24	59.89	77.65
T16:AH+40%CD	19.74	72.71	80.26	27.29	52.97	66.01	79.06	15.96	63.10	79.82

Table 4.9. Physical properties of *Arachis hypogaea* cake incorporated treatments
AH –*Arachis hypogaea* : CD – Cattle dung

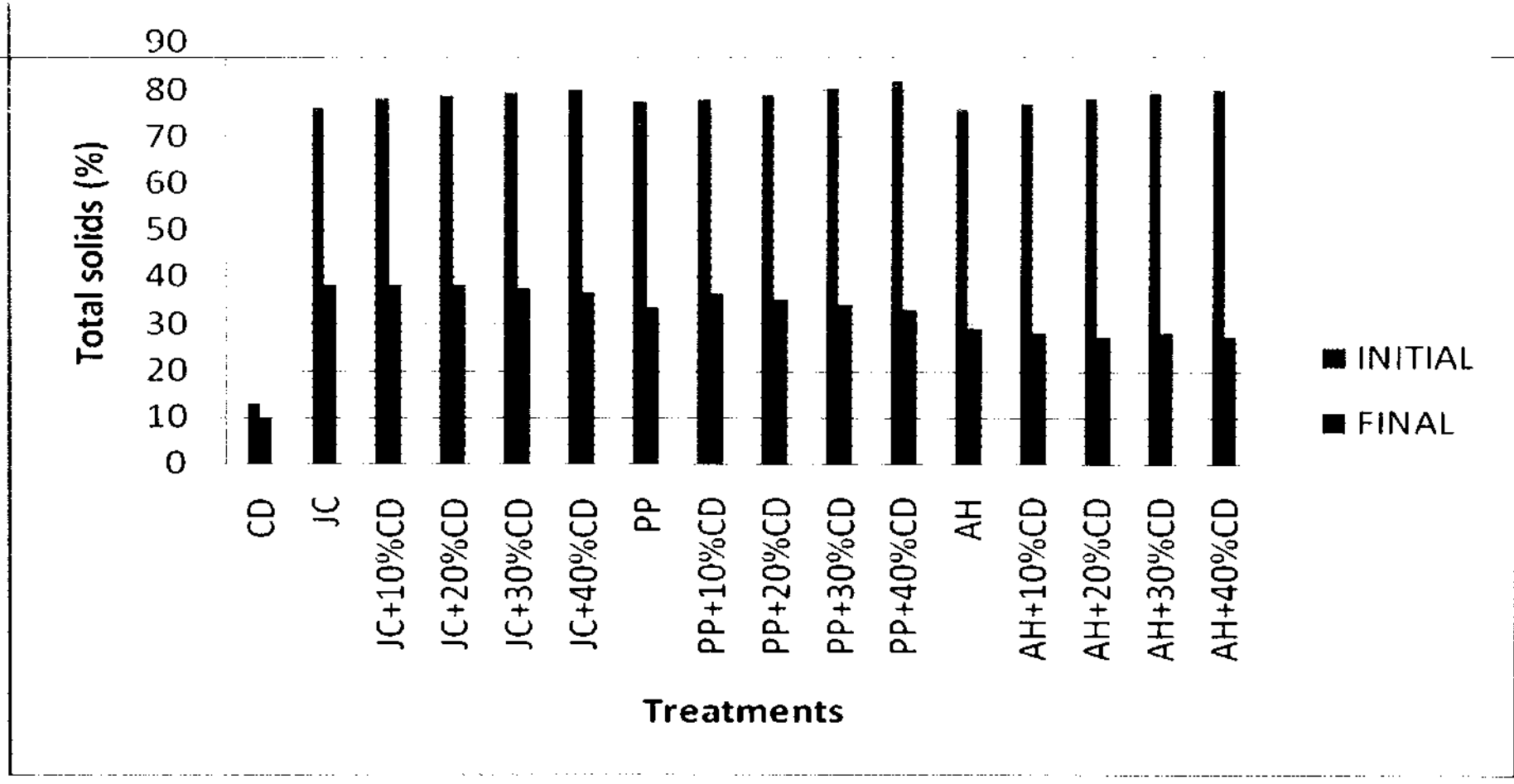


Fig 4.6. Total Solids (Initial and Final) % of various cake incorporated treatments

[CD-*Cattle dung* ; JC-*Jatropha curcas* ; PP-*Pongamia pinnata* ; AH-*Arachis hypogaea*]

