

UTILISATION OF NON-EDIBLE OIL SEED CAKES FOR OPTIMAL BIOGAS PRODUCTION

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BHUBANESWAR

2014

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A THESIS SUBMITTED TO

ORISSA UNIVERSITY OF AGRICULTURE AND TECHNOLOGY

BHUBANESWAR

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE

DEGREE OF

MASTER OF TECHNOLOGY

(AGRICULTURAL ENGINEERING)

IN

FARM MACHINERY AND POWER

BY

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This is to certify that the thesis entitled “**UTILISATION OF NON-EDIBLE OIL SEED CAKES FOR OPTIMAL BIOGAS PRODUCTION**” submitted in partial fulfillment for the degree of Master of Technology (Agricultural Engineering) in Farm Machinery and Power of Orissa University of Agriculture and Technology, Bhubaneswar is a faithful record of bonafied research work carried by Ms. Sushreesmita Mishra (2FMP/12) under my direct supervision and guidance. No part of the thesis has been submitted for any other degree or diploma.

This assistance and help received during the course of this investigation have been duly acknowledged by him.

Bhubaneswar

Dr. M.K. Mohanty

Date:

ACKNOWLEDGEMENT

Foremost, I would like to express my sincere gratitude to my guide Dr. M.K. Mohanty for the continuous support of my M. Tech study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of my research and writing the thesis. I could not have imagined a better guide and mentor for my M. Tech study.

Besides my guide, I would like to thank the rest of my thesis committee: Dr. D. Behera, Professor and Head, Farm Machinery and Power (FMP); Dr. B.K. Behera, Professor, Department of FMP; Dr. A.K. Parida, Associate Professor and Head, Department of Agriculture Statistics, College of Agriculture for their encouragement, useful discussions and contractive criticism throughout the pursuit of the study.

I do extend my hearty thanks to Dr. Md. Khalid Khan, DEAN, College of Agricultural Engineering and Technology (CAET), for providing facilities during the research work.

Words are no eloquent to thanks Dr. M. Mohapatra, Dr. N. Mohapatra, Dr. S.K. Mohanty, Dr. J.N. Mishra, Dr. P.L. Pradhan, Dr. A.K Goel, Dr. A.K. Das of Department of Farm Machinery and Power, CAET; Dr. S.K. Pattnaik, Department of Soil Science, College of Agriculture for providing valuable suggestions and guidance in the research work.

I would like to express my special thanks to Mr. Manmohan Nayak and Madhu bhaina for helping me while conducting the my research work.

I also thank my friends as their friendship has kept me sane during these years. I am most thankful to Sagarika, Smrutilipi, Minaketan, Pooja, Gitanjali, Dwarika and also my roommates Padmini, Tripti for sharing so many moments in my life for the deepest exchange of thoughts and for understanding me and my thesis worries.

My heartiest appreciation is also for the moral support given by my entire family, particularly my mother Mrs. Banita Rani Mishra, my sisters Bubuni and Kuni, my brother Dugulu. There are no words to thank you enough for the support and encouragement; I have been given throughout my life.

I am also thankful to Department of Science and Technology, Govt. of India for providing financial help for conducting the experimental works.

Last but the most important, I bow my head to the greatness of almighty for making me experience one of the most technologically glorifying moments of my life.

Date:

Place: Bhubaneswar

(Sushreesmita Mishra)

CONTENTS

CHAPTER NO.	TITLE	PAGE
	LIST OF TABLES	i
	LIST OF FIGURES	ii
	LIST OF ABBREVIATION	iv
I	INTRODUCTION	1-7
1.1	Present Energy Scenario in World	1
1.2	Future Energy Situation	1
1.3	Environmental Problems and its Alternatives	2
1.4	India Energy Scenario	2
1.5	Biogas	3
1.6	Potential of Non-edible Oil Seed and Cakes	5
1.7	Biogas Application in Engine	6
1.8	Justification of Research Work	6
II	REVIEW OF LITERATURE	8-16
2.1	Biogas Production From Biological Sources	8
2.1.1	Suitability of non-edible oil cakes for biogas production	10
2.1.2	Biogas production from de-oiled non-edible oil seed cakes	11
2.2	Operational factors affecting biogas production	13
2.2.1	Type of feed	13
2.2.2	Mixing ratio	13
2.2.3	Hydraulic retention time	14
2.3	Analysis of biogas by gas chromatographs	15
2.4	Biogas application in engine	16
III	THEORITICAL CONSIDERATION	17-24
3.1	Biogas production from de-oiled non-edible oil seed cakes	17
3.1.1	Hydraulysis	17
3.1.1	Acidogenesis	17

	3.1.2	Acetogenesis	18
	3.1.3	Methanogenesis	18
	3.2	Operational Parameters affecting biogas production	19
	3.2.1	Temperature	19
	3.2.2	Pressure	19
	3.2.3	Solid to moisture ratio	20
	3.2.4	pH value	20
	3.2.5	Carbon to nitrogen ratio (C/N) ratio	20
	3.2.6	Hydraulic retention time (HRT)	21
	3.2.7	Mixing or stirring	21
	3.2.8	Effect of toxic substances	21
	3.3	Botanical description of selected oil cake source (Kusum and Polanga)	21
	3.3.1	Kusum	21
	3.3.2	Polanga	22
IV		MATERIALS AND METHODS	25-37
	4.1	Substrate Collection	25
	4.2	Preliminary Test	25
	4.2.1	Moisture content determination	26
	4.2.2	pH determination	26
	4.2.3	N, P, K and C analysis of de-oiled seed cake	27
	4.2.3.1	Nitrogen analysis	27
	4.2.3.2	Phosphorus (P) and Potash (K) analysis	28
	4.2.3.3	Carbon	29
	4.3	Preparation of Feed for Biogas Production	29
	4.4	Experimental design	30
	4.5	Experimental apparatus set up	31
	4.6	Gas Chromatography test	32
	4.7	Experimental Procedures	33
	4.8	Pilot Scale Biogas Production	33
	4.9	Biogas Application in Engine	34
	4.9.1	Development of experimental engine test assemble	34

	4.9.2	Installation of the instrument control panel	35
	4.9.3	Modification of the air inlet pipe	36
V		RESULTS AND DISCUSSION	38-55
	5.1	Suitability of kusum and polanga seed cakes as feedstocks for biogas production	38
	5.1.1	Total solid and oil content of samples	38
	5.1.2	C/N ratio of samples	38
	5.2	Biogas production	39
	5.3	Effect of different variables on biogas production and methane content	43
	5.3.1	Effect of mixing ratio on biogas production	43
	5.3.2	Effect of retention time on biogas production	45
	5.3.3	Effect of mixing ratio on methane content of biogas	47
	5.3.4.	Effect of retention time on methane content of biogas	49
	5.3.5	Selection of best mixing ratio	50
	5.4	Selection of best retention time	51
	5.5	ANOVA table for quantity and quality of biogas	52
	5.6	Variation of pH before and after digestion	54
	5.7	Application of Biogas in Engine	55
	5.8	Fuel (diesel) consumption VS loads	55
VI		SUMMARY AND CONCLUSION	56-57
VII		SUGGESTIONS FOR FUTURE WORK	58
		REFERENCE	59-66
		APPENDIX	

LIST OF TABLES

Table No.	Title	Page
1.1	Trends in consumption of conventional energy in India	3
1.2	Some biogas equivalents	4
1.3	Biogas composition and qualities	4
1.4	Potential availability of selected non-edible seeds	5
4.1	Treatment table	31
4.2	Research plan	31
5.1	Composition of cow dung and oil cakes	38
5.2	Properties of slurries used for experiments	39
5.3	Analysis of variance for the effect on quantity of biogas produced	53
5.4	Analysis of variance for the effect on methane content of biogas produced	53
A.1.1	Daily biogas production	i-ii
A.1.2	Cumulative biogas yield in several days observation time	ii-iii
A.2	Calculation of quality of biogas produced	iii-v
B.1	ANOVA analysis data	xiii-xvi
C.1	Engine specification	xvii
C.2	Generator specification	xvii
C.3	Fuel consumption	xvii

LIST OF FIGURES

Figure No.	Title	Page
1.1	World population and energy distribution in developed and developing countries	1
3.1	Pathway of anaerobic digestion	18
3.2	Kusum tree with seeds	21
3.3	Kusum seeds with pods	21
3.4	Polanga tree with seeds	23
3.5	Polanga seed with pods	24
4.1 (a)	Ground kusum oil cake	25
4.1 (b)	Ground polanga oil cake	25
4.2	NIR Analyser	26
4.3	Digital pH meter	27
4.4 (a)	Ground kusum oil cake	30
4.4 (b)	Ground polanga oil cake	30
4.5	Preparation of feed material for biogas production	30
4.6	Experimental apparatus set-up	32
4.7	Schematic diagram of experimental apparatus	32
4.8	Gas Chromatograph	33
4.9 (a)	Biogas plant	34
4.9 (b)	Biogas storage balloon	34
4.10	Diesel engine used for experiment	35
4.11	Instrument control panel	35
4.12	Parts used for engine modification	36
4.13	Schematic diagram of engine set-up in dual fuel mode	37
5.1	Daily biogas production, m ³ / kg of slurry	41
5.2	Cumulative biogas production, m ³ /kg of slurry	42
5.3 (a)	Mean biogas production at different mixing ratios (30 days HRT)	43
5.3 (b)	Mean biogas production at different mixing ratios (40 days HRT)	43
5.3 (c)	Mean biogas production at different mixing ratios (50 days HRT)	44
5.3 (d)	Mean biogas production at different mixing ratios (irrespective of	44

	HRT)	
5.4 (a)	Mean biogas production at different retention time (15 % MR)	45
5.4 (b)	Mean biogas production at different retention time (30 % MR)	45
5.4 (c)	Mean biogas production at different retention time (45 % MR)	46
5.4 (d)	Mean biogas production at different retention time (irrespective of MR)	46
5.5 (a)	Effect of mixing ratio on methane content of biogas (30 days HRT)	47
5.5 (b)	Effect of mixing ratio on methane content of biogas (40 days HRT)	47
5.5 (c)	Effect of mixing ratio on methane content of biogas (50 days HRT)	48
5.5 (d)	Effect of mixing ratio on methane content of biogas (irrespective of HRT)	48
5.6 (a)	Effect of retention time on methane content of biogas produced (15 % MR)	49
5.6 (b)	Effect of retention time on methane content of biogas produced (30 % MR)	49
5.6 (c)	Effect of retention time on methane content of biogas produced (45 % MR)	50
5.6 (d)	Effect of retention time on methane content of biogas produced(irrespective of MR)	50
5.7	Best level of mixing ratio	51
5.8	Best level of retention time	52
5.9	Variation of pH before and after digestion	54
5.10	Fuel (diesel) consumption VS loads	55
A.1	GC data acquisition graphs of biogas on 30th days of observation	v-vii
A.2	GC data acquisition graphs of biogas on 30 th days of observation	viii-x
A.3	GC data acquisition graphs of biogas on 30 th days of observation	x-xii

LIST OF ABBREVIATIONS

Abbreviations	Description
Mtoe	Million ton of oil equivalent
TERI	The Energy and Research Institute
i.e.	That is
°C	Degree Celsius
abs	absolute
cm	centimeter
Fig.	Figure
Eqn	Equation
L/d ¹	Liter per day
FAO	Food and agriculture organisation
VS	Volatile solid
KOC	Kusum oil cake
POC	Polanga oil cake
CD	Cow dung
MR	Mixing ratio
HRT	Hydraulic retention time
N	Normality
NIR	Near infrared
GC	Gas chromatograph
ANOVA	Analysis of variance
DI	Direct ignition

INTRODUCTION

The contents of this chapter justify the basis on which this area has been chosen for present research. It covers with the necessity of proper balance among energy, environment and ecosystem without hampering the economy of the country.

1.1 Present Energy Scenario in World

Energy is one of the chief contributors for the economic growth of any country. The worldwide primary energy consumption at the end of 2012 was more than 10,000 Mtoe. Although 80 percent of the world's population lies in the developing countries (a four-fold population increase in the past 25 years), their energy consumption amount is only 40 percent of the world total energy consumption (fig. 1.1). Because of the high standards of living, the developed countries are attributable to high energy consumption levels. Also, the rapid population growth in the developing countries has kept the per capita energy consumption low compared with that of highly industrialized developed countries.

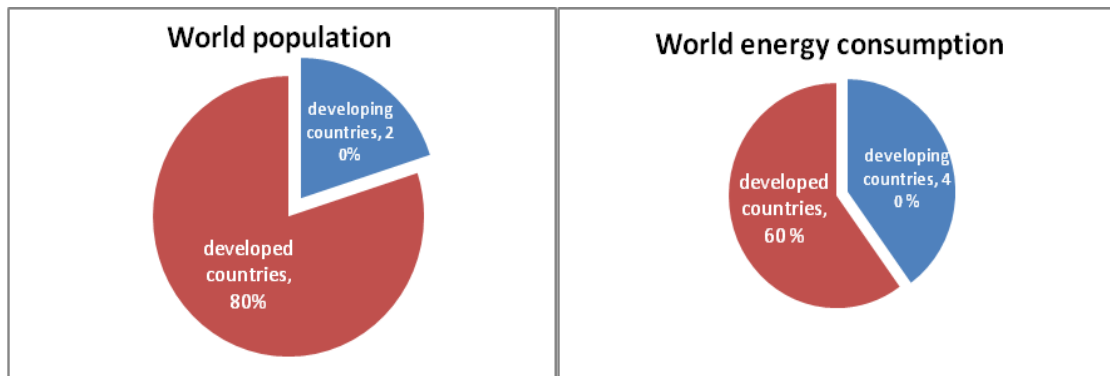


Fig.1.1 World population and energy distribution in developed and developing countries
(Source: Energy scenario)

1.2 Future Energy Situation

There will be severe energy shortage in the coming 50 years due to increasing demand. According to current research and future predictions, the crude oil will finish within 40 to 70 years, and natural gas will be broken down within 50 years (Courtney and Dorman, 2003).

1.3 Environmental Problems and its Alternatives

In twenty-first century world will face the challenge to meet the increasing demand of energy. This rising consumption of energy has increased the demand of fossil fuel such as coal, and petroleum products which has negative impact on environment due to release of huge amount of greenhouse gases. Some negative effects are depletion of ozone layer, global warming and significant raise of ocean level which cause massive concern worldwide. These days both energy crisis and climate change are key issues all over the world. Global warming as the result of climate change is a well-known fact. Global average temperature is expected to increase 1.4 to 5.8 °C by year 2100 and continue to rise long after that (Dow and Downing, 2006). So there is pressure on society to find alternative or renewable energy sources (Midilli *et al.*, 2006). Energy from renewable sources is a feasible substitute to the fossil fuel. Biomass such as agricultural waste is one of the promising renewable energy sources which can solve future world energy problem (Nallathambi, 1997). Bio-energy, biofuel and biogas can meet the future energy needs of world inhabitants.

1.4 India Energy Scenario

Being a developing country India needs much higher level of energy to sustain its rate of progress. But there is a limited quantum of petroleum-based mineral oil available at present. As per the current estimates, oil reserves in India will last for next 26 years (Crude oil imports, The Hindu, 2006). Energy is the important key of economic growth and responsible for sustenance of a modern economy. Future economic growth mainly depends on the availability of energy from sources that are affordable, accessible and environment friendly. Primary commercial energy consumption in the country for 2009-10 was around 316.29 Mtoe (TERI Energy Data Directory and Yearbook 2012-13). The estimate of annual energy consumption in India is about 7689.40 billion kWh for the year 2010-11. The annual growth rate of energy consumption from 2010-11 to 2011-12 was 0.60% (Energy statistics, 2013). The trend in conventional energy consumption in India is given in table 1.1. India ranks sixth in the world in total energy consumption and needs to accelerate the development of the sector to meet its growth goals. An American uses 32 times more commercial energy than an Indian. Thus, there is a huge scope for energy conservation in the country (Raghuraman and Ghosh, 2003). India, like many other developing countries, is a net importer of energy. More than 25 percent of primary

energy needs being met through imports mainly in the form of crude oil and natural gas. The rising oil import bill has been the focus of serious concerns. Due to this it has been placed on scarce foreign exchange resources and is also largely responsible for energy supply shortages. The huge consumption of commercial energy adversely affects the productive sectors, which in turn hampers economic growth and also encounters environmental pollution.

Table 1.1 Trends in Consumption of Conventional Energy in India (Peta Joules)

Source: Energy Statistics, 2013

Year	Coal and Lignite	Crude petroleum	Natural Gas	Electricity	Total
2000-01	5,396	4,331	1,073	11,398	22,198
2005-06	7,009	5,448	1,195	14,828	28,480
2006-07	7,459	6,136	1,208	16,407	31,210
2007-08	7,926	6,536	1,189	18,392	34,043
2008-09	8,476	6,732	1,223	20,264	36,695
2009-10	9,137	8,071	1,791	22,329	41,329
2010-11	9,207	8,632	1,974	24,636	44,448
2011-12	9,410	8,852	1,790	27,210	47,264

India, though rich in coal, is abundantly gifted with renewable energy in the form of solar, wind, hydro and bio-energy which is not properly explored till date. Bio-energy or biomass energy sources are bio-diesel, biogas etc. In this study we focus on the topic biogas.

1.5 Biogas

Biogas is a gas mixture mainly comprising more than 50 % methane and rest carbon dioxide. It is formed when organic materials, such as dung or vegetable matter are broken down by microbiological activity in the absence of air, at slightly high temperatures (most effective between 30 to 60°C). This is the same process which occurs naturally at the bottom of ponds and marshes and gives rise to marsh gas or methane. Biogas has a wide variety of applications. Biogas can be directly used for cooking, lightening, heat generation and also used as a fuel in diesel engine. Biogas is proved to be a clean fuel, in comparison with direct burning of biomass. Thus it reduces the levels

of indoor air pollution, a major cause of rural health problem table 1.2 shows equivalency of one m³ biogas equivalent for different applications.

Table 1.2 Some biogas equivalents (at 15°C and atmospheric pressure) (Biogas Technology Center (BTC), Chiang Mai University and (FAO, 1992))

Energy source	Equivalent to 1 m ³ of biogas
Petrol	0.53 - 0.75L
Diesel	0.48 - 0.68L
Firewood	1.50kg
Electricity	1.20kW/h
LPG	0.46kg

Biogas is constituted of different component gases the majority of them being methane (CH₄) and Carbon dioxide (CO₂), with traces of Sulphur Dioxide (H₂S), Hydrogen (H₂) gas and some amount of other gases. Composition of a typical biogas sample is given in the table below (Deublein and Steinhauser, 2008).

Table 1.3. Biogas Composition and Qualities (Deublein and Steinhauser, 2008)

Gas Composites/ Features	Formula	Units	Biogas Sources		
			Sewage	Agricultural	Landfill
Methane	CH ₄	% by vol.	65-75	45-75	45-55
Carbon dioxide	CO ₂	% by vol.	20-35	25-55	25-30
Carbon Monoxide	CO	% by vol.	<0.2	<0.2	<0.2
Nitrogen	N ₂	% by vol.	3.4	0.01-5.00	10-25
Oxygen	O ₂	% by vol.	0.5	0.01-2.00	1-5
Hydrogen	H ₂	% by vol.	trace	0.5	0.00
Hydrogen Sulphide	H ₂ S	mg/Nm ³	<8000	<8000	<8000
Ammonium	NH ₃	mg/Nm ³	trace	0.01-2.5	trace
CFC		mg/Nm ³	0	20-1000	n.a.
Net Calorific value		kWh/Nm ³	6.0-7.5	5.0-7.5	4.5-5.5

In the above table, we can see the combustible components of biogas are CH₄ and H₂. Other gases are not flammable at normal conditions and have no energy contribution in biogas. Also, among these two gases only CH₄ is present in a significant amount and hence, is considered in most cases involving biogas.

1.6 Potential of Non-edible Oil Seed and Cakes

In addition to these sources de-oiled oil cakes can be coincided as a major available source for biogas production. A large variety of oil seed trees grows in forest and non-agricultural lands of India. According to Ministry of New Renewable Energy (MNRE), around 400 oil seed species are found in India. The edible ones among these are already being used for human consumption but non-edible oils do not have a significant use. Some of the common non-edible oil seed trees seen in India are *Jatropha Curcas* (jatropha), *Madhuca indica* (mahua), *Pongamia Pinnatta* (karanja), *Scleicera oleosa* (kusum), *Azadirecta indica* (neem), *Callophyllum inophyllum* (polanga) etc.

Potential availability of some selected non-edible seeds in India is given in table 1.4. Annual growth in oil cake production is predictable to average 2.3% annually over the decade to 2010. Total production currently stands at over 25 million tonnes per annum while the exports account for over 4.3 million tonnes of oil cake (www.seaofindia.com).

Table 1.4 Potential availability of selected non-edible seeds (Radhakrishna, 2003).

Sl. No	General Name	Botanical Name	Potential, Million Metric Tonnes/Year			Oil Content, %
			Seed	Oil	Cake	
1	Karanja	<i>Pongamia pinnata</i>	0.20	0.055	0.145	27-39
2	Jatropha	<i>Jatropha curcas</i>	0.05	0.015	0.035	30-40
3	Kusum	<i>Scheleichera oleosa</i>	0.08	0.025	0.055	34
4	Neem	<i>Azadirecta indica</i>	0.50	0.100	0.400	20
5	Sal	<i>Shorea robusta</i>	1.50	0.180	1.320	12-13
6	Mahua	<i>Madhuca indica</i>	0.50	0.180	0.320	35

A small portion of the total non-edible seeds grown are collected in the villages and crushed to extract the oil. The oil is used to make cosmetics, shampoo, soaps, used for relieving arthritis and dermatitis and some are used as lubricants. In rural areas, there is demand of this non-edible oils which meet many needs of villagers. However, leads to production of oil cakes in a significant amount.

1.7 Biogas Application in Engine

Diesel engines have been widely used as power for engineering machinery, automobiles and rural agricultural sector over the last few decades. At the same time, diesel engines are major contributors of various types of air pollutant emissions such as carbon monoxides (CO), oxides of nitrogen (NO_x), particulate matter (PM) and other harmful compounds. With the increasing concern of environmental protection and more stringent government regulations on exhaust emissions, reduction in engine emissions has become a major research task in engine development. On the other hand, since the global energy crisis in the 1970's research for alternative and renewable fuels have become a very intense research for alternative and renewable fuels have become a very intense research area. Here biogas is chosen as an alternative fuel.

1.8 Justification of Research Work

India is a vast country having a major portion of population engaged in agriculture. The agricultural operations generate huge quantities of biomass that are not efficiently used. Biogas production from these biomasses from agricultural field has occupied a significant position in our society and the demand is growing rapidly. The anaerobic digestion of biomass requires less capital investment per unit production cost compared to other renewable energy sources, such as hydro, solar and wind energy (Rao *et al.*, 2010). Use of biogas plants for energy, manure and sanitation has made a significant impact on the quality of rural life in India (Planning Commission Report, 2002). As on 31st March 2009, 3.94 million family-type biogas plants were in operation in India (TERI, 2009). Animal dung for biogas production is limited and is available with small fraction of the rural households in India. It is only possible to meet the cooking energy needs of the rest of the rural families by using other types of commonly available biomass feedstock (Jagadish *et al.*, 1999).

Nowadays attempts are being made to utilize non-edible and under-exploited oils for biodiesel production which is used as a substitute to diesel. India has a requirement of biodiesel to the tune of 8.35 million ton by the end of 2016-17 (Malik, 2009). If these non-edible oils are to be used for biodiesel production, there will be availability of huge amount of oil seed cake. But due to the presence of toxic materials (crucin and saponins in jatropha, ricin in castor, karanjin and pongamol in karanja) in these cakes, it can neither be used for animal feeding nor can be used directly as fertilizer in agricultural farming (Gubitz *et al.*, 2004).

