Investigations on Co-digestion Scenarios of Agricultural and Municipal Organic Wastes for Enhanced Biogas Production

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By

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CERTIFICATE

This is to certify that the thesis titled **"Investigations on Co-Digestion Scenarios of Agricultural And Municipal Organic Wastes For Enhanced Biogas Production"** by Muramreddy Jugal Sukhesh is a bonafide research work carried out under my supervision and submitted to the Department of Civil Engineering, National Institute of Technology, Warangal for the award of degree of Doctor of Philosophy in Civil Engineering and has not been submitted elsewhere for the award of any degree or diploma.

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APPROVAL SHEET

This Thesis entitled "**Investigations on Co-digestion Scenarios of Agricultural and Municipal Organic Wastes for Enhanced Biogas Production**" by **Mr. Muramreddy Jugal Sukhesh** is approved for the degree of Doctor of Philosophy.

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DECLARATION

This is to certify that the work presented in the thesis entitled **"Investigations on Co-digestion Scenarios of Agricultural and Municipal Organic Wastes for Enhanced Biogas Production"** is a bonafide work done by me under the supervision of **Dr. P. Venkateswara Rao** and was not submitted elsewhere for the award of any degree. I declare that this written submission represents my ideas in my own words and where others ideas or words have been included, I have adequately cited and referenced the original sources. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea / data / fact /source in my submission. I understand that any violation of the above will be a cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

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Abstract

Increase in urbanization and consumption standards have been leading to the generation of different kinds of organic wastes from municipalities, agricultural and food-based industries. The generation of organic wastes and its open dumping causes unhygienic conditions. The open burning of organic wastes contributes to greenhouse gas emissions (GHGs), subsequently resulting in climate change. The increase in energy demand and continuous escalation of prices compel to look for self-reliable, cost effective, and environmentally friendly alternatives for energy production. Anaerobic digestion (AD) manages organic wastes with generation of energy in the form of biogas in an environmentally friendly manner. Even though AD is being encouraged with current guidelines of the Government of India, the method is not being implemented at its optimal capacities for organic waste management. One of the major reasons is that most of the AD plants are designed for use by a single feedstock. The lack of continuous feedstock supply makes the plants non-operational occasionally leading to the plant becoming non-functional. Further rejuvenation of AD system requires technical expertise. The difficulty can be solved with co-digestion of suitable organic wastes at optimal proportions. The present work aims to utilize the available, widely generating organic wastes for co-digestion in Warangal as well as other parts of the country. The work is carried out in three phases.

In Phase I, several agricultural crop residues are studied for energy generation through AD in the Indian context. The crop residues generating in India are estimated for their bio-energy potential and environmental impact for AD. It is observed that the usage of surplus rice, wheat, and maize crop residues as a feedstock for AD has bio-energy potential of 653×10^9 MJ/year. The bio-energy potential of surplus crop residues could substitute 52 Mt/year of coal from consumption. It is also observed that the AD of these residues could avoid 46 Mt GHG (CO_2) emissions/year from being released into the atmosphere.

In Phase-II, seven organic wastes that are widely being generated in the study area are identified based on local abundance, seasonal availability, economic feasibility and compatibility with AD. The identified organic wastes are lawn grass (LG), food waste (FW), fruit & vegetable waste (FVW), citrus pulp waste (CP), rice straw (RS), chicken manure (CM), and dairy manure (DM). The organic wastes are characterised for proximate and elemental analysis. Based on their

characterization four combinations of organic wastes are chosen. The four combinations of organic wastes are investigated for their co-digestion behaviour in four sets. Set I comprises CM and FVW, Set II comprises CM, CP, and LG, Set III comprises DM, FW, and FVW, and Set IV comprises DM and RS.

In Set-I, co-digestion experiments are carried out with CM and FVW as a feedstock for AD. Three variables viz., proportion of FVW (20-60 %), total solids (3-9 TS %) and inoculum to substrate (I/S) ratio (0.5-1.5) that influence the AD are chosen as variables. The experimental design is carried out with central composite design (CCD) and biogas production is analysed with response surface methodology (RSM). It is observed that with an increase in proportion of FVW (%) and total solids (TS %) in co-digestion resulted in an increase in biogas production till about 40 % and 7 %, and decreased thereafter respectively. The decreased biogas production may be due to the rapid acidification at high proportion of FVW and total solids (TS %). However, the I/S ratio is found to be not having any significant effect on biogas production. The maximum biogas production can be obtained with FVW (%) of 42 %, CM (%) of 58 %, and total solids (TS %) of 7.3%.

In Set II, co-digestion experiments are continued with CM, while choosing LG and CP as the co-digesting feedstock. The experimental design and analysis of biogas production are again carried out with CCD and RSM respectively, however the organic wastes are individually loaded at various total solids (TS %) loading and C/N ratios. It is observed that biogas production is found to be impacted more with respect to total solids (TS %) loading than C/N ratio of the co-digestion mix. The relative low influence of C/N ratio may be due to the prevalence of optimal C/N ratio of 16-33 in all co-digestion mixes. The maximum biogas production can be obtained with CP of 2 %, LG of 68 %, and CM of 29 %.

In Set-III, co-digestion experiments are continued with DM, FW, and FVW at various volume mix proportions. The experimental design and analysis of biogas production are carried out with simplex centroid mixture design (SCMD) and RSM respectively. It is observed that co-digestion of three organic wastes is better than co-digestion of two organic wastes due to more synergistic effect. The maximum biogas production can be obtained with DM of 40 %, FW of 26 %, and FVW of 34 %.

In Set IV, co-digestion experiments are continued with DM and RS as a co-digesting feedstock at various volume mix proportions. The kinetic behaviour of seven mix proportions of RS and DM (1:0,1:5,1;3, :1,1:3 ,1:5 and 0:5) is investigated with modified Gompertz model. It is observed that the co-digestion of organic wastes favoured the kinetic behaviour in terms of reduced lag phase time (5.7 days), improved process rate (5.8 mL of CH_4/g of VS. day) and improved biogas production (239.3 mL CH_4/g .VS). The maximum biogas production can be obtained for mix proportions RS and DM of 1:1, 1:3 and 1:5 with the highest being the mix proportion of 1:1.

In Phase -III, the energy and economic benefits are quantified for the mix proportions of four sets that maximise biogas production in Phase-II. In order to evaluate the net thermal and electrical energy production from AD process, several unit processes that consume energy are considered. The benefits are quantified in terms of cost of energy production and payback period. It is observed that among the organic waste mix combinations investigated, the co-digestion of Set IV (DM + RS) registered low cost of energy (Rs 1.9/- per kWh) and low pay-back period (2.0 years) on investment compared to other co-digestion mixes. The three organic waste mixes are financially feasible and preferable in the order of Set IV (DM + RS) > Set II (CM + CP + LG) > Set III (DM + FW + FVW).

The present study states that the single organic waste as a feedstock for AD may not be a wise option and recommends the co-digestion of various organic wastes for field scale implementation. The rural and municipal solid waste management authorities can adopt an appropriate policy for the collection and transportation of the suitable organic wastes to generate bio-energy and effective management of organic wastes.

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List of Acronyms

AD	Anaerobic Digestion
ANOVA	Analysis Of Variance
CCD	Central Composite Design
CCR	Capital Charge Rate
CHP	Combined Heat and Power generation
CM	Chicken Manure
C/N	Carbon to Nitrogen ratio
CP	Citrus Pulp
C_T	Total Annual Cost
DM	Dairy Manure
E_c	Electrical Energy Consumption
E_p	Electrical Energy Production
FVW	Fruit and Vegetable Waste
FW	Food Waste
GHG	Green House Gas emissions
HRT	Hydraulic Retention Time
I/S ratio	Inoculum to Substrate Ratio
LG	Lawn Grass
M	Methane Potential
η	Efficiency
NPV	Net Present Value
O&M	Operation and Maintenance
P_m	Capacity of the Motor
R_m	Maximum Methane Production Rate
RS	Rice Straw
RSM	Response Surface Methodology

SCMD	Simplex Centroid Mixture Design
SRT	Solids Retention Time
t	Operating Time
T_c	Thermal Energy Consumption
T_p	Thermal Energy Production
TAN	Total Ammonia Nitrogen
TS	Total Solids
VS	Volatile Solids
VFA	Volatile Fatty Acids
Y	Methane Yield
λ	Lag Phase

Chapter 1 Introduction

The aim of this chapter is to describe the background of the topic, motivation, and objectives of the study. It concludes with an outline of the thesis structure.

1.1 Background

Energy plays a vital role in fostering the economic development and its shortage jeopardizes the growth of the nation (Hiloidhari et al., 2014). In India, a large fraction of energy demand is met by imported fossil fuels, which is affecting the country's economy (NITI Aayog, 2015). India Energy Security Scenarios (NITI Aayog, 2015) estimated that the share of fossil fuel imports may raise from 32% (in the year-2012) to 59 % (in the year - 2047). Green House Gas emissions (GHGs) may raise threefold from 1.7 tons per capita (in the year 2012) to 5.8 tons per capita (in the year 2047) with current use of fossil fuels which may affect the environment adversely. It is necessary to look for self-sustainable, environmental friendly alternate sources of energy for meeting the needs of the country.

Consistent growth of agricultural sector in India leading to the generation of different kinds of crop residues which need to be handled properly (Cardoen et al., 2015). It is estimated that 686 Mt of crop residues are generated annually and about 34% (234 Mt) of residues is surplus after the primary utilisation (Hiloidhari et al., 2014). The crop residues are potential energy sources due to their reasonably high calorific value, high volatile matter, and cellulose content (Balachandra, 2011; Hiloidhari et al., 2014). The crop residues in India would meet the energy demand partially if used properly. In this context, it is important to consider crop residues for energy generation.

Increase in urbanization and consumption standards leading to the generation of different kinds of organic waste from municipalities. The generation and open dumping of organic waste causes unhygienic conditions (Fig. 1.1). The open burning of organic waste contributes to the emission of GHGs and resulting in climate change (Kumar et al., 2015). Proper management of generated organic wastes is necessary for a clean and healthy environment.

1.2 Motivation

Landfilling, gasification, composting, and anaerobic digestion (AD) are commonly used methods for organic waste management in India (Chandra et al., 2012a; Singh and Gu, 2010). AD scores several advantages as it generates energy in the form of biogas and fertile rich digestate while stabilising the organic waste (Fig 1.2). The fertile rich digestate improves the nutrient content and texture of the soil when applied to land resulting in better crop productivity (Pathak et al. 2010). AD of organic waste is a carbon neutral process as the carbon in organic matter is converted to biogas is originally fixing by photosynthesis. Moreover, the renewable energy generated from AD minimises the use of fossil fuels and controls the emission of GHGs (Tonini et al., 2016). In view of these multiple advantages, the proposed research work is motivated to adopt AD for organic waste management.

Fig. 1.1 Municipal solid waste dumping yard Madikonda, Warangal, India

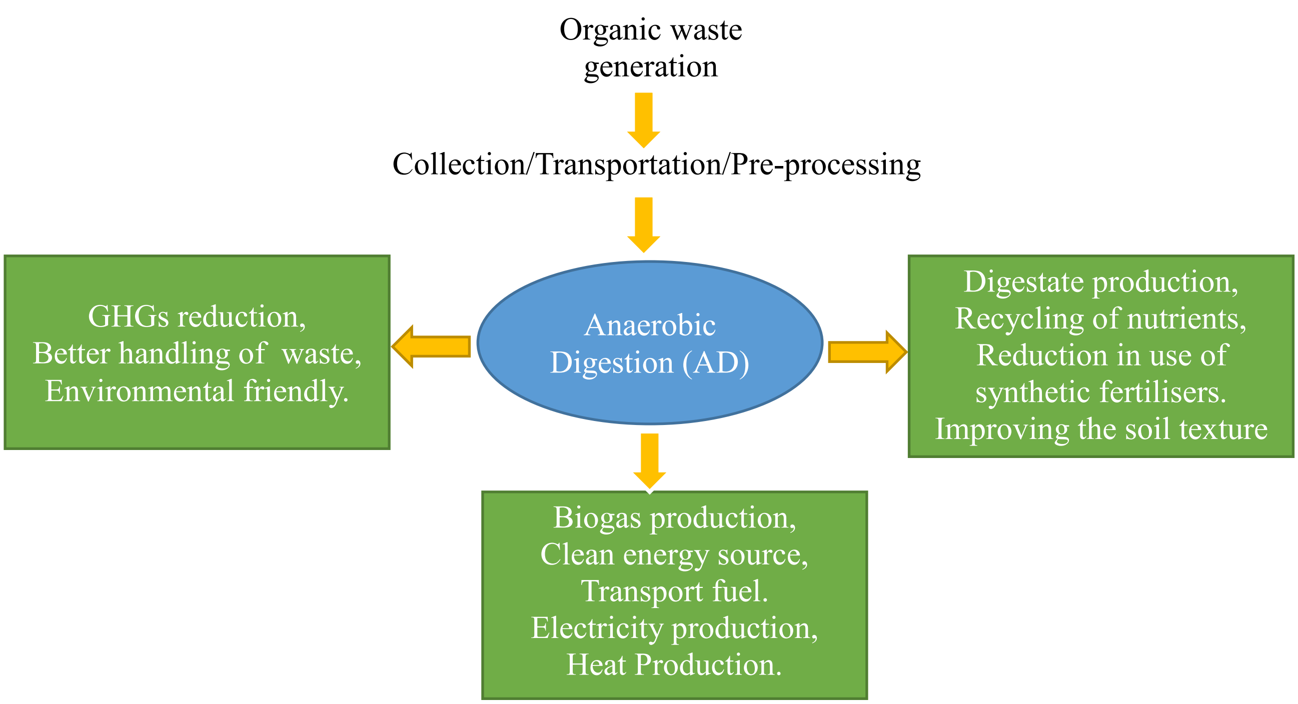

Fig. 1.2 Multiple benefits in AD

1.3 Anaerobic digestion (AD) process

AD is a biochemical process that degrades organic matter into biogas through a series of reactions and intermediary by-products in the absence of oxygen by a consortium of different microbial groups (Mussoline et al., 2012c). AD is one of the preferred methods used to manage organic wastes and popular in countries like Germany, Italy, and China for processing domestic, agricultural, and industrial organic wastes. AD converts a wide range of substances containing carbon atoms at different oxidation/reduction states to the most oxidized state (CO_2) and most reduced state (CH_4), collectively referred to as biogas. Minor amounts of other gases (<1 %) such as ammonia, nitrogen, hydrogen, and hydrogen sulphide can also be produced. AD is effectively used to manage the sludge generated in wastewater treatment plants (Pilli et al., 2016). The process results in lesser microbial biomass production compared to aerobic process. The process can be described in four sequential stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Fig. 1.3). The first stage is hydrolysis in which complex polymeric substances like carbohydrates, proteins, and lipids are hydrolyzed to monomers such as water-soluble sugars, amino acids, and long chain fatty acids. The second stage is called acidogenisis in which water-soluble monomers are converted to acids, alcohols, carbon dioxide and hydrogen. The third stage is acetogenesis in which products of acidogenesis are converted to acetic acid. The last stage is the most crucial stage called methanogenesis during which the formed intermediaries acetic acid, hydrogen, carbon dioxide are converted to biogas. The overall process efficiency depends on the balanced equilibrium of these four stages and are detailed as follows:

1.3.1 Hydrolysis

Organic matter is carbonaceous material comprising polymeric compounds such as carbohydrates, proteins, and lipids. Microorganisms cannot directly consume complex organic matter in the form of carbohydrates, proteins, or lipids. Hydrolysis is the first step that converts polymeric compounds into simple monomers. Extracellular enzymes released by fermentative bacteria break the polymeric compounds into their respective soluble substances such as sugars, amino acids, and fatty acids. Proteolytic bacteria release enzymes that solubilize proteins into amino acids. Cellulolytic bacteria and xylanolytic bacteria release enzymes that solubilize carbohydrates like cellulose and xylanose into simple glucose and xylose. Lipolytic bacteria release enzymes that solubilize lipids into long chain fatty acids and glycerol. Fermentative bacteria can easily absorb solubilized matter. Hydrolysis is often treated as rate limiting step for the lignocellulosic organic matter as lignin acts as a physical barrier that prevents the enzymatic attack of cellulose and hemicellulose. For this reason, lignocellulosic organic wastes degrades very slowly and thus yields low biogas production. For such organic wastes, the rate of biogas production depends on the rate of hydrolysis. Appropriate pre-treatment methods such as physical, chemical, and biological methods can improve hydrolysis. The hydrolysis of organic matter to glucose can be represented as follows (Eq. 1.1)

$$C_6H_{10}O_4 + 2\ H_2O \rightarrow C_6H_{12}O_6 + H_2 \qquad \text{Eq. 1.1}$$

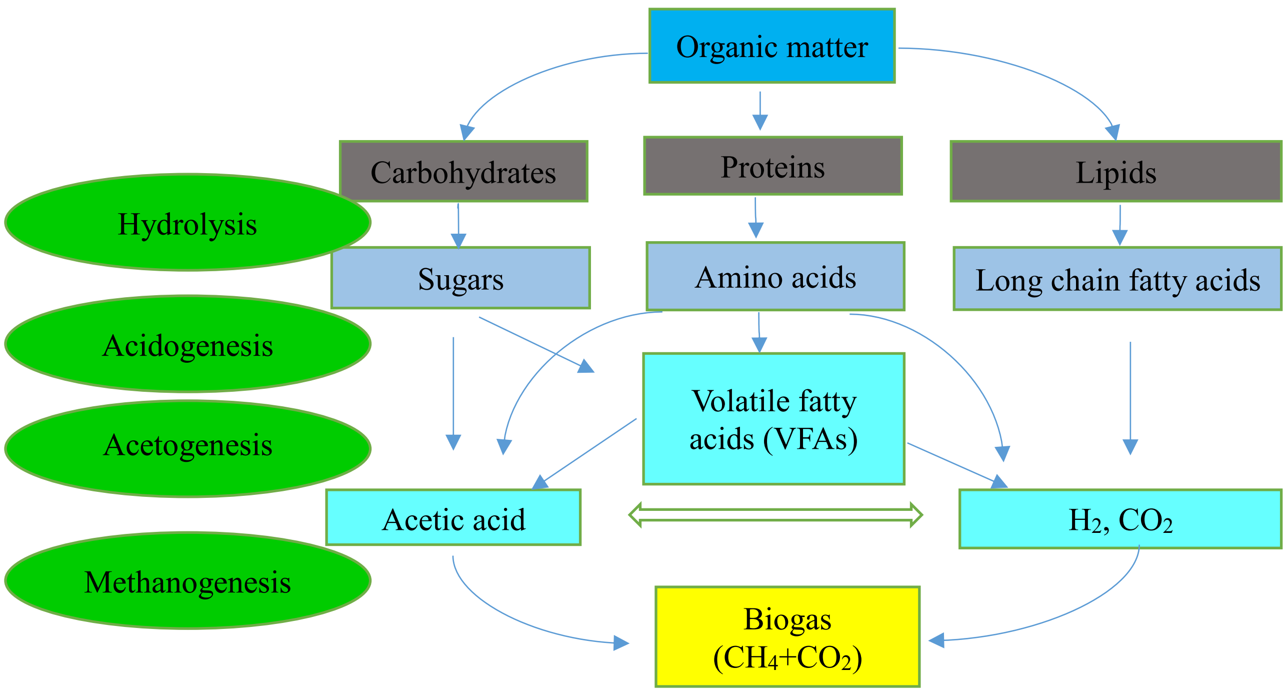

Fig. 1.3 Four stages of AD process (Mussoline et al., 2012c)

1.3.2 Acidogenesis

Hydrolysis is followed by acid forming stage known as acidogenesis. It converts the produced soluble matter in hydrolysis to methanogenic substrates (approximately 70 %) and non-methanogenic substrates (approximately 30 %). Methanogenic substrates comprise volatile fatty acids (VFAs), hydrogen, and carbon dioxide. Non-methanogenic substrates comprise lower fatty acids. The specific compounds formed at this stage vary with type of bacteria, pH, and temperature etc. Moreover, the presence of non-methanogenic substrates increases if the hydrogen formed is not consumed as fast as it is produced. Therefore, it is always important to have hydrogen at low partial pressure. Typical reactions in the acidogenesis are

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \quad \text{Eq. 1.2}$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O \quad \text{Eq. 1.3}$$

In equation (Eq. 1.2) glucose is converted to ethanol and CO_2. In equation (Eq. 1.3) glucose is converted to propionic acid. The accumulation of acids lowers the pH that may lead to the inhibition of methanogenic population required for subsequent stage of methanogenesis. In a well-functioning digester acidogenic population accounts for about 90% of total microbial population. Acidogenic microbial population grow relatively faster and are less sensitive to pH fluctuations compared to methanogenic population. Therefore, it is always important to avoid accumulation of acids in AD system.

1.3.3 Acetogenesis

The next stage is acetogenesis which is often considered to be part of acidogenesis. At this stage, the products of acidogenesis such as VFAs, hydrogen and carbon dioxide are converted to acetic acid. The bacteria involved are acetogenic bacteria, obligatory hydrogen-producing bacteria, and homeacetogenic bacteria. Acetogenic bacteria converts VFAs and alcohols to acetic acid. Obligatory hydrogen-producing bacteria converts protons (H^+) to hydrogen. Homoacetogenic bacteria converts H_2 and CO_2 to acetic acid. Acetogenesis requires a low partial pressure of hydrogen (<10^{-3} atm) as the high partial pressure of hydrogen inhibits propionate degradation as well as hydrogen formation from protons (H^+).

The following typical reactions i.e., conversion of propionate (Eq. 1.4), glucose (Eq. 1.5), ethanol (Eq. 1.6), and bicarbonate (Eq. 1.7) occur at this stage.

$$CH_3CH_2COO^- + 3\,H_2O \rightarrow CH_3COO^- + H^+ + HCO_3^- + 3H_2 \quad \text{Eq. 1.4}$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3CH_2COOH + 2CO_2 + 4H_2 \quad \text{Eq. 1.5}$$

$$CH_3CH_2OH + 2H_2O \rightarrow 2CH_3COO^- + H^+ + 2H_2 \quad \text{Eq. 1.6}$$

$$2HCO_3^- + H^+ + 4H_2 \rightarrow CH_3COO^- + H^+ + 4H_2O \quad \text{Eq. 1.7}$$

The acid forming stages may cause decrease in pH of the system. The low pH is beneficial to acidogenic and acitogenic bacteria as they prefer slightly acidic conditions (pH of 4.5-5.5). However, acidic conditions are problematic for methanogens involved in the next stage of methanogenesis. For a normal AD, acetic acid would prevail in the range of 50-250 mg/l. If the system balance is disturbed, the accumulation of VFAs continues to increase leading to a drop in pH. If corrective measures are not taken, the system may eventually fail.

1.3.4 Methanogenesis

Methanogenesis is the terminal step, which transforms acetate, hydrogen (H_2), and carbon dioxide (CO_2) to methane (CH_4). It occurs in two pathways one being acetoclastic/acetotrophic methanogenesis and the other hydrogenotrophic methanogenesis. The acetoclastic/acetotrophic methanogenesis converts acetic acid to methane which accounts for about 70 % of the total methane production (Eq. 1.8). Hydrogenotrophic methanogenesis converts H_2 and CO_2 to methane which accounts for about 30 % of the total methane production. (Eq. 1.9)

$$CH_3COOH \rightarrow CH_4 + CO_2 \qquad \text{Eq. 1.8}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \text{Eq. 1.9}$$

Methanogens prefers neutral to slightly alkaline conditions and are highly sensitive to pH fluctuations. If the pH drops below 6, methanogens cannot survive. Moreover, the growth of methanogens is slow compared to acidogens. For this reason, methanogenesis is considered as the critical stage.

Although AD is seen taking place in four stages, all the four stages occur syntrophically and simultaneously. The syntrophic relationship among the group of microorganisms in various stages is necessary for overall process balance (Rajesh Banu et al., 2018). The syntrophic relationship can be appropriately judged by the presence of intermediary compounds such as VFAs, pH, and alkalinity at appropriate levels. Several factors influence the presence of intermediary compounds and are detailed in Chapter 2.