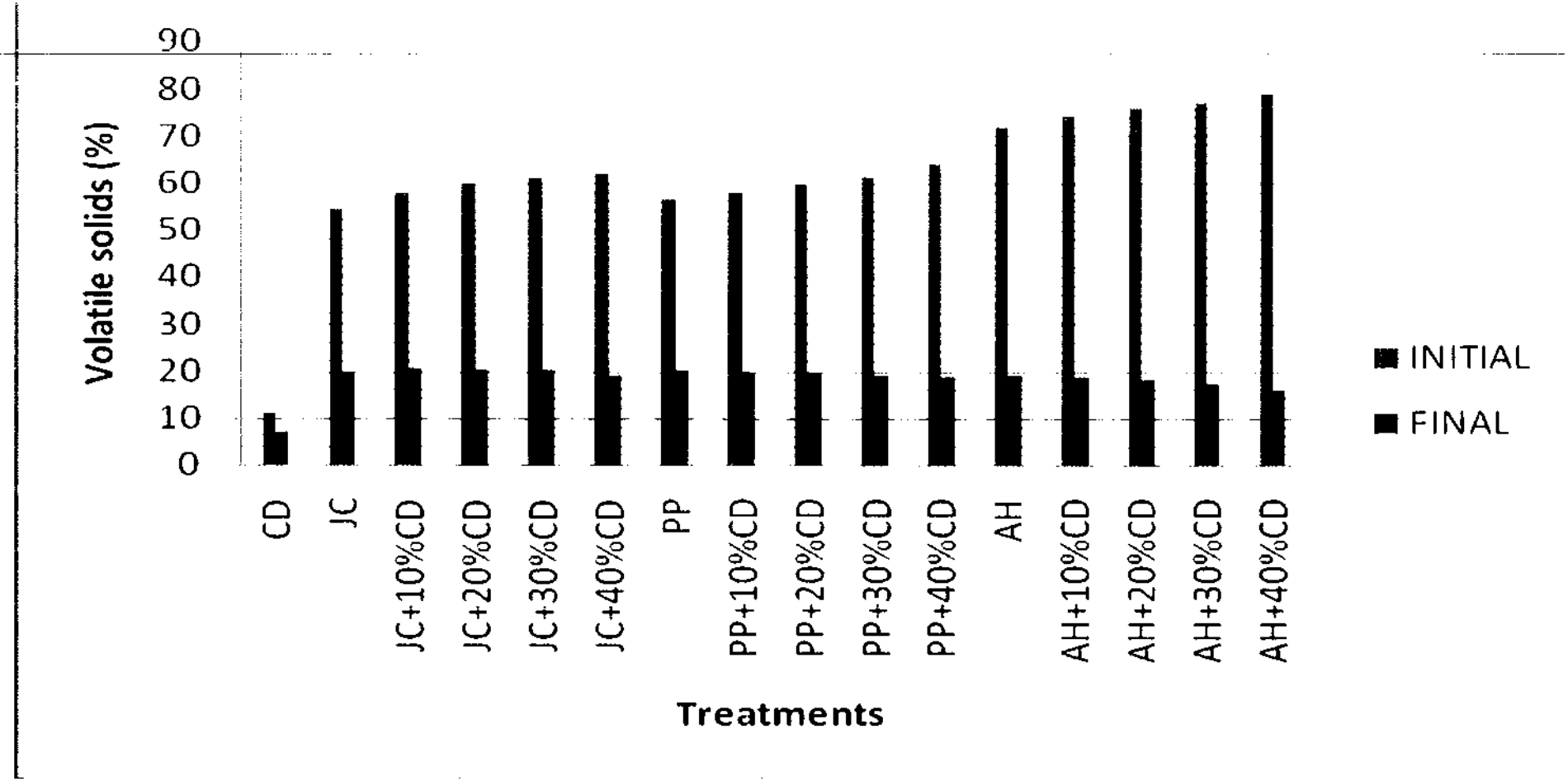


Fig 4.7. Volatile Solids (Initial and Final) % of various cake incorporated treatments

[CD-*Cattle dung* ; JC-*Jatropha curcas* ; PP-*Pongamia pinnata* ; AH-*Arachis hypogaea*]

4.2.5. ANALYSIS OF METHANE CONTENT

The Methane content of the biogas generated was estimated in the IV, V and VI weeks. The results are presented in Table 4.10, 4.11 and 4.12.

The Methane content of the biogas was observed to increase gradually with the increase in time. The initial methane content was high in treatment AH+40%CD (65 percent) and lowest in treatment CD (54.5 percent). The methane content estimated at the final stage of digestion ranged from 58 to 68 percent in treatments CD and AH+40%CD respectively. A qualitative presence of methane is confirmed, when a match stick is lit at the mouth of the measuring cylinder of the liquid displacement assembly. A blue colored flame is observed as in shown in Fig 4.8

Fig 4.8. Observation of blue colored flame

Treatments	Week IV (%)	Week V (%)	Week VI (%)
T1 : CD	54.5	56	58
T2 : JC	56	57	58
T3 : JC+ 10%CD	58	59	60.5
T4 : JC+ 20%CD	59.5	61.5	63
T5 : JC+ 30%CD	61	62	64
T6: JC+ 40%CD	62	63.5	65

Table 4.10. Methane content (in %) in the gas generated from *Jatropha curcas* cake incorporated treatments

CD = Cattle dung
JC = *Jatropha curcas*

Treatments	Week IV (%)	Week V (%)	Week VI (%)
T1 : CD	54.5	56	58
T7 : PP	56	57	58.5
T8 : PP+ 10%CD	58	59	61
T9 : PP+ 20%CD	60	61.5	63
T10: PP+ 30%CD	61	63	65
T11: PP+ 40%CD	63	64	66

Table 4.11. Methane content (in %) in the gas generated from *Pongamia pinnata* cake incorporated treatments

CD = Cattle dung
PP = *Pongamia pinnata*

Treatments	Week IV (%)	Week V (%)	Week VI (%)
T1 : CD	54.5	56	58
T12 : AH	59.5	61	63
T13 : AH+ 10%CD	61	62	64
T14 : AH+ 20%CD	62	63	65
T15 : AH+ 30%CD	63.5	64	66.5
T16: AH+ 40%CD	65	66.5	68

Table 4.12. Methane content (in %) in the gas generated from *Arachis hypogaea* cake incorporated treatments