The existing method to utilize non-edible oil seeds is only by extracting vegetable oil for biodiesel production and leaving a huge amount of unutilized biomass. Most tree born oil seeds yield about 25% oil, 70% oil cake and 5% losses in the oil extraction process using mechanical expeller (Chandra *et al.*, 2006). The presence of non-edible oil seed cakes in the open atmosphere would create environmental problems through generating various gases, such as CH₄, N₂O, H₂S, NH₃, CO₂, and volatile organic compounds (VOCs) by the action of various microorganisms (Singh and Mandal, 2012). Anaerobic digestion of these cakes could significantly reduce the gaseous emissions (CH₄, CO₂, VOCs, and H₂S) from waste disposal. Therefore, anaerobic digestion of these cakes would be a better way of cake utilization for energy generation and, further, effluent as enriched organic manure for organic farming (Singh *et al.*, 2008; Mahnert *et al.*, 2005; Marique *et al.*, 1989).

Objectives

Identifying the above problems, a research was undertaken on utilization of non-edible oil cakes for optimal biogas production with the following objectives.

1. To investigate the suitability of Kusum (*Schleichera oleosa*) and Polanga (*Callophylum inophyllum*) de-oiled seedcake for biogas production.
2. To study the effect of various operating parameters on biogas under anaerobic condition from non-edible oil cake.
3. To study the feasibility of using biogas on diesel engine as a substitute for diesel.

REVIEW OF LITERATURE

It covers exhaustive review of the work done by earlier researcher on biogas production from different biological sources and non-edible oil cakes. All these related information has been summarized and existing gaps in the field have been identified and presented under the following heads.

- Biogas production from biological sources
- Operational factors affecting biogas production
- Analysis of biogas by gas chromatograph
- Application of biogas in diesel engine

2.1 Biogas Production From Biological Sources

Pathe *et al.*, 1983 studied were also made on freshwater hyacinth and dried powder water hyacinth as additives with cattle dung. There was enhancement of gas production with respect to freshwater hyacinth.

Banerjee, 1987 studied Parthenium weed, which has allergy-causing potential, is a good source of biomass for biogas but due to its health hazard it did not receive much public attention.

Dar and Tandon, 1987 used alkali-treated (1% NaOH for 7 days) plant residues (lantana, wheat straw, apple leaf litter and peach leaf litter) as a supplement to cattle dung resulted in almost two-fold increase in biogas and CH₄ production.

Satyanarayan *et al.*, 1989 studied urea addition in cattle dung digesters at various organic loadings has been reported to be beneficial but has certain limitations, i.e. continuous addition of urea leads to decrease in biogas production and also ammonia toxicity sets in.

Shinnawi *et al.*, 1989 worked on addition of agricultural residues like maize stalks, rice straw, cotton stalks, wheat straw and water hyacinth each enriched with partially digested cattle dung enhanced gas production in the range of 10–80%.

Babu *et al.*, 1994 found improvement in bio-methanation of mango-processing wastes by several folds was observed by the addition of extracts of seeds of Nirmali, Common bean, Black gram, Gaur and Gaurgum at the rate of 1500 ppm.

Satyanarayan, 1998 used night soil as feed material which was found to be very useful in enhancing gas production in cattle dung digesters due to its richness of volatile solids content and nitrogen content but due to aesthetics and hygiene problems associated with it, it did not gain much momentum.

Sharma, 2002 found an increase of 40–80% in biogas production has been observed on addition of 1.0% onion storage waste to cattle dung in a 400 liter floating drum biogas reactor.

Satyanarayan *et al.*, 2003 observed increase in gas production upto 30% urine addition was observed, but beyond 30% urine addition gas production gradually decreases. At this urine addition about 31.6% more biogas was yielded.

Budiyono *et al.*, 2011 investigated the influence of total solid contents on biogas yield from cattle manure using rumen fluid inoculums. 100 g of fresh cattle manure was fed to each biodigester and mixed with fixed 50 mL of rumen fluid and different volumes oftap water resulting six different total solid contents, i.e., 2.6, 4.6, 6.2, 7.4, 9.2, 12.3 and 18.4%. The results showed that the best performance for biogas production was the digester with 7.4 and 9.2% of total solid i.e., gave biogas yield 184.09 and 186.28 mL gVS⁻¹, respectively after 90 days observation. While the other total solids content of 2.6, 4.6, 6.2, 12.3 and 18.4% gave the biogas yield 115.78, 122.33, 172.34, 137.99 and 54.87 mL gVS⁻¹, respectively. In all cases, there was no variation of pH, fat, protein and ash content in sludge after digestion at several variation of pH. During digesting, pH tends to increase to neutral pH, i.e., optimum pH for methanogenic bacteria.

Vivekanandan and Kamaraj, 2011 discussed biogas production from rice chaff as co-substrate with cow dung. The study was carried out at mesophilic condition between (26-30°C) for a period of 60 days with seven percent total solid concentration was taken for the fermentation slurry. Experiment study was conducted for three different proportions: (i) 50% weight of boiled rice chaff plus 50% weight of cow dung (ii) 75% weight of rice chaff (boiled) plus 25% weight of cow dung (iii) 50% weight of raw rice chaff (without boiled) plus 50% of cow dung. The result showed a cumulative biogas

production of 161.5ml in case (i) for the retention time of 60 days. In case (ii) showed the biogas production of 140.5 ml for the retention time of 70 days and in case (iii) there was no significant gas production due to high percent of lignin in raw rice chaffs.

Abubakar and Ismail, 2012 studied the effectiveness of cow dung for biogas production using a laboratory scale 10 litter bioreactor working in batch and semi-continuous mode at 53°C. In their study, anaerobic digestion seemed feasible with an organic loading of up to 1.7 kg volatile solids /L d⁻¹ and HRT of 10 days during the semi-continuous operation with total solid, volatile solid and removals amounted to 49% and 47% respectively.

Imam *et al.*, 2013 observed biogas production of 0.034 m³/kg, 0.058 m³/kg and 0.014 m³/kg respectively from cow dung, poultry waste and water hyacinth. Poultry waste produced maximum gas 0.026m³ at the 8th day whereas cow dung and water hyacinth produced maximum gas 0.0263 m³ and 0.012m³ respectively at the 26th day.

2.1.1 Suitability of non-edible oil cakes for biogas production

Randhawa and Parmar, 1996 *Azadirachta indica* cake contains 35 % digestible protein which confirms its suitability for biogas production.

Makkar *et al.*, 1998 found that jatropha seed cake contain a high amount of protein in the range of 50–62 %, and the level of essential amino acids except lysine is higher than the FAO reference protein.

Balguruswami and Ramaswami, 2007 concluded that de-oiled cake of most oilseeds contains high amounts of total solids, volatile solids, high percentage of proteins and starchy material, which make it a suitable feedstock for biogas generation.

Karve, 2007 also concluded that de-oiled cakes contain a higher percentage of sugar, carbohydrates and other starchy material which can be easily digested and hence requires a smaller size digester.

Sharma *et al.*, 2012 described that non edible oil cakes can also be used as low cost substrates for the growth of the fungus and nematodes; at the same time they can supply nutrients to the soil as organic fertilizers. The study also concluded that though the cakes have high nutritious quality, some oil cakes have toxic components in them. However, the toxicity of these cakes can be exploited by using them as bio-pesticides.

2.1.2 Biogas production from de-oiled non-edible oil seed cakes

Haridasan *et al.*, 2004 studied biogas yield from the *Jatropha curcas* seedcake. The substrate consisting of 1 kg of de-oiled seedcake of *Jatropha* mixed with 250g of cattle dung produced 180 litter of biogas.

Chandra *et al.*, 2006 showed that the *Jatropha curcas* and *Pongamia pinnata* oil seed cakes have biogas generation potential in the range of 220 to 250 and 240 to 265 liters per kg of cake respectively under mesophilic temperature range of anaerobic digestion. They observed the methane content of biogas derived from these non-edible oil seed cakes and it ranges from 65-70 % against 55 % from cattle dung. Their study also revealed that dilution ratio of cake is best at 1:4 (cake:water) for *Jatropha curcas* and 1:3.5 (cake:water) for *Pongamia pinnata* cakes. Total biogas generation potential from *Jatropha curcas* and *Pongamia pinnata* cakes in India has been estimated as 2, 550 and 377 million cubic metre respectively from 10.2 and 1.45 lakh metric tonnes of *Jatropha curcas* and *Pongamia pinnata* oil seed cakes.

Patel and Chellapandi, 2008 studied the anaerobic digestion process of cottonseed cake following a series of experiments. The study established mixed anaerobic consortia derived from fresh cattle dung and adapted (acclimatized) seed for their anaerobic digestion potentials. The intended results for the digestion rate of cotton seed cake and biogas generation were found out. 44% loss in total solids and 17-19% loss in organic nitrogen was achieved by using enriched consortia. The crucial importance and suitability of these developed consortia over fresh consortia have suggested for the improved anaerobic digestion process as well as suitability of cotton seed cake for biogas production.

Rajasekaran *et al.*, 2008 carried out experiment on biogas production using non-edible oil cakes along with cattle dung. The experimental data revealed a maximum gas output of *Arachis hypogaea* non-edible oil cake of 22815ml, followed by 20025 ml with *Pongamia pinnata* oil cake incorporated treatment along with cattle dung over a period of six weeks. The methane content ranged from 54.5 to 68 percent and the carbon dioxide content from 30 to 43.5 percent. The bio-digested slurry was analyzed for their nitrogen, phosphorous, and potassium contents which revealed their usefulness as manure for possible applications in soil fertilization procedures.

Satyanarayan *et al.*, 2008 reported a tremendous increase in volatile solids destruction, with a 12.2–13.08% increase in the case of 30% mustard cake addition with a corresponding gas production of 0.329 m³/kg VS with 4591 ml/day. There is almost a 63.44% increase in biogas production compared with only cattle dung, which resulted in 2809 ml/day. But based on the mustard cake availability, an optimum of 20% addition was suitable. In general, a biogas increase of 13.38%, 25.27%, 39.16%, 52.26% and 63.44% was observed at 10%, 15%, 20%, 25% and 30% mustard cake addition. Manurial value of the digested sludge was very good.

Ali *et al.*, 2010 used *Jatropha curcas* de-fatted waste as an alternative feed in biogas plant for its bio-methanisation. The study was conducted on a floating drum type biogas plant. It was observed that the biogas plant, initially charged with pure cattle dung, when gradually replaced with *Jatropha* oilcake (0 - 100%), it increased the biogas production up to approximately 25% in reasonable time duration. A significant increase in the percentage of nitrogen, phosphorus and potassium during the biofermentation process invokes the use of the effluent slurry as organic manure. Simultaneous reduction in the amount of the oil (5.67 to 3.95%) sustains the possibility of degradation of oil during methanisation. The study concluded that *Jatropha* de-fatted waste can successfully be used as a supplementation as well as substrate in already running cattle dung based biogas plant to get high yield of biogas in comparison to cattle dung feed.

Raheman and Mondal, 2012 studied biogas production from *Jatropha* seedcake (JSC) at different total solid (TS) contents and carbon to nitrogen ratio. Biogas production from kg of TS was found to be maximum i.e. 0.17 m³ at 20% TS of JSC slurry followed by 15%, 25% and 10% TS in that order as compared to 0.166 m³ in case of cow dung slurry alone. Gas production was found to be maximum when JSC percentage in the mixture was within 25%. The nitrogen content in the bio-digested JSC slurry was increased by 5.9% as compared to JSC alone and its use as fertilizer produced better growth of maize and tomato crops.

Singh and Mandal, 2012 used different proportions (i.e., 25, 50 and 75%) of each of the non-edible oil cakes such as *Jatropha*, *Karanja* and *Safflower* along with cow dung for biogas production in a 1 L batch reactor using mixed inoculum. This study found that the respective average methane yields in biogas were 2.5, 14.8 and 6.6% higher as

compared to cow dung alone (0.316 L/g VS) and other combinations of non-edible oil cakes and cow dung.

2.2 Operational Factors Affecting Biogas Production

The operation of biogas production or digestion process is affected by a number of factors. The research made in these parameters is described below.

2.2.1 Type of feed

Despande *et al.*, 2012 studied biogas generation from Mahua (*Madhuca indica*) and Hingan (*Balanites aegyptiaca*) oil seed cake. The study revealed that mahua seed cake has a mean biogas potential in the range 200 to 225 l/kg of seedcake and that for Hingan was 200 to 220 l/kg of seedcake.

Jekayinfa and Scholz, 2013 investigated biogas production from Cassava Tubers, Cassava Peels, and Palm Kernel Oil Residues. Measured biogas yields for cassava tuber, cassava peels, palm kernel cake, and palm kernel shell were 0.66, 0.66, 0.58, and 0.08 m³/ (kg VS), respectively, after 30 days digestion time. Methane production from cassava tuber, cassava peels, palm kernel cake, and palm kernel shell was 0.31, 0.28, 0.32, and 0.05 m³/ (kg VS), respectively.

2.2.2 Mixing ratio

Satyanarayan *et al.*, 2008 observed a tremendous increase in volatile solids destruction, with a 12.2–13.08% increase in the case of 30% mustard cake addition with a corresponding gas production of 0.329 m³ kg⁻¹ VSa with 4591 ml day⁻¹. This is almost a 63.44% increase in biogas production compared with only cattle dung, which resulted in 2809 ml day⁻¹. Results indicated that biogas production increases 13.38%, 25.27%, 39.16%, 52.26% and 63.44% at 10%, 15%, 20%, 25% and 30% mustard meal/cake addition.

Kasisira and Muiyiya, 2009 determined the effect of mixing pig and cow dung mixture in proportions of 1:0, 3:1, 1:1, 1:3 and 0:1 on biogas yield. Results from this study show that co-digestion of cow dung with pig manure increased biogas yield as compared to pure samples of either pig or cow dung. Comparing to samples of pure cow dung and pig manure, the maximum increase of almost seven and three fold was respectively achieved when mixed in proportions of 1:1.

2.2.3 Hydraulic retention time

Lu and Ahring, 2005 investigated the effects of temperature and hydraulic retention time on thermophilic anaerobic pretreatment of sewage sludge by running continuous stirred tank reactor the effects of different hydraulic retention times (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 days, respectively). Extension of hydraulic retention time did not significantly increase dissolved COD products Acidogenesis had the highest products when temperature was at 70°C or 75°C and for a hydraulic retention time around 2 days.

Demir *et al.*, 2011 studied the effect of HRT (20 days and 40 days) on organic material removal and biogas production in the anaerobic treatment of cattle manure. For HRT 20 days, VS removal efficiencies ranged from 23% to 30% and from 20% to 29% for mesophilic and thermophilic reactors, respectively. After increasing the HRT to 40 days VS removal efficiencies were about 41% for both reactors.

2.3 Analysis of Biogas by Gas Chromatographs

Since 1952 gas chromatography (GC) is a useful and accurate analysis tool that has been used for the analysis of liquid and gas mixtures.

Drs. James and Martin discovered the analytical method for separating volatile fatty acids. It immediately achieved credit among the petrochemical industries after its discovery (Bartle and Myers, 2002).

Though a gas chromatograph is made up of many complex working parts, its use is very simple. At first, a sample is input through an injection port and is subsequently separated in a column between a mobile gaseous phase and a stationary phase. Separation in the column occurs due to the affinity of the sample for the stationary phase. The mobile gaseous phase must be an inert gas, but the stationary phase can be made of either a liquid or a solid. Solid stationary phases are usually found in packed columns, made of a finely divided packing material like silica. The use of a packed or capillary column depends upon the amount of resolution needed. Capillary columns provide better separation, and therefore better resolution, due to their increased length over packed columns. This increased length allows for a much larger number of theoretical plates to be present. Once separation has been completed, the sample is analyzed as the mobile phase carries each analyte to the detector.

Skoog *et al.*, 2007 narrated that the thermal conductivity detector (TCD) is one of the earliest and widely used methods of detection for use with a GC. The advantages of using a TCD include its simplicity, its general response to both organic and inorganic species, and its nondestructive character, permitting collection of solutes after detection if desired. Other detectors, such as the flame ionization detector (FID), have sensitivities exceeding that of the TCD by factors of 10⁴ to 10⁷. The detector works through identifying differences in the thermal conductivities of the gas stream exiting the column. Helium and hydrogen, two of the most prominent carrier gases, have thermal conductivities that are approximately six to ten times greater than all organic compounds. Therefore, when any organic species passes through the detector, the thermal conductivity greatly decreases, resulting in a large increase in the temperature of the TCD.

2.4 Biogas Application in Engine

The use of biogas in internal combustion engine was practiced during Second World War when thousands of vehicles ran by sewage gas in Europe. After that many attempts were made to use biogas in diesel and petrol engine. The difficulties faced in these cases were due to lower heating value, corrosive compression and difficulties in transportation of fuel which is main challenge for biogas. After 1990s diesel engines were converted to dual fuel biogas engines.

Kerkhof, 2008 worked on application of jatropha oil and biogas in a dual fuel engine for rural electrification. He found that thermal efficiency of engine in dual fuel mode did not deteriorate up to 70% heat release fraction of methane at 10 kW load. Volumetric efficiency and air-excess ratio decreased under dual fuel operation as expected. The decrease did not result in a deficiency of oxygen. Enough oxygen was available to combust oil smoke-free. The amount of carbon dioxide in the biogas did not influence performance parameters; the smoke limit was not reached.

Thring, 1983 concluded that biogas would be just attractive when its production site would close to application site.

Deri and Mancini, 1990 converted a diesel engine to dual fuel engine and found more stable combustion in lean mixture because of using diesel to ignite the mixture.

However, it was difficult for separate control of air-gas mixture. Keeping above limits in mind, engineers found many solutions to solve these limits.

Swami Nathan *et al.*, 2010 compressed a homogeneous mixture of air and fuel is and allowed to self-ignite. Combustion is controlled by varying the temperature and composition of the charge. The NO level was less than 20 ppm and the smoke level was less than 0.1 BSU at all conditions.

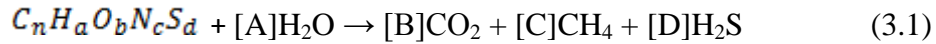
Dung, 2012 modified a direct-ignition, four cylinder diesel engine to replace diesel fuel system in order to supply gaseous fuel to the engine. In addition, engine management system with electronically controlled was used to control air-to-fuel ratio, ignition timing according to engine speed and load. The result showed that conversion biogas based diesel engine could operate fully with biogas (CH₄ 62%) at high compression ratio ($\epsilon=17$).

Mihic, 2004 presented that automatic control of speed or power can be done by changing the amount of diesel fuel injection because of existence of a governor at most diesel engines while the biogas flow remains uncontrolled. Biogas cleaning is not welcomed economically, therefore actions should be taken to increase engine tolerance against the impurities and extend the engine life and time between overhaul.

From the review work, it is revealed that no much work on application of biogas produced from kusum and polanga oil cake has been done. Hence in the present study, these potential seeds have been considered.

THEORITICAL CONSIDERATION

Biogas, as the name indicates, is produced from the decomposition of any biological source or organic matter. Biogas production is governed by an empirical equation given in Eqn. 3.1 (Ghani and Idris, 2009).



Where, $A = (n - a/4 - b/2 + 3c/4 + d/2)$

$B = (n/2 - a/8 + b/4 + 3c/8 + d/4)$

$C = (n/2 + a/8 - b/4 - 3c/8 - d/4)$

3.1 Biogas Production Stages

Biogas production is a multi-step biological process where the organic carbon is converted in to carbon dioxide and methane (Angelidaki *et al.*, 2003). The process can be divided into four steps: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Fig.3.1 shows the pathway of anaerobic digestion.

3.1.1 Hydrolysis

Hydrolysis is the first step in anaerobic digestion processes. During the hydrolysis step, complex organic matters, such as carbohydrates, proteins and lipids are hydrolyzed into soluble organic molecules such as sugars, amino acid and fatty acids by extracellular enzyme, i.e. cellulase, amylase, protease or lipase (Parawira *et al.*, 2005). Hydrolytic bacteria, which hydrolyze the substrate with these extracellular enzymes, are facultative anaerobes. Hydrolysis can be the rate-limiting step if the substrate contains large molecules (particulates) with low surface-to-volume ratio (Vavilin *et al.*, 1996). While if the substrate is readily degradable, the rate-limiting step will be acetogenesis and methanogenesis (Bjornsson *et al.*, 2001). When the substrate is hydrolyzed, it becomes available for cell transport and can be degraded by fermentative bacteria in the following acidogenesis step.

3.1.2 Acidogenesis

In the acidogenesis step, the soluble organic molecules from hydrolysis are utilized by fermentative bacteria or anaerobic oxidizers (Garcia-Heras, 2003). These microorganisms are both obligate and facultative anaerobes. In a stable anaerobic digester, the main degradation pathway results in acetate, carbon dioxide and hydrogen.

The intermediates, such as volatile fatty acids and alcohols, play a minor role. This degradation pathway gives higher energy yield for the microorganisms and the products can be utilized directly by methanogenic microorganisms (Schink, 1997). However, when the concentration of hydrogen and formate is high, the fermentative bacteria will shift the pathway to produce more reduced metabolites (Angelidaki *et al.*, 2002). The products from acidogenesis step consist of approximately 51% acetate, 19% H₂/CO₂, and 30% reduced products, such as higher VFA, alcohols or lactate (Angelidaki *et al.*, 2002). Acidogenesis step is usually considered the fastest step in anaerobic digestion of complex organic matter (Vavilin *et al.*, 1996).

3.1.3 Acetogenesis

Intermediates formed during acidogenesis, consist of fatty acids longer than two carbon atoms, alcohols longer than one carbon atom and branched-chain and aromatic fatty acids. These products cannot be directly used in methanogenesis and have to be further oxidized to acetate and H₂ in acetogenesis step by obligate proton reducing bacteria in a syntrophic relationship with hydrogen utilizers. The products from acetogenesis are then the substrates for the last step of anaerobic digestion, which is called methanogenesis.

3.1.4 Methanogenesis

In methanogenesis step, acetate and H₂/CO₂ are converted to CH₄ and CO₂ by methanogenic bacteria. The methanogenic bacteria are able to grow directly on H₂/CO₂, acetate and other one-carbon compound, such as formate and methanol (Schink, 1997). In the normal anaerobic digesters, acetate is the precursor for up to 70% of total methane formation while the remaining 30% originates from H₂/CO₂ (Klass, 1984). Moreover, the inter-conversion between hydrogen and acetate, catalyzed by homo-acetogenic bacteria, also plays an important role in the methane formation pathway. Homo-acetogens can either oxidize or synthesize acetate depending on the hydrogen concentration in the system (Kotsyurbenko, 2005). At higher temperatures, the acetate oxidation pathway becomes more favorable (Schink, 1997). It has been reported that methane formation through acetate oxidation can contribute up to 14% of total acetate conversion to methane under thermophilic conditions (60 °C) (Petersen and Ahring, 1991).