1.4 Limitations of AD process

The efficiency and stability of AD depends on the characteristics of the feedstock, more specifically, it depends on the nutritional balance of feed for anaerobic microorganisms (Abudi et al., 2016a). Organic waste such as fruit waste is easily biodegradable and acidic in nature. High moisture and organic content in fruit waste facilitate improved AD (Scano et al., 2014; Shen et al., 2013). However, AD of fruit waste may cause rapid acidification of the process leading to a drop in pH, and subsequently low biogas production (Callaghan et al., 2002a; Shen et al., 2013). Animal manures have high nitrogen content due to the presence of uric acid and undigested protein. The high nitrogen content releases toxic ammonia nitrogen that may disturb the process leading to lower biogas production (Li et al., 2013b; Y. Li et al., 2014a). Rice straw generating in crop fields is also a potential substrate for AD (Chandra et al., 2012a). However, high lignin and carbon to nitrogen (C/N) ratio in rice straw causes low and slow degradation (Chandra et al., 2012b). These kind of limitations may result in unstable behaviour leading to lower biogas production in AD. Furthermore, AD systems in India are mostly limited to animal manure and sewage sludge in spite of several organic wastes being generated and available abundantly. In certain cases, AD systems are found to be non-functional due to the non-availability of specific feedstock for which it is designed. The inappropriate selection of organic wastes, composition, and operating conditions may lead to process instability and low biogas production. These limitations need to be addressed for efficient utilization of organic wastes in AD.

1.5 Aim and objectives of the thesis

The primary objective of the study is to maximize biogas production from AD of the organic wastes generating in Warangal and other parts of India. The specific objectives of the present work are:

i. Quantification of bio-energy potential and environmental impact for AD of crop residues generating in India.

ii. Identification of suitable scenarios for co-digestion of generating organic wastes through characterization.

iii. Evaluation of optimal proportion of organic wastes in co-digestion for maximising the biogas production.

iv. Evaluation of energy-economics of co-digestion for the optimized organic waste combinations.

1.6 Organization of the thesis

The present thesis detailed in seven chapters with first being the introduction and the last, conclusions.

Chapter 1 presents a brief overview on need for AD of organic wastes and states the scope of research. The motive of the thesis is to improve the efficiency of AD to maximize the generation of biogas from locally available organic wastes.

Chapter 2 presents literature review on influencing factors such as temperature, pH, alkalinity, organic loading, retention time, VFAs, substrate composition, nutritional requirement, and toxic materials like ammonia, heavy metals, and hydrogen sulphide. The chapter also presents strategies that can be considered for enhancing the process performance. An overview on recent research on co-digestion has been presented.

Chapter 3 presents preparation of substrates for AD, analytical, and experimental methods used in the study.

Chapter 4 presents crop residues for AD, bio-energy potential and its environmental impact in Indian context.

Chapter 5 presents organic wastes that are commonly generated in Warangal and their characteristics. Four combinations of organic wastes are chosen based on their characteristics to investigate the co-digestion behaviour. Experimental investigations on four co-digestion combinations for maximum biogas production are presented.

Chapter 6 presents the energy and economic prospects of co-digestion for the optimal organic waste mix combinations obtained in Chapter 5. The net thermal and electrical energy production along with cost of electrical energy production is presented.

Chapter 7 presents the significant conclusions drawn from the study and perspectives for future research work.

Chapter 2 Review of Literature

The present chapter aimed to describe the operational and design factors that influence the AD process and strategies to improve the process performance. The chapter also describes the co-digestion of organic wastes, and importance of modelling and energy economics. Summary is presented at the end of the Chapter.

2.1 Factors influencing the AD process

AD is a sensitive process and several operational and design factors influence its efficiency. Following section thoroughly reviews the influence of pH, alkalinity, temperature, total solids (TS %), nutritional balance, and toxic compounds on AD.

2.1.1 pH and alkalinity

pH and alkalinity are interrelated factors that indicate the stability of the AD process. AD mainly involves two microbial groups, one is an acid forming group, and another is the methane forming group. The acid forming group works effectively at a wider pH range of 5.5-6.5 whereas methane-forming group works effectively at a very narrow pH range of 7.8-8.2. Methane forming group is highly sensitive to slight changes in pH than the acid forming group. The activity of methane forming group is just about 25 % at pH of 5 compared to its activity at neutral pH (Khanal, 2009). Hence, in an AD system where both microbiological groups work in a single digester, an optimal pH of 6.8-7.4 is widely recommended for efficient AD.

Several factors such as VFAs, carbon dioxide and ammonia influences the pH in AD process. The presence of VFAs and carbon dioxide decreases the pH, whereas the presence ammonia increases the pH. The accumulation of VFAs occurs when excess organic load is fed to the digester or due to the presence of toxic compounds inhibiting the methane producing microbial group. A drop in pH often arises due to the accumulation of VFAs. In such cases, alkalinity acts as a buffer against a drop in pH to certain extent. Optimal alkalinity for efficient biogas production in AD is 2000-5000 mg/l as $CaCO_3$ (titration to pH 4.3). The alkalinity in the digester neutralizes the accumulating VFAs as follows (Eq. 2.1).

$$HCO_3^- + CH_3COOH \Leftrightarrow H_2O + CO_2 \uparrow + CH_3COO^- \qquad \text{Eq. 2.1}$$

At a given pH, alkalinity in the digester is in equilibrium with the CO_2 in the biogas as follows (Eq. 2.2).

$$CO_2 \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow H^+ + CO_3^{-2} \qquad \text{Eq. 2.2}$$

In some cases, the alkalinity in digester may not suffice to neutralize the pH drop. The problem can be solved by feeding the organic waste at lower organic load into the digester which allows the consumption of accumulated VFAs. If the problem was not resolved, the alkalinity can be supplemented externally with high proteinaceous matter that releases amino groups ($-NH_2$) and ammonia (NH_3) leading to ammonia bicarbonate alkalinity. Bicarbonate alkalinity can act as a primary source of carbon for methane forming group. Carbohydrate-rich organic wastes could not contribute adequate alkalinity, as they do not contain noteworthy organic nitrogen. In such cases, the addition of external alkalinity is required.

The alkalinity can be supplemented externally with the addition of chemical compounds that generate alkalinity in the digester. Some of the chemical compounds are sodium bicarbonate, sodium carbonate, sodium hydroxide, potassium hydroxide, ammonium hydroxide, ammonia gas, and lime. Among the listed additives for alkalinity generation, lime is an inexpensive option and does not cause Ca^{+2} toxicity. However, lime addition may create negative pressure due to the over consumption of CO_2 in biogas of headspace if excessively added (Eq. 2.3). In such cases, it is advisable to supplement the alkalinity with sodium bicarbonate which draws 50% of less CO_2 in biogas than lime (Eq. 2.4).

$$Ca(OH)_2 + 2CO_2 \Leftrightarrow Ca^{+2} + 2HCO_3^- \qquad \text{Eq. 2.3}$$

$$Na_2CO_3 + H_2O + CO_2 \Leftrightarrow 2Na^+ + 2HCO_3^- \qquad \text{Eq. 2.4}$$

Gaseous ammonia can also be used to bring sufficient alkalinity as it produces ammonium bicarbonate with water and carbon dioxide. The produced bicarbonate alkalinity neutralizes the VFAs as follows (Eq. 2.5) (here, R symbolizes the non carboxyl group of VFA).

$$NH_4HCO_3 + RCOOH \Leftrightarrow RCOONH_4 + H^+ + HCO_3^- \quad \text{Eq. 2.5}$$

The pH in the digester can be easily measured, however it only indicates what has happened in the system. Alkalinity in digester sludge counteracts against initial acids accumulation, thus decrease in pH may not be visualized. Hence, alkalinity can be regarded as a best indicator to know what is happening in the system and accordingly early corrective measures can be taken. Excessive alkalinity addition may also be problematic and need to be avoided as it hampers microbial function. Compounds such as ferric chloride or citrate can be used to neutralize excessive alkalinity in AD.

2.1.2 Temperature

Like other biological processes, temperature is one of the most influential parameter of AD. It majorly effects the growth rate of microbial communities involved in AD (Chae et al., 2008). The physical factors such as viscosity and surface tension of digester contents are a function the digester temperature and influence the solid-liquid, liquid-gas mass transfer rates in production of biogas. Based on temperature, AD can be categorised to psychrophilic (<20ºC), mesophilic (20-45ºC), thermophilic (45-60ºC) and hyper thermophilic (>60ºC). Mesophilic and thermophilic temperature conditions are widely adopted globally due to high biogas production (Liu et al., 2017). AD at mesophilic conditions is stable and less sensitive, whereas AD at thermophilic is unstable and highly sensitive (El-Mashad et al., 2004). It is because of high metabolic growth rate and sensitive thermophilic microbial communities. However, maintenance of specific temperature requires external thermal energy if ambient temperature is low which may generally happen in winter season. It is important to evaluate the net energy output from the biogas to verify whether the improved biogas production is sufficient to maintain the respective temperature or not. The energy analysis may be used to choose appropriate temperature conditions for the reactor in practical application.

2.1.3 Total solids

Total solids (TS %) represents dry matter excluding the moisture content. Based on total solids (TS %) content, AD process can be categorized into two systems (Xu et al., 2014). AD which is carried out at total solids (TS) content <15% is a liquid state and total solids (TS) content >15% is solid state (Xu et al., 2014). Optimal total solids (TS %) content in AD is necessary to improve biogas production (Li et al., 2015a; Solli et al., 2014), which depends upon the type of organic waste (J. Li et al., 2014a) and mode of operation (Zuo et al., 2013). AD at very high total solids (TS %), may not be able to convert all organic matter loaded into digester and subsequently may fail. In such cases, the slowest process (generally either hydrolysis or methanogenesis) in overall degradation acts as a rate limiting step in biogas production. On the other hand, the process with low total solids (TS %) occupies more space of the reactor leading to the low volumetric biogas production that may not be economically feasible. Therefore, it is always important to maintain optimal total solids (TS %) for efficient process. Moreover, total solids (TS %) affects the rheology, viscosity, fluid dynamics, clogging, and solid sedimentation of the digester contents that further influence the mass transfer rates within the digesters (Karthikeyan and Visvanathan, 2013). AD of palm oil residues (analogous to organic wastes) has resulted in improved biogas production at a total solids (TS %) of 16% compared to higher total solids (TS %) of 25% and 35% (Suksong et al., 2017). The low biogas production at higher total solids (TS %) can be attributed to low mass transfer coefficient (Abbassi-Guendouz et al., 2012a), the formation of dead zones in the reactor (Sawatdeenarunat et al., 2014) and low microbial activity (Suksong et al., 2017). Hence, it is important to load the AD system with optimal total solids (TS %) for improved biogas production.

2.1.4 Hydraulic retention time

Hydraulic Retention time (HRT) is the average time of organic matter that stays in the digester. The generation time for the methanogens is high compared to acidoegens and methanogens need to be preserved for efficient AD. A minimum retention time of 12 days is required to prevent washout of the precious methanogens in AD. To prevent washout of the precious methanogens recycling of digestate, immobilization of microbia on to inert media, granulation (UASB) and microbial retention with the membrane can be carried out. Reasonably high HRT helps in improving the AD efficiency. However, AD at high HRT requires the large space of the digester that may escalate the cost of the digester. Hence, it is always recommendatory to optimize the HRT to have low digester space for the favourable economy of the AD system.

2.1.5 Volatile fatty acids

Volatile fatty acids (VFAs) are low molecular weight, short chain intermediary metabolites often represents the stability of the AD. The term volatile was used to these fatty acids as they get evaporated at atmospheric pressure. VFAs are not directly toxic in the system but it indicates the stability of the process. This means that high VFAs is the result of the process imbalance but not the cause for process imbalance. VFAs that are common in AD are formate (one carbon), acetate (two carbon), propionate (three carbon), and butyrate (four carbon). In typical AD process, 85 % of the VFAs occur in the form of acetate. The high organic loading into the system and inhibition of methanogen activity generally results in accumulation of VFAs in the digester.

Although there are contradictions about upper limits of VFAs in AD systems, acetic acid above 2000 mg/l, propionate concentration above 5 mg/l, and total VFAs concentration above 8000 mg/l can be regarded as upper limits. Some researchers considered the ratio between propionate and butyrate as an indicator for process imbalance. The propionate to butyrate ratio above 1.4 is an indication of process imbalance (Franke-Whittle et al., 2014) . The ratio VFAs to alkalinity ratio is also be regarded as an indicator of process stability (Kanhe et al., 2003). For a well-functioning AD system, VFAs to alkalinity ratio should be below 0.4 and the ratio above 0.8 indicates the instability of the process (Khanal, 2009). There are the instances where, even though the VFA/alkalinity ratio is about 0.2, the process inhibition was observed for proteinaceous organic wastes (Duan et al., 2012; Zeshan et al., 2012). It is because of buffering activity of ammonia- N of proteinaceous organic wastes that neutralizes acidification effect. In such cases it always necessary to consider both VFA to alkalinity ration and ammonia -N parameters in assessing the stability. The accumulation of VFAs in the digester can be neutralised with the addition of proteinaceous organic waste such as cattle manure or addition of alkali. Lowering the organic loading rate into the digester could also facilitate the consumption of VFAs, subsequently stable process.

2.1.6 Inoculum

Inoculum is the seed with active microbial population and low biodegradable matter. It facilitates the process with quick start-up and reduces the digestion time. The appropriate quantity of inoculum is essential for the stable and efficient performance of AD system (Li et al., 2011b). The low inoculum content (high S/I ratios) results in the accumulation of VFAs (acidification) subsequently inhibiting the methanogenic population (Xu et al., 2016), (Zhou et al., 2017). In AD of corn stover rapid acidification caused the accumulation of VFA with low inoculum content (high S/I ratio) (Li et al., 2011b). Inoculum content also affects the mass transfer of the substrate to microbial mass. In AD of rice straw, a low inoculum content caused poor mass transfer with low production of biogas (Zhou et al., 2017). Hence, the optimum inoculum content is required for the stable and optimal production of biogas in AD system.

The requirement of optimal inoculum is also different at mesophilic and thermophilic conditions (Li et al., 2011b). At mesophilic conditions, higher inoculum favoured biogas production, whereas in thermophilic conditions higher inoculum proportion retarded biogas production during AD of corn stover (Li et al., 2011b). The specific reason attributed for this effect is the low tolerance limit of free ammonia (4 N g /L) for thermophilic bacteria associated with the supply of high inoculum. Because the high ammonium nitrogen carried with the high quantity of inoculum supplementation into the digester inhibited thermophilic methanogens that have a low tolerance for ammonia. It is observed that the diluted inoculum facilitated the higher substrate loadings with improved biogas production compared to concentrated inoculum (Zhou et al., 2017). It is also observed that the supplementation of high inoculum (low S/I ratio of 2) resulted in higher biogas production during AD of corn stover and wheat straw (Liew et al., 2012). In this case, the corn stover and wheat straw resulted in biogas production of 81.2 mL CH_4/kg VS and 66.9 mL CH_4/kg VS respectively (at S/I ratio of 2). During solid state AD, addition of inoculum fetches additional moisture content and benefits quick mass transfer and microbial growth. For instance, additional moisture content improved the mass transfer of VFAs to methanogens in AD of rice straw that led to improved biogas production (Zhou et al., 2017). Hence, maintaining an optimal inoculum play a significant role in AD of organic wastes.

2.1.7 Nutritional balance

Nutritional balance of the feedstock influence the growth of microorganisms and it can be represented with carbon to nitrogen (C/N ratio), phosphorous and other trace elements. Generally, the manures are having the C/N ratio of 4-34, vegetable waste of 8-36, kitchen waste 26-30 and organic wastes of 40-151 (Siddique and Wahid, 2018). High C/N ratio in AD system may cause accumulation of VFAs whereas low C/N ratio may cause high total ammonia nitrogen (TAN) leading to low biogas production (Wang et al., 2012). The widely recommended optimal C/N ratio for efficient AD performance is 20-30 (Suksong et al., 2017; Wang et al., 2012; Yan et al., 2015; Yen and Brune, 2007). Optimal C/N ratio can be achieved with co-digestion of organic wastes with low and high C/N ratios at appropriate proportions (Wang et al., 2012). Several researchers optimised the nutritional balance with respect to C/N ratio for maximum biogas production. An optimal C/N ratio of 29.6 is suggested for AD of composted rice straw for high biogas production (Yan et al., 2015). An optimal range of C/N ratio of 20 -25 is suggested ((Yen and Brune, 2007) for the co-digestion of waste paper and algal sludge. Therefore, it is important to feed the AD with optimal C/N ratio for high biogas production.

The presence of nutritional elements such as phosphorous also plays an important role in AD. Addition of phosphorous in AD of rice straw accelerated the digestion process that caused 7-10 days of earlier appearance of biogas peaks (Lei et al., 2010). The presence of trace elements such as Fe, Ni, Co, Zn, W, and Se also improved the overall stability and AD efficiency (Demirel and Scherer, 2011). The depletion of trace elements may lead to souring of AD system , consequently low biogas production (Demirel and Scherer, 2011). The depletion of Fe and Ni resulted in the accumulation of VFAs during AD of wheat stillage (Schmidt et al., 2014). In this case, the depletion of Fe affected the methanogenic population and propionate oxidizing bacteria (Schmidt et al., 2014). The addition of Co, Ni, Mo, Se in AD of napier grass, caused 40% improvement in biogas production (Schmidt et al., 2014). The improved biogas production is attributed to higher conversion of VFA to biogas with addition of the micronutrients. Similarly, the addition of Fe, Ni, and Co improved biogas production by 35 % in the AD of corn residues (maize) (Hinken et al., 2008). However, the quantity of addition is also important as it may retard biogas production and may inhibit the process if excessively added. For instance, a higher concentration of Ni (greater than 1 g/m^3) inhibited methanogens in AD of sewage sludge (Tian et al., 2017). The trace elements can be supplemented with the co-digestion of organic wastes also. For example, wastewater sludge or animal manures that contains trace elements naturally can be used for co-digestion (Demirel and Scherer, 2011). Therefore, it is vital to supplement the optimal nutritional balance in the AD system for maximum biogas production.

2.1.8 Toxic compounds

Different groups of microorganisms mediate AD and several toxic compounds cause inhibition to microorganisms (J. L. Chen et al., 2014; Siddique and Wahid, 2018; Zhou et al., 2016). These compounds may cause inhibition either if they present in excess concentration or suddenly introduced into the system or both. Methanogenic microbial communities are highly sensitive to toxic compounds than acidogenic microbial communities. Toxic compounds in the system may come through either the influent feed (such as ammonia, heavy metals, cyanide, phenols, halogenated compounds) or intermediary product formation in the process (ammonia, sulfide, and long chain fatty acids). However, certain degree of contradiction exists to assess the toxic levels of AD depending upon the source of organic matter (Angelidaki et al., 2005; Mata-Alvarez et al., 2000). It also depends on the acclimatization of the microbial communities to the new toxic compound, the presence of other toxic materials, organic waste loading and operational conditions such as pH, temperature. Some common toxic compounds that cause inhibition are ammonia, hydrogen sulphide, and heavy metals detailed as follows:

2.1.8.1 Ammonia

Ammonia play a key role in inhibiting the AD particularly when the feed is from an animal source or comprising high proteinaceous matter (J. L. Chen et al., 2014). Ammonia-N serves as nitrogen source for microbial communities and also acts as a buffer. Microbial communities require certain extent of ammonia-N (200 mg/l) for their growth. However, excess ammonia-N causes inhibition to the microbial communities (Table 2.1). Ammonia-N in AD prevails in two forms, one is ionic ammonical nitrogen (NH_4^+) and other is non-ionic free ammonia (NH_3), which can be together termed as Total Ammonia Nitrogen (TAN) .

Table 2.1 Effect of total ammonia nitrogen (TAN)

TAN (mg/l)	**Effect**
50-200	Advantageous
200-1000	No effect
1500-3000	Adverse effect at high pH
>3000	Toxic at any pH

Free ammonia is highly toxic than ammonical nitrogen as it could penetrate through the cell membrane and damage methanogens. Free ammonia about 100-150 mg/l is generally toxic for un adopted cultures. However, it can tolerate up to 700 -800 mg/l of free ammonia in an adopted culture (Angelidaki and Ahring, 1994). The TAN concentration of greater than 3000 mg/l is toxic irrespective of pH (Table 2.1). The two forms of ammonia are in equilibrium as follows (Eq. 2.6)

$$NH_4^+ \Leftrightarrow NH_3 + H^+ \quad \text{Eq. 2.6}$$

The above equilibrium depends on pH and temperature. At neutral pH, the free ammonia constitutes about 0.5 % of TAN. The free ammonia increases with increase in pH and temperature. Hence, the inhibition of ammonia is higher under thermophilic conditions than mesophilic conditions due to the high formation of non-ionic free ammonia at high thermophilic temperature (Karthikeyan and Visvanathan, 2013). The free ammonia concentration can be mathematically correlated to pH and Ka as follows (Eq. 2.7). (Ka is dissociation constant which is temperature dependent)

$$NH_3(\%) = \frac{100}{1 + (\frac{[H^+]}{K_a})} \quad \text{Eq. 2.7}$$

The great feature of ammonia in AD is that it is "self-corrective". As the equilibrium reaction moves forward at higher pH, the activity of methanogen gets inhibited due to increase in high toxic free ammonia. It leads to accumulation of VFAs subsequently leading to decrease in pH. As the share of free ammonia is just about 0.5 % of TAN, at neutral pH, the free ammonia toxicity can be avoided by maintaining neutral pH.

2.1.8.2 Hydrogen sulfide

Microbial communities in AD require soluble sulphide (HS^-) to some extent for their growth and may cause inhibition if it exceeds. The toxicity of sulfide is more on methanogens than acidogens/acetogens and is also pH dependent. A decrease in pH results in increase in the formation of H_2S leading to more toxic conditions that reduce degradation of organic matter (Eq. 2.8, Eq. 2.9) (Omil et al., 1996). Aqueous hydrogen sulphide a weak acid and can cause inhibition with a concentration of 200 mg/l (at neutral pH). The non-iodised sulfide (H_2S) diffuses through the cell membrane of the microbial communities and impairs cell activity.

$$H_2S_{(aq)} \Leftrightarrow HS^- + H^+ \quad \text{Eq. 2.8}$$

$$HS^- \Leftrightarrow S^{-2} + H^+ \quad \text{Eq. 2.9}$$

However, the iodised sulfide (HS^-) cannot diffuse through the cell membrane effectively. The toxicity of sulfur speciation is in the order of H_2S > total sulfide > sulfite >thiosulfate > sulfate

(Abdel-Monaem Zytoon et al., 2014). The problem of high sulfide toxicity can be avoided by adding iron (Fe) that make to precipitate it into iron sulfide.

2.1.8.3 Heavy metals

Toxicity of heavy metals often arises in AD of sludge generated in wastewater treatment plants and industrial wastes (such as electroplating, metal processing, and tanneries). Heavy metals at low concentration activate the enzymes involved in AD. The moderate to excessive concentration heavy metals (10^{-3} to 10^{-4} M) inhibits the microbial microorganisms by adsorbing on to their cell wall, subsequently absorbed into the microbial bulk solution binding to thiol groups in enzymes. It leads to the inactivation of enzymes involved in biogas production.

Table 2.2 Summary of various factors influencing AD

Factor	**Optimal Range**	**Ref**
Nutritional Balance	C/N ratio: 20-30	Yan et al., 2015
Temperature	Psychrophilic (<20ºC), Mesophilic (20-45ºC), Thermophilic (45-60ºC) and hyper thermophilic (>60ºC).	Liu et al., 2017
Total Solid (TS%) content	Liquid state: 1 to 10 % TS, Hemi-solid state- 10 to 15 %, Solid state: 20% 30 %	Karthikeyan and Visvanathan, 2013
Substrate to inoculum ratio	0.5 to 3	Jacob & Banerjee, 2016
pH & Alkalinity	pH: 7.8 to 8.2 Alkalinity: 2000-5000 mg CaCO3/l	Khanal, 2009
Retention Time	10 to 50 days	Khanal, 2009
Toxic materials (VFAs, Ammonia, H_2S,)	VFAs- <8000 mg/l. Free Ammonia: <700 mg/l, H2S: < 200 mg/l	Khanal, 2009

Although several heavy metals present in AD, they cannot cause toxicity as they are in combined form, not free. The bacteria cannot adsorb the combined forms of heavy metals. Thus, the soluble forms of heavy metals are more toxic to AD than insoluble forms (Igiri et al., 2018). The formation of sulfide benefits the AD as it forms insoluble metal sulfides of heavy metals (except Cr). All heavy metals exert toxicity to AD with an exception of iron (Fe) as it mediates the sulfide toxicity effectively. The order of toxicity of heavy metals to AD is Ni > Cu > Pb > Cr > Zn (Nguyen et al., 2019) .