CD = Cattle dung
AH = *Arachis hypogaea*

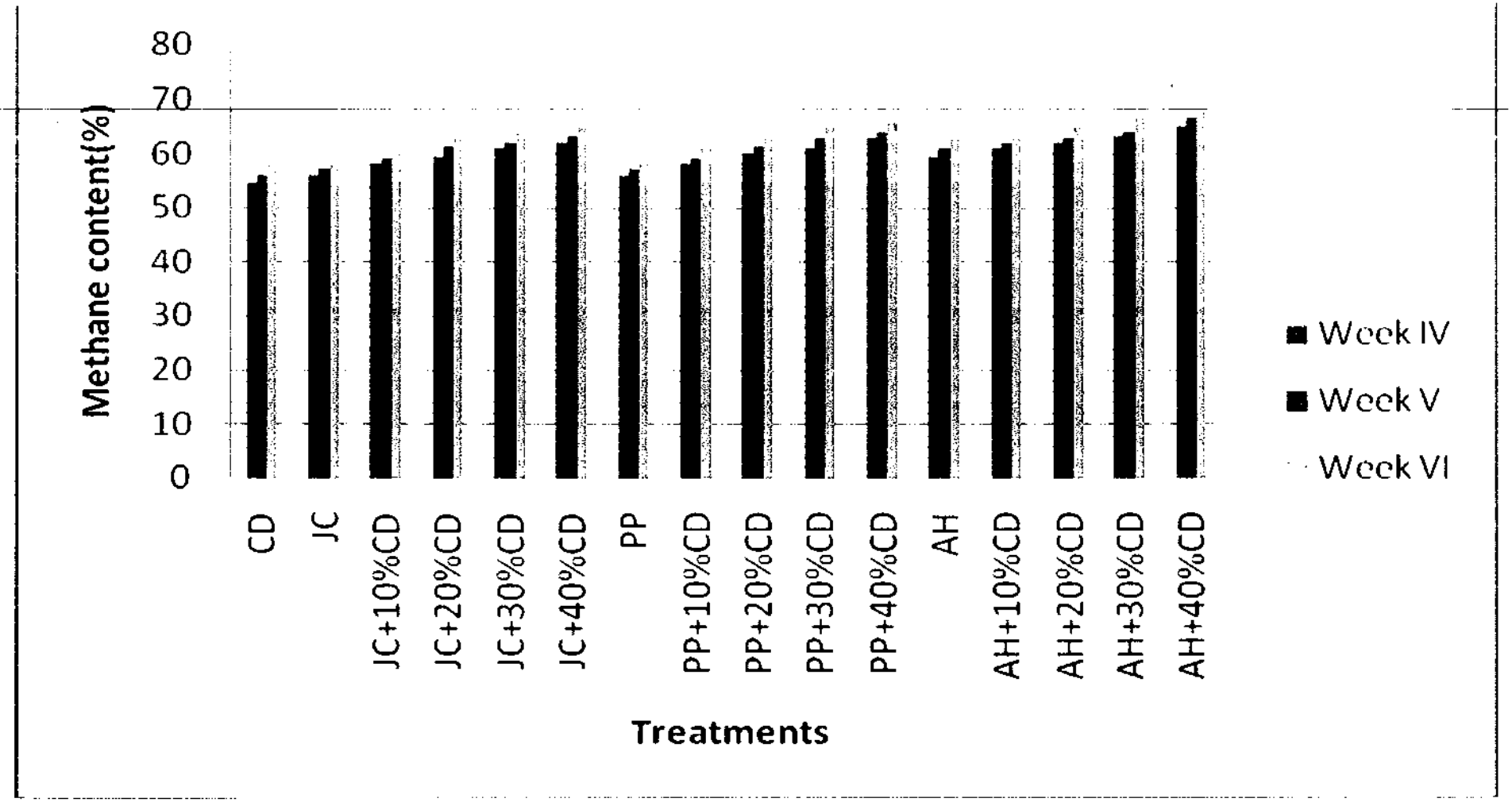


Fig 4.9. Methane content (%) of gas generated from various cake incorporated treatments

[CD-*Cattle dung* ; JC-*Jatropha curcas* ; PP-*Pongamia pinnata* ; AH-*Arachis hypogaea*]

4.2.6. ANALYSIS OF CARBON DIOXIDE CONTENT

The carbon dioxide content of the biogas generated was estimated in the IV, V and VI weeks. The results are presented in Table 4.13, 4.14 and 4.15.

The carbon-di-oxide content of the biogas was observed to decrease gradually with the increase in time. The initial CO_2 content was high in treatment CD (43.5 percent) and lowest in treatment AH+40%CD (33 percent). The carbon dioxide content estimated at the final stage of digestion ranged from 30 to 40.0 percent in treatments AH+40%CD and CD respectively.

Treatments	Week IV (%)	Week V (%)	Week VI (%)
T1 : CD	43.5	42	40
T2 : JC	42	41	40
T3 : JC+ 10%CD	40	39	37.5
T4 : JC+ 20%CD	38.5	36.5	35
T5 : JC+ 30%CD	37	36	34
T6: JC+ 40%CD	36	34.5	33

Table 4.13. Carbon dioxide content (in %) in the gas generated from *Jatropha curcas* cake incorporated treatments

CD = Cattle dung
JC = *Jatropha curcas*

Treatments	Week IV (%)	Week V (%)	Week VI (%)
T1 : CD	43.5	42	40
T7 : PP	42	41	39.5
T8 : PP+ 10%CD	40	39	37
T9 : PP+ 20%CD	38	36.5	35
T10: PP+ 30%CD	37	35	33
T11: PP+ 40%CD	35	34	32

Table 4.14. Carbon dioxide content (in %) in the gas generated from *Pongamia pinnata* cake incorporated treatments

CD = Cattle dung
PP = *Pongamia pinnata*

Treatments	Week IV (%)	Week V (%)	Week VI (%)
T1 : CD	43.5	42	40
T12 : AH	37.5	37	35
T13 : AH+ 10%CD	37	36	34
T14 : AH+ 20%CD	36	35	33
T15 : AH+ 30%CD	34.5	34	31.5
T16: AH+ 40%CD	33	31.5	30

Table 4.15. Carbon dioxide content (in %) in the gas generated from *Arachis hypogaea* cake incorporated treatments