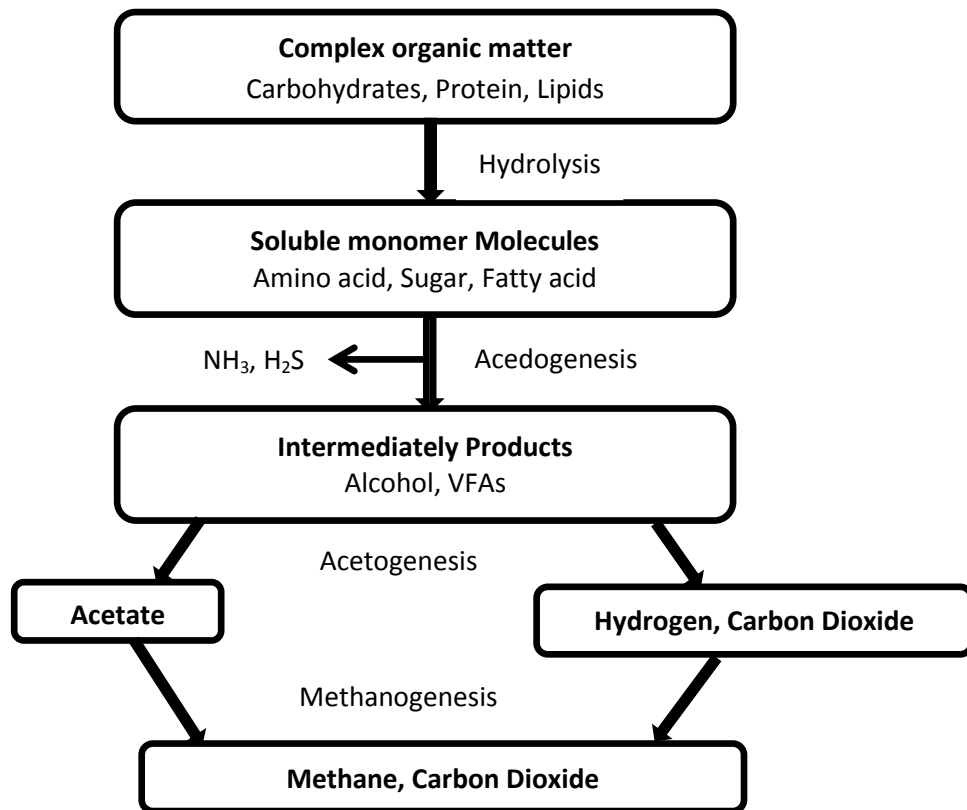


Fig. 3.1 Pathway of anaerobic digestion

3.2 Operational Parameters Affecting Biogas Production

The operation of biogas production or digestion process is affected by a number of factors, which are described as below.

3.2.1 Temperature

Methane forming bacteria work best in temperature ranges 20-55°C. Digestion at higher temperature proceeds more rapidly than at lower temperature, with gas yield rates doubling at about every 5°C increase in temperature. In cold climate regions the digester has to be heated to about 35°C, in most cases by using part of the biogas produced. The gas production decreases sharply below 20°C, and almost stops at 10°C. It is to be noted that raising the temperature accelerates the gas production; however its methane content gets relatively reduced.

3.2.2 Pressure

A minimum pressure of 6-10 cm of water column, i.e. 1.2 bar (abs) is considered ideal for proper functioning of biogas production and it should never be allowed to exceed 40-50 cm of water column. Excess pressure inhibits release of gas from slurry. It

also leads to leakage in digester structure. Also there is no advantage in maintaining negative pressure (vacuum) either, which is a costly and energy consuming option. Any leakage of air (oxygen) into the plant during negative pressure condition completely inhibits the growth of methane formers, as these are strictly anaerobic. Addition of oxygen also results in an explosive mixture raising safety concern. Hence, the digestion chamber should be completely leak proof.

3.2.3 Solid to moisture ratio

Water is essential for survival and activity of micro-organisms, hydrolysis process and activity of extra cellular enzymes. This helps in (a) better mixing of various constituents of the slurry, (b) movement of bacteria, and faster digestion rate. However, when water content is too much high, the mean slurry temperature decreases and hence, gas production drops. If water content is too low, acid accumulates and hinder fermentation process. The optimum solid concentration is 8-10%. Hence for various input materials, the optimum ratio of solid to moisture should be adjusted by mixing extra water, for best results. Raw cow dung contains about 80-82% moisture (by weight). It is usually mixed with equal amount of water to reduce solid content to 9-10%.

3.2.4pH value

In the initial acid forming stage of the digestion process, pH value may be around 6 or less. However, during methane formation stage, pH value of 6.5-7.5 is maintained, as methane forming bacteria are sensitive to acidity. Too much and sudden deviation from this value is likely to cause imbalance in bacteria population affecting the production of gas.

3.2.5 Carbon to nitrogen ratio (C/N) ratio

Carbon not only forms cytoplasm of micro-organisms, but also provides energy for their life activities. Nitrogen present in the feed stock has two benefits (i) it provides an essential element for synthesis of amino acids, proteins and nucleic acids, (ii) it is converted to ammonia which, as a strong base, neutralizes the volatile acids produced by fermented bacteria, and helps to maintain neutral pH conditions essential for cell growth. Presence of excess nitrogen in slurry produces excess ammonia which has toxic effects. Hence, the feed stock should contain proper amount of nitrogen to avoid either nutrient limitation (too little nitrogen) or ammonia toxicity (too much nitrogen). When carbon amount will increase nitrogen will be consumed fast and breaking down of organic

matter will be reduced. Hence an imbalance C/N ratio will affect gas production and microbial activity. Higher gas production from *Jatropha* seed cake slurry was observed when the carbon to nitrogen ratio (C:N) ratio was between 22:1 to 27:1 (by adding different quantity of paddy straw) (Raheman, 2012).

3.2.6 Hydraulic retention time (HRT)

HRT is the time duration for which the slurry remains inside the plant or the time that is available for bio-digestion. For pilot plant it is determined by the volume of digester divided by the volume of slurry added per day. Retention time is optimized to achieve a 70-80% complete digestion. The bio-degradability depends on the temperature and type of biomass. In India biogas plants are designed for retention period of 30, 40, and 50 days depending on the region.

3.2.7 Mixing or stirring

Mixing has three important effects: (a) maintains uniformity in substrate concentration, temperature and other environmental factors, (b) minimizes the formation of scum at the surface, and (c) prevents the decomposition of solids at the bottom. The masses that float at the top in the form of scum and that deposit at the bottom are not easily available to bacteria for bio-digestion. Stirring brings these masses to the reach of bacteria, thus helping in proper functioning.

3.2.8 Effect of toxic substances

High concentration of ammonia, antibiotics, pesticides, heavy metals are toxic to bacteria. Traces of pesticides and disinfectants may be present in farm products. Antibiotics given to animals in feed or injected to them will have its trace in the manure produced.

3.3 Botanical description of selected oil cake source (Kusum and Polanga)

Here in this study, kusum and polanga oilcake were used for biogas production. Hence the review is focused on these two oil cake sources. Botanical description of these two oil cakes has described below.

3.3.1 Kusum (*Schleichera oleosa*)

It is a medium-sized to large deciduous or nearly evergreen tree, up to 40 m in height, and 2-3.7 m in girth usually with a clean bole of about 6 m in length and a dense and spreading shady crown shown in fig.3.2. Potential availability of kusum seed, oil and

cake is 0.08, 0.025, 0.055 million metric tonnes per year. It belongs to the *Sapindaceae* family and found particularly in South and Southeast Asia. *Schleichera oleosa* is widely distributed in the sub-Himalayan region, throughout central and southern part of India, as well as in the forests of Bangladesh, Myanmar, China, Thailand, Sri Lanka, Indonesia and Malaysia. It is called as kusum in local area (India). Leaves, twigs and seed-cake are used as cattle-feed. The tree yields an excellent fuel and charcoal. Oil extracted from the seed (kusum oil) is a valuable component of true Macassar oil used in hairdressing, sometimes for cooking and lighting purposes and in traditional medicine. The tree is an important host for lacinsect (*Laccifer lacca*) and the finest quality of lac is obtained from this tree every second or third year.



Fig. 3.2 Kusum tree with seeds



Fig. 3.3 Kusum seeds with pods

3.3.2 Polanga (*Callophyllum inophyllum*)

Polanga (Undi in hindi) (*Callophyllum inophyllum*) is a medium-sized to large perennial tree, having height ranging from 8 to 20 m with a broad spreading crown of irregular branches. The tree supports a dense canopy of silky elliptical leaves, fragrant white flowers, and large round nuts shown in fig. 3.4 and 3.5. It rises along coastal areas and adjacent lowland forests, although it occasionally occurs inland at higher elevations. It is found in countries like Africa, India, South-east Asia, Australia and South Pacific. The tree is useful for coastal shelterbelts, windbreaks, and strand reforestation because it grows well despite the wind, salt spray, draught and occasional flooding common to beach environments. Oil extracted from this polanga seed has been used as a traditional medicine and cosmetic in India for centuries. The oil is greenish, thick and is easily absorbed into the skin. It is used as massage oil and skin moisturizer. In addition to this, traditionally it has been used to treat various skin injuries such as scraps, burns, insect bites, sunburn, and diseases and sores such as dry skin, ringworm and even diaper rash. Polanga oil has also been used to treat rheumatism and inflammation and is believed to help heal scars. Medical research has shown that this oil has anti-bacterial properties and may help promote healing of scars. Results of some studies have even shown that inophyllums, chemicals extracted from polanga oil, inhibit HIV reverse transcriptase in a novel way, which indicates that some day they may be used as part of a combination therapy for AIDS. The polanga oil is mainly utilised for coating the fishing boats and small sized ships. The wood of polanga tree is very useful for the construction of the ships and fishing boats.



Fig. 3.4 Polanga tree with seeds



Fig. 3.5 Polanga seed with pods

MATERIAL AND METHODS

The chapter deals with the experimental methods and techniques used in this research which is discussed in two sections; i.e., biogas production and application of biogas for engine operation. Biogas production was done from two oil cakes i.e. Kusum oil cake (KOC) and Polanga oil cake (POC) along with input or independent variables like type of cake, mixing ratio of oil cake (OC) with cow dung (CD) and retention time. Output or dependent parameters are quantity of biogas produced and methane content of each sample. An air cooled diesel engine was run by using biogas in the air suction inlet. The research experiments were conducted in College of Agricultural Engineering and Technology (CAET), Orissa University of Agriculture and Technology (OUAT), Bhubaneswar, Odisha.

The detailed procedures followed in carrying out the research work are presented under the following sections.

4.1 Substrate Collection

Fresh cattle manure used in this research was taken from cattle yard located at OUAT farm, Bhubaneswar. Oil cakes used in the experiment were bought from near-by oil expelling units present in Puri.



Fig. 4.1 (a) Kusum oil cake



Fig. 4.1 (b) Polanga oil cake

4.2 Preliminary Test

Cattle dung and the oil cakes were analyzed for their physical and chemical properties such as moisture content, pH, nitrogen (N) content, phosphorous (P) content, potassium (K) content, carbon(C) content. The experiment of N, P, K and C was

performed in Soil Science laboratory, College of Agriculture, OUAT, Bhubaneswar. The preliminary tests were done to ascertain the suitability of the substrate for producing biogas.

4.2.1 Moisture content determination

The moisture content of cow dung and oilcakes were determined by NIR analyzer (DICKEY John Company). The instrument should be calibrated first following the instruction given in the manual. The fine ground sample was placed in sample cup inside the sample drawer. When the INSERT SAMPLE message was displayed, sample drawer was closed. After certain time (about 20-30 sec.), it shows the moisture and oil content of that sample.



Fig. 4.2 NIR Analyser

4.2.2 pHdetermination

A digital pH meter is used to measure pH of all samples to ascertain the suitability of samples. As methane forming bacteria are sensitive to acidity. Too much and sudden deviation from this value is likely to cause imbalance in bacteria population affecting the production of gas.

The digital pH meter consists of a pH sensor, pH half cell; whose voltage varies proportionately to the hydrogen ion activity of the solution. A reference electrode, reference half-cell provides a stable and constant reference voltage. The pH electrode consists of a thin membrane of hydrogen sensitive glass, blown on the end of an inert glass tube. Because this is a special type of glass and very thin, the bulb is very fragile

and great care must be exercised in handling it. A small filter (diaphragm) connects this tube to the external liquid or sample. This system is called a reference half-cell.



Fig. 4.3 Digital pH meter

The cap of the digital pH meter was first removed and the sample was placed in it. The power button was turned on. Then the sensor was dipped in the sample at least 20 mm of test solution. Then it was stirred once and allowed the reading to stabilize. Then the measured value was noted which indicates the pH of the sample.

4.2.3 N, P, K and C analysis of de-oiled seed cake

N, P, K and C analysis of the de-oiled cake samples were carried out to identify its composition.

4.2.3.1 Nitrogen analysis

The organic carbon present in the seed cake was estimated using Kjeldahl method. The sample was taken for further analysis. The step wise procedure is as follows.

- 0.5 gm of sample oil cake was taken in a digestion flask.
- 10 ml of conc. H_2SO_4 was added to it. 1 gm of salicylic acid, 2 gm of digestion mixture ($K_2SO_4 : CuSO_4 = 10: 1$) and 1 crystal of Sodium thiosulphate ($NaHSO_4$) were added and the flask was shaken and kept overnight.

- Next day it was put for digestion (heated up) until the contents turned into Copper sulphate colour.
- After completion of digestion, the flask was allowed to cool and about 20 ml of water was added (slowly and with shaking). Then the flask was swirled to bring any insoluble material into suspension and the content was transferred to the distillation chamber of the Hoskins apparatus via the funnel of the apparatus. The Kjeldahl flask was rinsed three times with about 9 ml of water to complete the transfer. Enough water was added to the distillation chamber to bring the level of solution to the mark made previously to indicate a volume of 50 ml and the stopcock was closed connecting the funnel and distillation chamber. Then 5 ml of H_3BO_3 indicator solution was added to a 50 ml Erlenmeyer flask marked to indicate a volume of 35 ml and the flask was placed under the condenser of the distillation apparatus so that the end of the condenser was about 4 cm above the surface of the H_3BO_3 . Then 20 ml of 10N NaOH was added to the funnel of the apparatus and the alkali was run slowly into the distillation chamber by opening the funnel stopcock. When about 1 ml of alkali remained in the funnel, the funnel was rinsed rapidly with about 15 ml of water. Enough water was allowed to run into the distillation chamber to bring the level of the solution up to the mark made previously to indicate a volume of 80 ml. Then the funnel stopcock was closed and immediately distillation was commenced by closing the steam bypass tube at the base of the steam jacket of the distillation chamber. (It is not necessary to interrupt the flow of steam to the steam jacket of the distillation chamber before addition of the digest and alkali, but the bypass tube of the steam jacket must be kept open during these additions). When the distillate reached the 35 ml mark on the receiver flask, distillation stopped by opening the steam bypass tube, the end of the condenser was rinsed and NH_4^+ and N was determined in the distillate by titration with 0.01N H_2SO_4 using a 10 ml burette, graduated at 0.01 ml intervals (1 ml of 0.01N H_2SO_4 = 0.14 mg of NH_4^+ N). The colour changed from green to pink which indicate the end point of the process.

4.2.3.2 Phosphorus (P) and Potash (K) analysis

The sample was taken for potash and phosphorus analysis. The step-wise procedure is as follows.

- 0.5 ml of ground and oven dried oil cake sample was taken in a 100 ml conical flask.
- 5 ml of conc. HNO₃ acid was added and kept for overnight.
- Next day it was put for digestion on a hot plate.
- 5 ml di-acid (HNO₃ + HClO₄ = 3:2) was added to the flask when brown flumes ceased to come.
- Digestion was allowed till the content became colourless.
- The content was cooled and transferred to a 50 ml volumetric flask with repeated washing and the final volume was made up to 50 ml with distilled water.
- Potassium in the solution was estimated by flame photometric method as described by Pageet *al.*, 1982.
- Total phosphorous was estimated by spectro-photometrically at 470 nano meter wave length by using Vanadomolebedo phosphoric yellow colour method as described by Jackson.

4.2.3.3 Carbon: The organic carbon was determined by the following methods.

- About 0.05 gram of sample was taken in a 500 ml. conical flask.
- About 10 ml. of Potassium Dichromate and 20 ml. of H₂SO₄ was added and allowed to mix for 30 minutes.
- About four drops of ferroin indicator was added to it. It was then titrated against Ferrous Ammonium Sulphate to estimate the organic carbon.

4.3 Preparation of Feed for Biogas Production

Oil cakes were powdered to ensure homogeneity in particle size for reducing the degradation time.

Six different feed materials were prepared by mixing each of the non-edible oil cakes, such as kusum, polanga in different proportions (15, 30, and 45%). One sample was prepared only for cow dung, as control, to compare the performance with other treatments. Total 13 samples were prepared which was made 1200 grams by adding the appropriate amount of water for each reactor. The higher solid content in feed will lessen

cumulative biogas produced without depend on kinds of feed material. Literature review says, the optimum solid content obtained for biogas production is in the range 7-9% (Muryanto *et al.*, 2006; Balsam, 2002). Hence, total solid of each experiment vial was kept fixed i.e. 10%. Water was added to oil cakes in 1:8 ratios and with cow dung in 1:1 ratio to maintain solid content of slurry 10%. No pretreatment or chemical adjustment of the slurry was made before or during testing. The study was run under uncontrolled pH, which is without acid or base addition.



Fig. 4.4 (a) Ground kusum oil cake



Fig. 4.4 (b) Ground polanga oil cake



Fig.4.5 Preparation of feed material for biogas production

4.4 Experimental design

The influence of type of cake, mixing ratio (OC:CD), hydraulic retention time (HRT) on biogas production was studied by performing series of laboratory bio-digester in several levels of independent parameters. Two cakes such as kusum and polanga are mixed with cow dung at different mixing ratios (15%, 30% and 45%) which kept for

different levels of HRT (30, 40 and 50 days). All of treatments were carried out by triplication. Composition of 63 treatments was used in the study. Operating temperature was at room temperature which is attached in Appendix.A.

Table 4.1 Treatment table

Retention time, days	KOC+CD			POC+CD			CD
	15:85	30:70	45:55	15:85	30:70	45:55	
30	T30 ₁	T30 ₂	T30 ₂	T30 ₃	T30 ₄	T30 ₅	T30 ₆
40	T40 ₁	T40 ₂	T40 ₂	T40 ₃	T40 ₄	T40 ₅	T40 ₆
50	T50 ₁	T50 ₂	T50 ₂	T50 ₃	T50 ₄	T50 ₅	T50 ₆

Replication=3, Total combinations=63

Table 4.2 Research plan

Independent Variables	Level	Values
Cake type	2	kusum, polanga
Mixing ratio (OC:CD)	4	15:85, 30:70, 45:55, 0:100
Retention time, days	3	30, 40, 50

Design of Experiment: Complete randomized design

Dependent Variables: Quantity of biogas produced (l/kg of slurry),

Methane content, %

4.5 Experimental Apparatus Set Up

Laboratory test was carried out by using 2 liters bio-digester and was operated in batch system at mesophilic temperature range of 20°C to 30° C. The daily atmospheric temperature is given in Appendix. A. The main experimental apparatus consists of bio-digester and biogas measuring device (fig. 4.6). Bio-digester was made from glass bottle plugged with tightly plastic clips and was equipped with valve for biogas measurement. The opening of the reactor bottle was sealed perfectly to maintain anaerobic condition. Biogas generated was measured by liquid displacement method. The schematic diagram of experimental laboratory set up as depicted in fig. 4.7. Total 21 test vials are used for experimentation.



Fig. 4.6 Experimental apparatus set-up

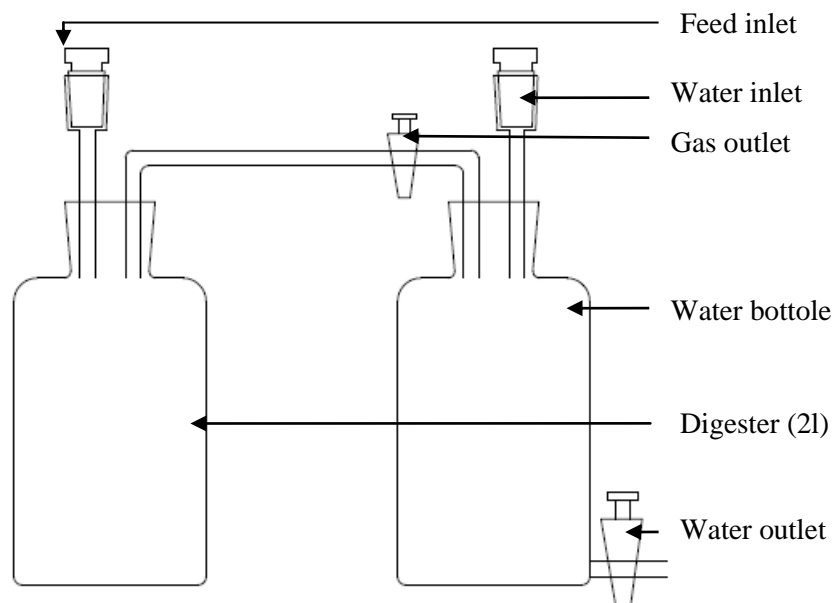


Fig. 4.7 Schematic diagram of experimental apparatus

4.6 Gas Chromatography (GC) Test

The biogas produced in the head space was analysed in every 30, 40 and 50 days of HRT by gas chromatography test. A gas tight syringe was used for sampling and tests were made without measuring the pressure inside the reactor.

A DANI Master GC gas chromatograph (GC) (fig. 4.8) equipped with a packed column and a DANI instruments actuator valve was used to analyze all gas samples.



Fig. 4.8 Gas Chromatograph

Hydrogen was used as the carrier gas and a TCD detector was utilized for the output signal. The elution time for each sample was 13.80 minute. The oven temperature was held at 50⁰C while the detector was held constant at 170⁰C. The sample continued to flow through the loop, pushing excess sample out the exit of the loop, ensuring that the sample loop only contains 1 mL for consistent sample size. When the run started, the loop closed immediately, pushing the sample into the column for analysis. After the predefined time, data acquisition curve was displayed on the monitor showing the percentage area of the gas constituents.

4.7 Experimental Procedures

The manure sample with research variables type of cake, mixing ratio, retention time was fed to different bio-digester. Biogas formed was measured every day and stopped after 50 days of retention time. The similar procedure was performed in three replications. Significance difference between treatments was determined statistically by complete randomized design (CRD). ANOVA table was drawn with the help of MSTAT C software. ANOVA table is given in table B.1.

4.8 Pilot Scale Biogas Production

After selection of best treatment among the above said treatments, biogas was produced in pilot scale biogas plant (fig. 4.9 (a)) of 0.25 m³ volume present in the

Renewable Energy Lab, CAET, OUAT. The biogas produced was stored in a one m³ biogas balloon (fig. 4.9 (b)).



Fig. 4.9 (a) Biogas plant



Fig. 4.9 (b) Biogas storage balloon

4.9 Biogas Application in Engine

In India nearly all agricultural tractors, pump sets, farm machinery and transport vehicles are run by DI diesel engines. Keeping the specific features of diesel engine in mind, a typical engine system, which is actually used in Indian context, has been selected for the present experimental investigations.

4.9.1 Development of experimental engine test assemble

A single cylinder, air cooled, direct injection, KIRLOSKAR make, TAF 1 model diesel engine was selected for the research work, which is primarily used for agricultural activities and house hold electricity generation as shown in fig. 4.10. The detailed specifications of theselected diesel engine have been given in Table. C.2.1. The objective here is to use biogas in dual fuel mode as mixture with air. For conducting the desired setof experiments and to gather required data from the engine, it is essential to mount various instruments at the appropriate location on the experimental setup as shown in fig. 4.11.