From the above discussion, it can be observed that the optimal levels of parameters facilitates the microbial activity in degradation and avoids inhibition that occurs in AD of organic wastes (Table) . The parameters described above need to be maintained carefully for enhanced biogas production. Several strategies proposed in the literature to avoid inhibition and achieve process enhancement with maximum biogas production, and detailed as follows:

2.2 Strategies for the process enhancement

Strategies such as pretreatment, co-digestion and some process modifications could enhance the biogas production. The effectiveness of these strategies and their practical applicability are detailed:

2.2.1 Pretreatment

One of the barriers in achieving the maximum biogas production is presence of lignin, protecting carbohydrates from effective biological degradation particularly crop residues. The lignin coat is a protective hydrophobic layer, prevents the microbial communities from the accessibility of carbohydrates such as cellulose and hemicellulose. It is reported that lignin in organic wastes reduces biogas productivity (Buffiere et al., 2008). Pre-treatment of organic wstes enables lignin degradation and facilitates the microbial action on carbohydrates. Possible pretreatment methods are physical, chemical and biological methods. Most of the physical pre-treatment methods (such as irradiation) are effective in lignin degradation, however it may require high energy input making them more expensive. The chemical pre-treatment methods (such as acids, alkali or ammonia pre-treatments) cause secondary pollution to the environment, corrosion of the equipment, releasing toxic furfural and phenolic compounds during pre-treatment that may harm the microbial communities (Jönsson and Martín, 2016). Biological pre-treatment methods (fungal treatment and aeration) requires larger time for pretreatment eventhough they involve mild operating conditions and environmentally friendly. Careful selection of the pre-treatment method among the available physical, chemical and biological methods is required in economic perspective.

2.2.2 Co-digestion

Optimal nutritional content in organic waste promotes the growth of the microbial communities in AD. Nutritional content in terms of carbon to nitrogen ratio (C/N ratio), phosphorous and trace elements required for the AD. Typically manures have C/N ratio about 4-34, vegetable waste about 8-36, kitchen waste about 26-30 and crop residues about 40-151 (Siddique and Wahid, 2018). AD performs well within the C/N ratio of 20-30 (Suksong et al., 2017; Wang et al., 2012; Yan et al., 2015; Yen and Brune, 2007). Some organic wastes such as fruit and vegetable wastes have high C/N ratio and its rapid acidogenesis may result in the accumulation of VFAs (Bouallagui et al., 2005). Whereas, manures have low C/N ratio that may release high total ammonia nitrogen (TAN) which is toxic to microbial communities (Wang et al., 2012).

Co-digestion with nitrogen rich organic matter or addition of nitrogen rich materials such as ammonia improves the C/N ratio (Wang et al., 2012). AD of composted rice straw mixed with urea resulted in C/N ratio of 29.6 that lead to enhanced biogas production (Yan et al., 2015). Co-digestion of waste paper with algal sludge enhanced biogas production with C/N ratio of 20 to 25 (Yen and Brune, 2007). The addition of phosphorous and trace elements such as Iron (Fe), Nickel (Ni), Cobalt (Co), Zinc (Zn), tungsten (W), and Selinium (Se) also enhanced biogas production. The addition of phosphorous in AD of rice straw enhanced biogas production (Lei et al., 2010). The addition of Fe, Ni, Co, Zn, W, and Se enhanced the biogas production (Demirel and Scherer, 2011). The depletion of trace elements in AD process may also cause low biogas production (Demirel and Scherer, 2011). The depletion of Fe effected the methanogenic population and propionate oxidizing bacteria (Schmidt et al., 2014). The depletion of Fe and Ni in AD of wheat stillage caused the accumulation of VFAs, subsequently low biogas production (Schmidt et al., 2014). However, the addition of Co, Ni, Mo, Se in the AD of napier grass, enhanced the biogas production by 40 % (Schmidt et al., 2014) . The enhanced biogas production is due to the presence of the micronutrients that lead to the higher conversion of VFA to biogas. Similarly, the addition of trace elements such as Fe, Ni, CO enhanced biogas production by 35% (Hinken et al., 2008).

Trace elements can also be found naturally in wastewater sludge or animal manures which can be used as a co-organic wastes to enhance biogas production (Demirel and Scherer, 2011). However, the quantity of addition is an important factor and may inhibit the process if excessively added. AD a higher concentration of Ni (>1 g /m^3) inhibited methanogens, that lead to low biogas production (Ashley et al., 1982). Hence, it is important to maintain the nutritionally balanced feed either through co-digestion or through external micro-nutrient supplementation for the efficient functioning of the microorganisms in AD system. Also, the organic wastes generated in different areas are varied in its characteristics and availability, and a detailed research is required to draw the concise conclusions for the implementation of co-digestion at field level.

2.2.3 Recirculation

The difficulties that are commonly found in AD system are clogging of pumping tubes, floatation of biomass, stratification and scum formation due to bulky nature of organic wastes (Li et al., 2011a). These difficulties in AD system can be partially overcome with recirculation of the leachate back into the system. As mentioned in Chapter 1, the stability and efficiency of AD system mainly depend upon the syntrophy in interlinked hydrolysis, acidogenesis, acetogenesis and methanogenesis phases. Sometimes, syntrophy is disturbed due to either slow hydrolysis or fast hydrolysis that causes either shortage of VFAs or accumulation of VFAs respectively, both affects the activity of methanogens (Schievano et al., 2010; Zhou et al., 2017). It has been reported that the supply of microbial population plays a key role than the supply of buffering capacity in enhancing biogas production (Charles et al., 2009). It is also to be noted that the growth of methanogenic microbial population is slower compared to acidogenic microbial population leading to imbalanced microbial population more specifically at higher substrate loadings. The recirculation of methanogenic rich digestate solves the problem of poor methanogenic population in AD system leading to balanced syntrophy of four stages. Moreover, it can enhance the nutritional balance, moisture content and reduces the lag phase time required for initial startup time for biogas production (Lü et al., 2008; Zuo et al., 2013). Even though recirculation of leachate is beneficial in improving the performance, the maintenance and operation of the system requires careful monitoring and technical skill in field level application.

2.3 Need for co-digestion

Even though AD is being encouraged with current guidelines of the Government of India, the method is not being implemented at its optimal capacities for organic waste management. One of the major reasons is most of the AD plants are designed for use of single feedstock. The lack of continuous feedstock supply making the plants non- operational, occasionally plant becoming non-functional too. Further, rejuvenation of AD system requires technical expertise. The difficulty can be solved with co-digestion of appropriate organic wastes at optimal proportions.

As mentioned in Sections 2.1.7 and 2.2.2 , optimal nutritional composition of feedstock is required for effective digestion (Siddique and Wahid, 2018). The co-digestion with complementary organic wastes fetches nutritional balance and evades the majority of limitations (Bouallagui et al., 2009; Y. Li et al., 2016; Wang et al., 2012). For the case of mono-digestion of animal manures, manures are having high nitrogen content, that frequently cause ammonia inhibition. For the case of digestion of crops and agro industrial wastes it is having low nitrogen content, leading to insufficient nitrogen for microbial growth. For the case of FVW, FW, and slaughterhouse wastes accumulation of long chain fatty acids is frequent phenomenon leading to souring of the digester. Co-digestion of two or more organic wastes in a single digester can overcome these limitations in effective manner (Dareioti et al., 2009; Dareioti and Kornaros, 2014). Moreover, co-digestion of different organic wastes in a single digester facilitates management of different organic wastes generated in a particular geographical area (Di Maria et al., 2014; Kalamaras and Kotsopoulos, 2014; Shah et al., 2015; M. X. Zhao et al., 2014). The co-digestion also facilitates the efficient use of equipment and ensures the continuous feedstock supply with enhanced stability of the digester. In view of these benefits, co-digestion of organic wastes may be an appropriate choice for AD. However, different kinds of organic wastes could be generated in a particular area which need to be investigated to adopt the co-digestion strategy for organic wastes generated in the Indian context.

2.4 Need for modelling in co-digestion

The better understanding and optimal performance of the AD process which is a complex biochemical process is required in terms of the effective mixture proposition for a particular type of feed used (Hagos et al., 2017). The classical optimization techniques optimize the process with a variation of one independent variable by keeping other variables constant. It causes difficulties in finding true optimum, because of the interaction among the factors being involved. Moreover, this method is time consuming due to the requirement of more number of experiments to draw a valid conclusion. The information on proportion of organic wastes to be used in co-digestion is limitedly reported (Karthikeyan and Visvanathan, 2013). The proportion of organic wastes can be evaluated with appropriate experimental design and a statistical approach such as response surface methodology (RSM).

The kinetic performance of the AD system is required for understanding the co-digestion behaviour. The kinetic performance can be evaluated using models available in literature. Several models are available for the kinetic analysis of the AD. First order kinetic model (S. Xie et al., 2011), modified Gompertz model (Kafle and Kim, 2013; Yan Yao, Rui Zhang, 2017), Chen and Hashimoto model (Ma et al., 2013) , ADM1 model (Wang et al., 2014) are well known models to understand the AD process.The modified Gompertz model is an empirical, non-linear regression equation that explains the kinetic behaviour of the co-digestion in effective manner (Kafle and Kim, 2013). The model estimates biogas production potential, lag phase time, maximum biogas production rate (Krishania et al., 2013). The model is successfully used to understand the kinetic behaviour in anaerobic co-digestion of apple waste with swine manure (Kafle and Kim, 2013), rice straw with pig manure (Li et al., 2015b) and chicken litter with yoghurt whey, organic fraction of municipal solid waste and hay grass (Zahan et al., 2018). The modified Gompertz model can be adopted to analyse the kinetic behaviour. In view of this, it is imperative to evaluate optimal proportion of organic wastes with suitable modelling approaches for maximum biogas production.

2.5 Need for energy-economic analysis

Even though, most methods reports enhanced process performance, they may not be economically feasible always as the cost they consume sometimes higher than that cost it incurs (Mansouri et al., 2019). There are enormous approaches in lab scale indicating the enhancement in biogas production. However, limited information exists regarding net energy and economic benefits involved for co-digestion. In order to decide the feasibility, energy economic analysis plays a key role in decision making (Scano et al., 2014). If a particular process is scaled up, it also attracts different unit operations which needs to be considered in assessing the feasibility (Ruffino et al., 2015). For this purpose, energy economic assessment is required to quantify the benefits in terms of net energy generation, unit cost of energy production (Rs./kWh) and payback period upon investment. Thus, the comparison of input energy spent and output energy obtained is required to estimate the economic viability to adopt at large scale.

2.6 Summary

From Chapter 1 and Chapter 2 it can be observed that

- AD is the preferable organic waste management method due to multifaceted benefits involved.
- Different kinds of crop residues are generating from agricultural sector in India. However, the bio-energy potential of the crop residues for AD and environmental impact is limitedly reported.
- AD is a complex biochemical process involving four stages, hydrolysis, acidogenesis, acetogenesis, and methanogenesis. The syntrophic relationship of four stages plays a significant role in the efficiency of AD.
- The syntrophic relationship can be improved with the co-digestion of complementary organic wastes in a single AD facility.
- The organic wastes are area specific and its composition varies geographically. The organic wastes need to be verified for their quality in co-digestion.
- The possible co-digestion scenarios utilising local organic wastes is limitedly reported and need to be investigated for maximum biogas production.
- The information regarding the proportion of organic wastes in co-digestion for maximum biogas production is limitedly reported and need to be evaluated for field application.
- Mathematical modelling approaches enables better understanding of the co-digestion behaviour of the system involving multiple variables.
- Energy economic study is required for the co-digestion to assess the viability at large scale.

Hence, based on literature it is proposed to study the crop residues as a feedstock for AD, its bio-energy potential and environmental impact in Indian context. It is also proposed to identify suitable mix of organic wastes and optimal proportion of organic wastes for co-digestion. Further, it is planned to assess the energy and economic benefits for the field scale implementation of co-digestion process.

Chapter 3 Materials and Methods

The present chapter is aimed to describe the materials, analytical methods, and experimental procedures carried out in the present study.

3.1 Bio-energy potential and environmental impact

Bio-energy potential and environmental impact for AD of rice, wheat and maize residues generated in India are assessed. The bio-energy potential is assessed based on the surplus amount of residue generation and biogas production through AD. The environmental impact with AD of these residues is assessed based on the assumption that produced bio-energy through AD substitutes the consumption of coal. The amount of coal substitution is estimated based on assumption that the generated bio-energy is utilised for thermal heating (instead of coal) according to the method prescribed (Eq. 3.1) in (Yanli et al., 2010). The amount of CO_2 emissions that can be avoided with coal substitution is estimated based on the assumption that combustion of coal is taken in an environment of sufficient air (Eq. 3.2).

$$\text{Coal substitution } (M) = \frac{(B \times P \times Q_m \times E_m)}{Q_c \times E_c} \quad \text{Eq. 3.1}$$

$$CO_2 \text{ emissions} = M \times (C_p - C_s) \times \frac{44}{12} \times C_o \quad \text{Eq. 3.2}$$

Where B is surplus crop residue (t), P is methane potential (m^3/t), Q_m is calorific value of methane (35.9 MJ/m^3), E_m is efficiency of methane for thermal heating (0.9), Q_c is calorific value of coal (20,900 MJ/ton), E_c is efficiency of coal for thermal heating (0.6), M is amount of coal substitution (t), C_p is percentage of carbon in coal (60 %), C_s is percentage of unburned carbon (10 %) ; C_o is carbon oxidation percentage (80 %) .

3.2 Material collection and preservation

Several kinds of organic wastes generated in Warangal district, Telangana, India (18.0°0' 0.19" N, 79° 35' 17.39" E) are considered for the present study. Food waste (FW) is widely being generated in hotels, academic institutions whose management is posing a challenge for municipal authorities. Fruit & vegetable waste (FVW) is widely being generated in local fruit vegetable markets, fruit industries, and local bench-scale juice units.. Food and agricultural organization of the united nation reported that worldwide production of citrus fruits reached 124 Mt in the year 2016 (Intergovernmental and Fruit, 2017). Grass is a widely generated organic waste in public green spaces and crop fields. Agricultural fields also generating residues after crop harvest. India is the fourth largest chicken producer and generating about 6.2-8.0 Mt of chicken manure (CM) annually (Prabu, 2009). CM is traditionally applied to the agricultural field as a soil conditioner (after stacking for 6-8 weeks). On the other hand, dairy manure (DM) is widely generated in rural areas and is also traditionally applied to the agricultural field as a soil conditioner and fertiliser (Rudra et al., 2015). Efficient utilization of generating organic wastes in appropriate manner is necessary for clean and healthy environment.

Seven different organic wastes viz., food waste (FW), fruit & vegetable waste (FVW), lawn grass (LG), citrus pulp waste (CP), rice straw (RS), chicken manure (CM), and dairy manure (DM) are identified (Fig. 3.1).These organic wastes are identified based on their local availability and suitability for AD in the study area. FW is collected from the hostel mess in National Institute of Technology Warangal campus. The FW is mixed and macerated to achieve homogeneity. FVW is collected from the nearby market in Warangal city. The composition of FVW chosen for study is tomato- 25%, leafy vegeatbles-25 %, orange- 12.5 %, banana- 12.5 %, lady finger- 12.5 %, cabbage- 12.5 % and potato- 12.5 %. The composition is selected based on physical observation over a month of the time period in local market in Warangal for the consistency of the experimental data. The defined FVW is also mixed and macerated. RS is collected from a paddy field located in Warangal district, India. The straw is shredded into small pieces using laboratory mixer followed by sieving to a size of 1 - 3 mm to fetch homogeneity and reduce crystallinity (Hendriks and Zeeman 2009). CP is collected from a bench-scale juice processor after juice extraction. While collecting CP, only pulp waste is collected without outer covering peel of citrus fruit since it contains high limonene which may be inhibitory to anaerobic microbes. It is air dried, ground to 1-3 mm size using a mixer grinder. LG is collected from public lawn spaces in the winter season at National Institute of Technology Warangal campus, India. It is also air dried, ground to 1-3 mm size using a mixer grinder. DM and CM are collected from the respective farms available locally. The coarse material is removed manually from it. Inoculum for the experimental work is obtained from a working anaerobic digester that processes FW generated in the institute campus. All the organic wastes are preserved at a temperature of 4 °C in refrigerator until further use to maintain freshness and prevent possible degradation. The generating organic wastes are area specific, and their composition is spatio-temporal in nature (Panigrahi and Dubey, 2019). In order to use the organic wastes for AD, they are analysed as follows:

Lawn grass (LG)

Dairy manure (DM)

Rice straw (RS)

Fruit and vegetable waste (FVW)

Chicken Manure (CM)

Fig. 3.1 Materials for co-digestion study

3.3 Analytical methods

All the organic wastes are analysed for their proximate and elemental characteristics. The organic wastes are analysed in triplicates, and their average values are taken to represent the sample. The characteristics of the organic wastes are measured in accordance with APHA standard methods (APHA, 2017). The proximate analysis is carried out to determine the moisture content, total solids (TS), volatile solids (VS), and ash content. The elemental analysis is carried out to determine the carbon, hydrogen, nitrogen and sulfur composition of organic wastes on a weight basis using Euro EA Elemental Analyser.

Compositional analysis of biogas is carried out weekly once with a gas chromatograph system (Fig. 3.4: YL Instruments Model 6500). It is equipped with a thermal conductivity detector and a stainless steel column length of 4m packed with Porapak Q (80-100 mesh). Hydrogen is used as a carrier gas, and the temperature of the injection port, column oven, and detector are maintained at $40^{o}C$, 50^{o} C and 100^{o} C respectively. A standard mixture of methane and carbon dioxide (CO_2 of 51.65%, and CH_4 of 48.35% by volume) is used for calibrating the system.

3.4 Experimental setup

AD experiments are carried out using batch reactor comprising an air tight glass of volume 120 mL (Fig. 3.2). Each reactor is fed with appropriate proportions of feedstock and inoculum. Enough space is left for biogas generation and collection in each reactor. After the addition of appropriate contents, headspace of reactors is flushed with nitrogen gas and bottles are sealed with aluminum crimps. All the reactors are maintained with duplicates for consistency in biogas volume measurements and average readings are taken for interpretation. The experiments are performed at mesophilic temperature (35^{O} C) and biogas production is measured daily with downward water displacement method using 0.6 mm needle (Rao and Baral, 2011). The gas pressure is released into the water column by piercing the septum with a needle (Fig. 3.3). Biogas obtained from all the reactors is corrected by subtracting biogas produced in control digester that contains only inoculum (Jagadabhi et al., 2010). Each reactor is shaken manually every day before taking biogas volume measurement for proper mixing.

Fig. 3.2 Biogas experiments

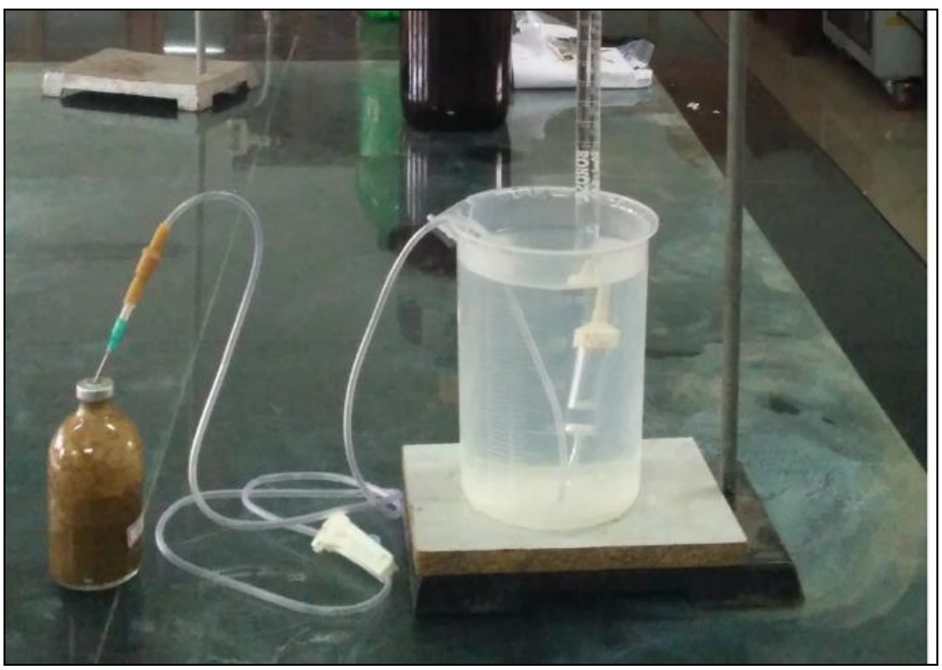

Fig. 3.3 Biogas measurement by the downward water displacement method

Fig. 3.4 Gas Chromatography system for biogas analysis

3.5 Design of experiments

Design of experiments faciliate to analyse the influence of several factors on output response variable (Tiwari et al.,2017). The designs such as central composite design (CCD) and simplex centroid mixture design (SCMD) are widely used to study the interactions in a biochemical process (Kim et al., 2007). The main advantage of CCD and SCMD is that it requires a fewer experimental combinations and creates a wealth of information with minimal experimental errors. The CCD and SCMD estabish response surface model of continuous variables and interactive effects of each factor on response variable (Wang et al., 2013). In the present work, CCD and SCMD are used for the experimental design of the influencing factors in AD.

3.5.1 Central composite design

Central composite design (CCD) is a mathematical design used to analyze the relationship between influencing factors and response variable (Wei and Manickam, 2012). CCD facilitate to establish a response surface model of continuous variables and interactive effects of each component on response (Wang et al., 2013). In the present work, CCD (face centered type) and CCD (circumscribed type) are used for the analysis of the influencing parameters in AD. The distance of axial points in CCD (circumscribed type) from the central point (α) is calculated as follows (Eq. 3.3)

$$\alpha = 2^{k/4} \qquad \text{Eq. 3.3}$$

Where 'k' is the number of factors i.e three in present work. The 'x_i' is coded form of variable X_i according to Eq. 3.4 given below, such that X_i^* represents the central value.

$$x_i = \frac{(X_i - X^*_i)}{\Delta X_i} \qquad i = 1, 2, 3......k \qquad \text{Eq. 3.4}$$

Where, x_i = coded value of an independent variable for the i^{th} test, X_i = real value of an independent variable for the i^{th} test, X_i^*=real value of an independent variable at the centre point, ΔX_i = step difference.

3.5.2 Simplex centroid mixture design

Simplex-centroid mixture design (SCMD) is a mathematical design widely used to analyze the relationship for mix proportion of components on response variables such as biogas production (Rao and Baral, 2011; Wang et al., 2013). The three factor design is a triangle whose vertices correspond to pure mix (100 % of a sole component) and triangle space correspond to mix of three components (Douglas C. Montgomery, 2000). SCMD design also facilitate to establish a response surface model of continuous variables and interactive effects of each component on response variable (Wang et al., 2013). In the present work, SCMD is used for the experimental design in the co-digestion of three organic wastes.

3.6 Response surface methodology

Response surface methodology (RSM) is used to establish the relationship between influencing factors and response i.e., biogas production (mL). RSM uses different statistical and mathematical techniques to analyse the influence of different factors on the response. The successful implementation of the RSM is carried out by several researchers for optimization of biogas production (Jacob and Banerjee, 2016; Zou et al., 2016). The relationship between biogas production and the set of factors can be explained by choosing one of the best models from the following widespread models (Eq. 3.5,Eq. 3.6,Eq.3.7,Eq. 3.8).