CD = Cattle dung
AH = *Arachis hypogaea*

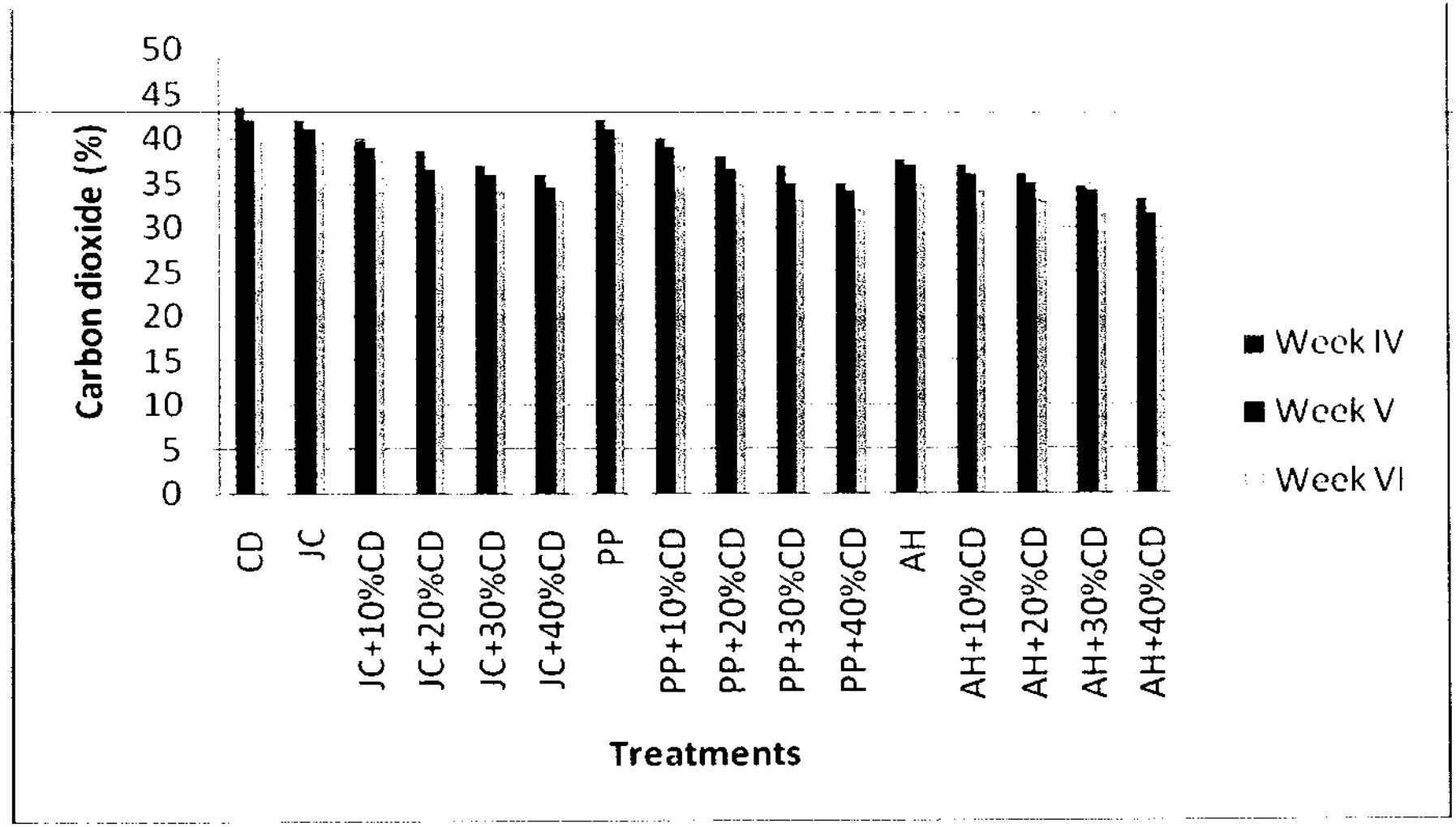


Fig 4.10 Carbon dioxide (%) of gas generated from various cake incorporated treatments

[CD-*Cattle dung* ; JC-*Jatropha curcas* ; PP-*Pongamia pinnata* ; AH-*Arachis hypogaea*]

4.2.7. MANURIAL VALUE OF BIODIGESTED SLURRY SAMPLE

The manurial values of biodigested slurry samples of various treatments are presented in Table 4.16, 4.17 and 4.18

4.2.7.1. Total nitrogen

The nitrogen contents of various slurry samples ranged from 1.61 to 6.49 percent in treatments CD and JC+40%CD respectively. The next best treatment was AH+40%CD (5.68 percent) followed by JC+10%CD (5.67 percent) and JC+30%CD (5.59) respectively.

4.2.7.2. Phosphorous

The highest phosphorous content of 0.95 percent was estimated in the treatment AH+30%CD. The next best treatment was PP+10%CD (0.86 percent), AH (0.82 percent) and AH+40%CD (0.78 percent). The least phosphorous content of 0.25 percent was estimated in JC+30%CD .

4.2.7.3. Potassium

The potassium content varied with various treatments. The potassium content ranged from 0.19 (AH+20%CD) to 0.78 (CD) percent.

Treatments	Nitrogen (%)	Phosphorous (%)	Potassium (%)
T1 : CD	1.61	0.64	0.78
T2 : JC	5.34	0.49	0.34
T3 : JC+ 10%CD	5.67	0.37	0.45
T4 : JC+ 20%CD	4.98	0.56	0.32
T5 : JC+ 30%CD	5.59	0.25	0.37
T6: JC+ 40%CD	6.49	0.43	0.44

Table 4.16. Manurial values of *Jatropha curcas* cake incorporated treatments

CD = Cattle dung
JC = *Jatropha curcas*

Treatments	Nitrogen (%)	Phosphorous (%)	Potassium (%)
T1 : CD	1.61	0.64	0.78
T7 : PP	2.39	0.43	0.31
T8 : PP+ 10%CD	1.98	0.86	0.28
T9 : PP+ 20%CD	2.57	0.37	0.37
T10: PP+ 30%CD	2.12	0.39	0.25
T11: PP+ 40%CD	2.76	0.26	0.23

Table 4.17. Manurial values of *Pongamia pinnata* cake incorporated treatments

CD = Cattle dung
PP = *Pongamia pinnata*

Treatments	Nitrogen (%)	Phosphorous (%)	Potassium (%)
T1 : CD	1.61	0.64	0.78
T12 : AH	4.23	0.82	0.22
T13 : AH+ 10%CD	3.87	0.76	0.31
T14 : AH+ 20%CD	4.17	0.65	0.19
T15 : AH+ 30%CD	3.62	0.95	0.35
T16: AH+ 40%CD	5.68	0.78	0.24

Table 4.18. Manurial values of *Arachis hypogaea* cake incorporated treatments

CD = Cattle dung
AH = *Arachis hypogaea*

The results obtained from the batch digestion of various treatments are discussed below.