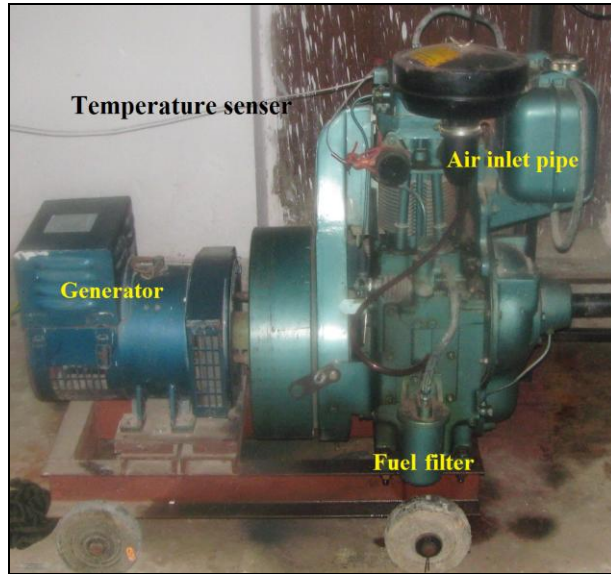


Fig. 4.10 Diesel engine used for experiment

4.9.2 Installation of the instrument control panel

After finalizing the procedures for data collection and procurement of the desired documents, they are put on a panel. Instrument such as voltmeter, ammeter, RPM indicator, 4 channel digital temperature displays were mounted on the front side of the control panel. Electrical load banks, i.e., 8 bulbs each of 500 watts were mounted on the top of the control panel and their switches were provided on the same side as shown in fig. 4.11.



Fig. 4.11 Instrument control panel

4.9.3 Modification of the air inlet pipe

A slight modification was made in the air inlet pipe of the diesel engine. A 3” diameter cut piece was welded to that air inlet pipe. A gate valve was attached to it. Another 3” diameter cut piece was connected to that gate valve for connecting the biogas ballon. Fig. 4.13 indicates the schematic diagram of engine set-up in dual fuel mode.



Fig. 4.12 Parts used for engine modification

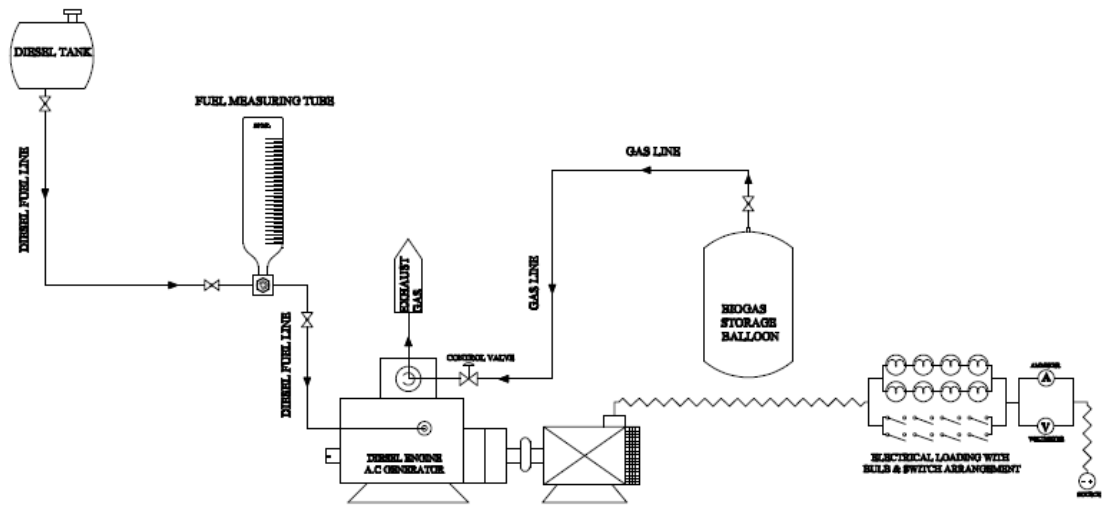


Fig. 4.13 Schematic diagram of engine set-up in dual fuel mode

RESULTS AND DISCUSSION

In the present study feasibility of de-oiled kusum and polanga cakes were analyzed for biogas production. Then biogas was produced in lab-scale by using biogas digesters from different samples, having different mixing ratios of oil cakes and cow dung. Variation of retention time on biogas production has also been investigated. The main target of the study is to identify the sample of oil cake and cow dung mixture for best quantity and quality biogas production. This chapter deals with the analysis of produced biogas and its feasibility for engine application.

5.1 Suitability of Kusum and Polanga Seed Cakes as Feed Stocks for Biogas Production

Each sample of KOC and POC were tested in the laboratory for evaluating their physical and chemical properties which are explained below.

5.1.1 Total solid and oil content of samples

Total solid was calculated from by deducting moisture content of each sample from its total weight. Moisture content was determined by NIR (near infrared) analyser. The detailed data is given in table 5.1 below. High percentage of total solid suggests their suitability as feed stock for bio-methanation process. Oil content of KOC and POC was found out to be 10.41% and 9.53% respectively.

Table 5.1 Composition of cow dung and oil cakes

Samples	Moisture content, %	Total solid, %	Oil content, %
Cowdung	81.60	18.40	Nil
Kusum oil cake	12.05	87.95	10.41
Polanga oil cake	9.26	90.74	9.53

5.1.2 C/N ratio of samples

C/N ratio of around 8-10 makes the feed stock suitable for biogas generation, while a ratio of around 25-30 is optimum (Mittal, 1996). It is observed that C/N ratio of all slurries that is used in the experiment varies from 12.00 to 17.62 with an average of 14.62 which confirms the suitability of KOC and POC seed cakes for biogas production.

High percentage of protein also leads towards acceptance of these two cakes for anaerobic digestion (table 5.2).

Table 5.2 Properties of slurries used for experiments

Samples	Carbon, %	Nitrogen, %	C/N ratio	Protein, %
Cowdung	35.20	1.55	22.71	9.69
Kusum oil cake	39.60	4.99	7.94	31.19
85% CD+15% KOC	35.86	2.07	17.36	12.91
70% CD+30% KOC	36.52	2.58	14.14	16.14
55% CD+45% KOC	37.18	3.10	12.00	19.36
Polanga oil cake	35.16	4.53	7.76	28.31
85% CD+15% POC	35.19	2.00	17.62	12.48
70% CD+30% POC	35.19	2.44	14.40	15.28
55% CD+45% POC	35.18	2.89	12.17	18.07

For optimal growth and activity of bacteria, it is essential that required nutrients are available in correct chemical form and concentration. Carbon (in carbohydrates) and nitrogen (in proteins, nitrates etc.) are the main nutrients for anaerobic bacteria. While carbon supplies energy, nitrogen is needed for building up the cell structure (i.e. growth). Deviation from the required range (8-30) ratio slows down the digestion process.

5.2 Biogas Production

Biogas produced every day was measured by water displacement method. The research was carried out in triplication. The data obtained from the study then was averaged and daily and cumulative volume of biogas production was observed. Numerical values of daily biogas yield and cumulative biogas production for several days observation time are presented in Appendix A.1.1 and A.1.2 respectively.

Fig. 5.1 and 5.2 shows daily biogas production and cumulative biogas production respectively for all samples including cow dung.

Biogas production was less both at the beginning and at the end period of observation. This is predicted due to the fact that growth of methanogenic bacteria is not prominent during these periods (Nopharatana *et al.*, 2007). Biogas production was slow in the first 4-5 days of observation due to the lag phase of microbial growth. In the range of 5-30 days observation, biogas production was significantly increased due to

exponential growth of micro-organisms. After about 30 days of observation, biogas production tends to decrease due to stationary phase of microbial growth. This is also due to reduction in nutrients, which affects the growth of micro-organisms.

Fig. 5.1 shows that biogas production starts from the next day of start of experiment. Average volume of biogas production for the sample 45% POC+55% CD is 0.072 m^3 and has a higher value than that of other combinations i.e. 0.056, 0.043, 0.053, 0.065, 0.067 m^3 in case of 15:85 KOC:CD, 30:70 KOC:CD, 45:55 KOC:CD, 15:85 POC: CD, 30:70 POC: CD, 45:55 POC: CD respectively. This amount is also close to the value of cow dung which was used as control i.e. 0.073 m^3 .

Fig. 5.2 shows that, in general, cumulative biogas production rate tend to obey sigmoid function (S curve) as generally occurred in batch growth curve and also has been resulted by Budiyo *et al.* (2009). Cumulative biogas production for the sample 45% POC+55% CD is highest compared other mixture and cow dung only. This may be due to the fact that it contains high amount of protein. Though the sample 45% KOC+55% CD contains more protein than that of 45% POC+55% CD, due to better degradability of POC it produces more quantity of gas.

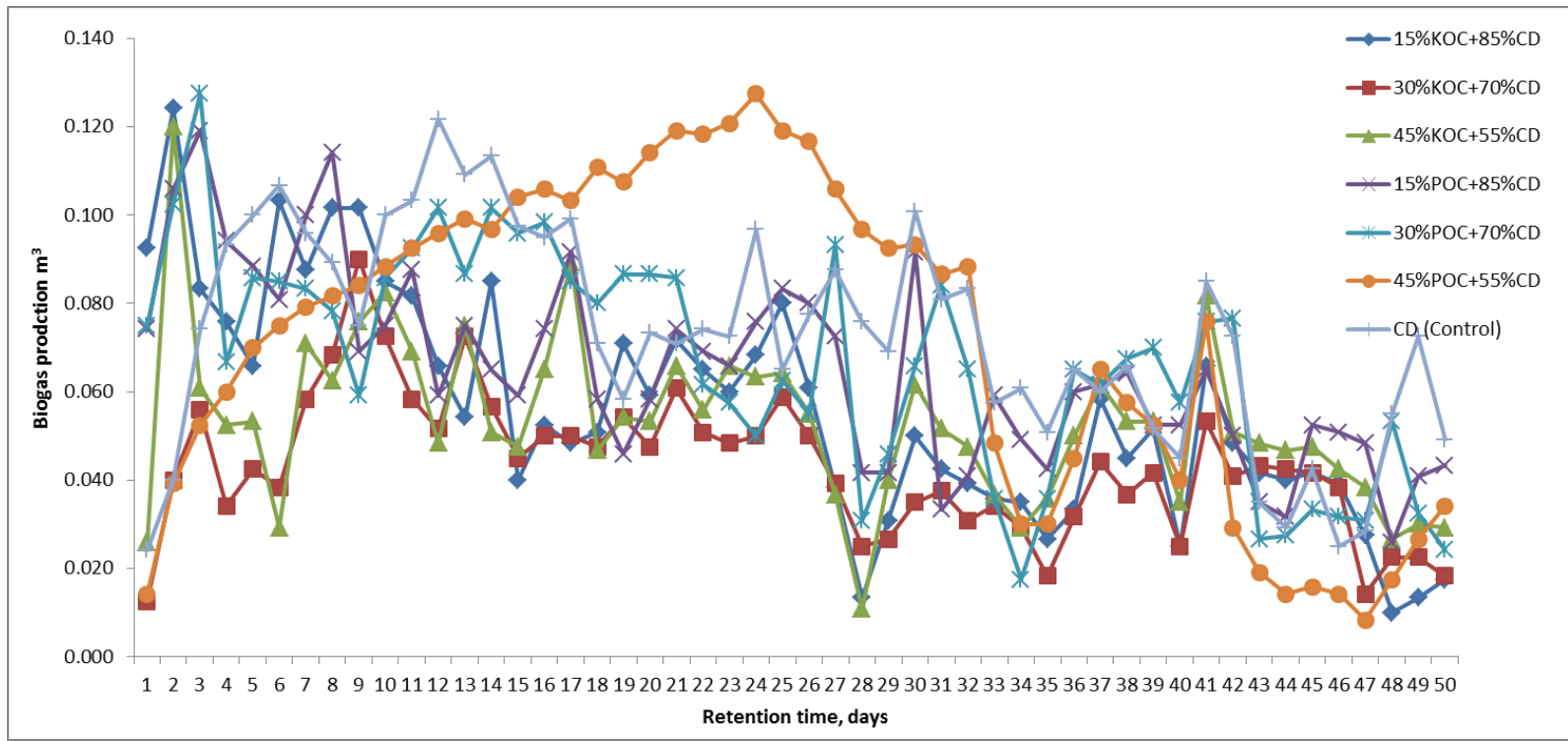


Fig. 5.1 Daily biogas production, m³

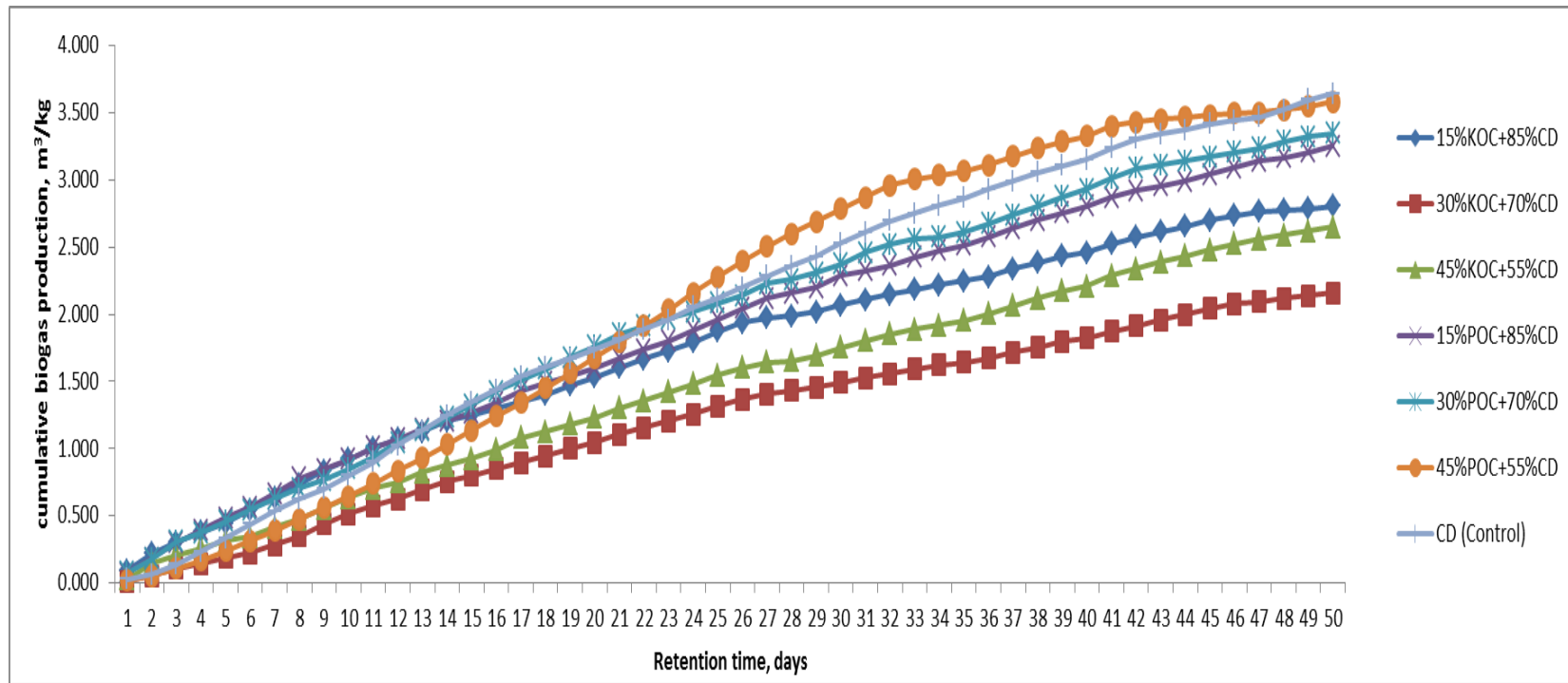


Fig. 5.2 Cumulative biogas production, m³/kg of slurry

5.3 Effect of different variables on biogas production and methane content

The effect of research variables such as cake type, mixing ratio of OC and CD, HRT on biogas production and methane content of biogas produced was analysed. The mean table is attached in Appendix B and the results are discussed as below.

5.3.1 Effect of mixing ratio on biogas production

The effect of mixing ratio (MR) of oil cake to cow-dung on biogas production was studied by varying oil cake MR at three levels i.e. 15%, 30% and 45% with cow dung. Figs. 5.3 (a), 5.3 (b), 5.3 (c), 5.3 (d) represents the mean biogas produced at different levels of mixing ratios. The values are also compared with cow dung.

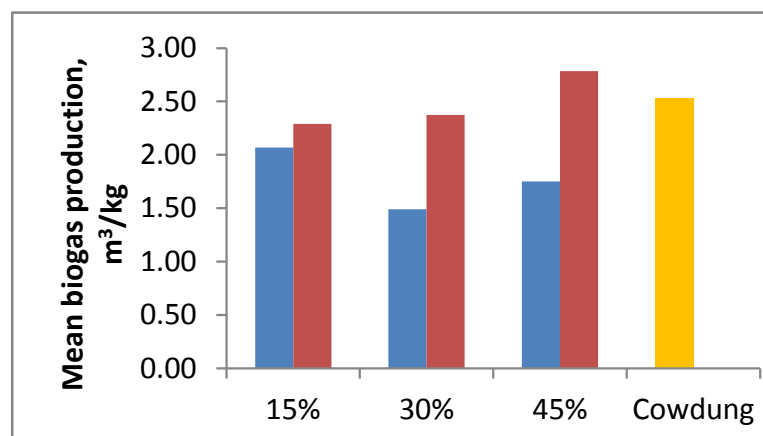


Fig.5.3 (a) Mean biogas production at different mixing ratios (30 days HRT)

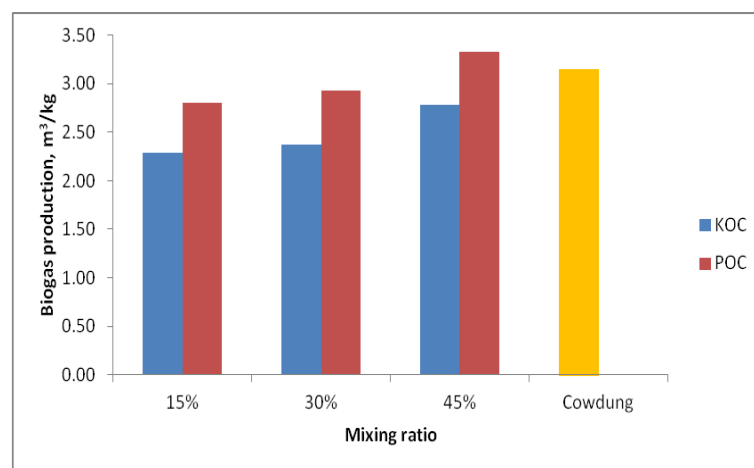


Fig. 5.3 (b) Mean biogas production at different mixing ratios (40 days HRT)

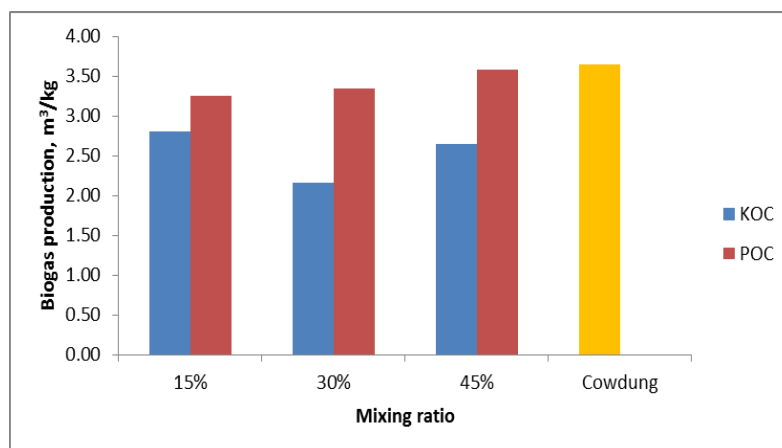


Fig. 5.3 (c) Mean biogas production at different mixing ratios (50 days HRT)

It is evident from the figs. 5.3 (a), 5.3 (b) and 5.3 (c) that biogas production volume per kg of sample increases by increasing oil cake percentage in the substrate mixture. In case of KOC mixture at 30% mixing level, little decrease in biogas production is observed during 30 days and 50 days HRT. But a regular increase in biogas production is observed in case of POC mixture for all HRT.

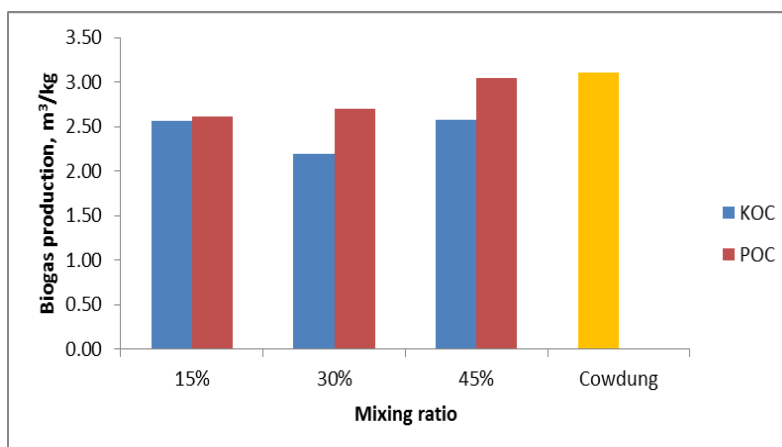


Fig. 5.3 (d) Mean biogas production at different mixing ratios (irrespective of HRT)

Mean biogas produced from KOC and POC mixtures irrespective of HRT is shown in fig. 5.3 (d). The figure indicates a continuous increase in biogas production by increasing POC in the substrate mixture. At 45% of POC mixing level highest biogas production is observed, which is nearly equal to biogas produced from pure cow dung. In case of KOC mixture biogas production is little lower at 30% mixing level but it is also further improved at 45% mixing level. It is predicted due to the presence of more amount of protein i.e. 18.07 % (table 5.2) in that sample.

5.3.2 Effect of retention time on biogas production

Variation of biogas production with retention time, at different mixing ratios of all samples including CD slurry is given in figs. 5.4 (a), 5.4 (b),5.4 (c).