Linear model:

$$Y = \beta_0 + \beta_1 * A + \beta_2 * B + \beta_3 * C \qquad \text{Eq. 3.5}$$

Two-factor interaction model ((2FI):

$$Y = \beta_0 + \beta_1 * A + \beta_2 * B + \beta_3 * C + \beta_{12} * AB + \beta_{13} * AC + \beta_{23} * BC \qquad \text{Eq. 3.6}$$

Quadratic model:

$$Y = \beta_0 + \beta_1 * A + \beta_2 * B + \beta_3 * C + \beta_{12} * AB + \beta_{13} * AC + \beta_{23} * BC + \beta_{11} * A^2 + \beta_{22} * B^2 + \beta_{33} * C^2 \qquad \text{Eq.3.7}$$

Cubic model:

$$Y = \beta_0 + \beta_1 * A + \beta_2 * B + \beta_3 * C + \beta_{12} * AB + \beta_{13} * AC + \beta_{23} * BC + \beta_{11} * A^2 + \beta_{22} * B^2 + \beta_{33} * C^2 + \beta_{123} * ABC + \beta_{112} * A^2B + \beta_{113} * A^2C + \beta_{122} * AB^2 + \beta_{133} * AC^2 + \beta_{223} * B^2C + \beta_{233} * BC^2 + \beta_{111} * A^3 + \beta_{222} * B^3 + \beta_{333} * C^3 \qquad \text{Eq. 3.8}$$

Where *Y* represents biogas production (mL), A, B and C are influencing factors. β_0 is constant, β_1 , β_2 , β_3 are linear coefficients, β_{12}, β_{13}, β_{23} are cross-product coefficients, β_{11}, β_{22} , β_{33} are quadratic coefficients, and β_{123}, β_{112}, β_{113}, β_{122}, β_{133}, β_{223}, β_{233}, β_{111}, β_{222} , β_{333} are cubic coefficients. The fitness of the model equation is determined by using the coefficient of determination (R^2), and the standard deviation. Its statistical significance is checked using F-test. The model with the best statistical fitness is selected for the estimation of response. After selection of the appropriate model, the influence of each factor and their interactions are evaluated with a significance test and analysis of variance (ANOVA).

3.7 Modified Gompertz model

Understanding the basic mechanism of complex process involving various groups of microorganisms is necessary for efficient process development (Shin et al., 2008). Various kinetic models are available for the performance evaluation of AD as discussed in Section 2.4. In the current study, modified Gompertz model is adopted for the performance evaluation of the co-digestion due to its robustness. The model is based on the assumption that the methane yield (mL

CH_4/g VS) from AD is a function of microbial growth (Jagadish H. Patil, Malourdu Antony Raj, P. L. Muralidhara, S. M. Desai, 2012). The model is expressed as (Eq. 3.9).

$$Y = M.\exp\{-\exp[\frac{R_m \times 2.71}{M}(\lambda - t) + 1\}] \qquad \text{Eq. 3.9}$$

Where 'Y' is accumulated methane yield (mL) at time t, 'M' is methane potential, R_m is the maximum methane production rate, 'λ' is lag phase time in days. Kinetic parameters M, R_m and λ are estimated using nonlinear least-square regression method using experimentally obtained methane yield. The kinetic parameters are used to predict the methane yield. The predicted methane yield from the model is plotted with the obtained methane yield in the AD experiments. The goodness of fit for the kinetic parameters is diagnosed using coefficient of determination (R^2).

3.8 Energy-economic analysis

Energy-economic analysis is required to plan and execute the project at a large scale as discussed in Section 2.5. If a particular process is scaled up, it attracts different unit operations which needs to be considered in deciding the feasibility (Ruffino et al., 2015). For this purpose, a large scale AD plant of 200 m^3 volume and a combined heat and power generation (CHP) system with a heat recovery facility is considered. The CHP system converts the produced biogas from AD plant to electrical and thermal energy. Apart from production of energy, several physical operations in AD plant consume energy. The consumption of energy and various costs involved for the AD plant are estimated and detailed as follows:

3.8.1 Energy analysis

The net energy production from the AD system is evaluated by subtracting the energy consumed for internal maintenance of plant from the energy produced. Four unit operations are considered in assessing the electrical and thermal energy requirements. Four unit operations are pulverisation, pumping system, conveyance, heating system (Deublein, Dieter Steinhauser, Angelika, 2010). However, the energy required for mechanical agitation in the AD plant is neglected due to their low energy requirement as it consumes less than 2 % (Abudi et al., 2016a; Scano et al., 2014). The energy requirements for four unit operations are assessed based on following specifications.

3.8.1.1 Pulverisation

Organic waste needs to be pulverised to reduce size and improve surface area for effective microbial action. The motor capacity of pulveriser is 9 kW that can process 400 kg of organic waste in one hour with efficiency of 50%. The small variations in electric power requirements for different organic wastes due to their texture variations are neglected. The manures such as DM and CM do not require pulverisation as they are fine-textured.

3.8.1.2 Pumping system

Pumping system is required to supply the feedstock and withdraw the finished digestate. Two pump motors are required: one is to supply the feedstock from the feed tank to the digestion tank and another is to withdraw the finished digestate. The capacity of the pump motor is 0.5 kW that can deliver the feedstock of density 1100 kg/m^3 with a flow capacity of 10 m^3/h. The efficiency of centrifugal pump is 50%.

3.8.1.3. Conveyance

Conveyance of the feed material from the silo (storage tower) to the feed tank is supportive for smooth flow feedstock to plant (Deublein and Steinhauser, 2010).Two series-connected screw conveyors between the silo and feed tank, each with a motor capacity of 5 KW is considered (Deublein and Steinhauser, 2010). The conveyor is operated once in a day for 1h/day (with a flow capacity of 1 m^3/h). The efficiency of conveyance motor is 50%.

3.8.1.4. Heating system

In India, a low ambient temperature (≈25^{o}C) arises in winter and night hours (Kothawale and Rupa Kumar, 2005) that may cause low rate of biogas production in AD plants. In order to overcome this difficulty, thermal energy is required in two means. One is to raise the digestion temperature of feed, second is to maintain the temperature against heat losses. The energy required to raise the temperature is assessed based on specific heat of feedstock (Cp) and quantity of feedstock (m_F). Whereas thermal losses considered to be 20 % of thermal energy required in raising the temperature (Scano et al., 2014; Valenti et al., 2018). The efficiency of heating system is 80% and the energy requirement is calculated as follows (Eq. 3.10).

$$\text{Thermal energy} = \text{Thermal energy}_{\text{Temperature raise}} + \text{Thermal energy}_{\text{Heat losses}} \qquad \text{Eq. 3.10}$$
$$= m_F .\, Cp \,.\, (T_R - T_A) \; + \; 0.20 \; (m_F .\, Cp \,.\, (T_R - T_A))$$

Where, m_F = quantity of feeding substrate (5830 kg/day), Cp=Specific heat capacity of the feedstock (4187 J/kg/K), T_R = digestion temperature (35^O C), T_A= ambient temperature (25^O C),

The electrical energy consumption (kWh) for the pulverisation, pumping system, conveyance are calculated as follows (Eq. 3.11).

$$E_C = \frac{P_m}{n_m} * t \qquad \text{Eq. 3.11}$$

Where P_m is capacity of the system (kW), n_m is efficiency, and t is operating time (hours).

The net energy production is assessed by subtracting the energy consumption (input energy) from energy produced (output energy). The net electrical and thermal energy production is calculated as follows (Eq. 3.12, Eq. 3.13).

$$\text{Net electrical energy production} = E_P - E_C \qquad \text{Eq. 3.12}$$

$$\text{Net thermal energy production} = T_P - T_C \qquad \text{Eq. 3.13}$$

Where E_p is electrical energy production (kWh), E_c - electrical energy consumption (kWh), T_p is thermal energy production of (kWh), T_c is thermal energy consumption (kWh).

3.8.2 Economic analysis

Economic analysis plays a key role in decision making about the viability of the project. It can be assessed based on costs incurred (investment) and financial benefits that can be obtained over a period. Total annual costs (C_T) incurred for the production of electricity is calculated from capital cost (fixed cost) and O&M costs (variable cost). Capital cost is the expenses incurred for the installation of the digestion tank, pulveriser, conveyor, pumping system, heating system and other miscellaneous items. O&M costs are the costs associated with operation & maintenance of the AD plant. Using the data obtained from energy analysis, unit cost of energy, payback period upon investment and net present value (NPV) are quantified as follows.

3.8.2.1 Cost of energy:

Cost of energy for a particular process (Rs./kWh) is required to compare with present market price of energy. It is estimated through the ration between total annual cost *(C_T)* and annual electricity production.

$$\text{Cost of energy}\left(\frac{\text{Rs/-}}{\text{kWh}}\right) = \frac{\text{Total annual cost } C_T \text{ (Rs/-)}}{\text{Annual electricity production (kWh)}} \qquad \text{Eq. 3.14}$$

Where total annual cost (C_T) incurred in a year is evaluated by considering capital cost and O&M costs as follows (Eq. 3.15).

Total annual cost, C_T = Capital cost *CCR+ O&M cost   Eq. 3.15

CCR is the capital charge rate and is calculated as follows (Eq. 3.16)

$$CCR = \frac{i}{1-(1+i)^{-n}} \quad \text{Eq. 3.16}$$

Where, *i* is interest rate (10%), *n* is operating life (20 years)

3.8.2.2 Pay-back period:

Pay-back period (discounted) indicates amount of time it takes to recover the cost of an investment. It is estimated through the ration between capital investment and net cash out flow in a year measured in today's currency based on discount rate of 10 %.

$$\text{Payback period} = \frac{-\ln(1-\frac{\text{capiatal cost} \times \text{discount rate}}{\text{net cash flow}})}{\ln(1+\text{discount rate})} \quad \text{Eq. 3.17}$$

3.8.2.3 Net present value:

Net present value (NPV) is expected cash flows to receive in the future in today's currency. It is estimated through the sum of expected net cash flows (*NCF*) in todays currency based on discount rate of 10 % (*r*).

$$NPV = \sum_{t=0}^{n} \frac{NCF}{(1+r)^t} \quad \text{Eq. 3.18}$$

Based on the materials and methods presented in this Chapter, the study carried. The detailed results and discussion presented in Chapters 4, 5, and 6.

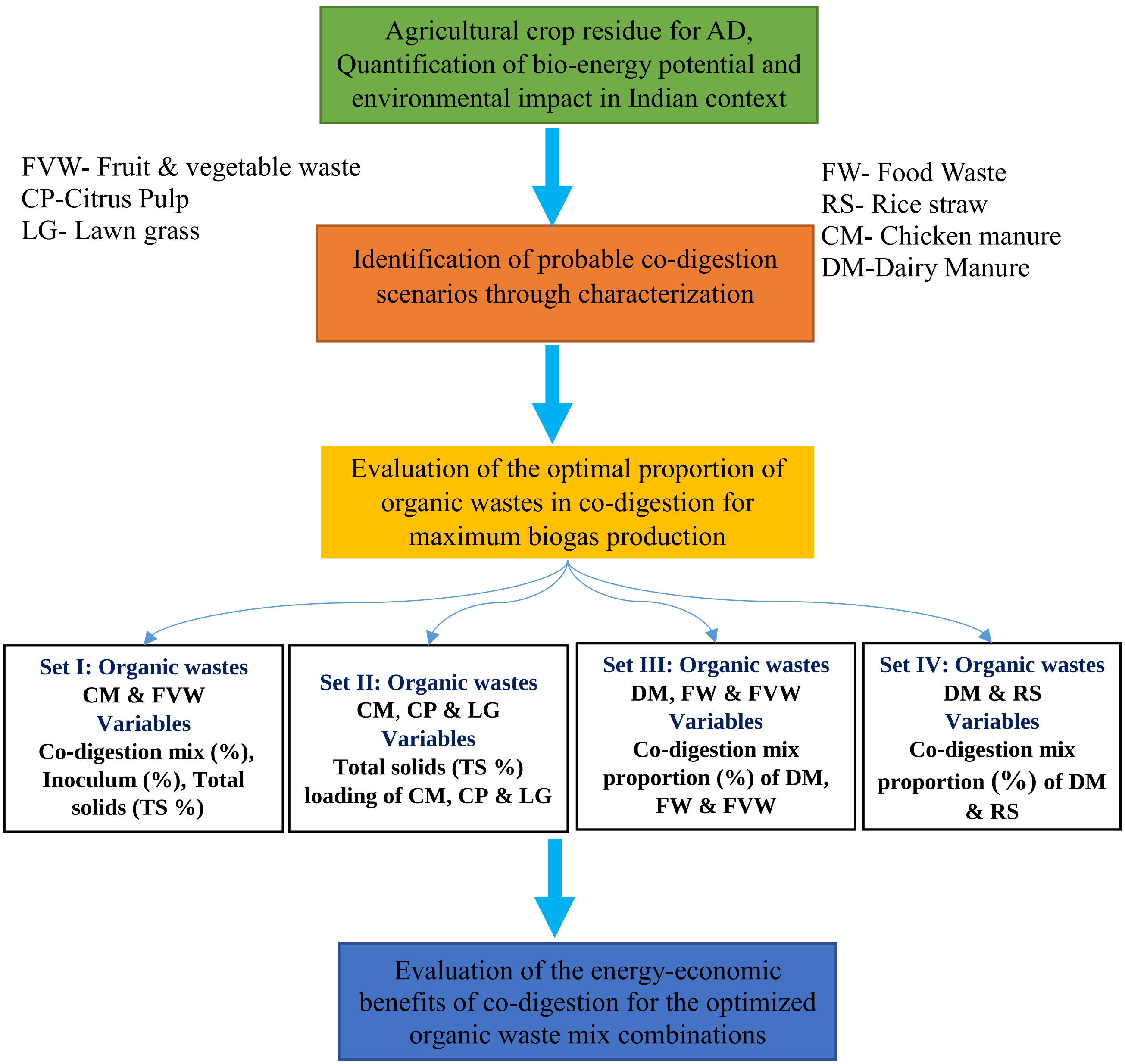

Fig. 3.5 Work flow

Chapter 4 AD of Agricultural Crop Residues

The present chapter is aimed to describe the crop residue generation and issues associated with crop residue based AD planning in Indian context. Bio-energy potential and environmental impact is also estimated for crop residue based AD. Summary is presented at the end of the Chapter.

4.1 Crop residue generation in India

Consistent growth of agricultural sector causing the augmented generation of crop residues in India (Cardoen et al., 2015). Common practices for utilisation of crop residue include feeding the cattle, using for domestic fuel, roof thatching, fencing and packaging (Milhau and Fallot, 2013). The unutilised surplus residues are either left uncollected or burnt openly in the crop field itself (Cardoen et al., 2015). It is estimated that 686 Mt of crop residues are generated annually and about 34% of residues (234 Mt) is surplus quantity (Hiloidhari et al., 2014). In another study, it is estimated that 611 Mt of crop residues are generated annually and 25% of generated residues (158 Mt) is the surplus quantity (Cardoen et al., 2015). In India, major cultivating crops are rice (*Oryza sativa)*, wheat (*Tritium aestivum)*, and maize (*Zea mays)* that occupies about 45 % of the cultivation area (Cardoen et al., 2015) (Fig. 4.1). Rice and wheat merely occupies about 40%, whereas maize occupies about 5% of the cultivation area (Cardoen et al., 2015). The crops generates about 3.2 to 4.5 tons of residues per hectare of cultivation (Cardoen et al., 2015). In India, rice generating about 154 Mt of residue /year which is the highest among the crops. After primary use for animal feeding and other domestic purposes, it is resulting in surplus residue about 28% (43.5 Mt). Wheat contributes about 131 Mt of residue/year and resulting in surplus residue about 21 % (28.4 Mt). Maize contributes about 35.8 Mt of residue/year and resulting in surplus residue about 25 % (9 Mt) (Hiloidhari et al., 2014). The three crops together making about 81 Mt of surplus residue (Table 4.1) and need to be handled in sustainable manner.

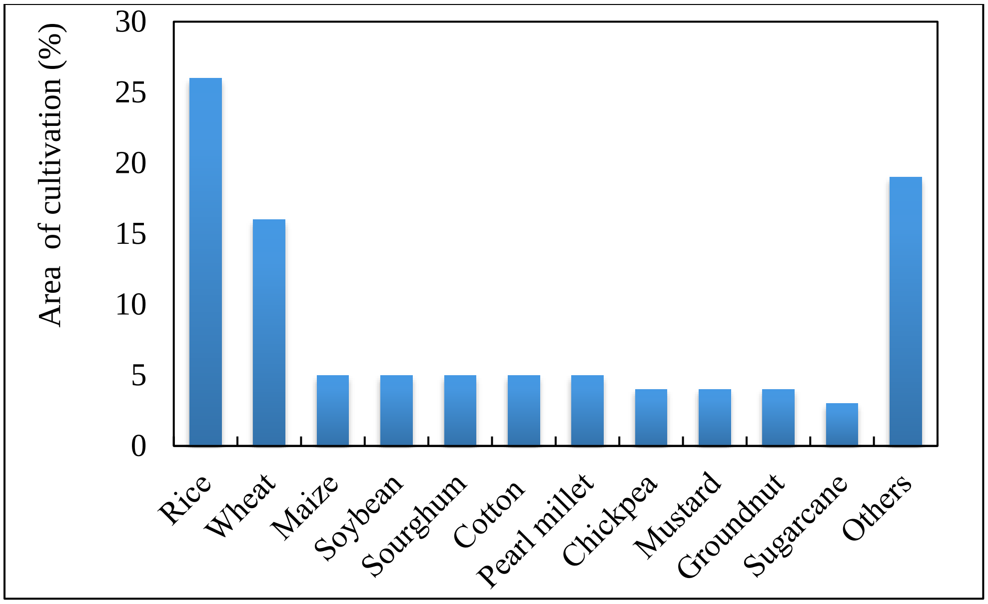

Fig. 4.1 Percentage (%) of cultivation area of crops

Table 4.1 Gross and surplus residue potential of major crops In India

Crop	Gross potential (Mt)	Surplus potential (Mt)
Rice	154.0	43.5
Wheat	131.1	28.4
Maize	35.8	9.0
Total	320.9	80.9

4.2 Utilization of crop residue for AD

In order to use crop residue for any alternative management, composition of residue indicates its suitability (Amon et al., 2007). The crop residue primarily consists of cellulose, hemicellulose, and lignin. Cellulose is a linear polymer of cellulobiose units and hemicellulose is a branched network of pentose and hexose units whereas, lignin is the three-dimensional network of phenyl propanoid units (Martínez et al., 2005). The three components of cellulose, hemicellulose, and lignin intermeshed with each other making as complex structure. Cellulose is linked physically with hemicellulose whereas linked physically and chemically with lignin. Lignin is linked chemically to hemicelluloses with ester or ether bonds.

Crop residue contains cellulose about 30-44%, hemicellulose about 30-50% , and lignin about 8-21% (Chandra et al., 2012a). The cellulose and hemicellulose fractions are predominantly available fractions for biological degradation. Crop residue also contains little amounts of proteins (3-4%) and fats(1-2%) (Chandra, 2015). Principal composition of the rice, wheat, and maize residues are presented in Table 4.2. From the table it can be understood that the crop residues are potential energy sources due to its reasonable volatile matter, and cellulose content. Due to richness in biodegradable fraction (volatile matter) crop residues can be used as a feedstock for AD (Chandra et al., 2012a). In Germany, 50% of the AD plants are based on crop residues and are successful in tapping the energy from AD (Li et al., 2011a). From the experience of Germany, AD can be practiced for energy generation in sustainable manner in India.

Table 4.2 Composition of crop residues

Crop residue	Volatile matter (%)	Cellulose (%)	Hemi cellulose (%)	Lignin (%)	Ref.
Rice straw	82.5	34.9	12.5	11.8	(Candia-García et al., 2018)
Wheat straw	88.3	45.6	33.4	6.4	(Xavier et al., 2015)
Maize straw	89.4	32.8	44.1	1.9	(Cuetos et al., 2013)

From the above discussion, it is evident that agriculture sector generating large amount of crop residues and significant portion of the generating residues is surplus. Due to richness in biodegradable fraction, the surplus residues can be used as feedstock for AD. However, AD being a complex biochemical process, several issues need to be considered for the AD based planning of crop residue and detailed as follows:

4.3 Considerations in crop residue based AD

Several factors influence the biological degradation of crop residue in anaerobic conditions (Amon et al., 2007). In addition to the factors mentioned in Section 2.1, the composition of residue, stage of harvest of the crop, pattern of harvest also influence the biological degradation, subsequently its efficiency (pictorially represented in Fig. 4.2). It is reported that silaged maize residue (preserved pasture) produced 25% of higher biogas production than non-silaged maize residue due to the pre-decomposition of the crude fiber in silaging (Amon et al., 2007). Also, the maize residues harvested at the stage of milk ripeness produced 16-27% of higher biogas production than maize residue harvested at the stage of full ripeness. The variations in biogas production are due to changes in residue composition over harvesting period (Amon et al., 2007). However, biogas production per hectare of crop area is highest for the maize residue harvested at full ripens stage. It is due to the more residue generation per hectare at full ripens stage (Amon et al., 2007). Furthermore, the type of harvesting (mechanical/manual) influences the structure of residues. The manual harvesting preserves the original structure of the residue. Mechanical harvesting shreds the residue to small pieces affecting its structure, which is favorable for the better AD. Moreover, the climatic conditions vary with geographical loacation and affects the composition, subsequently biogas production (Amon et al., 2007). Therefore, the time of harvest, harvesting pattern (mechanical/manual), silaging of residue and climatic conditions influence the composition and texture, subsequently AD.

Several researchers mathematically correlated the composition to biogas production to investigate its effect (Table 4.3). A positive correlation for biogas production is observed with crude protein, crude fat and hemicellulose (Amon et al., 2007; Dandikas et al., 2014; Rath et al., 2013). A negative relationship for biogas production is observed with the lignin content (Li et al., 2013a; Liu et al., 2015; Triolo et al., 2011). The kinetic investigations implied that low rate of biogas production (0.05-0.06 1 of CH_4/d) for the residues with high lignin (Li et al., 2013a). The low rate of bio production is mainly due to the protective action of the lignin coat preventing the biodegradation of cellulose and hemicellulose.

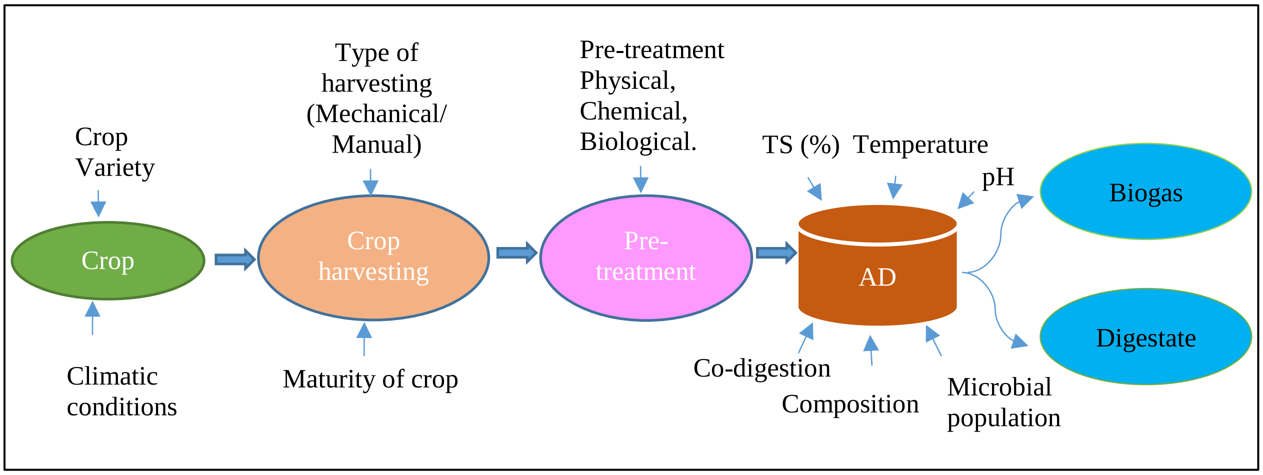

Fig. 4.2 Influencing factors in AD of crop residues

Table 4.3 Relation between composition and methane yield

Crop residue	No of samples	Methane yield (Y_m)	R^2	Reference
Energy crops	41	$Y_m = 371 + 0.13 \times HC - 2\ ADL$	0.80	(Dandikas et al., 2014)
Maize	12	$Y_m = 19.05 \times CP + 27.73\ CF + 1.8 \times C + 1.7 \times HC$	-	(Amon et al., 2007)
Energy crops	10	$Y_m = -2.58 \times L + 460.6$	0.76	(Triolo et al., 2011)
Crop residues	14	$Y_m = 113.14 \times (C/L\ ratio) - 26.62$	0.78	(Liu et al., 2015)

Y_m –Methane yield; C-Cellulose; HC – Hemicellulose; L-Lignin; ADL-Acid detergent lignin; CP-Crude protein CF-Crude fat; R^2 –Correlation coefficient; C/L ratio- cellulose to lignin ratio

The depolymerization of lignin can be achieved with pre-treatment before AD (Reilly et al., 2015). Several physical (Chandra et al., 2012c; Ferreira et al., 2014, 2013), chemical (Khatri et al., 2015; Reilly et al., 2015; Song and Zhang, 2015; Yuan et al., 2015) and biological pre-treatments (Mustafa et al., 2016; J. Zhao et al., 2014; Zhou et al., 2017) have been proven to be effective in degrading the lignin content. However, the high energy and costs associated with the pre-treatment methods preventing their practical application (Abudi et al., 2016a, 2016b). Therefore, low cost and energy efficient methods are necessary for the lignin degradation in crop residues for their sustainable utilisation.