4.2.8. DISCUSSION ON PHYSICAL PROPERTIES

The physical properties of the raw materials used viz Cattledung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake varied widely. The moisture content was observed high in was 86.14 percent (CD). Similar observations were also recorded by Sharma *et al.*, (1980). Depending upon the nature of cake materials, the total solids ranged from 13.88 to 86.2 percent for cattle dung and *Arachis hypogaea* cake respectively. The volatile solids varied from 12.12 to 79.6 percent for cattle dung and *Arachis hypogaea* cake respectively. The volatile solids content of *Jatropha curcas* cake and *Pongamia pinnata* cake recorded was 78.32 and 78.4 respectively.

4.2.9. DISCUSSION ON CHEMICAL PROPERTIES.

The total nitrogen content of the various cakes ranged from 1.53 to 5.12 for cattledung and *Arachis hypogaea* cake respectively. The total organic carbon varied from 31.88 (*Arachis hypogaea* cake) to 47.43 percent (*Pongamia pinnata* cake). The C: N ratio of the various waste materials ranged from 7.97 to 23.36 percent for *Arachis hypogaea* cake and *Pongamia pinnata* cake respectively. The phosphorous content varied from 0.18 to 0.70 percent for *Arachis hypogaea* cake and cattle dung respectively. The potassium content varied from 0.30 to 1.31 percent for *Pongamia pinnata* cake and *Arachis hypogaea* cake respectively.

In general the *Jatropha curcas* cake recorded a higher nitrogen and carbon when compared to the other cakes like cattledung, *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake.

4.2.10. DISCUSSION ON GAS PRODUCTION

Variations in the gas output were recorded with the various treatments. The maximum weekly gas output of 22815 ml was recorded in the treatment T16 (AH+40%CD) and the minimum of 9680 ml in the control of cattle dung alone. In general the *Arachis hypogaea* cake incorporated treatments gave comparatively higher gas output than that of other treatments.

4.2.11. DISCUSSION ON PHYSICO-CHEMICAL ANALYSIS OF BIODIGESTED SLURRY OF VARIOUS CAKE INCORPORATED TREATMENTS

4.2.11.1. Moisture content

The initial moisture content of the various slurry samples analyzed ranged from 91.98 (MW) to 92.81 (SLL) percent. The final moisture content of slurry samples of the various treatments varied from 95.21 (CD+MW) to 96.85 (MW) percent. The apparent increase in moisture content of the biodigested slurry might be due to the accumulation of excess water liberated during degradation of various cakes in the digester. In other words about one third of the material added is utilized by the microorganisms for the liberation of biogas. So, the remaining water that was not utilized resulted in the increase in the moisture content (Murugesan 1982).

4.2.11.2. Total solids

The initial total solids percentage of the various treatments range from 81.97 (PP+40%CD) to 12.83 (CD) percent. The final total solids percentage ranged from 9.53 (CD) to 27.15 (AH+20%CD) percent. The decrease in total solid content of the fermented slurry was observed maximum to 52.97 percent in *Arachis hypogaea* cake incorporated treatment.

The *Arachis hypogaea* cake incorporated treatment showed relatively increased degradation of total soids. The gas generation as well as maximum total solid destruction were reported earlier by several workers (Acharya (1958), Singh (1982) and Summers and Bousfield (1980)).

4.2.11.3. Volatile solids

The initial volatile solids content ranged from 10.89 to 79.06 percent. The cattle dung treatment recorded 10.89 and the *Arachis hypogaea* cake incorporated treatment gave 79.06 percent. The gas generation is not only induced by the quantity but also the quality. This is supported by the findings of Varel et al (1977).

4.2.11.4. Percentage degradation of total solids

The percentage degradation of Total solids of various cake incorporated treatments were analyzed and found to ranged from 46.79 to 66.01. The percentage degradation was highest in the AH+40%CD treatment and lowest in the CD treatment.

4.2.11.4. Percentage degradation of volatile solids

At the end of the experiment , the percentage degradation of the volatile solids were obtained and the highest being in the treatment AH+40%CD (79.82) and the lowest in the treatment CD (60.85)

4.2.12. DISCUSSION ON ANALYSIS OF BIOGAS FOR ITS CARBON DIOXIDE CONTENT

The percentage of carbon dioxide was analyzed in the biogas generated from the various treatments. The trend of the data revealed higher content of carbon dioxide in the initial stages of digestion. This may be due to anaerobic predigestion of cakes resulting in the release of higher carbon

dioxide in the initial stage of digestion. The highest carbon dioxide content observed in treatment in the initial week is CD treatment(43.5).

4.2.13. DISCUSSION ON ANALYSIS OF BIOGAS FOR ITS METHANE CONTENT

The percentage of methane content was analyzed in the biogas generated from the various treatments. The trend of the data revealed higher content of methane in the final stages of digestion. This may be due to different microorganisms that help in the digestion of cakes and since it is a slower process, the methane content is increased at the final stages of digestion. The highest methane content in the final weeks was observed in AH+40%CD treatment (68), then in AH+30%CD treatment (66.5) and then in PP+40%CD treatment (66).The gas burnt well on ignition indicating that the methane content is much pronounced in all the cakes incorporated treatments.

4.2.14. DISCUSSION ON MANURIAL VALUES OF BIODIGESTED SLURRY

The biodigested slurry samples from the various cakess incorporated treatments were analyzed for their manurial values.

4.2.14.1. Nitrogen content

The treatment JC possessed the highest nitrogen content (6.49 percent). In general, all the treatments possessed higher nitrogen content than the control (CD-1.61 percent) . The increase in the nitrogen content of the treatments might be attributed to high initial nitrogen content of the wastes in addition to the build up of microbial biomass, conversion of ammoniacal nitrogen to nitrates in an anaerobic environment.

4.2.14.2. Phosphorous

The phosphorous contents of the slurry samples varied with various cakes. The maximum phosphorous content of 0.95 percent was estimated in the treatment, AH+30%CD. *Arachis hypogaea* cake incorporated treatments possessed higher phosphorous content than the control. The results obtained are in agreement with that of Singh (1982) and Rajasekaran (1980a).