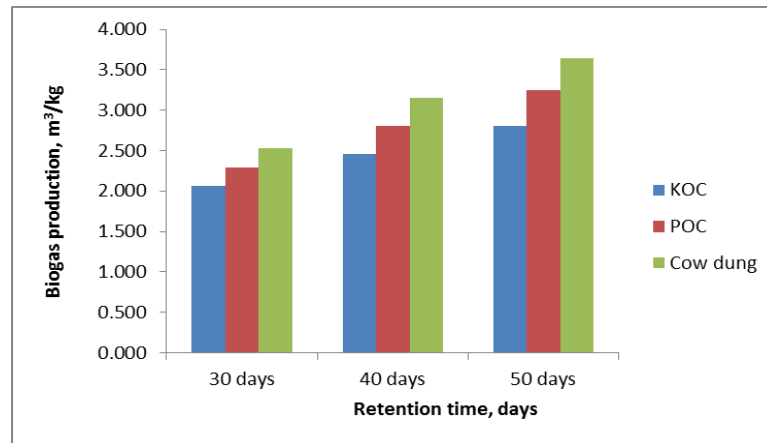


Fig.5.4 (a) Mean biogas production at different retention time (15 % MR)

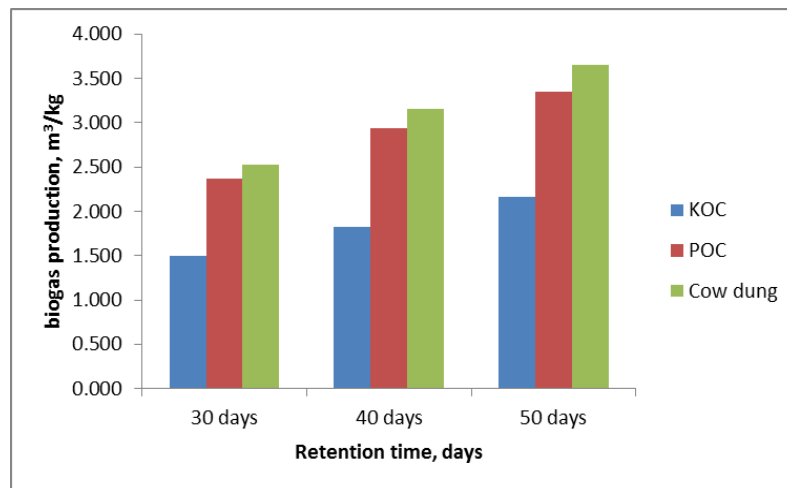


Fig. 5.4 (b) Mean biogas production at different retention time (30 % MR)

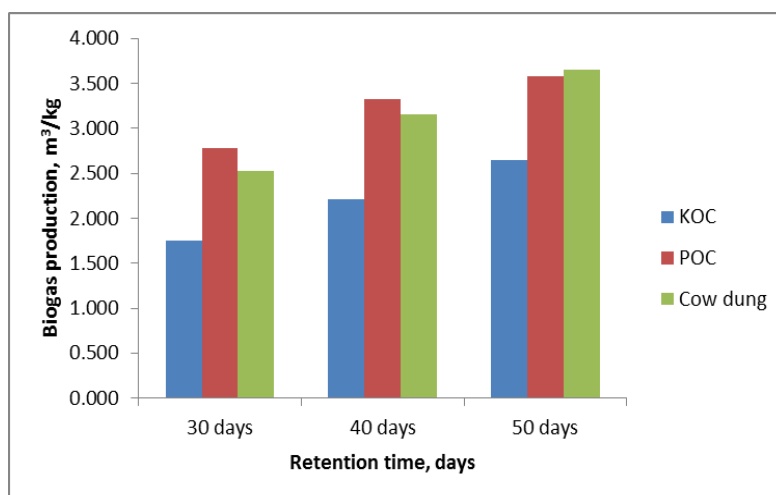


Fig. 5.4 (c) Mean biogas production at different retention time (45 % MR)

Effect of variation in HRT on biogas production for mixed samples and pure cow dung is shown in figs. 5.4 (a), 5.4 (b) and 5.4 (c) at different mixing levels. The figures indicate a continuous increase in biogas production with increases in retention time irrespective of cakes type and the same is also true for pure cow dung.

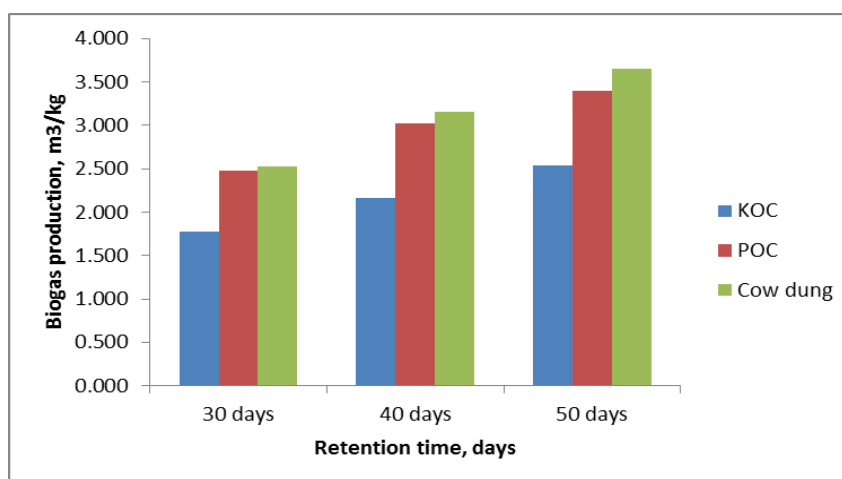


Fig. 5.4 (d) Mean biogas production at different retention time (irrespective of MR)

Fig. 5.4 (d) indicates variation of mean biogas production irrespective of oil cake mixing level. It is evident from the figure that there is a regular improvement in biogas production with respect to the increasing retention time. It is an obvious fact that, in general, quantity of biogas production increases with increases in no of days of digestion.

5.3.3 Effect of mixing ratio on methane content of biogas

Effect of mixing ratio (3 levels: 15%, 30%, 45%) of oilcake to cow dung is analyzed from mean table obtained after statistical analysis. The figs. 5.5 (a), 5.5 (b), 5.5 (c) represents mean methane content of biogas at different levels of mixing ratios. The values are then compared with cow dung.

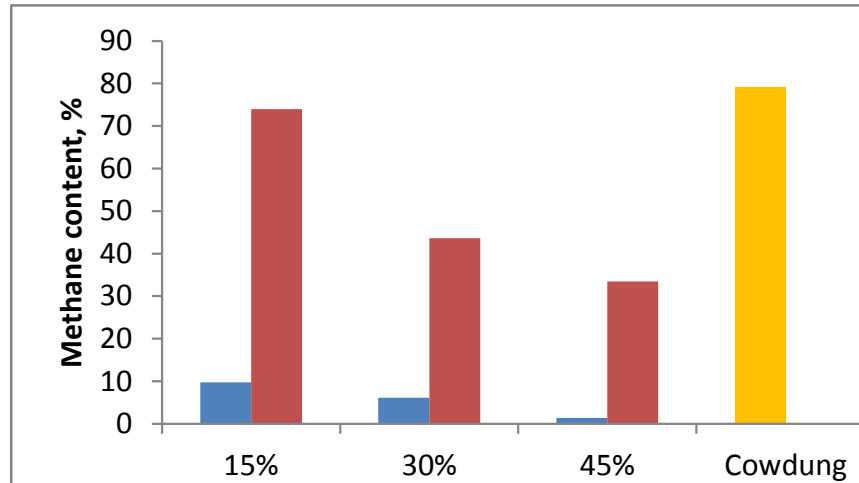


Fig. 5.5 (a) Effect of mixing ratio on methane content of biogas (30 days HRT)

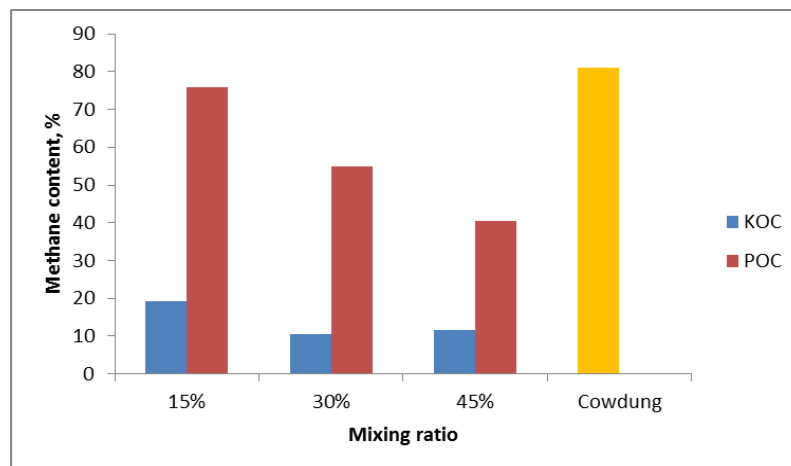


Fig. 5.5 (b) Effect of mixing ratio on methane content of biogas (40 days HRT)

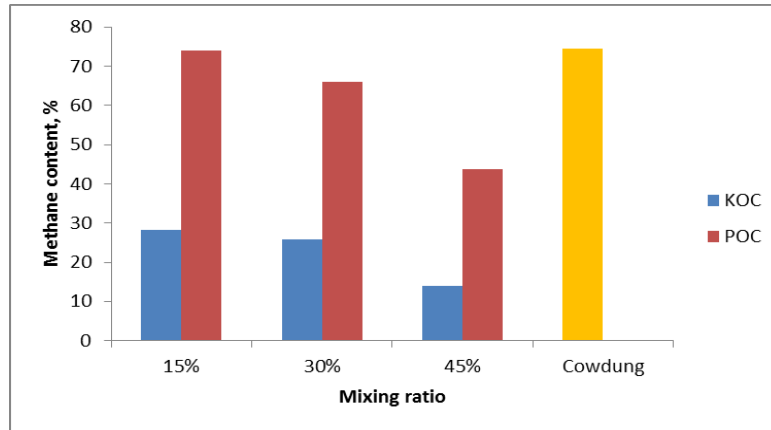


Fig. 5.5 (c) Effect of mixing ratio on methane content of biogas (50 days HRT)

Effect of mixing ratio on biogas quality is shown in figs. 5.5 (a), 5.5 (b) and 5.5 (c) for 30, 40 and 50 days HRT time respectively. It is evident from the figures that biogas quality reduction occurs with increase in level of oil cake in the sample. Highest methane content was found at 15% mixing level of both KOC and POC with cow dung. It is also observed that POC mixed samples produced significantly higher quality biogas than that of KOC mixtures for all mixing levels at all HRT. POC at 15% mixing level produces highest quality biogas, equivalent to cow dung.

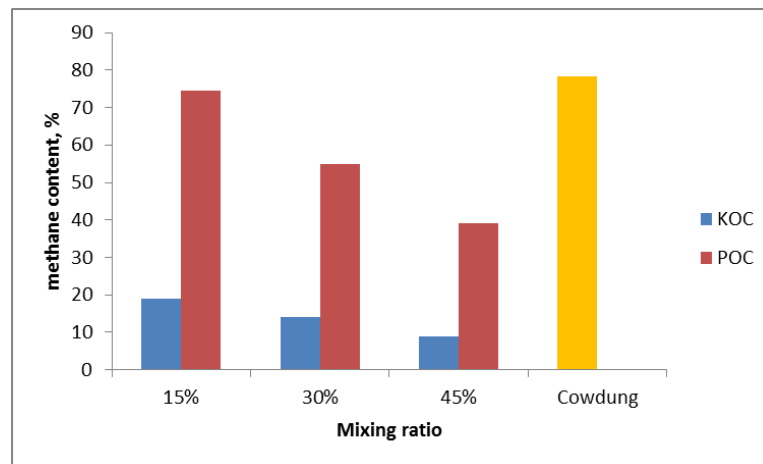


Fig. 5.5 (d) Effect of mixing ratio on methane content of biogas (irrespective of HRT)

Fig. 5.5 (d) indicates the effect of methane content in biogas production irrespective of HRT for both POC and KOC mixture. It is evident from the figure that POC at 15% mixing level gives best quality biogas than other treatments. It may be due to gradual decrease of C/N ratio with addition of OC. If we compare two oil cakes i.e. KOC and POC, methane content of POC is higher than that of KOC. Because KOC takes

more time to degrade because of its more oil content i.e. 10.41 % while in case of POC, it is 9.53%.

5.3.4 Effect of retention time on methane content of biogas

Variation of methane content of the biogas produced from different cakes with retention time, at different mixing ratios is given in fig. 5.6 (a), 5.6 (b) and 5.6 (c). The numerical values are given in Appendix A.2.

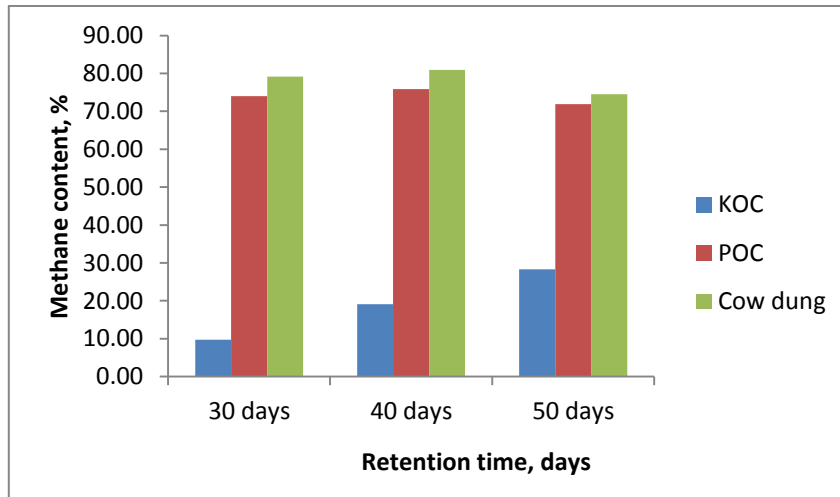


Fig. 5.6 (a) Effect of retention time on methane content of biogas produced(15 % MR)

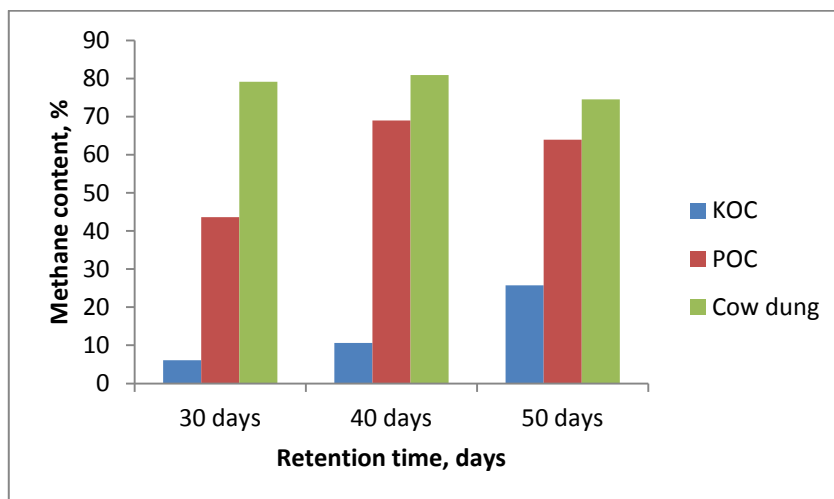


Fig. 5.6 (b) Effect of retention time on methane content of biogas produced(30 % MR)

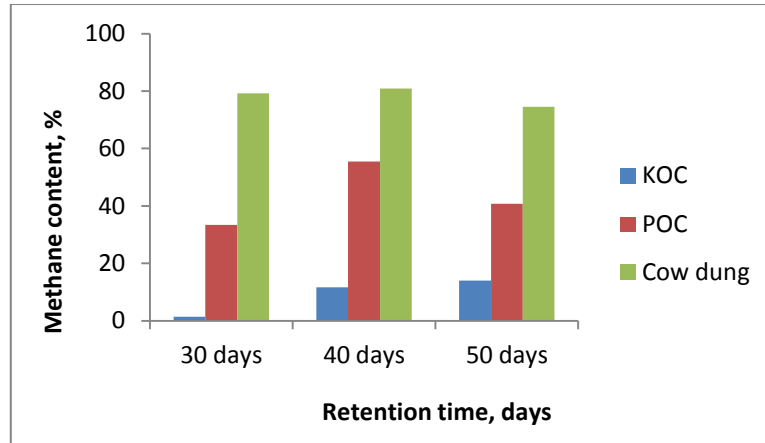


Fig. 5.6 (c) Effect of retention time on methane content of biogas produced(45 % MR)

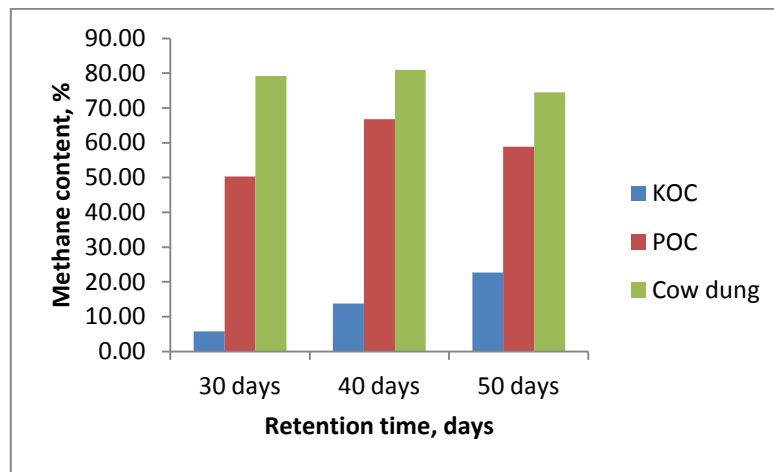


Fig. 5.6 (d) Effect of retention time on methane content of biogas produced(irrespective of MR)

The graph reveals that with retention time, methane content of biogas produced increases in case of KOC. In other two cases (POC and CD), methane content is highest in 40 days. This means that HRT for KOC may be 50 days or higher than 50 days and for POC and CD, HRT is 40 days after which methane content falls.

5.4 Selection of Best Mixing Ratio

Effect of oil cakes (i.e. both POC and KOC) mixing levels on biogas quantity and quality irrespective HRT are obtained from mean table B.1 are plotted in a scatter diagram and the best level of mixing ratio was selected considering both quantity and quality of biogas which is represented in fig. 5.7.

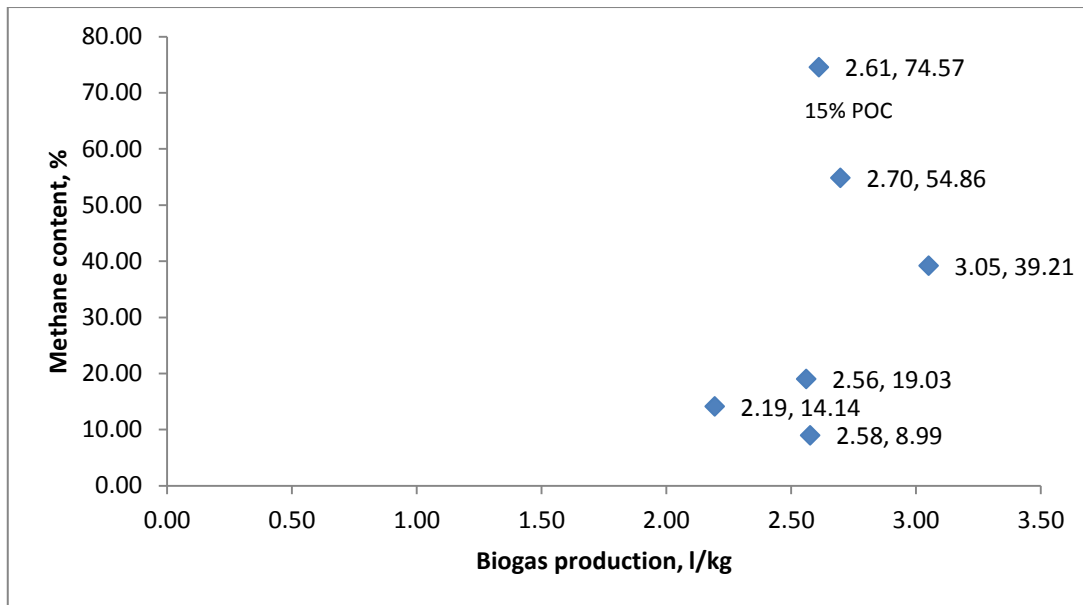


Fig. 5.7 Best level of mixing ratio

From the diagram it is clear that POC at 15% mixing level is positioned at right hand top corner in the scatter plot, means it has highest methane content and highest biogas production volume compared to other mixing levels of POC and KOC. Hence, from the above analysis POC at 15% mixing level is selected as the best among all experimental treatments.

5.5 Selection of Best Retention Time

Effect of HRT of oil cakes (i.e. both POC and KOC) on biogas quantity and quality irrespective MR are obtained from mean table B.1 are plotted in a scatter diagram and the best level of mixing ratio was selected considering both quantity and quality of biogas which is represented in fig. 5.8.

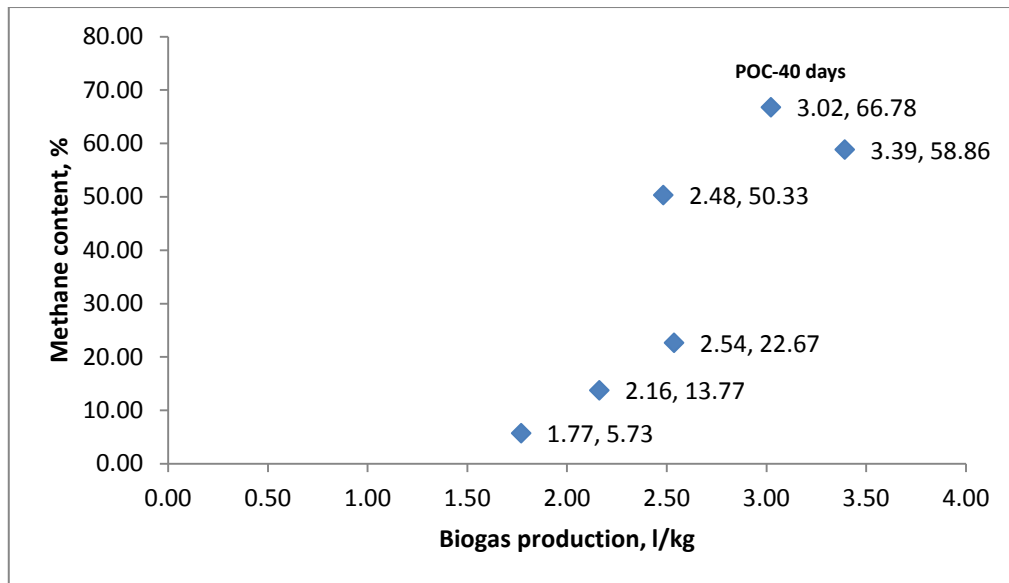


Fig. 5.8 Best level of retention time

From the diagram it is clear that POC at 40 days retention time is positioned at right hand top corner in the scatter plot, means it has highest methane content and highest biogas production volume compared to other mixing levels of POC and KOC. Hence, from the above analysis POC at 40 days retention time is selected as the best among all experimental treatments.

5.6 ANOVA Table for Quantity and Quality of Biogas

Analysis of variance for the effect of type of cake used, mixing ratio (MR) and retention time (RT) on quantity of biogas produced and methane (CH₄) content was derived from ANOVA which is given in table 5.3, 5.4. The detail ANOVA analysis data is attached in Appendix B.

Factor A (Var 2: cake) with values from 1 to 2

Factor B (Var 3: mixing ratio) with values from 1 to 4

Factor C (Var 4: retention time) with values from 1 to 3

No. of replications=3

Table 5.3 Analysis of variance for the effect on quantity of biogas produced

Source	Degree of freedom	sum of square	mean square	F _{cal}	CD, 5% level
Factor A	1	6.745	6.745	5.575*	0.528
Factor B	3	5.058	1.686	1.395*	0.001
AB	3	3.796	1.265	1.046 ^{NS}	1.056
Factor C	2	9.589	4.795	233.487*	0.084
AC	2	0.048	0.024	1.161*	0.119
BC	6	0.112	0.019	0.911*	0.168
ABC	6	0.092	0.015	0.744*	0.238
Error	32	0.657	0.021		
Total	71	45.440			

Coefficient of Variation: 5.33%

Table 5.4 Analysis of variance for the effect on methane content of biogas produced

Source	Degree of freedom	Sum of square	Mean square	F _{cal}	CD	
					5% level	1% level
Factor A	1	17993.045	17993.045	107599.80**	1.225	0.264
Factor B	3	27785.08	9261.693	55385.66**	0.434	0.373
AB	3	8902.62	2967.540	17746.12**	0.613	0.528
Factor C	2	190.943	95.471	885.25**	0.408	0.259
AC	2	750.556	375.278	3479.732**	0.577	0.367
BC	6	756.478	126.08	1169.06**	0.464	0.519
ABC	6	1233.133	205.522	1905.69**	0.656	0.734
Error	32	3.451	0.108			
Total	71	57617.981				

Coefficient of Variation: 5.30%

* Significant

** Highly significant

^{NS} Not significant

From the results of the experiments conducted as well as from the analysis of variance carried out from experimental data, it was found that type of cake used, MR and HRT as well as their interaction have significant effect on yield of biogas at 5% level ($p < 0.05$). But, the interaction between factor A and B, i.e., type of cake and mixing ratio

was found to be not significant. It can be said that all input variables such as type of cake used, MR and HRT have significant effect on methane content of biogas production even at 1% level.