From the above discussion, it can be understood that composition, stage of harvesting, pattern of harvesting, climatic conditions, and silaging of residue influence the biological degradation, subsequently AD performance.

4.4 Rice, wheat and maize residues for AD

The present section discusses rice, wheat, and maize residues in crop wise manner for AD process. The critical observations for improved AD performance in various scientific studies are presented.

4.4.1 Rice

Rice is largely cultivated food crop in India generating highest quantity of crop residue (Fig. 4.3) (Mussoline et al., 2012c). It is largely being cultivated in West Bengal, Andhra Pradesh, Telangana and Punjab (Gadde et al., 2009b). The yield of one kg of grain generates about 1.7 kg of straw and husk (Hiloidhari et al., 2014). In northern parts of India, rice is being cultivated on a rotation basis with the wheat crop. The utilisation of the rice residue is different throughout the country. In some parts of India, wheat straw is preferred as animal fodder than rice straw. The farmers leave the surplus rice residues in the field itself and are burnt subsequently (Gadde et al., 2009b). The open burning of rice straw results in the emission of GHGs such as carbon dioxide, carbon monoxide, methane, and nitrous oxide and affecting the environment (Gadde et al., 2009a).

Fig. 4.3 A field of rice in India

Several researchers have considered the rice residues for process enhancement. A wide range in experimental methane production (193-535 mL of CH_4/g VS) have been observed in AD of rice residues (Table 4.4**)**. The wide range in methane production is due to different operating conditions, pre-treatment methods and co-substrates used in the studies. As already mentioned in Section 2.2., co-digestion with nitrogen rich materials and pre-treatment methods improve the methane production. The co-digestion of rice straw with nitrogen rich manures (dairy manure, chicken manure and swine manure) improved the methane production about 33% to 43% (Wang et al., 2013). The improved methane production is due to synergistic effect between rice straw and nitrogen rich manures. Rice straw when pre-treated with fungi improved the methane production about 31% to 46% (Ghosh and Bhattacharyya, 1999). Some researchers also carried pre-treatment with acids, alkalis & hydrogen peroxide. The acid pre-treatment (HCl) of rice straw is found to be better compared to alkali pre-treatment (NaOH) that caused 43% of higher methane production (Wang et al., 2015). The alkali pre-treatment (NaOH) of rice straw is better compared to hydrogen peroxide (H_2O_2) pre-treatment that caused 20% of higher methane production (Abudi et al., 2016b). However, the improved methane production with pre-treatment may not be sufficient to cover the extra expenses incurred for pre-treatment (Abudi et al., 2016a). Whereas, the combined co-digestion and pre-treatment may sometimes make the process economically feasible (Abudi et al., 2016a). The other residue rice husk is shown to be improved the methane production when co-digested with poultry droppings (Okeh et al., 2014). It is estimated that 100-ha of rice field could generate 10^5 Mm^3 of methane annually that could yield 328 MWh of electricity (Mussoline et al., 2012a). The various pre-treatment methods and co-digestion substrates considered for rice residues comprehensively reported in Table 4.4. From the table it can be observed that the co-digestion with nitrogen rich manures and pre-treatment methods improves the methane production.

4.4.2 Wheat

Wheat is a second most cultivated food source in India (Fig. 4.4) and occupies about 16 % of the cultivation area (Cardoen et al., 2015). It is largely being cultivated in Uttar Pradesh, Punjab, Haryana, Madhya Pradesh, Bihar, and Rajasthan (Cardoen et al., 2015). One kg of grain yield from wheat generates about 1.8 kg of residues (Hiloidhari et al., 2014). In terms of area of cultivation, wheat generates about 4.5 t of residues per hectare of cultivation. After the primary utilisation for cattle feed and domestic use, the wheat generates about 28 Mt of surplus residues annually in India (Hiloidhari et al., 2014).

Fig. 4.4 A field of wheat in India

The conversion of wheat straw to methane is energetically most efficient process (Kaparaju et al., 2009). The methane production of wheat straw is found to be improved with various pre-treatment conditions, co-digestion substrates. The co-digestion of untreated wheat straw with cattle manure at 40:60 ratio resulted in improved methane production (Krishania et al., 2013). The additional alkali and combinational calcium hydroxide and sodium carbonate pre-treatments decomposed lignin that lead to improvement in methane production by 94%-99% (370-380 mL CH_4 /g of VS) (Krishania et al., 2013). Pre-treatment of wheat straw with H_2O_2 improved the soluble fraction of wheat residues by 30.5-77.3%. Among the tested concentrations of H_2O_2 (1%, 2%, 3% and 4%), pre-treatment of wheat straw with 3% of H_2O_2 resulted in maximum methane production (Krishania et al., 2013). The steam explosion pre-treatment also improved the methane production by 27% (Ferreira et al., 2014).

It is crucial to consider net energy balance for practical implementation for chosen pre-treatment (Ferreira et al., 2014). The microwave pre-treatment of wheat straw improved the methane production with structural modifications of wheat straw (Jackowiak et al., 2011). However, the improved methane production could not compensate the energy consumed for the microwave pre-treatment (Jackowiak et al., 2011). The operating conditions of AD process also influenced the AD performance significantly. It is reported that co-digestion of wheat straw (9% on fresh matter basis) with cattle manure (91% on fresh matter basis) under thermophilic (50º C), liquid state conditions (TS:14.8%) resulted in methane production of 351 mL of CH_4/g VS (Xavier et al., 2015). Whereas, the co-digestion of wheat straw with cow feces under psychrophilic (20º C), solid state conditions (TS-27%) resulted in just 187 mL of CH_4/g VS which is comparatively lower. The lower methane production is also attributed to the higher substrate loadings and lower operating temperature (Saady and Massé, 2015). Several pre-treatment methods and co-digestion materials that have been used for AD of wheat residues are summarised in Table 4.6. From the table a wide range in experimental methane yields in the range of 67- 380 mL of CH_4/g VS can be observed for wheat residues. Hence, proper pre-treatment method, co-digestion substrate, and operating conditions play a significant role for the improvement of methane production.

4.4.3 Maize

Maize (corn) is the third most cultivated cereal crop that occupies about 5 % of gross cultivation (Fig. 4.5) (Cardoen et al., 2015). It is largely cultivated in Andhra Pradesh, Karnataka, Bihar, Gujarat, Himachal Pradesh, Jharkhand, Rajasthan Madhya Pradesh, and Uttar Pradesh (Cardoen et al., 2015). One kg of corn yield generates about 2.3 kg of residue which is high compared to rice (1.7 kg) and wheat (1.8kg) (Hiloidhari et al., 2014). After the primary utilisation for cattle feed and domestic use, maize generates about 9 Mt of surplus residue annually in India (Hiloidhari et al., 2014).

Several pre-treatment, and co-digestion strategies are widely reported for maize residues to improve the methane production. A wide range in experimental methane yields (81- 383 mL of CH_4/g VS) have been observed for AD of maize residues (Table 4.6).. Corn straw when pre-treated under thermophilic (55ºC), microaerobic conditions (5 mL of oxygen load/ g VS) improved the methane production by 16 % due to improved hydrolysis of straw (Fu et al., 2014). Corn straw when with ammonia pre-treatment also improved the methane production by 26% (Yuan et al., 2015). The ammonia pre-treatment also reduced the digestion time from 52 days to 37 days in producing 90 % of methane.

Fig. 4.5 A field of maize in India

The combined effect of pre-treatment and co-digestion is also investigated**.** The pre-treated of corn stover with co-digestion of food waste improved the methane production by 12 % at C/N ratio of 20 (Zhou et al., 2014). The co-digestion of corn straw with blue algae improved the methane production by 46% at same C/N ratio of 20 (Zhong et al., 2013).The co-digestion of cornstalk with vermicompost with 60:40 proportion lead to improved methane production (Chen et al., 2010). Co-digestion of corn stover with chicken manure improved methane production that lead to energy of 8.0 MJ/kg VS with synergistic effect (Y. Li et al., 2014b). Hence, the appropriate pre-treatment method and co-digestion substrate could improve the methane production of maize residues.

Table 4.4 Summary of experimental conditions and methane production of rice residues

Substrate	Co-substrate	Pre-treatment	Mode	Operating conditions	Methane production	Remarks	Reference
Rice straw	Food waste	Size reduction 0.5-1 cm and alkaline pre-treatment of rice straw	Batch	Mesophilic, food waste to rice straw ratio -3.88 and S/I ratio -0.5 based on VS,	535 mL of CH_4/g of VS	High methane production obtained with butyric acid fermentation.	(Chen et al., 2015)
Rice straw	Kitchen waste and pig manure	Size reduction- <1 mm	Batch	Mesophilic, ratio of kitchen waste, pig manure, and rice straw is 0.4:1.6:1 (C/N ratio-21.7)	383 mL of CH_4/g VS of methane	VFAs accumulation was observed at high kitchen waste loading (>26%).	(Ye et al., 2013)
Rice straw	Chicken manure	Size reduction 2-3cm	Batch	Mesophilic, TS-8%, rice straw to chicken manure ratio -50:50	378 mL of CH_4/g of $VS_{removed}$	Co-digestion of substrates improved the stability	(Zhang et al., 2014)

Rice Husk	Food waste	Size reduction <10 mm	Batch	Mesophilic, C/N ratio 20, S/I ratio 0.25.	307 mL of CH_4/g VS*	Co-digestion avoided VFAs inhibition	(Haider et al., 2015)
Rice straw	-	Size reduction- <2mm, alkali, acid pre-treatments	Batch	Mesophilic, alkali- NaOH acid-HCl	287 mL of CH_4/ g COD(HCl) 193 mL CH_4/g COD (NaOH)	Acid pre-treatment resulted in higher methane yield compared to alkali pre-treatment	(Wang et al., 2015)
Rice straw	Sewage sludge	Size reduction - 2mm	Batch	Thermophilic, two stage system, sewage sludge-150 mL and rice straw-27g, TS-17%.	266 mL of CH_4/g of VS	Two stage system resulted in higher methane yield compared to one stage system	(Kim et al., 2013b)
Rice straw	-	Size reduction, fungal pre-treatment	Batch	Mesophilic, solid state conditions, moisture content 75%, 20 days	263 mL of CH_4/g VS	Fungal pre-treatment enhanced the methane yield by 120%.	(Mustafa et al., 2016)

Rice straw	-	Size reduction and pre-aeration for 2 days at 35º C	Batch	Mesophilic, TS-16%, I/S ratio of 2	234 mL of CH_4/g VS	Pre-aeration and inoculum dilution improved the hydrolysis.	(Zhou et al., 2017)
Rice straw	-	Size reduction, extrusion pre-treatment	Batch	Mesophilic, OLR is 50 kg/m^3 and I/S ratio of 2.5	227 mL of CH_4/g VS	Extrusion pre-treatment of rice straw reduced the digestion time.	(X. Chen et al., 2014b)
Rice Husk	Food waste	Size reduction <10 mm	Plug flow	Mesophilic, C/N ratio 28, OLR of 5 kg VS/ m^3 /day	245 mL of CH_4/g VS*	Inhibition VFAs was observed at high OLR	(Jabeen et al., 2015)

Rice straw	Pig manure	Size reduction- 1 mm	Batch, contin uous	Mesophilic, rice straw : pig manure 1:1 on VS basis 6-8 kg $VS/m^3/day$	220-247 mL of CH_4/g VS*	Stable biogas production was found at an OLR of 6-8 kg $VS/m^3/day$	(Li et al., 2015b)
Rice straw	-	Size reduction, composting	Batch	Mesophilic, C/N ratio of 30	194 mL of CH_4/g VS*	Composting enhanced the biodegradation.	(Yan et al., 2015)
Rice straw	Cow manure	Size reduction- 1 mm	Batch, contin uous	Mesophilic, rice straw : Cow manure 1:1 on VS basis 6kg $VS/m^3/day$	193 mL of CH_4/g VS	Stable biogas production was found at an OLR of 3-6 kg $VS/m^3/day$	(Li et al., 2015b)

Rice straw	Pig manure, clay residues	Size reduction	Batch	Thermophilic - 20.1 g VSS/L of manure+ 10.18 g VSS/L of straw + 3.05 g VSS/L of clay residue	1.38 g CH_4-COD/ g VSS/day	Presence of high amount of clay residue reduced the methane production	(Jiménez et al., 2014)
Rice straw	Pig manure, clay residues	Size reduction	Batch	Mesophilic, manure(28.35 g VSS/ L) + straw(17.6 g VSS /L) + clay residue (8.3 g VSS/L)	1.31 g CH_4-COD/ g VSS/day	Clay residues had higher influence on methane production compared to rice straw	(Jiménez et al., 2014)
Rice straw	Goat manure (GM)	Size reduction-2-3 cm	Batch	Mesophilic, GM: rice straw ratios of 30: 70 and 50:50, TS-8%, 700 mL working volume	8,584 mL of CH_4 * in 55 days (30:70) 8633 mL of CH_4 * in 55 days (50:50)	Co-digestion of substrates improved biogas production due to improved nutrient balance.	(Zhang et al., 2013)

Rice straw	Dairy manure	Size reduction-2-3 cm	Semi-cont	Mesophilic, TS-8%, rice straw to dairy manure ration of 5:5 on a mass basis,	286 mL of CH4/L/day* in the first stage of stabilization	All co-digestion proportions improved biogas production, except 9:1.	(J. Li et al., 2014b)

TCL-Treatment cycle length, OLR-Organic loading rate, S/I ratio = substrate to inoculum ratio, TS-Total solids, VS- Volatile solids, VSS- volatile suspended solids (VSS), * reported biogas yield was converted to methane yield with the conversion factor of 0.55 (methane content-55%).

Table 4.5 Summary of experimental conditions and methane production of wheat residues

Substrate	**Co-substrate**	**Pre-treatment**	**Mode**	**Operating conditions**	**Methane production**	**Remarks**	**Reference**
Wheat straw	Cattle manure	Size reduction (2-3 mm), ($Ca(OH)_2$-Na_2CO_3)	Batch	Mesophilic, cattle manure-60%, total solids -10%, inoculum of 10 %, 3% $Ca(OH)_2$ + 3% Na_2CO_3, Time- 48 h	380 mL of CH_4/g VS	Pre-treatment improved the CH_4 yield	(Krishania et al., 2013)
Wheat straw	Cattle manure	Size reduction (2-3 mm), alkali	Batch	Mesophilic, cattle manure of 60%, total solids -10%, inoculum -10%, NaOH - 2%	370 mL of CH_4/g VS	The increase of CH_4 yield by 94% with alkali pre-treatment of wheat straw	(Krishania et al., 2013)
Wheat straw	Cattle manure	Briquetting -20 mm	Cont	Thermophilic, wheat straw – 9%, cattle manure-91%	351 mL of CH_4/g VS	Co-digestion improvement the methane yield by 33%	(Xavier et al., 2015)
Wheat straw	Chicken manure	Size reduction 2-3cm	Batch	Mesophilic,TS-8%, wheat straw to chicken manure	345 mL of CH_4 /g of $VS_{removed}$	Co-digestion with chicken manure improved the stability	(Zhang et al., 2014)

				ratio -50:50 on a dry basis			
Wheat straw	Cattle manure	Size reduction 20-30 mm and H_2O_2	Batch	WS:CM ratio 40:60, inoculum-200 gr, total solids-8%, 3% H_2O_2	320 mL of CH_4/g VS	Pre-treatment and co-digestion at 40: 60 improved the CH_4 production	(Song and Zhang, 2015)
Wheat straw		Size reduction (3,2, 1.25 mm) and enzymatic	Batch	Mesophilic, S/I ratio 0.66 based on VS	307-335 NmL of CH_4/g VS	Combined size reduction and enzymatic treatment improved the CH_4 production	(Reilly et al., 2015)
Wheat straw	-	Size reduction (3,2, 1.25 mm) and alkali	Batch	Mesophilic, S/I ratio 0.66 based on VS	301 to 320 mL of CH_4/g VS for all particle sizes	Cost effective pre-treatment with particle size reduction to 3 mm compared to enzymatic pre-treatment	(Reilly et al., 2015)
Wheat straw	Sewage sludge	Size reduction - 3 mm	Cont	Mesophilic, OLR-2 g VS/L/day, recirculation of digestate	296 mL of CH_4/kg VS	Co-digestion of sewage sludge and digestate liquor	(Peng et al., 2016)

						recirculation improved the CH_4 production	
Wheat straw	-	Steam explosion and water impregnation	Batch	Mesophilic, S/I ratio-0.5 based on VS	293-323 mL of CH_4/g VS	Impregnation had negligible effect on methane production	(Ferreira et al., 2014)
Wheat straw	-	Steam explosion	Batch	Mesophilic, S/I ratio-0.5 based on VS	288-296 mL of CH_4/g VS	Steam explosion improved the methane production by 24-27%	(Ferreira et al., 2014)
Wheat straw	-	Size reduction- 10-20 mm, steam, enzymatic	Batch	Mesophilic I/S ratio -2.	280 mL of CH_4/g VS	Pre-treatment improved the methane yield by 57%	(Nkemka and Murto, 2013)
Wheat straw		Size reduction(3 ,2,1.25 mm)	Batch	Mesophilic, S/I ratio 0.66 based on VS	268 N mL of CH_4/g VS	Size reduction had negligible effect on methane production	(Reilly et al., 2015)
Wheat straw	Cattle manure	Size reduction (2-3 mm)	Batch	Mesophilic, cattle manure of 60%,total solids -	241 mL CH_4/g VS	Co-digestion of wheat straw and cattle	(Krishania et al., 2013)

				10%, inoculum-10%,		manure improved the methane production	
Wheat straw	Dairy manure(DM) and chicken manure(CM)	Size reduction - 2-3 cm	Batch	Mesophilic, S/I ratio-0.5, DM/CM ratio of 50:50 based on VS	234 mL of CH_4/g VS	Co-digestion of wheat straw with two manure improved the biogas production compared with single manure	(Wang et al., 2012)
Wheat straw	-	Size reduction 3-5 cm and < 1 mm	Batch	Mesophilic, S/I ratio-0.5 based on VS	232-245 mL of CH_4/g VS	Size reduction had negligible effect on methane production	(Ferreira et al., 2014)
Wheat straw	Dairy Manure	Size reduction	Sequential batch	Psychrophilic (20º C) S/R-1.7, OLR-3.7, TS-27%, TCL-21 days	193 mL of CH_4/g VS	Psychrophilic dry AD is as efficient compared to mesophilic dry AD.	(Saady and Massé, 2015)
Wheat straw	Urea	Size reduction and alkali	Batch	Mesophilic, S/I ratio 1 based on VS, C/N ratio 25.0,	165 mL of CH_4/g VS	Alkali pre-treatment improved the methane production by 111.6%	(Chandra et al., 2012d)

				NaOH-4%,			
Wheat straw	Cattle manure	Size reduction- 10 mm and steam explosion	Cont	Temperatures- 37,44, 55 º C, OLR-0.28 g VS/L/day, a steam explosion at 210º C, 10 min, retention time-25 days	130 to 210 N mL of CH_4/g VS	Co-digestion with cattle manure and pre-treatment by Steam explosion had not improved the methane production	(Risberg et al., 2013)
Wheat straw	Cattle manure	Size reduction (2-3 mm) and acid	Batch	Mesophilic, cattle manure-60%,total solids -10%, inoculum -10%, 2% H_2SO_4 -121º C, time-30 min, pressure of 100 kPa	125 mL of CH_4/g VS	Acid pre-treatment reduced the CH_4 production	(Krishania et al., 2013)
Wheat straw	Urea	Size reduction and hydrothermal		Mesophilic, S/I ratio- 1 (based on VS), C/N ratio 25.0, temp-200 ºC, 10 min, 1.5 Mpa	94 mL of CH_4/g VS	Hydrothermal pre-treatment improved the methane production by 20.0%	(Chandra et al., 2012d)

Wheat straw	-	Size reduction-9 mm	Batch	Mesophilic, TS=22%,S/I ratio=2	67 mL of CH_4/g VS	Cellulose and hemicelluloses are main contributors for methane yield	(Liew et al., 2012)
Wheat straw	Dairy manure	Size reduction- 2-3 cm	Semi-cont	Mesophilic, TS-8%,wheat straw to dairy manure ration of 5:5 on a mass basis, working volume - 800 mL	10,519 mL of CH4* after 47 days of digestion	Improved production, except of 9:1 ratio	(J. Li et al., 2014b)
Wheat straw	Goat manure (GM)	Size reduction 2-3 cm	Batch	Mesophilic, GM: Wheat straw ratios of 30: 70 ,TS-8%, working volume - 700 mL	7,020 mL of CH_4* in 55 days	Co-digestion with goat manure improved the stability	(Zhang et al., 2013)

VSS-Volatile suspended solids, BMP- Biochemical methane potential, TS-Total solids; VS- Volatile solids, OLR-Organic overloading rate, * reported biogas yield was converted to methane yield with the conversion factor of 0.55 (methane content-55%).