4.2.14.3. Potassium

The potassium content of the biodigested slurry samples varied with the treatments. The higher potassium content was estimated in the treatment CD (0.78 percent). The least potassium content was observed in treatments AH+20%CD (0.19 percent).

Conclusion

5. CONCLUSION

In India, there are many varieties of non-edible oil seed crops where Jatropha and Pongam have great potential for the production of biodiesel. These trees could be cultivated on waste and degraded land. Even 5% replacement of petroleum fuel by biodiesel can help India to save Rs.4000 crores in foreign exchange. Hence ,production of biodiesel has to be exploited at a industrial level.

Considering the future scenario of non-edible oil seeds utilization for biodiesel production from *Jatropha curcas* and *Pongamia pinnata* , there is need for efficient utilization of their cakes. These oil cakes could thus be profitably utilized for bio gas generation as a supplementary feedstock along with cattle dung. Anaerobic digestion of oil cakes is a good way of cake disposal which provide a better quality renewable gaseous fuel (biogas) than cattle dung generated biogas.

In Tamilnadu, a huge quantity of about 10,000 tones of oil cakes are disposed as waste. By utilizing such a huge amount of oil cakes for biogas generation, we can solve the energy crisis which is on the increase day by day. This will also help in making our environmental clean and healthy. This will avoid pollution problem faced by mankind. Thus wealth from oil cakes such as *Jatropha curcas* cake, *Pongamia pinnata* cake and *Arachis hypogaea* cake in the form of biogas could be possible. This has to be exploited in a bigger way. The methane content is much pronounced in all the cakes incorporated treatments. Besides the methane rich biogas the biodigested slurry obtained serves as a potential source of organic manure rich in plant food nutrients like N, P, K for application to the fields for improving crop productivity.

References

6. REFERENCES

1. Acharya, C.N. (1958) 'Preparation of fuel gas and manure by anaerobic fermentation of organic materials', *ICAR Research series Bulletin*, **15.**
2. Alok Kumar Tiwari, Akhilesh Kumar and Hifjur Raheman (2007) 'Biodiesel production from jatropha oil (*Jatropha curcas*) with high free fatty acids: An optimized process', *Biomass and Bioenergy.*, **31**:569-575.
3. Anthony Mshandete and Amelia Kivaisi (2004), 'Anaerobic batch co-digestion of sisal pulp and fish wastes ', *Bioresource Technology* ., **95:**19-24.
4. Avinash Kumar Agarwal.(2007) 'Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines', *Progess in Energy and Combustion science.*, **33**:233-271.
5. Banapurmath, N.R., Tewari, P.G. and Hosmath, R.S. (2007) 'Performance and emission characteristics of a DI compression ignition engine operated on Honge, Jatropha and sesame oil methyl esters', *Renewable energy.*,
6. Barnett, A., Pyle, L. and Subramanian, S.K. (1978) 'Biogas technology in the third world A Multidisciplinary Review', *Bioresource Technology* ., **17**:28-110.
7. Beckwith, C.P. and Parsons, J.W (2005) 'The influence of mineral amendments on the changes in the organic nitrogen components of composts', *J.Plant and Soil.*, **54**:259-270.
8. Callaghan , Wase, K. Thayanithy and Forster (1999), 'Co-digestion of waste organic solids: batch studies ', *Bioresource Technology* ., **67**:117-122.
9. Cenni, F., Dondo, G. and Tombetti, F. (1982) 'Anaerobic digestion of tannery wastes', *Agricultural Wastes*, **4**:241-243
10. Converse, J.C., Graves, R.E. and Evans, C.W. (1977) 'Anaerobic degradation of dairy manure under mesophilic and thermophilic temperatures'. *Trans. ASAE*, 336-340.
11. David J. Hills (1979), 'Effects of carbon: Nitrogen ratio on anaerobic digestion of dairy manure ', *Agricultural Wastes* ., **1**:268-279.
12. DeepakAgarwal., LokeshKumar., and Avinash Kumar Agarwal.(2008)

'Performance evaluation of a vegetable oil fuelled compression ignition engine', *Renewable energy.*, **33**:1147-1156.
13. Dennis, M., Sievers and Brune, E. (1978) 'C: N ratio and anaerobic digestion of swine wastes', *Trans. ASAE*, 537-541.
14. Dohia, A.K. and Vasudevan, P. (1986) 'Biogas plant slurry as an alternative to chemical fertilizers', *Biomass.*, **9**:67-74.
15. Fischer, J.R, Iannotti, E.L. and. Sievers, D.M. (1975) 'Anaerobic digestion of manure from swine fed on various diets', *Agric. Wastes*,. **3**:201-214.
16. Fischer, J.R., Iannotti, E.L. and Fulhage. C.D. (1981) 'Production of methane gas from combinations of wheat straw and swine manure', *Trans. ASAE.*
17. Fischer, J.R, Sievers, D.M. and Fulhage, C.D. (1983) 'Energy consumption from farm animal manure methane generation', *Trans.ASAE*, 223-227.
18. Fry, L.T. (1974) 'Practical building of methane power plants for rural energy independence', O.A. Knox, Great Britain, 62.
19. Fujita, M., Scharer, J.M. and Moo-Young (1980), ' Effect of corn stover addition on the anaerobic digestion of swine manure', *Agricultural Wastes.*, **2**:177-184
20. Gollakota, K.G., and Jayalakshmi, B.(1983) 'Biogas production by anaerobic digestion of oil cake by a mixed culture isolated from cow dung' *Biochemical and Biophysical Research Communications.*, . **110**:32-35.
21. Gollakota, K.G., and Meher, K.K.(1988) 'Effect of particle size, temperature, loading rate and stirring on biogas production from castor cake (oil expelled) *'Biochemical and Biophysical Research Communications.*, **24**:243 – 249.
22. Gunnarson, S.,Malmberg, A., Mathisen, B.,Theander,R.O.,Thyselius,L. and Wunsche (1985) 'Jerusalem artichoke (Helianthur tuberosus) for biogas production', *Biomass.*, 7:85 -97.
23 Gupta, A.P., Gupta, V.K., Antil, R.S. and Jagannath (1986) 'Possible losses of plant nutrients from biogas slurry', *Agric. Waste.*, **12**:317-320.
24. Hak-Joo Kim., Bo-Seung Kang., Min-Ju Kim., Young Moo Park., Deog-Keun Kim', Jin-Suk Lee., and Kwan-Young Lee. (2004)'Transesterification of vegetable oil to biodiesel using heterogeneous base catalyst', *Catalysis Today.*, **93-95**:315-320.
25. Hashimoto, A.G., Varel, V.H. and Chen, R. (1981) 'Ultimate methane yield from beef cattle manure effect of temperature, ration constituents,