5.7 Variation of pH Before and After Digestion

pH is expressed by the concentration of the hydrogen ions. The relationship between ammonium (NH_4^+) and ammonia (NH_3) is determined by a chemical equation regulated by the hydrogen ion concentration which is given in Eqn. 5.1. An increased concentration of hydrogen ions results in a decreased pH. pH of each sample before and after digestion is shown in fig. 5.9.

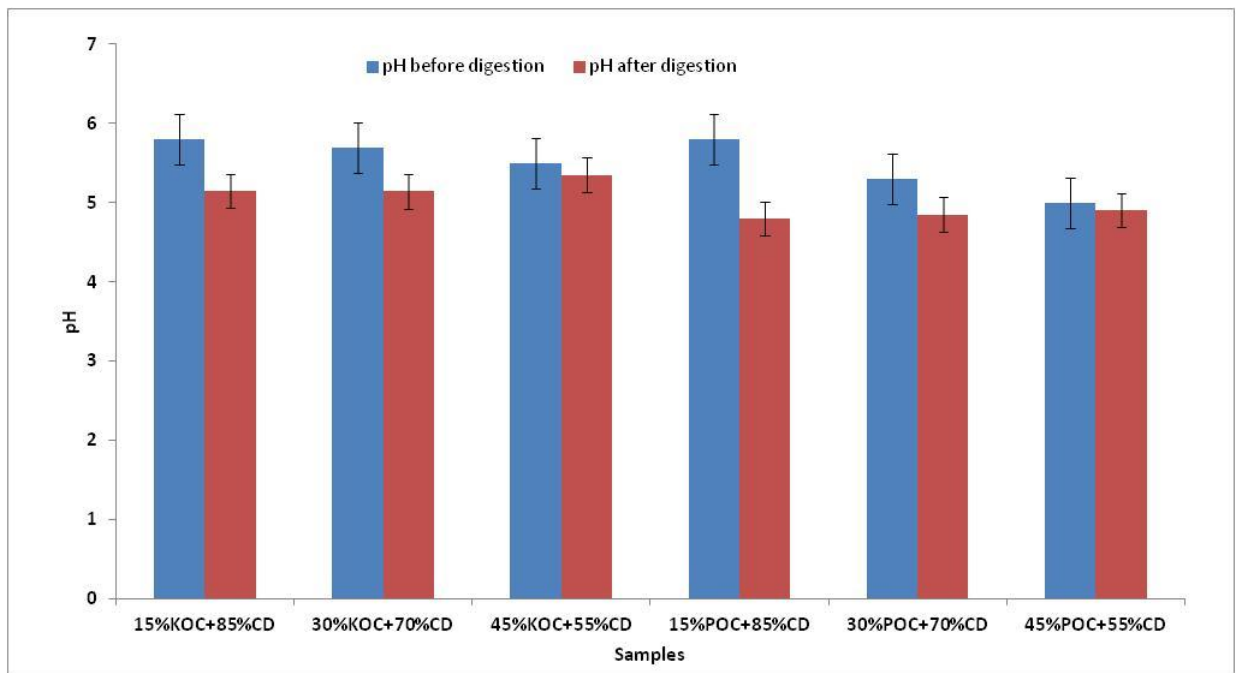


Fig. 5.9 Variation of pH before and after digestion

Before digestion, pH of all samples was slightly acidic with a standard deviation (S.D.) of 0.29. The pH of each samples after digestion decreased with S.D. of 0.20. This is because of the reason stated above.

5.8 Application of Biogas in Engine

Biogas was premixed with the intake air as gaseous fuel and the diesel engine was run at different electrical loads. The results obtained is analysed and fuel consumption vs load graph has been plotted from these results which is narrated in fig.

5.10. The numerical values of fuel consumption at two running modes of engine (i.e. diesel only and dual fuel mode) are given in Appendix C.

5.8.1 Fuel (diesel) consumption VS loads

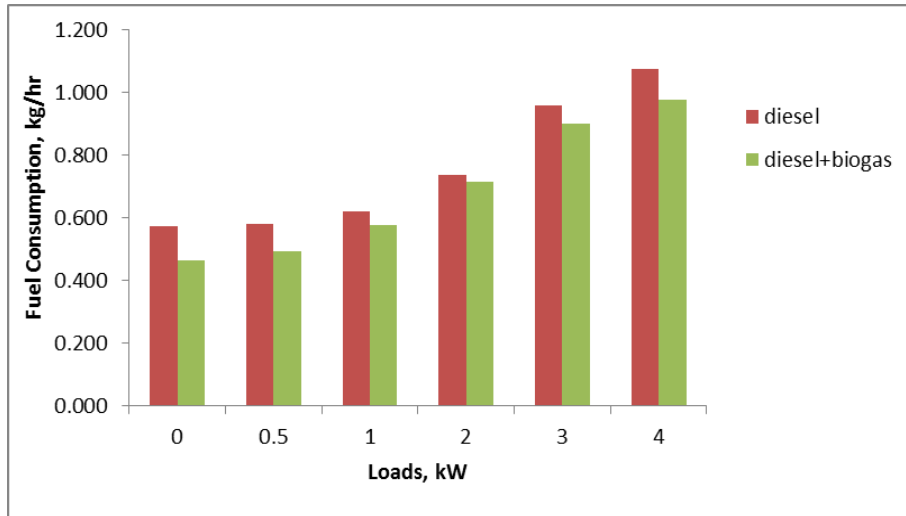


Fig. 5.10 Fuel (diesel) consumption VS loads

As expected, the diesel consumption decreased when engine was operated in dual fuel mode. The graph also illustrates that when load increases, diesel consumption increases at both condition. The biogas fulfills its aim of replacing the diesel fuel.

SUMMARY AND CONCLUSION

The increasing consumption of energy results in decrease of fossil fuel stock as well as increasing environmental problem which directly putting a great pressure on the society to find renewable alternatives. Biogas can be considered as one of the best non-conventional source of energy which is helpful to reduce this problem. India is endowed with a huge amount of biomass which can be used for biogas production, thus meeting the energy demand. Among the locally available biomass de-oiled oil seed cakes can be considered as a potential source for biogas production. The non-edible oil cakes in spite of having high nutrient content cannot be used as animal feed due to the presence of toxic components in them and are getting wasted. However, it is best suitable for biogas production as it contains a good amount of protein. Attempts are being made to produce biogas from these non-edible oil cakes considering different factors like cake type, cow dung to oilcake mixing ratio, retention time. The present dissertation work is mainly focused on biogas production as a waste management tool from two byproducts of the oil expelling unit, i.e. KOC and POC. Study revealed that KOC produces less biogas than POC, also contains very less amount of methane.

Based on the results obtained in the study, the following specific conclusions can be drawn:

1. The outcomes of preliminary test of feed materials for biomethanation process confirm that KOC and POC de-oiled cakes are rich in total solid content i.e. 87.95% and 90.74 % respectively. KOC have also a good proportionate of protein i.e. 31.19 % and 28.31 % respectively which is higher than that of cow dung (9.69%). It further confirms the suitability of KOC and POC for biogas production.
2. Though KOC and POC cannot be alone used for biogas production due to low C/N ratio (i.e. 7.94 and 7.76 respectively), it can be used for same purpose as a supplementation with cow dung. C/N ratios of the slurries 15:85 KOC:CD, 30:70 KOC:CD, 45:55 KOC:CD, 15:85 POC:CD, 30:70 POC:CD, 45:55 POC:CD was

found out to be 17.36, 14.14, 12.00, 17.62, 14.40, 12.17 respectively which suggest their suitability for biogas production.

3. Biogas production decreases with increasing addition of CD, but methane content increases for POC. In case of KOC, with increases in addition of CD, biogas production decreases up-to 30% mixing ratio, but at 45% mixing ratio this amount increases. Similarly with increase in CD addition, methane content increases for KOC.
4. For KOC, as the retention time increases biogas production and methane content increases. For POC, as the retention time increases biogas production increases and methane content increases upto 40 days, then decreases.
5. The variables cake type, mixing ratio and retention time have significant effect at 5% level. Similarly, regarding methane content, all the three variables have significant effect on it even at 1% level.
6. It was also found that there is no significant improvement in average biogas yields with mixed feed material as compared to cow dung slurry. Though the maximum biogas production was found in case of 45:55 (POC:CD) slurry with HRT 50 days i.e. 3.582 l/kg, the optimum process parameter found in case of 15:85 (POC:CD) having HRT 40 days due to high methane content i.e. 75.867%.
7. When the diesel engine run in dual fuel mode (diesel + biogas), the fuel (diesel) consumption is less as compared to when the engine run in diesel fuel only.

SUGRESSION FOR FUTURE WORK

This study deals only with composition of feed, quantity of biogas production and methane content of biogas. These factors vary according to cake type, mixing ratio of OC and CD and retention time. For further research, it can be recommended as follows:

1. Study biogas production by adding alkali or base material to increase the pH.
2. To find out other gas components like H_2 , NH_3 by running these standards in GC.
3. After digestion oil cake can be used as organic fertilizer.
4. Studies can be made on long term effect on diesel engine by running it in dual fuel mode (diesel + biogas).

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APPENDIX A

A.1 Calculation Sheet of Daily Biogas Produced

Daily biogas produced was measured in liter per 400 gm of slurry. Then biogas produced in m³/kg of slurry was calculated from these readings.

Table A.1.1 Daily biogas production

Temperature (°C)	Daily biogas production, m ³						Cow dung
	KOC:CD			POC:CD			
	15:85	30:70	45:55	15:85	30:70	45:55	
23.1	0.093	0.013	0.026	0.074	0.075	0.014	0.024
22.6	0.124	0.040	0.120	0.106	0.103	0.039	0.040
22.0	0.083	0.056	0.061	0.119	0.128	0.053	0.074
22.5	0.076	0.034	0.053	0.094	0.067	0.060	0.093
23.1	0.066	0.043	0.053	0.088	0.086	0.070	0.100
23.1	0.103	0.038	0.029	0.081	0.085	0.075	0.107
22.8	0.088	0.058	0.071	0.100	0.083	0.079	0.096
22.5	0.102	0.068	0.063	0.114	0.078	0.082	0.089
23.3	0.102	0.090	0.076	0.069	0.059	0.084	0.075
23.6	0.085	0.073	0.083	0.075	0.086	0.088	0.100
23.3	0.082	0.058	0.069	0.088	0.093	0.093	0.103
23.0	0.066	0.052	0.048	0.059	0.102	0.096	0.122
22.6	0.054	0.073	0.075	0.075	0.087	0.099	0.109
22.4	0.085	0.057	0.051	0.065	0.102	0.097	0.113
22.1	0.040	0.045	0.048	0.059	0.096	0.104	0.098
21.8	0.053	0.050	0.065	0.074	0.098	0.106	0.095
22.1	0.048	0.050	0.089	0.092	0.085	0.103	0.099
22.4	0.051	0.048	0.047	0.058	0.080	0.111	0.071
22.6	0.071	0.054	0.054	0.046	0.087	0.108	0.058
23.2	0.059	0.048	0.053	0.058	0.087	0.114	0.073
24.1	0.072	0.061	0.066	0.074	0.086	0.119	0.071
24.7	0.065	0.051	0.056	0.069	0.062	0.118	0.074
25.0	0.060	0.048	0.066	0.066	0.058	0.121	0.073
25.3	0.068	0.050	0.063	0.076	0.050	0.128	0.097
26.6	0.080	0.059	0.064	0.083	0.063	0.119	0.065
26.6	0.061	0.050	0.055	0.080	0.055	0.117	0.078
26.6	0.038	0.039	0.037	0.073	0.093	0.106	0.088
26.0	0.013	0.025	0.011	0.042	0.031	0.097	0.076
25.6	0.031	0.027	0.040	0.042	0.046	0.093	0.069
26.0	0.050	0.035	0.062	0.092	0.066	0.093	0.101
26.0	0.043	0.038	0.052	0.033	0.084	0.087	0.081
26.0	0.039	0.031	0.048	0.041	0.065	0.088	0.083
24.5	0.036	0.034	0.037	0.059	0.036	0.048	0.058

22.4	0.035	0.029	0.029	0.049	0.018	0.030	0.061
22.1	0.027	0.018	0.036	0.043	0.036	0.030	0.051
22.6	0.033	0.032	0.050	0.060	0.065	0.045	0.065
24.1	0.058	0.044	0.062	0.062	0.062	0.065	0.060
24.4	0.045	0.037	0.053	0.064	0.068	0.058	0.066
25.3	0.052	0.042	0.053	0.053	0.070	0.053	0.052
25.0	0.025	0.025	0.035	0.053	0.058	0.040	0.045
25.9	0.066	0.053	0.082	0.065	0.076	0.076	0.085
26.3	0.048	0.041	0.051	0.050	0.077	0.029	0.073
26.0	0.042	0.043	0.048	0.035	0.027	0.019	0.035
27.3	0.040	0.043	0.047	0.032	0.028	0.014	0.029
27.3	0.042	0.042	0.048	0.053	0.033	0.016	0.043
26.8	0.039	0.038	0.043	0.051	0.032	0.014	0.025
25.6	0.028	0.014	0.038	0.048	0.031	0.008	0.028
25.3	0.010	0.023	0.027	0.026	0.053	0.018	0.055
25.1	0.013	0.023	0.030	0.041	0.033	0.027	0.073
24.4	0.018	0.018	0.029	0.043	0.024	0.034	0.049

Table A.1.2 Cumulative biogas yield in several days observation time

Temperature (°C)	Cumulative biogas production, m ³ /kg						
	KOC:CD			POC:CD			Cow dung
	15:85	30:70	45:55	15:85	30:70	45:55	
23.1	0.093	0.013	0.026	0.074	0.075	0.014	0.024
22.6	0.217	0.053	0.146	0.180	0.178	0.053	0.064
22.0	0.300	0.108	0.207	0.299	0.305	0.106	0.138
22.5	0.376	0.143	0.259	0.393	0.372	0.166	0.232
23.1	0.442	0.185	0.313	0.482	0.458	0.236	0.332
23.1	0.545	0.223	0.342	0.563	0.543	0.311	0.438
22.8	0.633	0.282	0.413	0.663	0.626	0.390	0.534
22.5	0.734	0.350	0.475	0.777	0.704	0.472	0.623
23.3	0.836	0.440	0.551	0.846	0.763	0.556	0.698
23.6	0.921	0.513	0.633	0.921	0.849	0.644	0.798
23.3	1.003	0.571	0.703	1.008	0.942	0.737	0.902
23.0	1.068	0.623	0.751	1.068	1.043	0.833	1.023
22.6	1.123	0.695	0.826	1.143	1.130	0.932	1.133
22.4	1.208	0.752	0.877	1.208	1.232	1.028	1.246
22.1	1.248	0.797	0.924	1.267	1.328	1.133	1.343
21.8	1.300	0.847	0.989	1.341	1.426	1.238	1.438
22.1	1.348	0.897	1.078	1.433	1.511	1.342	1.538
22.4	1.399	0.944	1.125	1.491	1.591	1.453	1.608
22.6	1.470	0.998	1.179	1.537	1.678	1.560	1.667

23.2	1.529	1.046	1.233	1.595	1.764	1.674	1.740
24.1	1.601	1.107	1.298	1.669	1.850	1.793	1.811
24.7	1.666	1.158	1.354	1.738	1.912	1.912	1.885
25.0	1.726	1.206	1.420	1.804	1.969	2.033	1.958
25.3	1.794	1.256	1.483	1.880	2.019	2.160	2.054
26.6	1.874	1.315	1.548	1.963	2.082	2.279	2.119
26.6	1.935	1.365	1.603	2.043	2.137	2.396	2.197
26.6	1.973	1.404	1.639	2.116	2.230	2.502	2.284
26.0	1.987	1.429	1.650	2.158	2.261	2.598	2.360
25.6	2.018	1.455	1.690	2.199	2.307	2.691	2.429
26.0	2.068	1.490	1.752	2.291	2.373	2.784	2.530
26.0	2.110	1.528	1.803	2.324	2.457	2.871	2.611
26.0	2.149	1.559	1.851	2.365	2.522	2.959	2.694
24.5	2.185	1.593	1.888	2.424	2.558	3.008	2.752
22.4	2.220	1.622	1.917	2.473	2.575	3.038	2.813
22.1	2.247	1.640	1.953	2.516	2.611	3.068	2.863
22.6	2.280	1.672	2.003	2.576	2.676	3.113	2.928
24.1	2.338	1.716	2.064	2.638	2.738	3.178	2.988
24.4	2.383	1.753	2.118	2.702	2.805	3.235	3.054
25.3	2.435	1.795	2.171	2.754	2.875	3.288	3.106
25.0	2.460	1.820	2.206	2.807	2.933	3.328	3.151
25.9	2.526	1.873	2.288	2.872	3.008	3.403	3.236
26.3	2.574	1.914	2.338	2.922	3.085	3.433	3.308
26.0	2.616	1.957	2.387	2.957	3.112	3.452	3.343
27.3	2.656	2.000	2.433	2.988	3.139	3.466	3.373
27.3	2.698	2.041	2.481	3.041	3.173	3.482	3.415
26.8	2.737	2.080	2.523	3.092	3.204	3.496	3.440
25.6	2.764	2.094	2.562	3.140	3.235	3.504	3.468
25.3	2.774	2.116	2.588	3.166	3.288	3.522	3.523
25.1	2.788	2.139	2.618	3.207	3.321	3.548	3.596
24.4	2.805	2.157	2.648	3.250	3.345	3.583	3.645

A.2 Methane content of biogas produced

Methane content of biogas produced was measured in every 0, 40 and 50 days by gas chromatography test by clarity software. Some of the data acquisition graphs are shown in figs. A.1, A.2, A.3.

Table A.2 Calculation of quality of biogas produced

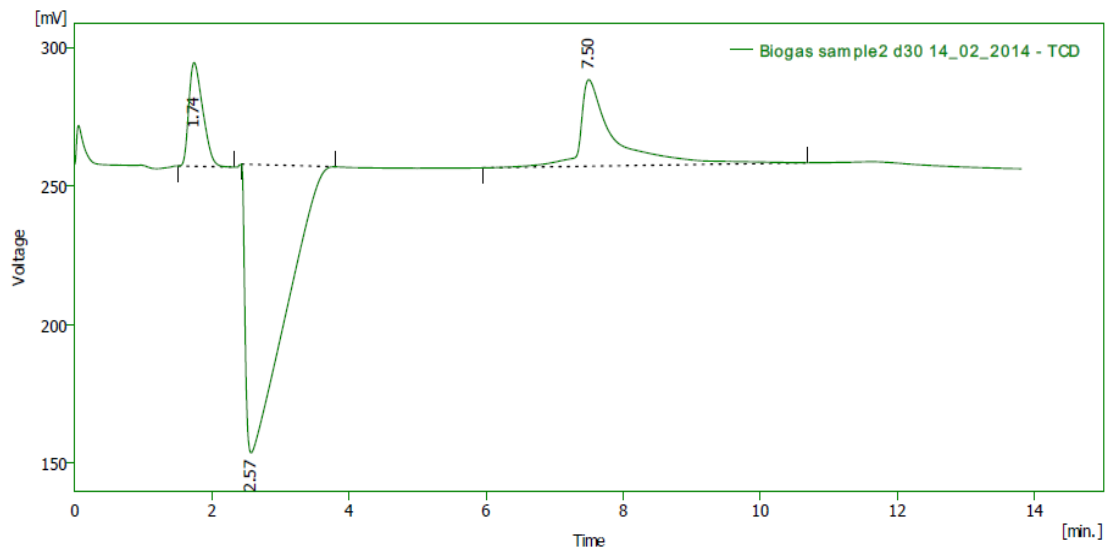
Replication	Cake	MR	HRT	CH ₄ Content (%)
1	1	1	1	9.7
1	1	1	2	19.1
1	1	1	3	13.9
1	1	2	1	6.0
1	1	2	2	10.6
1	1	2	3	25.7

1	1	3	1	1.3
1	1	3	2	11.6
1	1	3	3	28.3
1	1	4	1	78.9
1	1	4	2	81.0
1	1	4	3	74.6
1	2	1	1	73.9
1	2	1	2	75.9
1	2	1	3	73.8
1	2	2	1	43.5
1	2	2	2	54.9
1	2	2	3	65.9
1	2	3	1	33.4
1	2	3	2	40.5
1	2	3	3	43.7
1	2	4	1	78.9
1	2	4	2	81.0
1	2	4	3	74.6
2	1	1	1	9.5
2	1	1	2	19.3
2	1	1	3	14.2
2	1	2	1	6.2
2	1	2	2	10.5
2	1	2	3	25.6
2	1	3	1	1.5
2	1	3	2	11.5
2	1	3	3	28.1
2	1	4	1	80.2
2	1	4	2	81.3
2	1	4	3	74.5
2	2	1	1	73.8
2	2	1	2	76.2
2	2	1	3	74.0
2	2	2	1	43.9
2	2	2	2	54.5
2	2	2	3	66.3
2	2	3	1	33.2
2	2	3	2	40.6
2	2	3	3	43.6
2	2	4	1	80.2
2	2	4	2	81.3
2	2	4	3	74.5
3	1	1	1	9.9
3	1	1	2	18.9
3	1	1	3	28.5

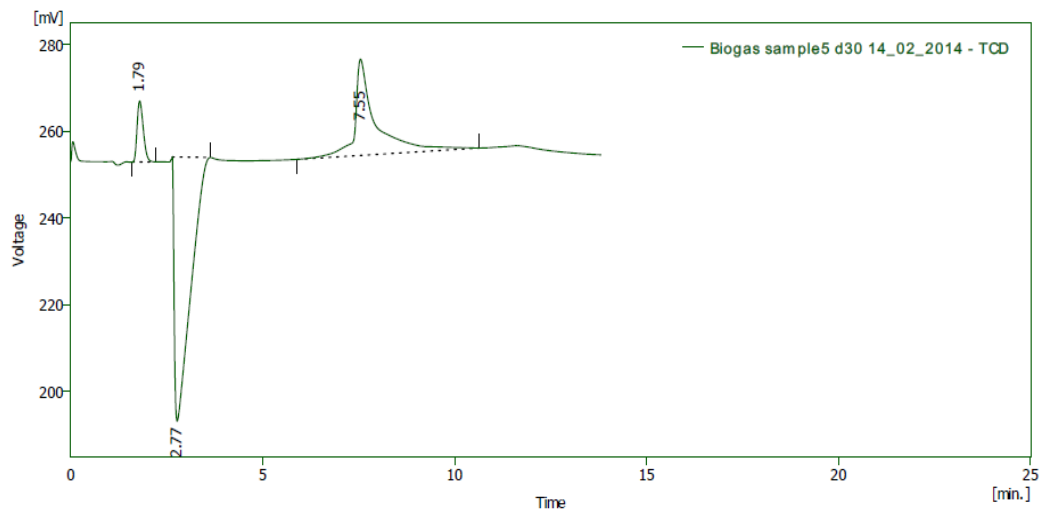
3	1	2	1	6.1
3	1	2	2	10.7
3	1	2	3	25.9
3	1	3	1	1.4
3	1	3	2	11.7
3	1	3	3	13.8
3	1	4	1	78.4
3	1	4	2	80.5
3	1	4	3	74.4
3	2	1	1	74.2
3	2	1	2	75.5
3	2	1	3	73.8
3	2	2	1	43.4
3	2	2	2	55.6
3	2	2	3	65.7
3	2	3	1	33.7
3	2	3	2	40.3
3	2	3	3	43.9
3	2	4	1	78.4
3	2	4	2	80.5
3	2	4	3	74.4