Table 4.6 Summary of experimental conditions and methane production of maize residues

Substrate	**Co-substrate**	**Pre-treatment**	**Mode**	**Operating Conditions**	**Methane production**	**Remarks**	**Ref**
Corn stalk	Chicken manure	Size reduction 2-3cm	Batch	Mesophilic, TS-8%, cornstalk to chicken manure ratio of 50:50 on dry matter basis	383 mL CH_4 /g of $VS_{removed}$	Co-digestion improved the stability	(Zhang et al., 2014)
Corn straw	-	Size reduction - 5mm, thermophilic (55^o C) micro-aerobic pre-treatment (TMP)	Batch	Mesophilic, I/S ratio-0.5 based on TS, Shaking speed-130 rpm, oxygen load - 5mL/g of VS	325 mL of CH_4/g of VS	Pre-treatment improved (TMP) the hydrolysis and reduced lag phase time	(Fu et al., 2014)
Corn Stover	Chicken manure	Size reduction-< 30 mm	Batch	Mesophilic, C/N ratio -20, Loading- 3 g VS/L, S/I ratio 0.5	281 mL of CH_4/g of VS	Biodegradability of 62%	(Y. Li et al., 2014b)

Corn stalk	Vermi compost	Size reduction corn stalk-10-20 mm; vermi compost-0.8mm	Batch	Mesophilic, Inoculum-400 g Vermi compost -40% , TS- 6%	259 mL of CH_4/g TS	Co-digestion with vermicompost improved the biodegradability	(Chen et al., 2010)
Corn Stover	-	Size reduction-<5mm,ammonia pre-treatment	Batch	Mesophilic, 4% NH_3,70% moisture content, Inoculum- 15 [MLSS] g/l,	256 mL of CH_4 /g VS	Ammonia pre-treatment improved biogas production by 26.70%	(Yuan et al., 2015)
Corn straw	Blue algae	Size reduction- 5 to 10 mm	Cont	Mesophilic, C/N ratio -20, OLR- 6 g VS/L, HRT-10 days	234 mL of CH_4 /g VS	Co-digestion with corn straw improved the methane production by 46%.	(Zhong et al., 2013)
Corn Stover (CS)	Chicken manure (CM)	Size reduction-< 30 mm	Cont	Mesophilic, C/N ratio -20, CM:CS - 1:1.4, TS- 12%, OLR -4 g VS/L	223 mL of CH_4/g of VS	Stable methane production at OLR of 4 g VS/L	(Y. Li et al., 2014b)

Maize residues	Poultry blood	Size reduction-3mm	Batch	Mesophilic, 200 rpm, I/S ratio-1-2 maize to poultry blood mixture - 70:30 on VS basis	188 mL of CH_4/g VS	Co-digestion of maize leaves with poultry blood improved the methane yield	(Cuetos et al., 2013)
Maize residues	Poultry blood	Size reduction-3mm	Semi-cont	Mesophilic, HRT- days36. OLR-3.1 g VS/L/day, TS-12.6%, Maize-60% based on VS	165 mL of CH_4/g of VS	VFAs accumulation caused inhibition at OLR of 3.1 g VS/L/day.	(Cuetos et al., 2013)
Corn stover	-	Size reduction	Batch	Mesophilic TS=22%,S/I ratio=2,	81 mL of CH_4 / kg of VS	Cellulose and hemicelluloses are mainly contributed methane yield	(Liew et al., 2012)
Corn stalks	Goat manure (GM)	Size reduction 2-3 cm	Batch	Mesophilic, GM: corn stalks ratio is 70: 30 ,TS-8%, working volume - 700 mL	8,812 mL of CH_4 * in 55 days	Co-digestion improved the biogas production	(Zhang et al., 2013)

Corn stalk	Dairy manure	Size reduction-2-3 cm	Semi-contin uous	Mesophilic, TS-8%, corn stalk to dairy manure ration of 5:5 on a mass basis, working volume - 800 mL	10,685 mL of CH_4/g TS* after 47 days of digestion	Optimal biogas yield obtained at corn stalk to dairy manure ratio of 5:5 (mass basis)	(J. Li et al., 2014b)

MLSS= mixed liquor suspended solids; HRT=Hydraulic retention time, TS= total solids, VS- Volatile solids, * reported biogas yield was converted to methane yield with the conversion factor of 0.55 (methane content-55%).

Table 4.7 Bio-energy potential and CO_2 emission reduction in AD of crop residues

Crop residue	Surplus quantity, *B* (Mt)	CH_4 potential, *P* (m^3/ton)	Methane potential (Mm^3)	Bio-energy potential ($\times 10^9$ MJ)	Net bio-energy potential ($\times 10^9$ MJ)	Coal Substitution, *M* (Mt)	CO_2 emission reduction (Mt)	Net CO_2 emission reduction (Mt)
Rice	43.50	231*	10,049	360	352	27.1	41	25
Wheat	28.40	221*	6300	226	220	16.9	26	15
Maize	9.00	258*	2328	84	81	6.3	9	6
Total			**18,677**	**670**	**653**	**52**	**76**	**46**

* Values adopted from (Chandra, 2015) and converted to methane production of fresh mass based on the assumption that crop residues are having TS=85% and VS=80%

From the above discussion, it can be understood that co-digestion of rice, wheat and maize residues with nitrogen rich organic substances and appropriate pre-treatment methods could improve the AD performance. The further section discusses bio-energy potential and environmental impact with AD of rice, wheat and maize residues.

4.5 Bio-energy potential and environmental impact

Bio-energy potential and environmental impact is required for crop residue based AD planning. The surplus rice, wheat, and maize residues is estimated to have methane potential about 18,677 Mm^3/year (Table 4.7). The corresponding bio-energy potential is estimated to be 670×10^9 MJ (Table 4.7). However, energy is also consumed for various unit operations involved in AD. One of the major energy consumptions is pulverisation of residue before feeding into the AD system. The energy required for pulverisation is about 207 MJ/ ton (Adl et al., 2012). After the deduction of energy for pulverisation (207 MJ/ ton), the net bio-energy potential is estimated to be 653×10^9 MJ for three crop residues. Other energy requirements such as mixing, feeding the feedstock and withdrawal of digested material are neglected due to their low energy requirement. Among the crop residues, rice is having highest bio-energy potential followed by wheat and maize (Fig. 4.6). The bio-energy potential of three crop residues could meet about 5.3% of electricity demand in India (1,021 TWh of electrical energy demand from coal in 2018-19).

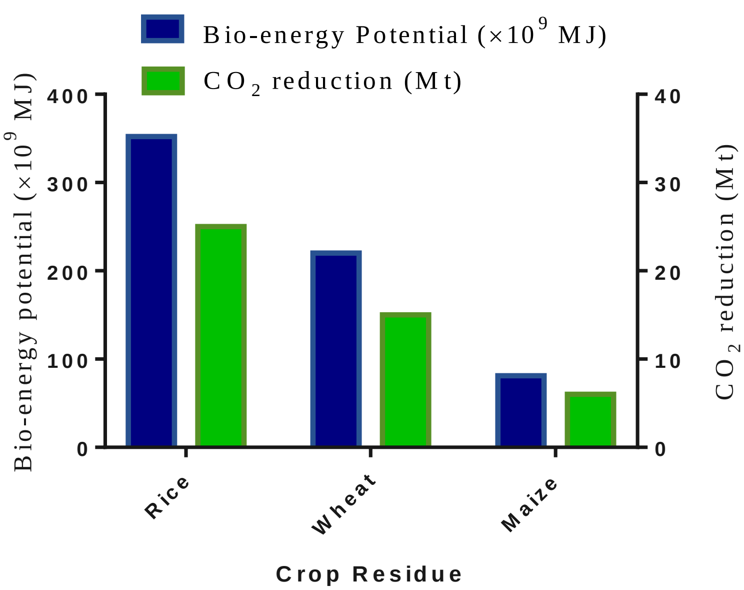

Fig. 4.6 Bio-energy potential and CO_2 emission reduction

Further, environmental impact is estimated for crop residues as per method described in Section 3.1. The environmental impact is assessed based on assumption that produced bio- energy from the AD substitutes the consumption of coal. The amount of coal that can be substituted is estimated by assuming the bio-energy produced from AD is used for thermal heating as given in (Yanli et al., 2010). The amount of coal that can be substituted is found to be 52 Mt. The reduction in CO_2 emission is estimated based on substituted amount of coal. It is observed that 76 Mt of CO_2 emissions from coal could be avoided from releasing into environment. However, CO_2 emissions could also be produced when the residues are transported to the centralised AD facility, and it need to be considered (Singh and Maurya, 2016). For this purpose, a vehicle is assumed to carry 2 ton of crop residues over a haul distance of 5 km with a mileage of 35 km/L of diesel is considered. One liter of diesel emits 2.6 kg of CO_2 into the atmosphere in vehicular transportation (Canada, 2016). The net CO_2 emissions reduction is estimated after the deduction of CO_2 emissions of vehicle during transportation of residues to AD plant. After subtracting the emissions of vehicular transportation, the net CO_2 emissions are found to be 46 Mt. The corresponding CO_2 emissions are about 3.4% of emissions currently released into the atmosphere in India (2,194 Mt of CO_2 emissions /year in 2018-19). The estimates implies that the AD of these surplus crop residues has significant bio-energy potential and it avoids significant CO_2 emissions from releasing into the atmosphere. Hence, crop residues can be considered for bio-energy generation with AD to meet the energy demand of the nation.

4.6 Summary

From the present study, it can be observed that

- The bio-energy production from AD of crop residues can be improved with co-digestion and pretreatmen methods by enhancing the nutritional balance and degradation.
- The selection of appropriate substrate for co-digestion and appropriate pre-treatment techniques for crop residue is required to improve the AD process performance.
- The surplus rice, wheat, and maize residues as a feed stock for AD has bio-energy potential of about 653×10^9 MJ/year in India.
- The bio-energy potential of surplus crop residues could substitute 52 Mt/year of coal from consumption.

- The coal substitution could avoid 46 Mt of CO_2 emissions/year from releasing into the atmosphere.
- The collection and transportation of the residues for AD process remains a challenge and may be practically feasible if the governing states adopt an appropriate policy for their effective use.

Among the crop residues studied in this chapter, rice is abundantly available in Warangal district and is selected for the process enhancement. As mentioned in Chapter 2, AD is a syntrophically connected biochemical process and co-digestion is preferable for stable and efficient biogas production. Several organic wastes are generated locally, their characteristics and co-digestion performance is investigated with an aim to maximise biogas production and detailed in Chapter 5.

Chapter 5 Co-digestion of Agricultural and Municipal Organic Wastes

The present chapter is aimed to describe the characteristics of organic wastes, options for process enhancement through co-digestion, and data analysis. Summary is presented at the end of the chapter.

5.1 Characterization of organic wastes

Different kinds of organic wastes are generated from municipalities, agricultural, and food based industries in the study area. Seven different organic wastes viz., food waste (FW), fruit & vegetable waste (FVW), lawn grass (LG), citrus pulp (CP), rice straw (RS), chicken manure (CM), and dairy manure (DM) are identified for the current work. These organic wastes are identified based on their local availability and suitability for AD in the study area. All the organic wastes are characterised in triplicates and their average value is taken to represent the sample. The obtained properties of proximate and elemental analysis are detailed as follows:

5.1.1 Proximate analysis

Proximate properties indicate the potential suitability of organic waste for AD. The proximate analysis gives moisture content, total solids content, volatile content, and ash content.

Moisture content represents the water content per unit mass of biomass. It affects the heating value of organic waste. High moisture content indicates the low heating value since heat is required to evaporate the moisture contained. Moisture content of the organic wastes is presented in Fig. 5.1. It can be observed from the figure that DM, FW, FVW, and CP are having high moisture content (83 to 89 %) and RS is having low moisture content (7 %). Whereas, LG and CM are having moisture content about 57-59 %.

Total solids content represents organic and inorganic content in biomass. Total solids (TS%) content of the organic wastes is presented in Fig. 5.2. It can be observed from the figure that RS, LG, and CM are having high total solids (TS %) content relatively compared to CP, FVW, FW, and DM.

Volatile solids content represents the probable biodegradable organic fraction of biomass. Volatile solids (% of TS) of the organic wastes are presented in Fig. 5.3. It can be observed that the selected organic wastes are having quite a good amount of volatile matter (60-92 %) indicating the potential for biological degradation and subsequent biogas production.

(RS: rice straw, CP: citrus pulp, LG: lawn grass, FW: food waste, FVW: fruit and vegetable waste, CM: chicken manure, DM: dairy manure)

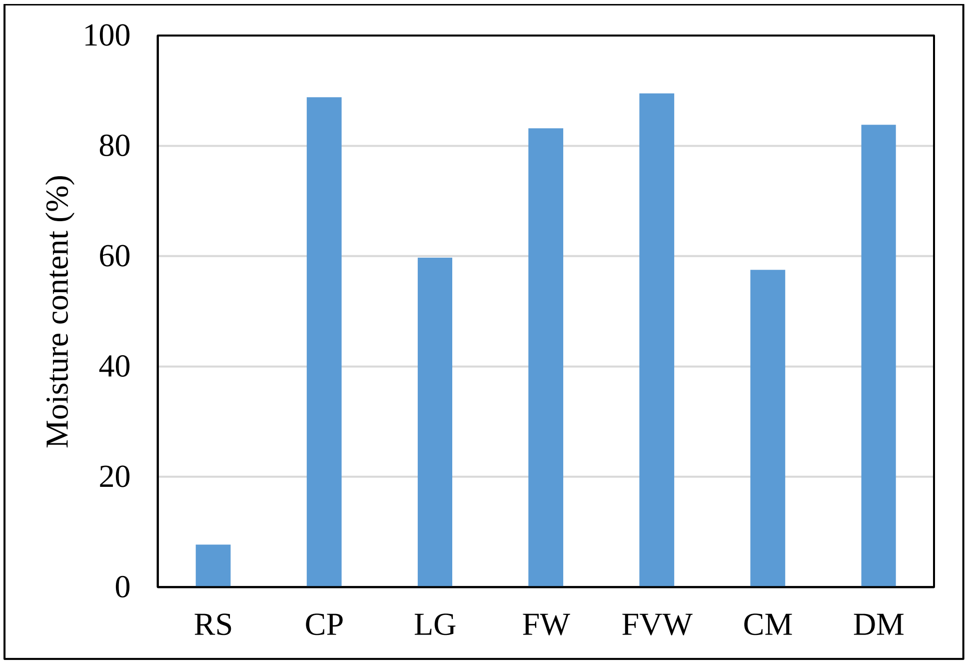

Fig. 5.1 Moisture content of organic wastes

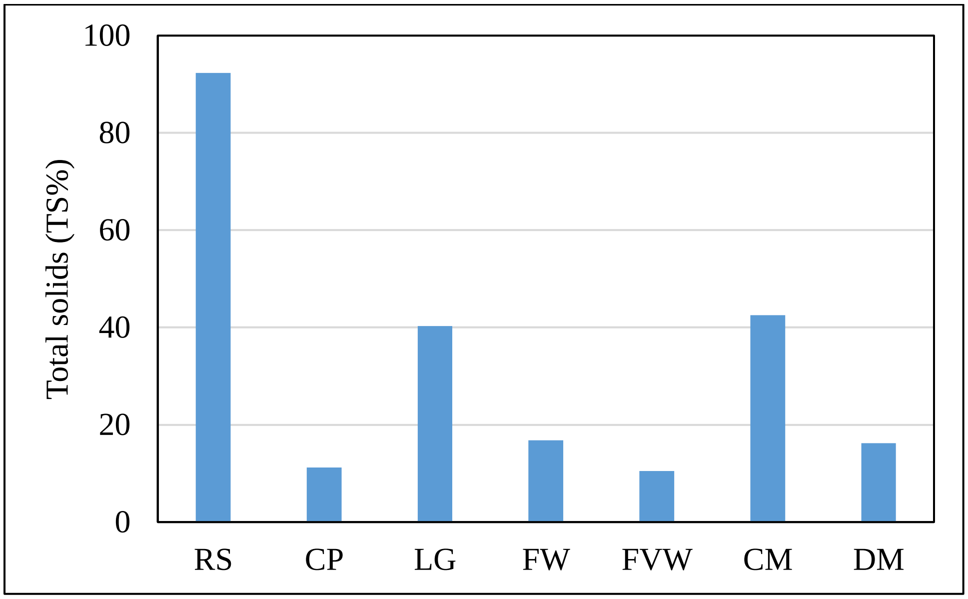

Fig. 5.2 Total solids content of organic wastes

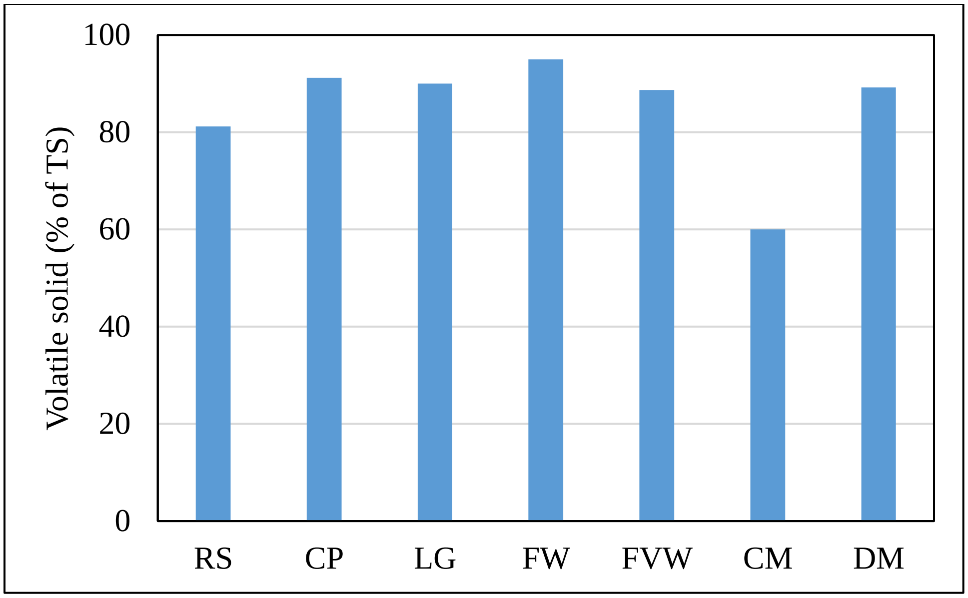

Fig. 5.3 Volatile solids content of organic wastes

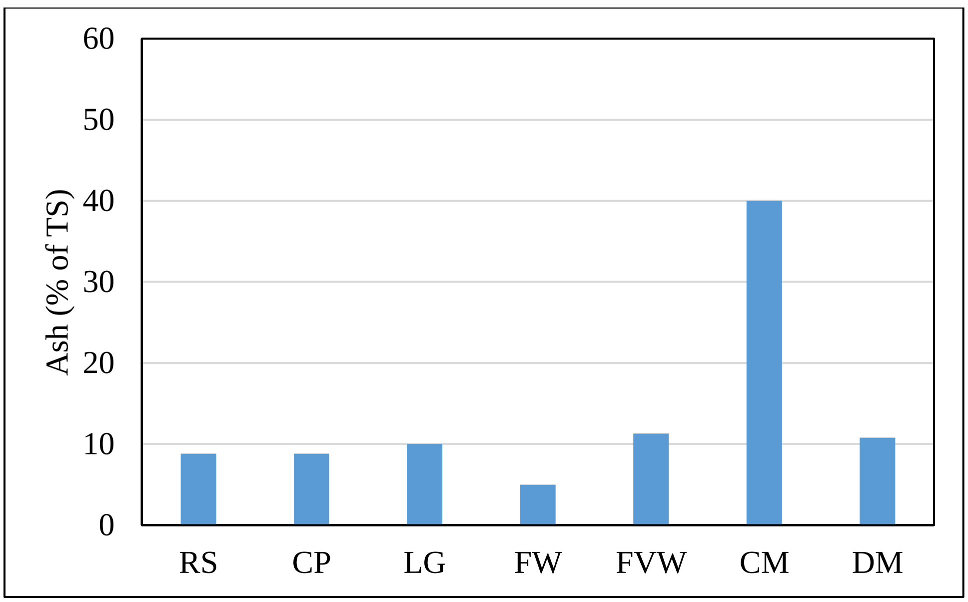

Fig. 5.4 Ash content of organic wastes

Ash content is the non-volatile organic matter left after thermal digestion at 550^{O} C. The organic waste with lower the ash content indicates the better substrate for AD. Ash content for all the organic wastes is presented in Fig. 5.4. It can be observed from the figure that all the organic wastes are having low ash contents (8 to 40 %) indicating the feasibility of organic wastes for AD.

5.1.2 Elemental analysis

Elemental analysis is carried to determine the composition of carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) content of organic wastes on weight basis. Elemental composition of the organic wastes is represented in Table 5.1. It can be observed that the selected organic wastes are having a reasonably good amount of carbon content (25.0-52.8%). The organic wastes such as DM, CM are relatively having high nitrogen content (>2.0 %) compared to other organic wastes. The variations in elemental composition are due to the diverse source of organic wastes and constituents present in it. For example, CM has high nitrogen content due to the presence of uric acid and undigested protein (Abouelenien et al., 2014; Y. Li et al., 2014a; Zhang et al., 2014).

Table 5.1 Elemental analysis of organic wastes (weight %)

Organic Waste	**C (%)**	**H (%)**	**N (%)**	**S (%)**
RS	38.2± 0.0	5.4± 0.0	0.68± 0.0	0.72± 0.0
CP	42.4± 0.2	7.3± 0.0	1.7± 0.0	-
LG	37.0 ± 0.1	4.90± 0.0	0.71± 0.0	-
FW	52.8 ± 0.0	7.8± 0.1	1.5± 0.0	0.29± 0.0
FVW	41.5± 0.0	5.1± 0.1	1.2± 0.0	-
CM	25.0 ± 0.0	5.0± 0.0	4.1± 0.0	-
DM	41.6± 0.0	6.11± 0.1	2.5± 0.0	0.35± 0.0

C/N ratio represents the carbon matter per unit of nitrogen and is a better indicator to represent the nutritional content of organic waste for microorganisms (Kainthola et al., 2019). C/N ratios of the organic wastes analysed in the present study shown in Fig. 5.5. The presence of a high C/N ratio (low nitrogen content) may cause the system devoid of nitrogen, which is a structural element for microorganisms. The presence of a low C/N ratio (high nitrogen content) may release toxic ammonia nitrogen that could affect the microbial communities in AD (Li et al., 2013b; Y. Li et al., 2014a). The imbalanced nutritional characteristics of the organic matter may not yield biogas at its optimal level although it has good potential for biogas production (Abouelenien et al., 2014; Chen et al., 2008). The balancing of nutritional content is necessary for optimal biogas production.

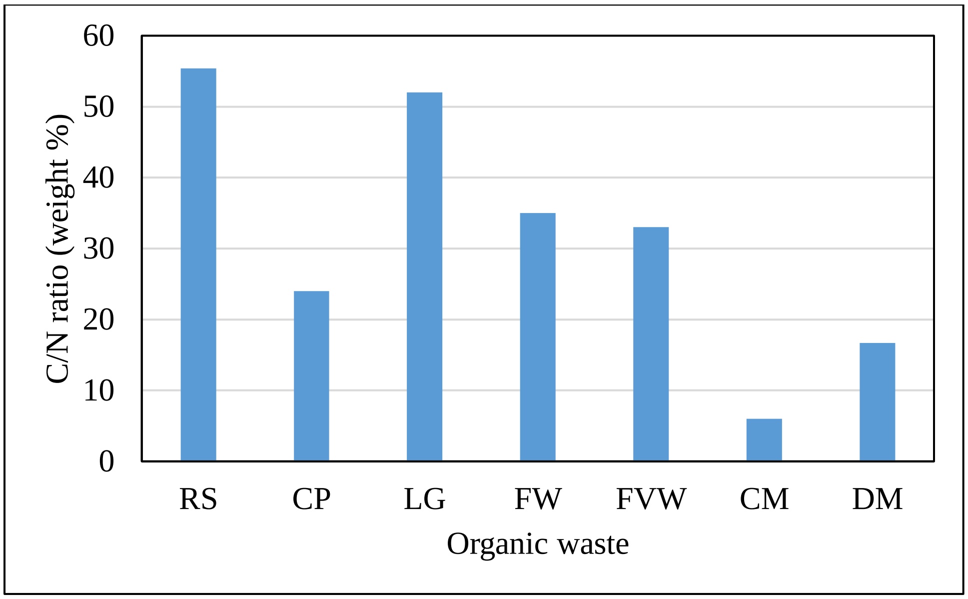

Fig. 5.5 C/N ratio of organic wastes (weight %)

From the characterization of organic wastes, it can be observed that organic wastes are having high volatile content indicating good potential for biogas production. However, the inappropriate nutrient content of the organic wastes may not translate high potential organic waste to high performing organic waste in the AD system. The specific technical limitations that may arise in AD of agricultural and municipal organic wastes detailed as follows:

5.2 AD of agricultural and municipal organic wastes

Efficiency of AD depends on the characteristics of the organic matter fed to the system. High moisture and degradable fractions in FVW facilitate AD (Scano et al., 2014; Shen et al., 2013). However, FVW is a readily biodegradable and acidic in nature that instantly may result in VFAs accumulation under anaerobic conditions (Mata-Alvarez et al., 2000). The accumulation of VFAs causes a drop in pH, and inhibition for the growth of methanogens (Panigrahi and Dubey, 2019). The pH below 5 does not favour the growth of methanogens (Khanal, 2009). The low growth rate of methanogens may lead to low biogas production, sometimes even process failure (Callaghan et al., 2002a; Shen et al., 2013).

RS comprises cellulose (~40%), hemicellulose (~18%), and non-biodegradable lignin (~7 %) (Jingura and Kamusoko, 2017). The non-biodegradable lignin and imbalanced nutrient composition of RS may cause slow degradation of organic matter (Chandra et al., 2012c; Ye et al., 2013). The slow biodegradability is due to the outer covering layer of lignin over the cellulose and hemicellulose that repels from the microbial action (C. Li et al., 2016). Also, low nitrogen (0.68% on dry basis) and low phosphorus (0.044% on dry basis) in the RS limits the growth of anaerobic microorganisms (Lei et al., 2010).