antibiotic and manure age', *Agric wastes*,. **3**:241-256.
26. Hills, D.J. (1982) 'Optimum operational design criteria for anaerobic digestion of animal manure', *Trans ASAE*, 1029-1030.
27. Hills, D.J. (1983) 'Intermittently mixed and plug flow digestion ofbeef feed lot manure at various water contents', *Trans. ASAE*, 884-889.
28. Hills, D.J. and Roberts, D.W. (1979) 'Effects of C: N ratio on anaerobic digestion of daily manure', *Agri .wastes*, **1**:267-278.
29. Hills, D. J. and Roberts, D.W. (1981) 'Anaerobic digestion of diary manure and field crop residues', *Agric. Wastes*, . **3**:179-189.
30. Hills, D.J, Young, D.T. and Norostedt. R.A. (1981) 'Continuously expanding anaerobic digestion, a technology for the small animal producer', *Trans. ASAE*, 731-736.
31. Hills, D.J and Roberts, D.W. (1982) 'Conversion of tomato,peachand honeydew solid waste into methane gas', *Trans. ASAE*, 820-826.
32. Hills, D.J and Prince, TJ. (1983) 'Dynamic of farmstead methane production', *Trans. ASAE*, 194 -199.
33. Jain, M.K., Rajendra Singh and Tauro, P. (1981) 'Diurnal variationin gas production from biogas plant' *Khadigramadyong*, **879**:314-315.
34. Joelianingsih., Hitoshi Maeda., Shoji Hagiwara., Hiroshi Nabetani., Yasuyuki Sagara., Tatang, H., Soerawidjaya., Armansyah, H., Tambunan., and Kamaruddin Abdullah.(2008) 'Biodiesel fuels from palm oil via the non-catalytic transesterification in a bubble column reactor at atmospheric pressure: A kinetic study' , *Renewable energy*., **33**:1629-1636.
35. Krishnan Vijayaraghavan., Desa Ahmad., Mohd Khairil Bin Ibrahim., and Haryati Naemmah Binti Herman.(2006) 'Isolation of hydrogen generating microflora from cow dung for seeding anaerobic digester',*International Journal of Hydrogen Energy*., . **31**:708-720.
36. Liao, P.H. and Lo, K.V. (1985) 'Two Pase thermophilic anaerobic digestion of screened dairy manure', *Biomass*, **8**:185-194.
37. Lingaiah, V., and Rajasekaran , P. (1986) ' Biodigestion of Cowdung and organic wastes mixed with oil cake in relation to energy', *Agricultural Wastes* ., . **17**:161-173.
38. Lo, K.V, Liao, P.H, and Whitehead, A.J. (1985) 'Methane production at 22$ of laboratory -scale fixed film reactors receiving screened dairy manure', *Energy in Agric*, **4**:1-14.
39. Lo, K.V and Liao, P.H. (1986) 'Methane production from fermentation of winery wastes', *Biomass*, . **9(1)**:19-27.
40. Lo, K. V and Liao, P .H. (1986) 'Mesophilic anaerobic digestion of screened dairy manure using a two phase reactor', *Energy in Agric*.

5:81-88.
41. Lo,K.V., March, A.C. and Liao, P.H. (1985) 'Determination of optimal feed strength for the thermophilic production of methane from dairy manure filtrate', *Energy in Agric*, .**4**:217-226.
42. Madamwar, D. B. and Mittal, B.M. (1986) 'Effect of pecting on anaerobic digestion of cattle dung', *Biotech. and Bioengg*, **25**: 624- 626.
43. Mohibbe Azam, M., Amtul Waris and Nahar, N.M. (2005) 'Prospects and potential of fatty acid methyl esters of some non traditional seed oils for use as biodiesel in India', *Biomass and Bioenergy* .,. **29**:293-302.
44. Murugesan, K. (1982) 'Effect of temperature on the microbial digestion of organic wastes in relation to bio gas generation', M.Sc., Thesis, TNAU, Coimbatore.
45. Nallathambi Gunaseelan (1995) ' Effect of inoculum/substrate ratio and pretreatments on methane yield from *Parthenium*', *Biomass and Bioenergy* ., .**8**:39-44.
46. Olezzkiewick (1985) 'Aerated Lagoon treatment ofPiggery wastes, kinetics of carbon removal', *Agric . wastes*, . **16**:121-134.
47. Pathak, B.S, Jain, R.K and Jon, D.S. (1985) 'Biodigestion of cattle dung and cattle dung- rice straw moisture at different solid concentrations', *Agric. Wastes*, . **13**:251-259.
48. Radhakrishna, P., and Gollakota, K.G.(1989) 'A pilot plant design and performance for biomethanation of non-edible oil cakes',*Energy*., **14**:771-772.
49. Raheman, H., and Ghadge, S.V.,(2005) 'Performance of diesel engine with biodiesel at varying compression ratio and ignition timing', *Fuel*.
50. Rajasekaran, P. (1980) 'Microbiological changes accompanying degradation of water hyacinth in an anaerobic digester', *Madras. Agric.J.*, .**67**:39-41
51. Rajasekaran, P. (1980a) 'Biogas production through microbial digestion of sewage sludge', *Madras Agric. J.*, . **67**:32-37.
52. Rajasekaran, P. and Oblisami (1980) 'Recycling of silkworm wastes for biogas production proceedings of sericulture', Symposium and seminar, 236-259.
53. Roskilly, A.P., Nanda, S.K., Wang, Y.D ., and Chirkowski, J. (2008) 'The performance and the gaseous emissions of two small marine craft diesel engines fuelled with biodiesel',*Applied Thermal Engineering*., **28**:872-878.
54. Roy D.R.Holmberg, Hill, D.J., Prince, J.J. and Vandyke, J. (1983) 'Potential of solid - liquid separation of swine wastes for methane