Fig. A.1 GC data acquisition graphs of biogas on 30th days of observation

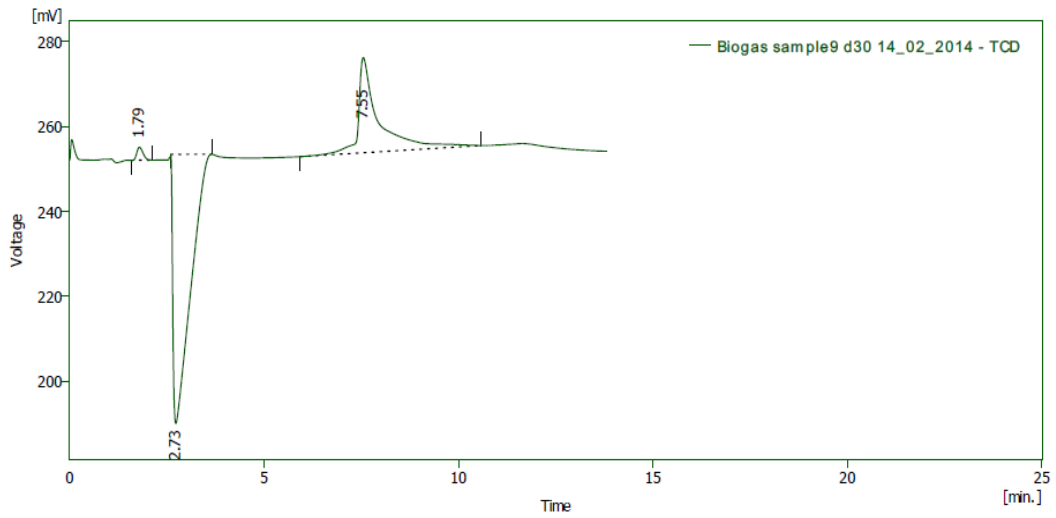
Slurry: 15%KOC+85%CD: Methane area: 9.7%



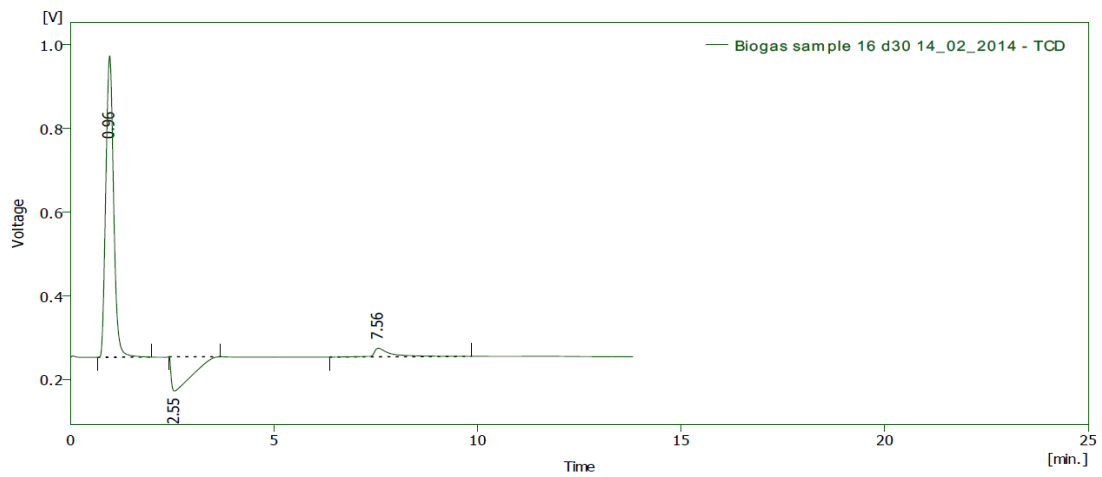
Slurry: 30%KOC+70%CD: Methane area: 6 %



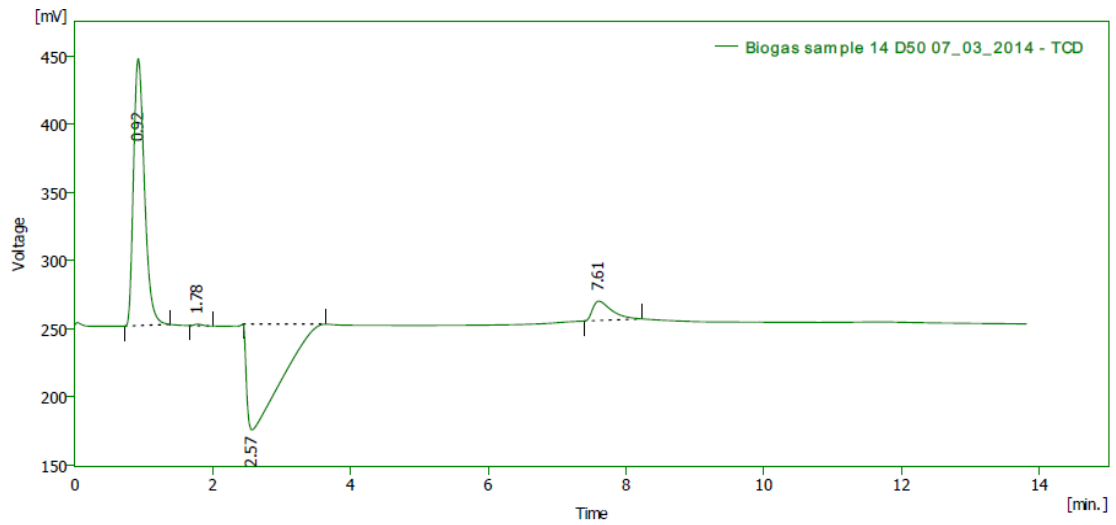
Slurry: 45%KOC+55%CD: Methane area: 1.3 %



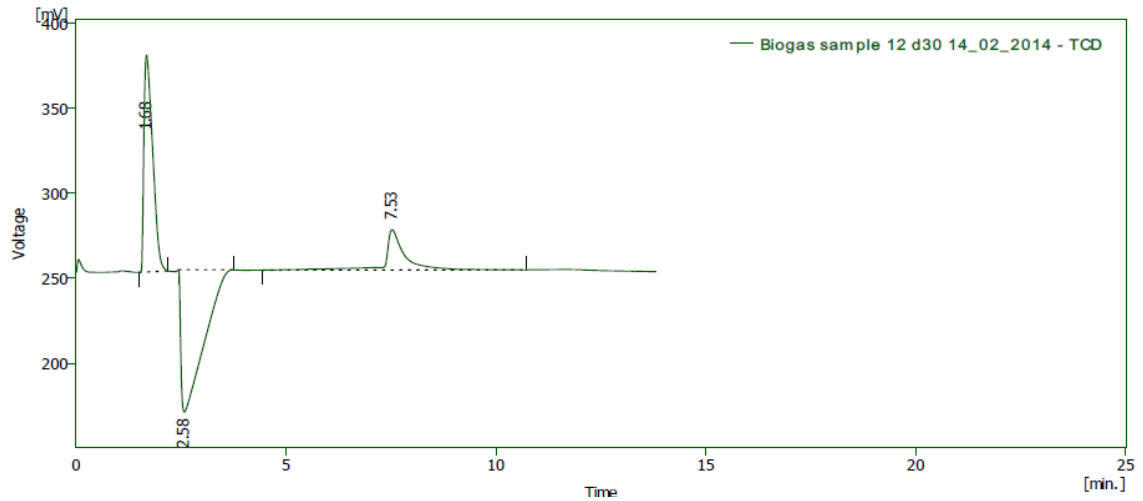
Slurry: 15%POC+85%CD: Methane area: 74.0 %



Slurry: 30%POC+70%CD: Methane area: 43.5%



Slurry: 45%POC+55%CD: Methane area: 33.4 %



Slurry: 100 % CD: Methane area: 78.9 %

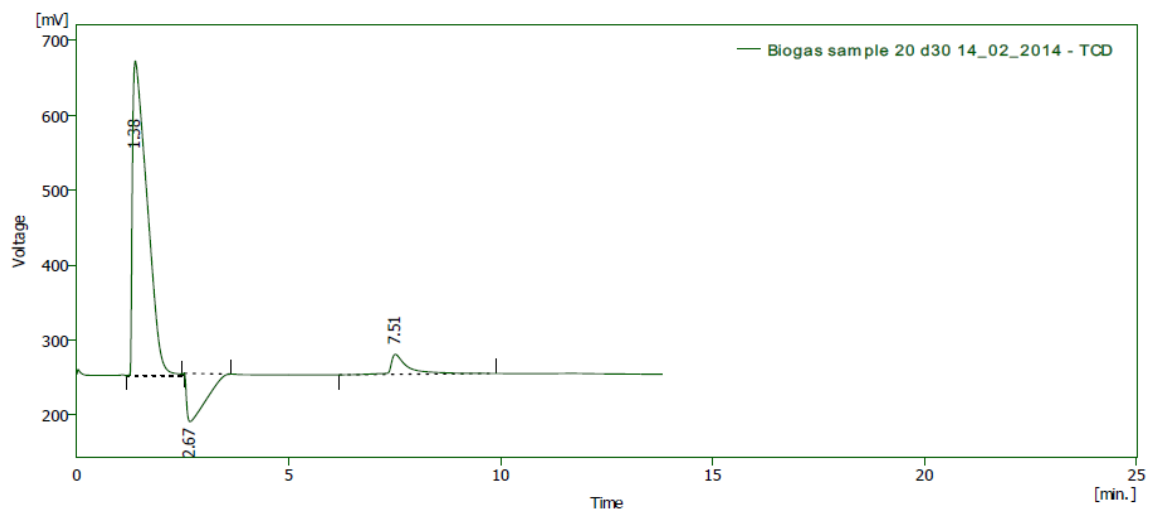
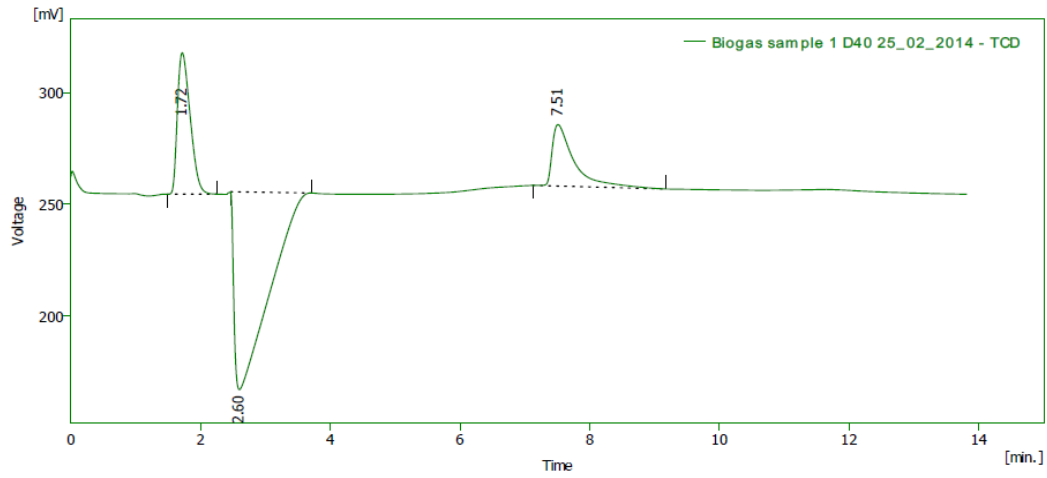
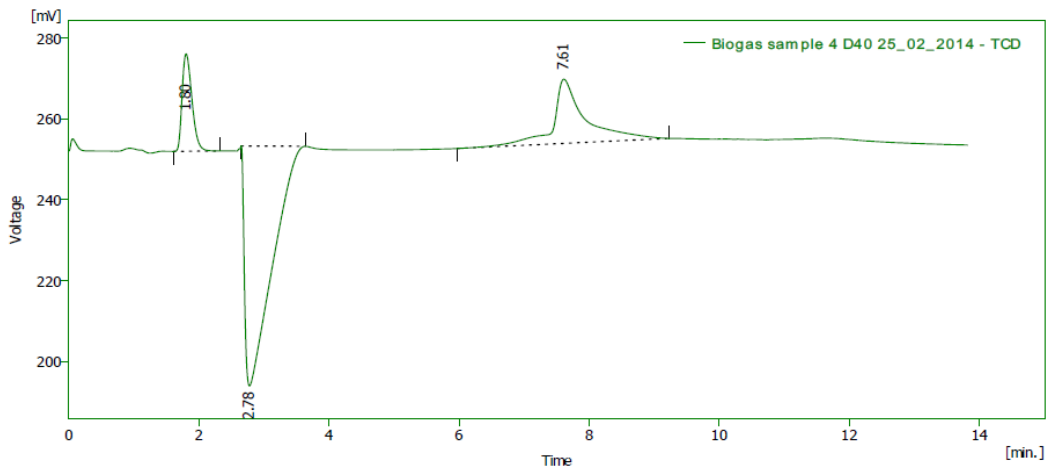


Fig. A.2 GC data acquisition graphs of biogas on 40th days of observation

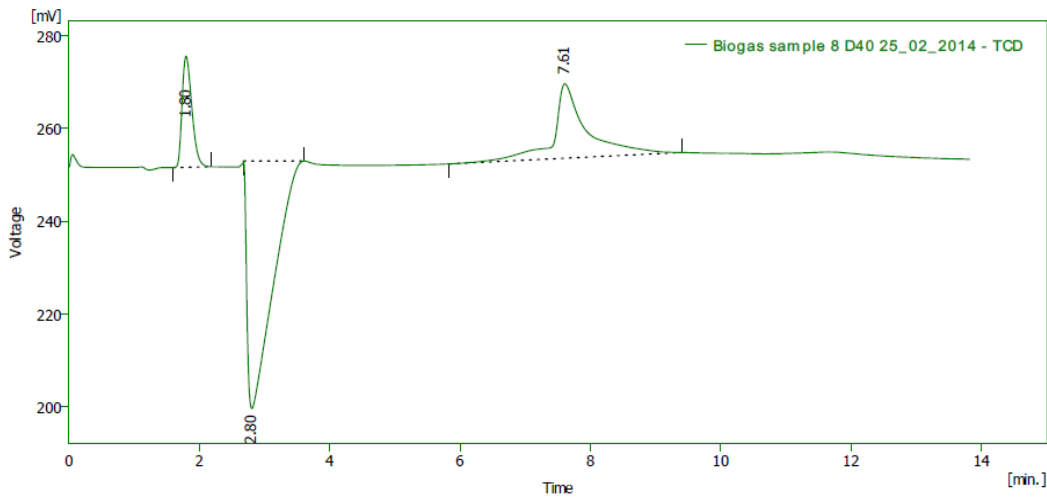
Slurry: 15%KOC+85%CD: Methane area: 19.1%



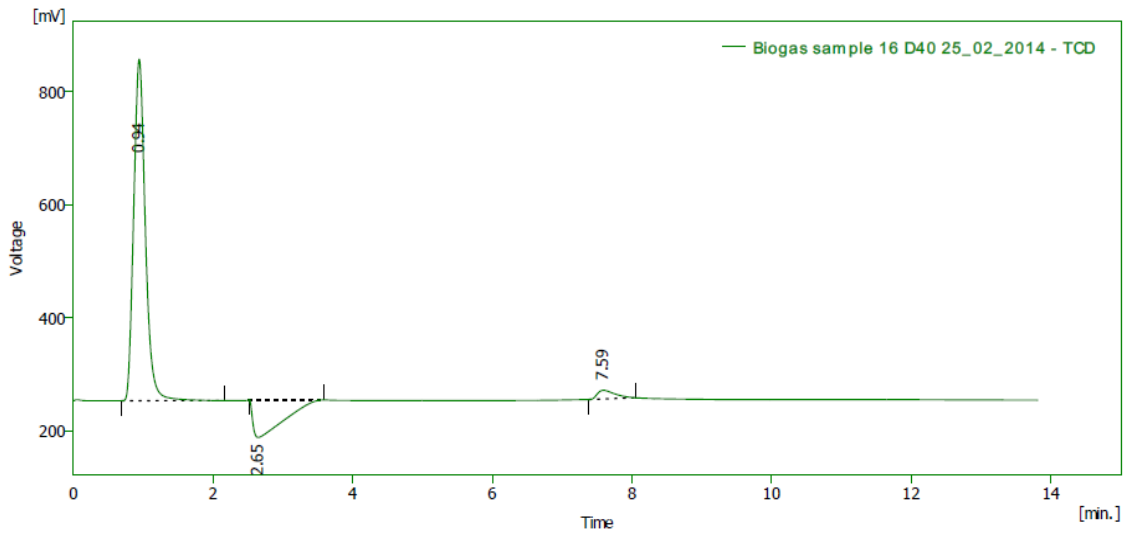
Slurry: 30%KOC+70%CD: Methane area: 10.6 %



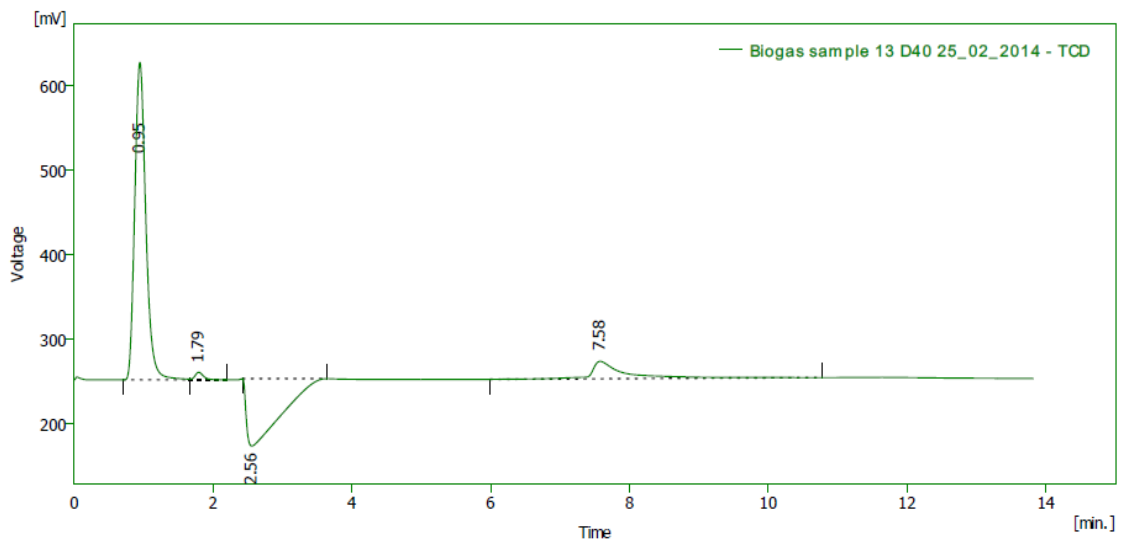
Slurry: 45%KOC+55%CD: Methane area: 11.6 %



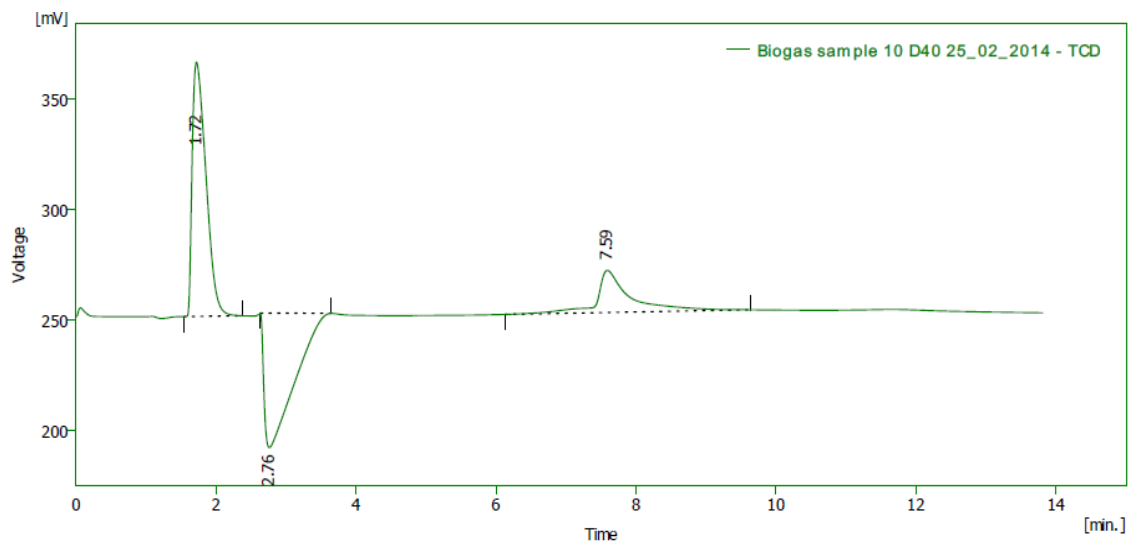
Slurry: 15%POC+85%CD: Methane area: 75.9 %