LG generating in public green spaces is a potential organic waste for AD (Alfa et al., 2014; Yu et al., 2014a). However, high lignin content and imbalanced nutrient composition in the grass may also result in slow degradation (Yu et al., 2014b).

DM has good moisture content (83.8%) and widely used as feedstock for biogas production. It has C/N ratio of 16.7±0.1, which is slightly lower to the optimal C/N ratio of 20-30. CM has high nitrogen content (low C/N ratio) due to the presence of uric acid and undigested protein (Abouelenien et al., 2014; Y. Li et al., 2014a; Zhang et al., 2014). The high nitrogen content may release toxic ammonia nitrogen that disturbs the growth of methanogenic population, consequently poor performance (Callaghan et al., 1999; Li et al., 2013b; Y. Li et al., 2014a; Sebastian et al., 2016).

The above-mentioned limitations are necessary to be addressed for effective utilisation of organic matter in AD. As mentioned in Section 2.3, the limitations can be addressed with the improvement of the characteristics of the feedstock. Co-digestion is better option to improve the characteristics of feedstock without incurring much additional cost. The optimal characteristics can be achieved with co-digestion of two or more organic wastes. For this purpose, the appropriate selection of organic wastes is beneficial for maximum biogas production.

5.3 Selection of organic waste combinations for co-digestion

Characteristics of organic waste play a key role for appropriate selection of organic wastes in co-digestion. Co-digestion of grass silage with nitrogen-rich pig manure improved the buffering capacity that lead to improved biogas production compared to mono digestion (S Xie et al., 2011).

Co-digestion of potato waste and nitrogen-rich aquatic weed also improved biogas production (Jacob and Banerjee, 2016). Co-digestion of vegetable processing waste with nitrogen-rich swine manure and CM improved biogas production (Molinuevo-Salces et al., 2010).

Co-digestion of RS with suitable co-organic wastes having balancing nutrients improves the AD efficiency (J. Li et al., 2014b). The C/N ratio of RS is high (55.4±0.1) which is not within the range of suggested optimal C/N ratio (20-35) for AD. Co-digestion of RS with nitrogen-rich organic matter supplies missing nutrients and microbial population for effective degradation (Zhou et al., 2016), improves the buffer capacity for optimal pH (Mussoline et al., 2012b), avoids free ammonia inhibition that generally occurs in mono-digestion of nitrogen-rich manures (Li et al., 2017). The co-organic wastes that can be used to improve the nutrient balance of RS are FW (Chen et al., 2015), sewage sludge (Kim et al., 2013a) , pig manure (Li et al., 2015b), DM and CM (Zhang et al., 2014) etc. DM has the advantage in terms of availability near RS cultivation. DM is an effective buffering agent to avoid drop in pH and favours the growth of microorganisms if used as a co- feedstock. Co-digestion of RS and DM can translate to superior quality feedstock with respect to nutrient balance (C/N ratio) when compared to mono-digestion.There are instances where more than two organic wastes are also lead to an improvement in biogas production (Rao and Baral, 2011; Wang et al., 2012). Co-digestion of fruit waste with FW and CM improved the buffering capacity and enhanced biogas production (Callaghan et al., 2002b; Lin et al., 2011).

From the above discussion, it can be observed that the characteristics of organic wastes can be improved with co-digestion of organic wastes having low C/N ratio and high C/N ratio. Four co-digestion scenarios are selected for organic waste management in study area to achieve efficient biogas production. The scenarios are selected with at least one organic waste having low C/N ratio and other one or two having high C/N ratio (Fig. 5.5). Following four sets of organic waste combinations may have good chances to yield high biogas production with co-digestion.

1 Set I : Co-digestion of CM and FVW

2 Set II : Co-digestion of CM , CP, and LG

3 Set III : Co-digestion of DM, FW, and FVW

4 Set IV : Co-digestion of DM and RS

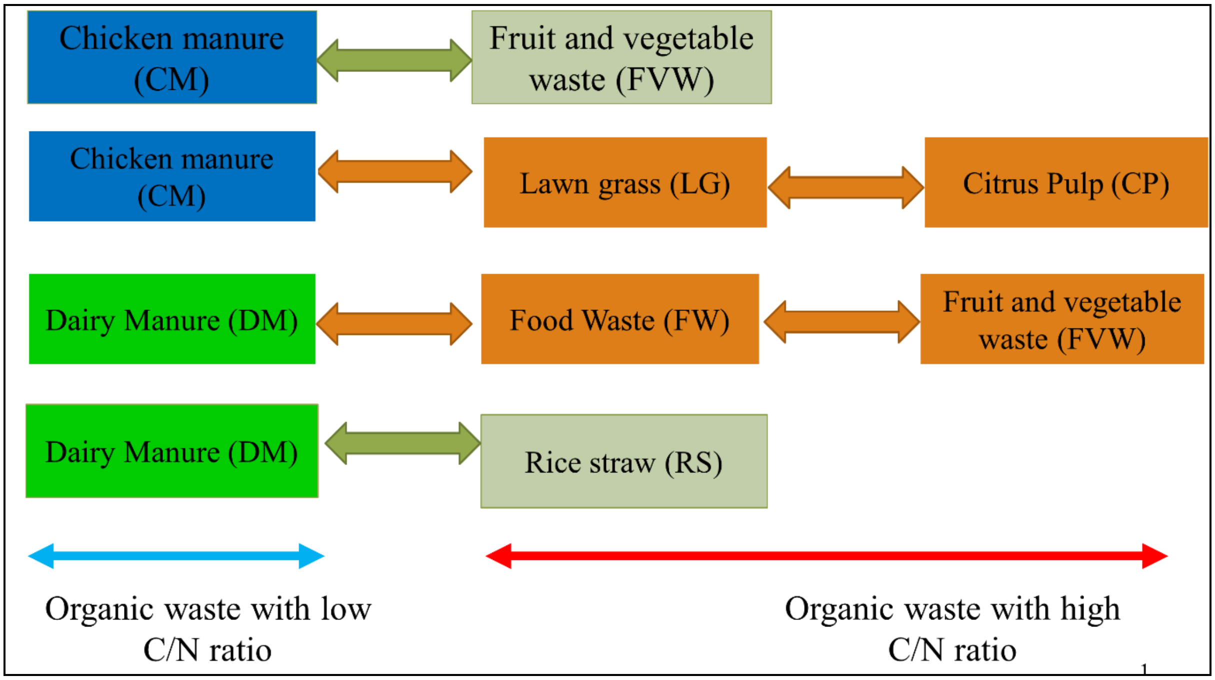

Fig. 5.6 Co-digestion mix combination of organic wastes

Theoretically, random mixtures of the above organic waste combinations can be used as a feedstock for AD. But, it is more desirable that they actually mixed according to some proportions instead of random mixtures. It requires understanding and optimisation of the composition for maximum biogas production (Hagos et al., 2017). Nevertheless, factors such as total solids (TS %) content, I/S ratio influence the AD process and are necessary to be investigated. Following section discusses the effect of these factors by considering the above four sets of combinations.

5.4 Co-digestion of FVW and CM: Set I

In the present set, co-digestion of FVW mixed with CM is studied to evalaue the biogas production. Preliminary study carried out to assess the feasibility and formulating detailed further investigation.

5.4.1 Preliminary study

Preliminary study carried out for mono-digestion of FVW, CM and co-digestion of FVW with CM (50:50 based on TS). The experiments are carried for 45 days at total solids (TS %) of 6 % and I/S ratio of one as per the method described in Section 3.4. It is observed that co-digestion has given high biogas production (316 mL) compared to mono-digestion of FVW (205 mL) and CM (176 mL). Biogas production of co-digestion is higher by 54 % and 79 % compared to mono-digestion of FVW and CM respectively (Fig. 5.7). It indicates that co-digestion of FVW and CM improves the AD performance. The methane (CH_4) content in biogas is found to be varying between 55-61 %.

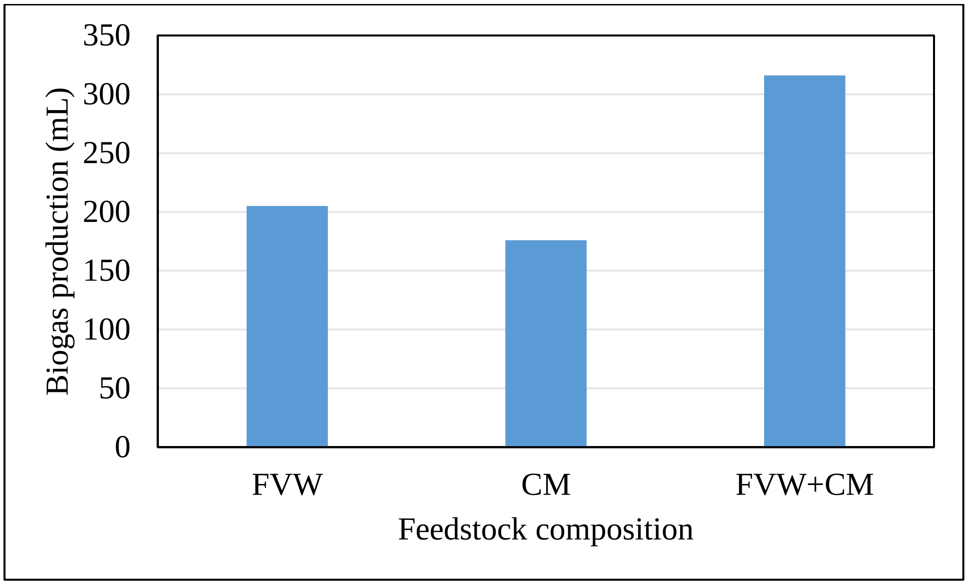

Fig. 5.7 Biogas production (mL) of mono-digestion and co-digestion: Set I

Total solids (TS %) content in AD affects the rheological behaviour of digester contents and microbial communities (Yi et al., 2014). It mainly influences the hydrolysis stage in AD process, consequently biogas production (Abbassi-Guendouz et al., 2012b; Cecchi et al., 1988; Gujer and Zehnder, 1983). Appropriate total solids (TS %) content facilitates maximum biogas production. Also, inoculum content influences the performance of AD process in biogas production (Charles et al., 2009; Jacob and Banerjee, 2016). Inoculum is active microbial population and is commonly measured in relative to the unit mass of substrate load i.e. Inoculum to Substrate ratio (I/S ratio). A low quantity of inoculum may not digest the organic matter effectively. It even leads to the accumulation of VFAs and process failure (Charles et al., 2009; Jacob and Banerjee, 2016). Sufficient I/S ratio must be present for efficient utilisation of organic matter. Thus, influence of total solids (TS %) and I/S ratio need to be evaluated to generate reasonable inferences.

5.4.2 Experimental design

Appropriate experimental design is supportive to understand the influence of multi-factors in AD (Wang et al., 2013). In the present Set-I of study, three factors viz., proportion of FVW %

(remaining is CM), total solids (TS %) content, and I/S ratio are chosen to evaluate their influence on biogas production. CCD (face-centered type) described in Section 3.5.1 is used for the experimental design of three influencing factors. The factors analyzed at low, high and central levels to estimate the experimental variability (Table 5.2). The experimental design yielded 20 runs and one central point replicated six times (14+6=20) (Table 5.3). The central point replicated six times, as it is very critical point. The central runs provide a valuable means of estimating the experimental errors. Factorial design levels are coded as -1, 0, and +1 at low, central and high levels. The organic waste mix proportions in the reactors are prepared as per design and experiments carried as per method described in Section 3.4. Inoculum is collected from the working anaerobic digester at National Institute of Technology, Warangal. The characteristics of inoculum are total solids (TS %)- 8.84 %, volatile solids (% of TS) content - 88.9%, C/N ratio - 20.2, and pH -7.2. Inoculum content in respective experimental combination is calculated as follows (Eq. 5.1)

$$\frac{I}{S}\ \text{ratio} = \frac{\text{Inoculum }(g_{vs})}{\text{Substrate i.e organic waste}(g_{vs})} \qquad \text{Eq. 5.1}$$

Table 5.2 Real values of coded factors: Set I

Factors	Coded values		
	-1	**0**	**+1**
A: FVW (%)	20	40	60
B:Total solids (TS %)	3	6	9
C:I/S ratio	0.5	1.0	1.5

5.4.3 Biogas production

CCD experimental design involving three factors is presented in Table 5.3. AD experiments are carried out as per the design and corresponding biogas production (mL) recorded. Biogas production is recorded for a period of 45 days, thereafter experiments are terminated due to negligible biogas production. A lag phase of around 5 to 10 days is observed in all the co-digestion mixes except run 11 (20, 80, 3,0.5) that has long lag phase around 20 days (Fig. 5.8). The longer lag phase may be due to the relatively low quantity of inoculum (I/S raio of 0.5). A high biogas production is obtained in co-digestion mix of run 1 (368 mL) and run 8 (328 mL). The corresponding biogas productions are higher than the mono-digestion of FVW (205 mL) and CM

(176 mL). The methane (CH_4) content in biogas is found to be varying between 57-62%. The methane yields in run 1 and run 8 are 94 mL of CH_4/g VS_{added} and 73 mL of CH_4/g VS_{added}, respectively. The C/N ratio of high biogas produced co-digestion mixes is 17. The high biogas production can be attributed to optimal nutritional balance with C/N ratio. It is in consistent with the widely suggested optimal C/N ratio of 17-33 (Shah et al., 2015). Low biogas production is obtained in run 2 (152 mL), run 10 (164 mL), and run 11 (132 mL) whose corresponding C/N ratio is 12. The low biogas production may be due to ammonia accumulation with high percentage of nitrogen (low C/N ratio) in these runs (CM of 80%). Similar kind of low biogas production is reported in co-digestion of vegetable processing waste with poultry litter having high nitrogen content (Molinuevo-Salces et al., 2010). Thus, high biogas production in co-digestion mixes can be attributed to the improved nutritional characteristics.

Table 5.3 Experimental design and biogas production: Set I

Run	FVW(%)	CM (%)	TS (%)	I/S ratio	Biogas production(ml)
1	40	60	6	1	368
2	20	80	3	1.5	152
3	40	60	6	1	344
4	60	40	3	0.5	188
5	40	60	6	1	315
6	40	60	6	1.5	304
7	40	60	6	1	316
8	40	60	9	1	328
9	40	60	6	0.5	297
10	20	80	9	1.5	164
11	20	80	3	0.5	132

12	60	40	3	1.5	213
13	20	80	6	1	183
14	40	60	6	1	321
15	60	40	9	1.5	268
16	40	60	6	1	324
17	40	60	3	1	243
18	60	40	6	1	256
19	20	80	9	0.5	238
20	60	40	9	0.5	186

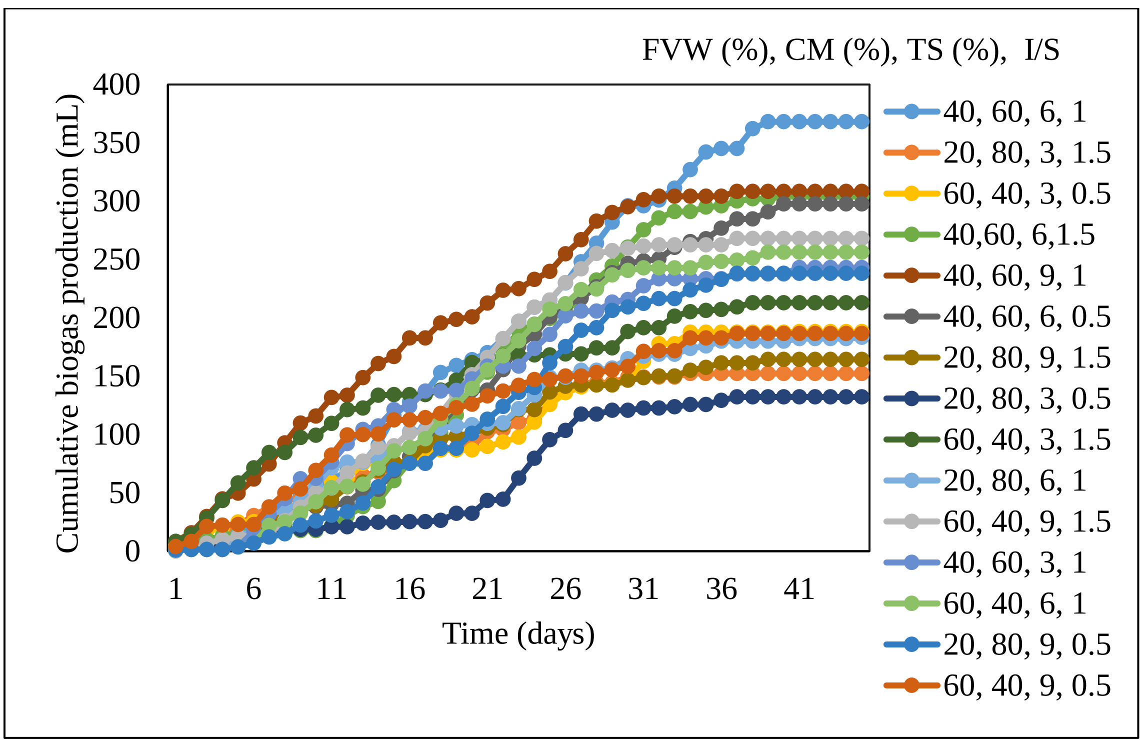

Fig. 5.8 Cumulative biogas production (mL): Set I

5.4.4 Data analysis

Response surface methodology (RSM) is used to study the relationship between influencing factors and biogas production (response) in AD. The relationship can be explained by choosing one of the best model described in Section 3.6.The fitness of the model equation is determined by using the coefficient of determination (R^2), and the standard deviation. Its statistical significance is checked using F-test. The model with the best statistical fitness is selected for the estimation of response . After selection of the appropriate model, the influence of each factor and their interactions are evaluated with a significance test and ANOVA.

The obtained experimental data of biogas production is fitted to linear, two-factor interaction (2-FI), quadratic, and cubic models. Statistical summary of each model is given in Table 5.4. Adjusted R^2 is used instead of R^2 to reduce insignificant terms in the model. Because, R^2 always increases as terms are added to the model even if they are not significant, whereas adjusted R^2 decreases if non-significant terms are added. For a given study, better response can be predicted by the model with lower standard deviation and higher adjusted R^2. In this study, quadratic and cubic model can be selected due to lower standard deviation and higher adjusted R^2. Quadratic model is selected to evaluate the influence of factors on biogas production. The R^2 and adjusted R^2 of the quadratic model are found to be 0.92 and 0.85 respectively. It indicates that the majority of the data obtained can be explained by using the model. Optimisation of anaerobic co-digestion of FW and sewage sludge resulted in R^2 and adjusted R^2 values of 0.88 and 0.73 (Kim et al., 2007) and are comparable to the present study.

Table 5.4 Model suitability check: Set I

Model	Stand. Deviation	R^2	Adjusted R^2
Linear	72.07	0.12	0.01
2-FI	78.04	0.16	0.21
Quadratic	26.78	0.92	0.85
Cubic	24.92	0.96	0.87

Note: 2FI: two factor interaction

After the selection of the quadratic model, ANOVA is carried out to evaluate the significance of the model and model terms (Table 5.5). The significance of the model and model terms are verified based on individual P values that are less than 0.05 . The obtained p-value with F-test of less than 0.05 indicates the significance. The p-values of the quadratic model is observed to be <0.05 respectively. It indicates that the model is significant at a confidence level of 95 % (p<0.05). The model adequacy is tested through lack of fit F-tests. The lack of fit which had an F-value of 2.30 and a p-value of 0.20 shows that it is not significant. It indicates that the model has good fit for prediction. The coded equation (Eq. 5.2) is used to ascertain the relative impact of each factor by comparing with its factor coefficients. From the coefficient terms in equation, it can be observed that the influence of FVW % (A), TS % (B) is high compared to I/S ratio (C) on biogas production. In the equation, the high level of factors is coded as +1, while the low levels are coded as -1.

$$\begin{aligned}\text{Biogas production}(\text{mL}) &= 322 + 24(A) + 23(B) + 6(C) - 8(AB) + 20(AC) \\ &- 4(BC) - 90(A^2) - 34(B^2) - 9(C^2)\end{aligned} \qquad \text{Eq. 5.2}$$

Table 5.5 ANOVA for the quadratic model: Set I

	Sum of square	**Degrees of freedom**	**Mean**	**F-value**	**p-value**	
Model	87732	9.0	9748.1	13.6	0.00	Significant
A: FVW (%)	5856	1.0	5856.4	8.2	0.02	Significant
B: TS (%)	5569	1.0	5569.6	7.8	0.02	Significant
C: I/S	360	1.0	360.0	0.5	0.49	
AB: FVW (%) *TS (%)	528	1.0	528.1	0.7	0.41	
AC: FVW(%) *TS (%)	3240	1.0	3240.1	4.5	0.06	
BC: TS * I/S	171	1.0	171.1	0.2	0.64	
A^2 : FVW(%)^2	22320	1.0	22320.0	31.1	0.00	Significant
B^2 -TS (%)^2	3196	1.0	3196.0	4.5	0.06	Significant
C^2 -I/S^2	227	1.0	227.3	0.3	0.59	
Lack of fit	5002	5	1000	2.3	0,20	Insignificant

The equation in terms of actual factors (Eq. 5.3) can be used to make predictions about the response for given levels of each factor. The levels are specified with the original units in Eq. 5.3.

$$\text{Biogas production}(\text{mL}) = -288 + 18(\text{FVW}) + 61(\text{TS}) + 22(\text{I/S}) - 0.1(\text{FVW}*\text{TS}) + 2(\text{FVW}*\text{I/S}) - 3(\text{TS}*\text{I/S}) - 0.2(\text{FVW}^2) - 3(\text{TS}^2) - 36(\text{I/S}^2) \quad \text{Eq. 5.3}$$

In this study, FVW (A), TS (B), FVW^2 (A^2), and TS^2 (B^2) are identified as significant terms ($p<0.05$). The other terms that have insignificant influence on biogas production can be eliminated. After eliminating the insignificant terms, the model can be re-written as the following (Eq. 5.4).

$$\text{Biogas production}(\text{mL}) = -288 + 18(\text{FVW}) + 61(\text{TS}) - 0.2(\text{FVW}^2) - 3(\text{TS}^2) \quad \text{Eq. 5.4}$$

The influence of input variables on biogas production (response variable) can be well understood with 3D response surface plots. It can be seen from the figures (Fig. 5.9, Fig. 5.10, Fig. 5.11) that biogas production increased with an increase in FVW (%) up to a certain level thereafter decreased. The decrease in biogas production is may be due to accumulation of VFAs as high FVW rapidly acidifies (Callaghan et al., 2002a; Shen et al., 2013). The high accumulation of acids cause drop in pH, consequently low biogas production. A similar low biogas production is reported (Molinuevo-Salces et al., 2010) when vegetable waste is co-digested with chicken litter. Further, biogas production increased with an increase in total solids (TS %) loading up to a certain level thereafter decreased. It may be due to the substrate overloading, changes in rheology of digester contents after reaching optimal total solids (TS %) level. (Aboudi et al., 2017) observed that high biogas production at 8 % of total solids (TS %) when compared to 5 % of total solids (TS %) in co-digestion of sugar beet by-products with livestock manures and is in consistent with the present study. However, the I/S ratio is not having any significant effect on biogas production potential at all studied I/S ratios. It indicates that shortage of inoculum is not controlling even at I/S ratio of 0.5 and any I/S ratio between 0.5 to 1.5 is adequate for effective degradation of the organic matter in co-digestion of FVW and CM.