production', *Trans. ASAE*,1803-1807.
55. Saraswat, N. and Khanna, P. (1986) 'Methane recovery from water hyacinth through anaerobic activated sludge process', *Biotech. and Bio engg*, . **2**:240-46.
56. Sellami, F., Jarboui., Hachicha, S., Medhioub, K., and Ammar, E. (2008)'Co-composting of oil exhausted olive cake, poultry manure and industrial residues of agro-food activity for soil amendment', *Bioresource Technology.*, **110**:32-35.
57. Sérgio Machado Corrêa .,and Graciela Arbilla. (2008) 'Carbonyl emissions in diesel and biodiesel exhaust' ,*Atmospheric Environment.*, **42**:769-775.
58. Sharma, V.P., Paul, T.M. and Zariwaler (1980) 'Recycling of waste materials, their chemical composition and utilization', *Indian.sci.* **50**:407-410.
59. Sharma, Y.C., and Singh, B.(2008) 'Development of biodiesel from karanja a tree found in rural India', *Fuel.*, . **87**:1740-1742.
60. Shanta Satyanarayan., Paresh Murkute., and Ramakant. (2008) 'Biogas production enhancement by *Brassica compestries* amendment in cattle dung digesters', *Biomass and Bioenergy.*, . **32**:210-215.
61. Shivappashetty, T.G., Nandahishore, M.R., Rangava Reddy and Patil, R.B. (1978) 'Silkworm waste as a substrate for biogas production', Abst. All India Symp., *Sericulture sci.*, 8-12.
62. Shyam, M., and Sharma, P.K.(1994) 'Solid-state anaerobic digestion of cattle dung and agro-residues in small-capacity field digesters', *Bioresource Technology.*, . **48**:203-207.
63. Singh,R., Jain, M.K. and Auro,P.T. (1982) 'Rate of anaerobic digestion of cattle wastes', *Agric. Waste*, . **4**:267-272.
64. Sleat and Robinson,T.P. (1984) 'The bacteriology of aromatic compounds and methanogenic fermentation of aromatic compounds', *J. Appl.Bacteriol.*, . **57**:381-394.
65. Smith, P.H. and Hungate, R.E (1958) 'Isolation and characterization of Methanobacterium tuminantium Sp.',*J. Bacteriol.*, .**75**:713 -718.
66. Srivathsan Vembanur Ranganathan., Srinivasan Lakshmi Narasimhan., and Karuppan Muthukumar.(2008) 'An overview of enzymatic production of biodiesel', *Bioresource Technology.*, **99**:3975-3981.
67. Stephenson, R. and Loster, J .N. (1986) 'Evaluation of start up and operation of four anaerobic processes treating a synthetic meat waste', *Biotech. and Bioengg*, **28**:372-380.
68. Sumitra Ramachandran., Sudheer Kumar Singh., Christian

Larroche.,Carlos Ricardo Soccol., and Ashok Pandey.(2007) 'Oil cakes and their biotechnological applications' *Bioresource Technology.*, **98**:2000-2009.

69. Sushil Kumar , Jain and Chhonkar (1987) ' A note on stimulation of biogas production from cattle dung by addition of charcoal', *Biological Wastes* .,**20**:209-215.
70. Summers, R. and Bousfield (1980) 'A detailed study of piggery waste anaerobic digestion', *Agric waste*, **2**:61-78.
71. Vaidynathan, S., Kavadia, K.M., Bonar, P., Mahajan. S.P. (1985) 'Optimal size hydraulic retention time and atile solids loading rate of biogas unit using water hyacinth', *J. Chem. Tech. Biotechnol.*, **35**:121 - 125.
72. Vandenberg, L., Patel, G.B., Clam and Lentz, P. (1976) 'Factors affecting rate of methane fermentation from acetic acid by enriched Methonogenic cultures', *Can. J. Microbiol*, **22**:1312 - 1319.
73. Van Valsen, A.F., Lettinga, M.G. and Denottee Lander, J. (1979) 'Anaerobic digestion of piggery waste, influence of temperature', *Neth. J. Agric. Sci.*, .**27**:255-67.
74. Varel, V.H., Isaacuson, H.R. and Bryant, H.P. (1977) 'Thermophilic methane production from cattle waste', *Appl. Environ.Microbiol* ., **33**:298-307.
75. Varrier, D., Morfaux, J.N., Albagnac, G. and Touzel, J.P. (1982) 'The french Programme on methane production', Bio mass, . **2**:17-28.
76. Walker, L .P., Pellerin, R.A., Heisler, M.G., Farmer, G.S. and Hills, L.A. (1985)' Anaerobic digestion on a dairy farm, over view', *Energy in Ag.*, . **4**:347-364.
77. Warman, P.R. and Termeer, W.C. (2005) 'Evaluation of sewage sludge, septic waste and sludge compost applications to com and forage: yields and N, P and K content of crops and soils', *Bioresource Technology*, . **96**:955-961.
78. Webb and Freda R. Hawkes (1985), 'The anaerobic digestion of poultry manure: Variation of gas yield with influent concentration and ammonium-nitrogen levels', *Agricultural Wastes,* **14**:135-156
79. Yeole T.Y., Ranade, D.R. and Godbole, S.H. (1987), 'Production of biogas from market waste', *Biomass,* **13**:147-153
80. Yong Wang., Shiyi Ou., Pengzhan Liu., and Zhisen Zhang.(2007) 'Preparation of biodiesel from waste cooking oil via two-step catalyzed process', *Energy conversion and management*, . **48**:184-188.

81. Zeeman, G., Wiegant, W.M., Koster-Treffers, M.E. and Lettinga, G. (1985), 'The influence of the total-ammonia concentration on the thermophilic digestion of cow manure', *Agricultural Wastes*, . **14**:19-35