Slurry: 30%POC+70%CD: Methane area: 54.9 %



Slurry: 45%POC+55%CD: Methane area: 40.5 %



Slurry: 100 % CD: Methane area: 81.0 %

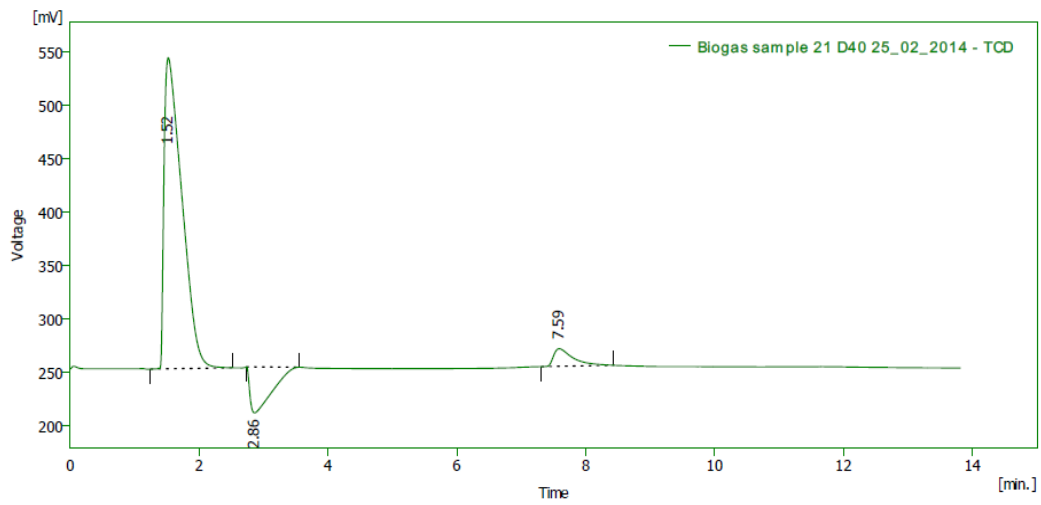
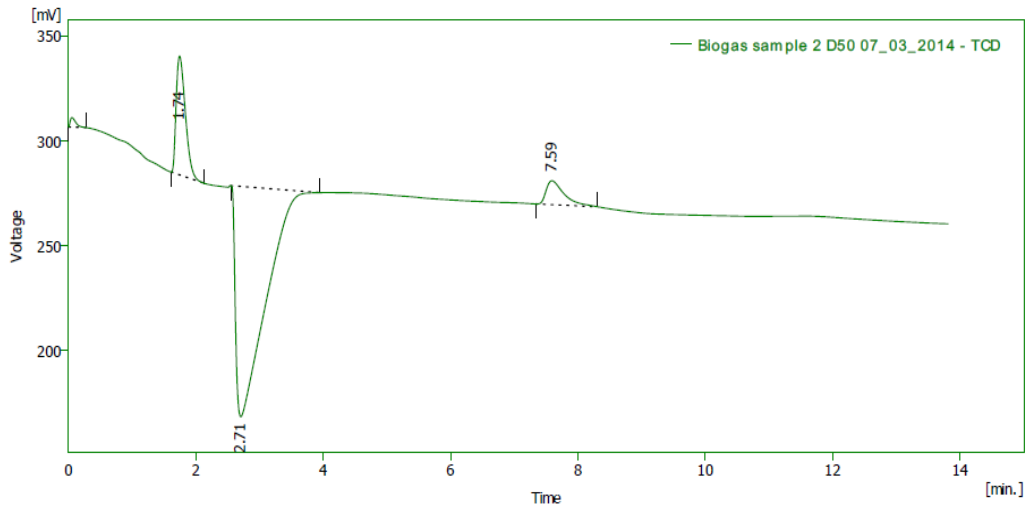
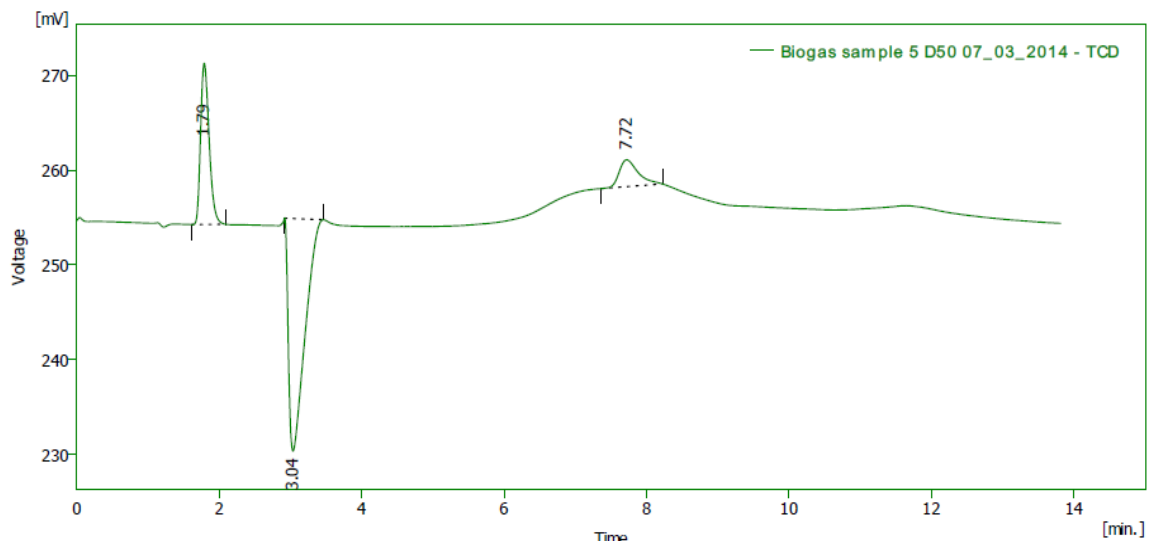


Fig. A.3 GC data acquisition graphs of biogas on 50th days of observation

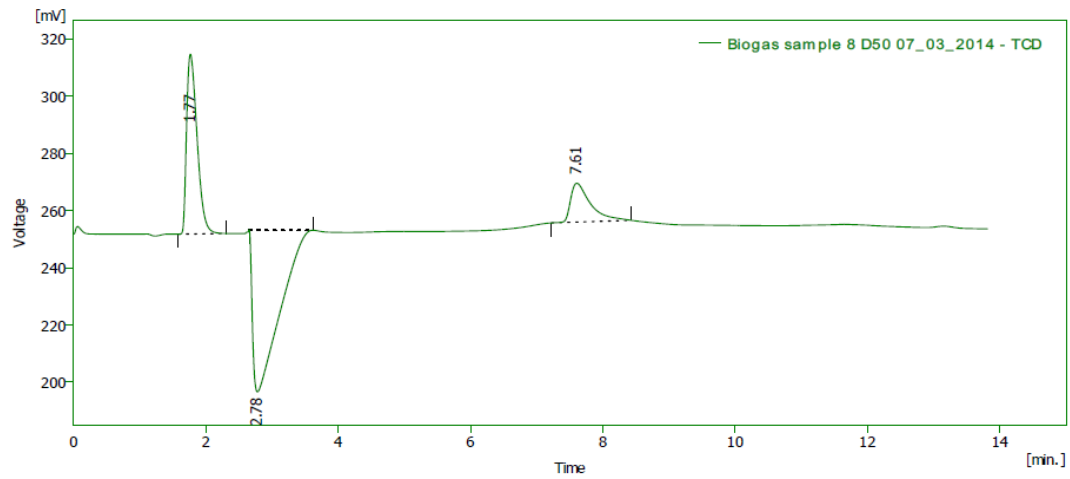
Slurry: 15%KOC+85%CD: Methane area: 13.9%



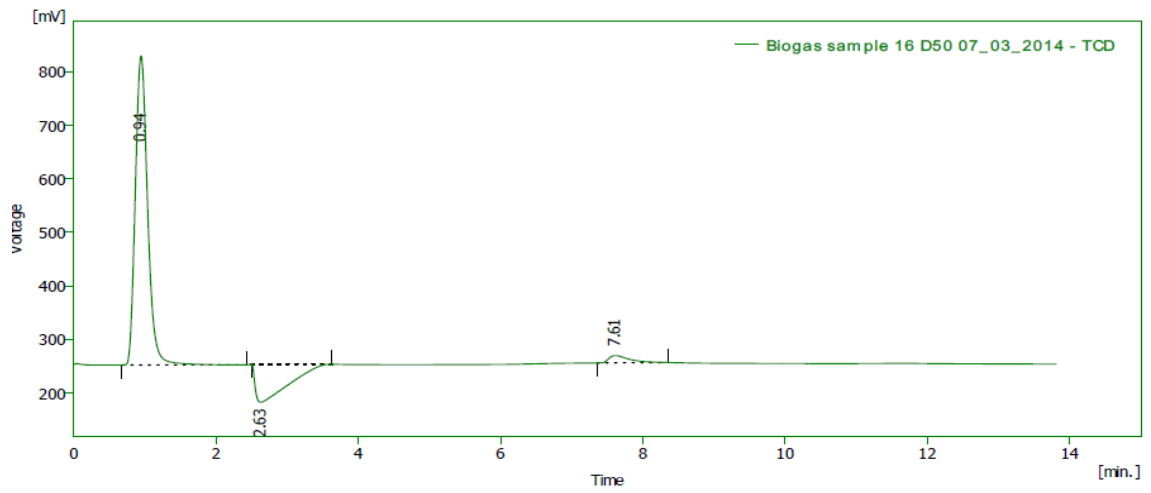
Slurry: 30%KOC+70%CD: Methane area: 25.7%



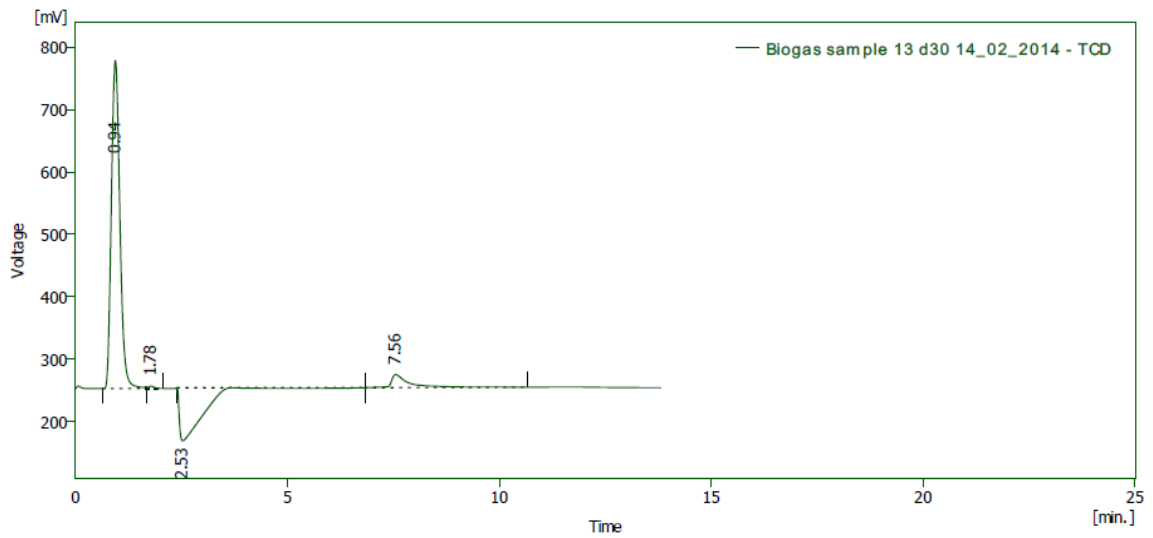
Slurry: 45%KOC+55%CD: Methane area: 28.3%



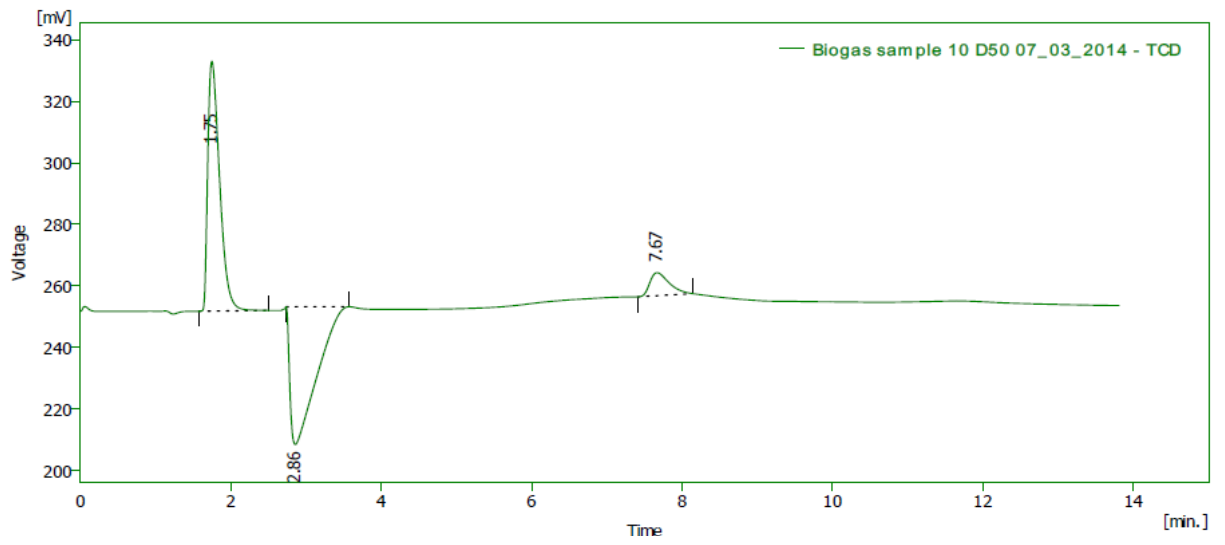
Slurry: 15%POC+85%CD: Methane area: 73.8%



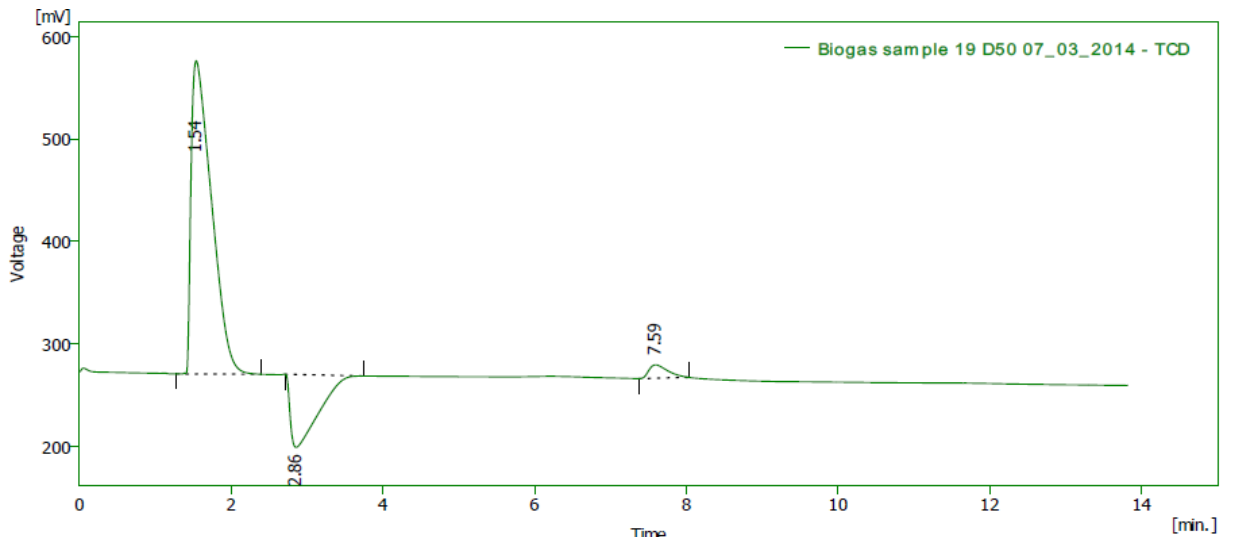
Slurry: 30%POC+70%CD: Methane area: 65.9 %



Slurry: 45%POC+55%CD: Methane area: 43.7%



Slurry: 100 % CD: Methane area: 74.6 %



APPENDIX B

B.1 Statistical analysis

Analysis of variance for the effect of type of cake used, mixing ratio (MR) and retention time (RT) on quantity of biogas produced and methane (CH₄) content was derived from ANOVA. The details of the variation on quantity of biogas produced and methane content of that biogas are given below in Table. A. 4.

Table B.1 ANOVA analysis data

```
Data file:SUSHREE
Title:      mishra
Function:   FACTOR
Experiment Model Number 5:
Completely Randomized Design for Factors A and B, Factor C is a Split Plot on A
and B
Data case no. 1 to 72.
Factorial ANOVA for the factors:
Replication (Var 1: replication) with values from 1 to 3
Factor A (Var 2: cake) with values from 1 to 2
Factor B (Var 3: mixing ratio) with values from 1 to 4
Factor C (Var 4: retention time) with values from 1 to 3
Variable 5: quantity
Grand Mean = 2.689   Grand Sum = 193.597   Total Count = 72
```

T A B L E O F M E A N S

1	2	3	4	5	Total

*	1	*	*	2.383	85.780
*	2	*	*	2.995	107.817

*	*	1	*	2.613	47.040
*	*	2	*	2.343	42.175
*	*	3	*	2.717	48.897
*	*	4	*	3.082	55.485

*	1	1	*	2.444	21.997
*	1	2	*	1.803	16.225
*	1	3	*	2.202	19.815
*	1	4	*	3.082	27.742
*	2	1	*	2.783	25.043
*	2	2	*	2.883	25.950
*	2	3	*	3.231	29.082
*	2	4	*	3.082	27.742

*	*	*	1	2.225	53.392
*	*	*	2	2.726	65.412
*	*	*	3	3.116	74.792

*	1	*	1	1.955	23.460
*	1	*	2	2.400	28.805
*	1	*	3	2.793	33.515
*	2	*	1	2.494	29.932
*	2	*	2	3.051	36.608
*	2	*	3	3.440	41.278

*	*	1	1	2.179	13.075
*	*	1	2	2.633	15.800
*	*	1	3	3.028	18.165
*	*	2	1	1.922	11.530
*	*	2	2	2.366	14.197
*	*	2	3	2.741	16.448
*	*	3	1	2.268	13.608

*	*	3	2	2.767	16.600
*	*	3	3	3.115	18.690
*	*	4	1	2.530	15.180
*	*	4	2	3.136	18.815
*	*	4	3	3.582	21.490

*	1	1	1	2.067	6.202
*	1	1	2	2.460	7.380
*	1	1	3	2.805	8.415
*	1	2	1	1.471	4.412
*	1	2	2	1.800	5.400
*	1	2	3	2.138	6.413
*	1	3	1	1.752	5.255
*	1	3	2	2.206	6.617
*	1	3	3	2.647	7.942
*	1	4	1	2.530	7.590
*	1	4	2	3.136	9.408
*	1	4	3	3.582	10.745
*	2	1	1	2.291	6.873
*	2	1	2	2.807	8.420
*	2	1	3	3.250	9.750
*	2	2	1	2.372	7.117
*	2	2	2	2.933	8.798
*	2	2	3	3.345	10.035
*	2	3	1	2.784	8.352
*	2	3	2	3.327	9.982
*	2	3	3	3.582	10.747
*	2	4	1	2.530	7.590
*	2	4	2	3.136	9.408
*	2	4	3	3.582	10.745

A N A L Y S I S O F V A R I A N C E T A B L E

K Value	Source	Degrees of Freedom	Sum of Squares	Mean Square	F Value	Prob
2	Factor A	1	6.745	6.745	5.5794	0.0312
4	Factor B	3	5.058	1.686	1.3946	0.2807
6	AB	3	3.796	1.265	1.0465	0.3990
-7	Error	16	19.343	1.209		
8	Factor C	2	9.589	4.795	233.4872	0.0000
10	AC	2	0.048	0.024	1.1615	0.3259
12	BC	6	0.112	0.019	0.9111	
14	ABC	6	0.092	0.015	0.7441	
-15	Error	32	0.657	0.021		
	Total	71	45.440			

s_	for means group 2:	0.1833	Number of Observations: 36
y			
s_	for means group 4:	0.2592	Number of Observations: 18
y			
s_	for means group 6:	0.3665	Number of Observations: 9
y			
s_	for means group 8:	0.0293	Number of Observations: 24
y			
s_	for means group 10:	0.0414	Number of Observations: 12
y			
s_	for means group 12:	0.0585	Number of Observations: 6
y			
s_	for means group 14:	0.0827	Number of Observations: 3
y			

=====
Variable 6: quality

Grand Mean = 45.900 Grand Sum = 3304.800 Total Count = 72
 T A B L E O F M E A N S

1	2	3	4	6	Total
* 1 *	1	*	*	30.092	1083.300
* 2 *	2	*	*	61.708	2221.500
* *	1	*	*	45.228	814.100
* *	2	*	*	34.500	621.000
* *	3	*	*	25.672	462.100
* *	4	*	*	78.200	1407.600
* 1 1 *	1	1	*	15.889	143.000
* 1 2 *	1	2	*	14.144	127.300
* 1 3 *	1	3	*	12.133	109.200
* 1 4 *	1	4	*	78.200	703.800
* 2 1 *	2	1	*	74.567	671.100
* 2 2 *	2	2	*	54.856	493.700
* 2 3 *	2	3	*	39.211	352.900
* 2 4 *	2	4	*	78.200	703.800
* * *	1	*	1	40.817	979.600
* * *	2	*	2	46.813	1123.500
* * *	3	*	3	50.071	1201.700
* 1 * 1	1	*	1	24.092	289.100
* 1 * 2	1	*	2	30.558	366.700
* 1 * 3	1	*	3	35.625	427.500
* 2 * 1	2	*	1	57.542	690.500
* 2 * 2	2	*	2	63.067	756.800
* 2 * 3	2	*	3	64.517	774.200
* * 1 1	*	1	1	41.833	251.000
* * 1 2	*	1	2	47.483	284.900
* * 1 3	*	1	3	46.367	278.200
* * 2 1	*	2	1	24.850	149.100
* * 2 2	*	2	2	32.800	196.800
* * 2 3	*	2	3	45.850	275.100
* * 3 1	*	3	1	17.417	104.500
* * 3 2	*	3	2	26.033	156.200
* * 3 3	*	3	3	33.567	201.400
* * 4 1	*	4	1	79.167	475.000
* * 4 2	*	4	2	80.933	485.600
* * 4 3	*	4	3	74.500	447.000
* 1 1 1	1	1	1	9.700	29.100
* 1 1 2	1	1	2	19.100	57.300
* 1 1 3	1	1	3	18.867	56.600
* 1 2 1	1	2	1	6.100	18.300
* 1 2 2	1	2	2	10.600	31.800
* 1 2 3	1	2	3	25.733	77.200
* 1 3 1	1	3	1	1.400	4.200
* 1 3 2	1	3	2	11.600	34.800
* 1 3 3	1	3	3	23.400	70.200
* 1 4 1	1	4	1	79.167	237.500
* 1 4 2	1	4	2	80.933	242.800
* 1 4 3	1	4	3	74.500	223.500
* 2 1 1	2	1	1	73.967	221.900
* 2 1 2	2	1	2	75.867	227.600
* 2 1 3	2	1	3	73.867	221.600
* 2 2 1	2	2	1	43.600	130.800
* 2 2 2	2	2	2	55.000	165.000
* 2 2 3	2	2	3	65.967	197.900
* 2 3 1	2	3	1	33.433	100.300
* 2 3 2	2	3	2	40.467	121.400

*	2	3	3	43.733	131.200
*	2	4	1	79.167	237.500
*	2	4	2	80.933	242.800
*	2	4	3	74.500	223.500

 A N A L Y S I S O F V A R I A N C E T A B L E

K Value	Source	Degrees of Freedom	Sum of Squares	Mean Square	F Value	Prob
2	Factor A	1	17993.045	17993.045	3058.0195	0.0000
4	Factor B	3	28491.568	9497.189	1614.1008	0.0000
6	AB	3	8258.525	2752.842	467.8610	0.0000
-7	Error	16	94.142	5.884		
8	Factor C	2	1057.651	528.825	89.3831	0.0000
10	AC	2	69.491	34.745	5.8727	0.0067
12	BC	6	1315.015	219.169	37.0444	0.0000
14	ABC	6	149.219	24.870	4.2036	0.0032
-15	Error	32	189.324	5.916		
Total		71	57617.981			

 Coefficient of Variation: 5.30%

s_	for means group 2:	0.4043	Number of Observations: 36
Y			
s_	for means group 4:	0.5717	Number of Observations: 18
Y			
s_	for means group 6:	0.8086	Number of Observations: 9
Y			
s_	for means group 8:	0.4965	Number of Observations: 24
Y			
s_	for means group 10:	0.7022	Number of Observations: 12
Y			
s_	for means group 12:	0.9930	Number of Observations: 6
Y			
s_	for means group 14:	1.4043	Number of Observations: 3
Y			

APPENDIX C

Table C.1 Engine specification

Make	Kirloskar
Model	TAF 1
Rated brake power (bhp/kW)	6/4.4
Rated speed (RPM)	1500
Number of cylinder	One
Bore (mm)	87.5
Stroke (mm)	110
Compression ratio	17.5: 1
Specific fuel consumption (gm/bhp/hr)	185
Cooling system	Air cooled

Table C.2 Generator specification

Make	Kirloskar
Model	KBM 103
Output (kVa)	3
Volt	230
Ampere	13
Frequency (Hz)	50
Phase	Single phase line
Speed (RPM)	1500
Power factor	1
Generator efficiency, %	95

Table C.3 Fuel consumption

loads,kW	Fuel Consumption, kg/hr	
	Diesel	Diesel + biogas
0	0.575	0.463
0.5	0.580	0.492
1	0.621	0.578
2	0.738	0.717
3	0.960	0.901
4	1.075	0.976