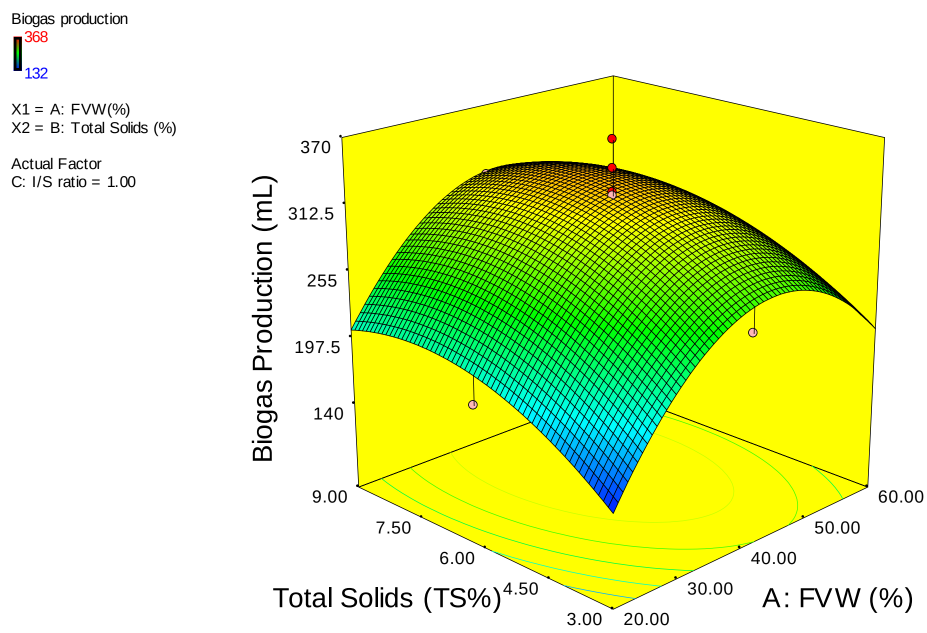

Fig. 5.9. Interactive effect of total solids (TS %) and FVW (%) on biogas production (mL)

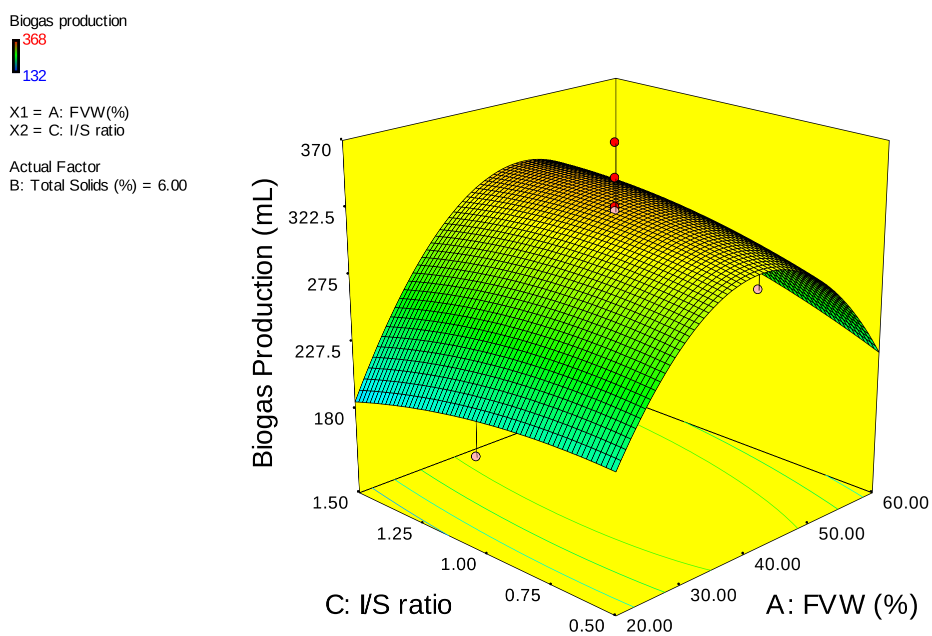

Fig. 5.10. Interactive effect of I/S ratio and FVW (%) on biogas production (mL)

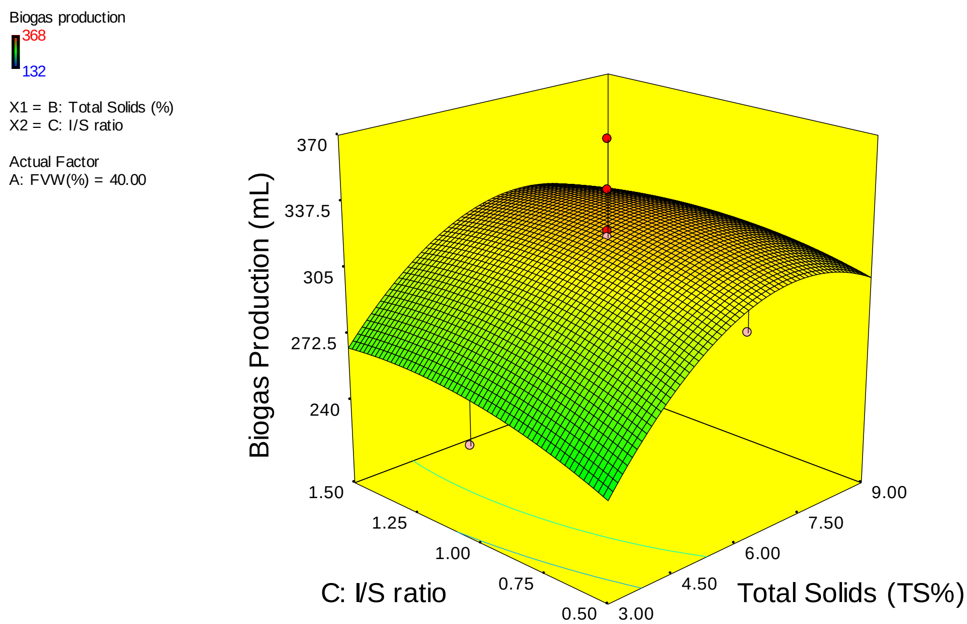

Fig. 5.11. Interactive effect of I/S ratio and total solids (TS %) on biogas production (mL)

The optimal points of each factor are evaluated from the model for maximum biogas production. The optimal points corresponding to the maximum biogas production (337 mL) are FVW (%) of 42 %, total solids (TS%) of 7.3 % and I/S ratio of 1. The optimal points from the model are verified through confirmatory experiment. The maximum biogas production obtained from the confirmatory experiment is found to be 358 mL,which closely agrees with the predicted biogas production (337 mL) of the model. Hence, the quadratic model adopted in the present study is validated reasonably and can be used to predict biogas production.

From the above discussion, it can be observed that mix proportion of organic waste and total solids (TS %) influence biogas production significantly and are to be chosen carefully for maximum biogas production. The maximum biogas production can be obtained with mix proportion of FVW (%) of 42 % and total solids (TS %) of 7.3 % in anaerobic co-digestion of FVW with CM.

5.5 Co-digestion of CP, LG and CM: Set II

From the previous Set-I, it is observed that co-digestion of FVW mixed with CM improves biogas production. The present Set II continued the possibilities of improving biogas production further by considering the additional organic wastes viz., CP and LG along with CM. Preliminary study carried for mono-digestion and co-digestion, and is detailed as follows:

5.5.1 Preliminary study

Preliminary study is carried out for mono-digestion and co-digestion of CP, LG and CM (33.3: 33.3: 33.3 based on TS). Experiments carried as per the method described in Section 3.4 for 60 days at total solids (TS %) content of 5 % and I/S ratio of one. It is observed that co-digestion of CP, LG and CM has given the maximum biogas production (312 mL) compared to mono-digestion of CP (250 mL), LG (135 mL) and CM (202 mL) (Fig. 5.12). Biogas production in co-digestion is higher by 25 %, 131 % and 54 % compared to mono-digestion of CP, LG, and CM respectively. It indicates the co-digestion of CP, LG and CM could be an appropriate choice for improving biogas production. The methane (CH_4) content in biogas is found to be varying between 57-61 %.

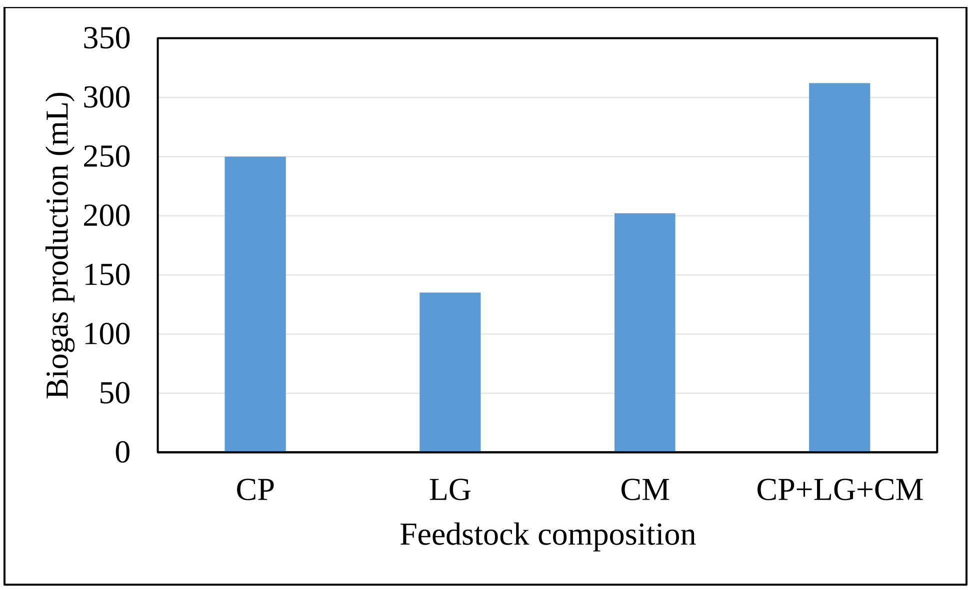

Fig. 5.12. Biogas production of mono-digestion and co-digestion: Set II

From the Set-I, it is observed that total solids (TS %) content having significant influence on AD. The total solids (TS %) loading of each organic waste in co-digestion acts as a key operational factor in AD and need to be chosen optimally for maximum biogas production (Molinuevo-Salces et al., 2010; Yan et al., 2015). In the present work, influence of total solids (TS %) loading of the organic waste in co-digestion of CP, LG, and CM is studied and detailed as follows:

5.5.2 Experimental design

In the present work, CCD (circumscribed type) is used for the co-digestion of ternary organic waste mix. Total solids (TS %) loading of three organic wastes are chosen as three variables. The chosen total solids (TS %) loading ranges for CP, LG and CM are 0.0-2.4%, 1.4-9.5%, and 3.4-11.5% respectively. The axial points are considered and their distance (α) from the central point is calculated as described in Section 3.5.1. The design consists of 20 experimental and one central point replicated six times (14+6=20) (Table 5.7). The factorial design levels of three organic wastes are coded from -1.68, -1, 0, and +1, +1.68 (Table 5.6). The organic waste mix composition is prepared in the reactors as per design.

Table 5.6 Real values of coded factors: Set II

Factors	Coded values				
	-1.68	**-1**	**0**	**1**	**+1.68**
A: Citrus Pulp (CP)	0	0.5	1.2	2.0	2.4
B: Lawn Grass (LG)	1.4	3	5.5	8.0	9.5
C: Chicken Manure (CM)	3.4	5	7.5	10.0	11.5

Table 5.7 Experimental design and biogas production (mL): Set II

Run	CP (%TS)	LG (%TS)	CM (%TS)	Biogas production (mL)
1	1.2	5.5	7.5	350
2	0.5	8.0	10.0	300
3	2.0	3.0	10	380
4	0.5	3.0	5.0	494
5	2.0	8.0	5.0	361
6	0.5	8.0	5.0	610
7	2.0	8.0	10.0	340
8	0.5	3.0	10.0	600

9	2.0	3.0	5.0	300
10	1.2	9.5	7.5	370
11	1.2	5.5	3.4	351
12	2.4	5.5	7.5	300
13	1.2	1.4	7.5	413
14	0.0	5.5	7.5	550
15	1.2	5.5	11.5	345
16	1.2	5.5	7.5	352
17	1.2	5.5	7.5	338
18	1.2	5.5	7.5	354
19	1.2	5.5	7.5	358
20	1.2	5.5	7.5	362

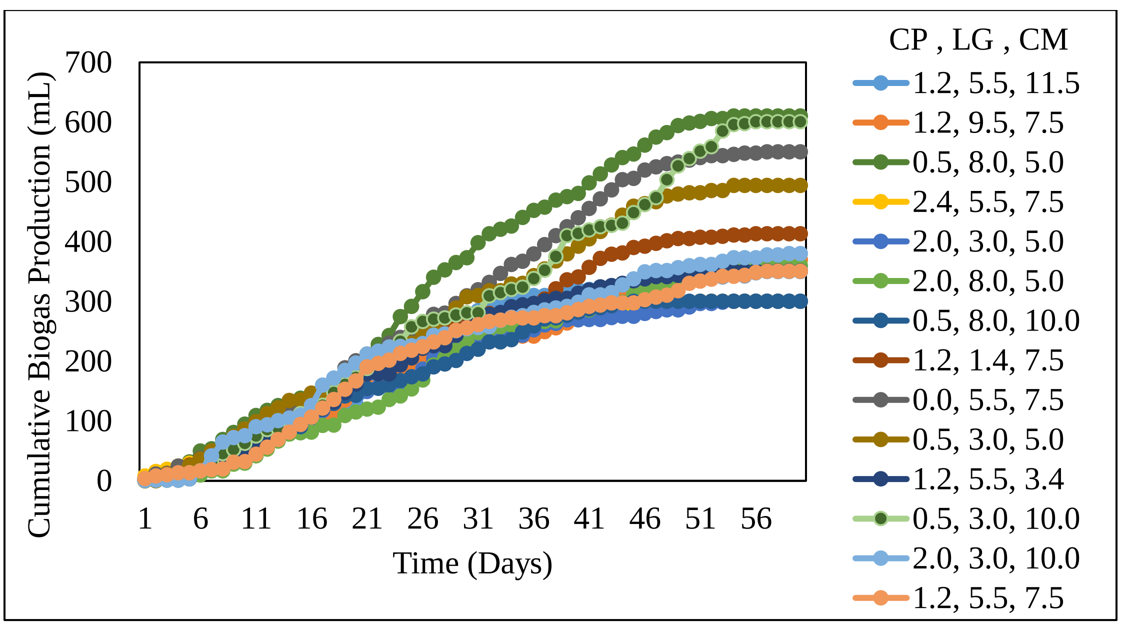

Fig. 5.13. Cumulative biogas production (mL): Set II

5.5.3 Biogas production

AD experiments are carried as per design and corresponding biogas production (mL) is recorded (Table 5.7). Biogas production is observed for a period of 60 days, thereafter the experiments are terminated due to negligible biogas production. A lag phase of around 5 days is observed in all the co-digestion mixes (Fig. 5.13). High biogas production is obtained in co-digestion mix of run 6 (610 mL) and run 8 (600 mL). The methane (CH_4) content in biogas is found to be varying between 55-65%. The methane yields in run 6 and run 8 are 171 mL of CH_4/g VS_{added} and 196 mL of CH_4/g VS_{added}, respectively. The corresponding methane yields are higher than the reported methane yield for mono-digestion of CM (126 mL of CH_4/g VS_{added}) (Wang et al., 2012) and co-digestion of switchgrass and DM (1:1 ratio) (158 mL of CH_4/g VS_{added}) (Zheng et al., 2015). The C/N ratio in corresponding high biogas produced co-digestion mixes are 33 (run 6) and 16 (run 8). It is in consistent with the reported (Wilawan et al., 2014) high biogas production at C/N ratio of 30 and 20. Low biogas production is obtained in run 2, 9, and 12 whose corresponding C/N ratio is 26, 23, and 25, respectively. From the Fig. 5.14.a, it can be observed that the C/N ratio of co-digestion mixes had not considerably influenced the biogas production. The C/N ratio in all co-digestion mixes are in the range of 16-33. The low influence of C/N ratio may be due to prevalence of optimal C/N ratio in all co-digestion mixes. Trace elements (Demirel and Scherer, 2011), buffering capacity (Murto et al., 2004), and toxic compounds (Ahring et al., 1992; Wang et al., 2012) also influence biogas production in co-digestion. (J. Li et al., 2014b) attributed the variation in biogas production to factors such as phosphorous and trace elements than C/N ratio. (Wang et al., 2012) reported variable biogas productions (mL) at the same C/N ratio. The variation in biogas production may be due to other factors such as supplementation of phosphorous, trace elements but not limited to C/N ratio in co-digestion.

Total solids (TS %) content influences the rheology and viscosity of digester contents, consequently the biogas production (Karthikeyan and Visvanathan, 2013). In the present study, the total solids (TS %) of co-digestion mix appears to be having a considerable influence on biogas production (Fig. 5.14b). Low biogas production (300 mL) is obtained in run 2, 9 and 12 at total solids (TS %) loading of 6.2, 3.3, and 5.2 respectively. It can be observed that lower biogas production is observed at two points. One at lower total solids loading (3.3 %) and another at higher total solids (TS %) loading (5.2 and 6.2%). High biogas production (610 and 600 mL) are obtained in run 6 and 8 whose total solids (TS %) loading is 4.5 %. The obtained high biogas production at total solids loading of 4.5 %, is may be due to optimal total solids (TS %) loading for the co-digestion mix. The higher total solids (TS%) loading than optimal level may cause acidification and subsequently low biogas production (Yao et al., 2014). Thus, total solids (TS %) need to be chosen optimally for high biogas production in co-digestion.

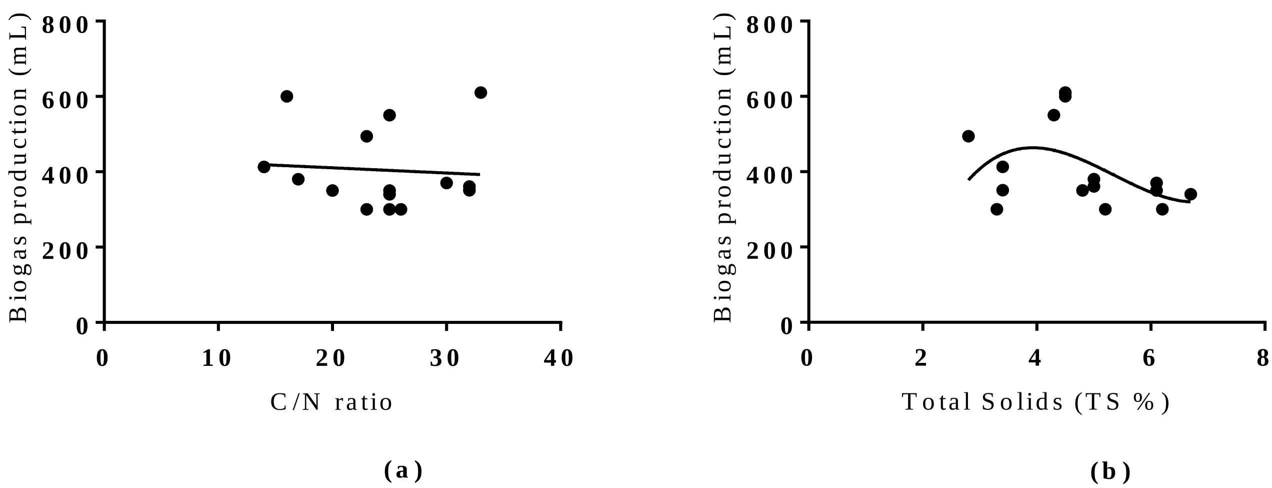

Fig. 5.14 Effect of C/N ratio (a) and total solids (TS %) (b) on biogas production (mL)

5.5.4 Data analysis

The obtained experimental data is fitted to linear, two-factor interaction (2FI), quadratic, and cubic models. Statistical summary of each model is presented in Table 5.8. The quadratic model is found to be fitting better for the experimental data with lower standard deviation and higher adjusted R^2. The R^2 and adjusted R^2 of the quadratic model is found to be 0.90 and 0.81 respectively. It indicates that the majority of the data obtained can be explained by using the model. The quadratic model in anaerobic co-digestion of FW and sewage sludge resulted in R^2 and adjusted R^2 values of 0.88 and 0.73 (Kim et al., 2007) and are comparable to the present study.

After selection of the quadratic model, ANOVA is carried out to evaluate the significance of the model and model terms (Table 5.9). The significance of the model and model terms are verified based on individual P values that are less than 0.05. The F and P values of the quadratic model are observed to be 10.44 and 0.0005 respectively. It indicates that the model is significant at a confidence level of 95 % ($p<0.05$). The model adequacy is tested through lack of fit F-tests. The lack of fit which had an F-value of 8.2 and a p value of 0.3 shows that lack of fit is insignificant. It indicates that the model has good fit for prediction.The coded equation (Eq. 5.5) is used to ascertain the relative impact of each factor by comparing with its factor coefficients. In the equation, the high level of factors are coded as +1, while the low levels are coded as -1.

$$\text{Biogas production}(\text{mL}) = 348 - 77(A) - 17(B) - 11(C) + 25(AB) + 32(AC) - 65(BC) + 33(A^2) + 21(B^2) + 7(C^2) \quad \text{Eq. 5.5}$$

Table 5.8 Model suitability check: Set II

Model	Stand. Deviation	R^2	Adjusted R^2
Linear	72.86	0.50	0.40
2FI	53.80	0.78	0.67
Quadratic	41.12	0.90	0.81
Cubic	72.86	0.98	0.94

Note: 2FI= two factor interaction

Table 5.9 ANOVA for quadratic model: Set II

Source	Sum squares	Degree of freedom	Mean Square	F-Value	P-Value	
Model	153900	9	17100	10.44	0.00	significant
A: CP	80198	1	80198	48.94	0.00	significant
B: LG	3913	1	3913	2.39	0.15	
C: CM	1647	1	1647	1.01	0.33	
AB: CP *LG	5253	1	5253	3.21	0.10	
AC: CP* CM	8646	1	8646	5.28	0.04	significant
BC: LG* CM	33411	1	33411	20.39	0.00	significant
A^2: CP^2	15884	1	15884	9.69	0.01	significant
B^2: LG^2	6746	1	6746	4.12	0.06	
C^2 : CM^2	692	1	692	0.4225	0.53	
Lack of fit	16910	5	3382	8.2	0.3	insignificant

The equation in terms of original units (Eq. 5.6) can be used to make predictions about the response for given levels of each factor. The levels are specified with the original units for each factor in Eq. 5.6.

$$\text{Biogas production } (\text{mL}) = 646 - 457(\text{CP}) + 13(\text{LG}) + 13(\text{CM}) + 13(\text{CP}*\text{LG}) + 17(\text{CP}*\text{CM}) - 10(\text{LG}*\text{CM}) + 59(\text{CP}^2) + 3.6(\text{LG}^2) + 1.1(\text{CM}^2) \qquad \text{Eq. 5.6}$$

In this study, CP (A), CP^2 (A^2), CP *CM (AC), and LG*CM (BC) are identified as significant terms ($p<0.05$). Other terms such as LG (B), CM (C), CP*LG (AB), LG^2 (B^2), CM^2 (C^2) are identified as insignificant terms, indicating that they did not influence biogas production considerably ($p>0.05$) (Table 5.9). After eliminating the insignificant terms from the above model, it can be re written as the following.

$$\text{Biogas production } (\text{mL}) = 646 - 457(\text{CP}) + 17(\text{CP}*\text{CM}) - 10(\text{LG}*\text{CM}) + 59(\text{CP}^2) \qquad \text{Eq. 5.7}$$

The influence of input factors on biogas production (response variable) is presented in Fig. 5.15, Fig. 5.16, Fig. 5.17. The less curvature in Fig. 5.15 indicates that the interaction between the total solids (TS %) loading of CP and LG is minimal on biogas production. It is also evident from Fig. 5.15 that biogas production decreased with an increase in total solids (TS %) loading of CP. The curvature in Fig. 5.16 indicates significant interaction between total solids (TS %) of CP and LG. It is also evident from Fig. 5.16 that biogas production decreased with increase of total solids (TS %) of CP. The decrease in biogas production may be due to high sugar content in the CP that might have caused the acidification of digester contents, and subsequently a drop in pH and inhibition of methanogenesis (Callaghan et al., 2002a; Shen et al., 2013). The response surface plot in Fig. 5.17, shows high biogas production at two regions of the plot. The high biogas production is obtained at low amount of LG and high amount of CM as well as high amount of LG and low amount of CM. The high biogas production at the two regions may be due to their interactive synergistic effect with co-digestion.

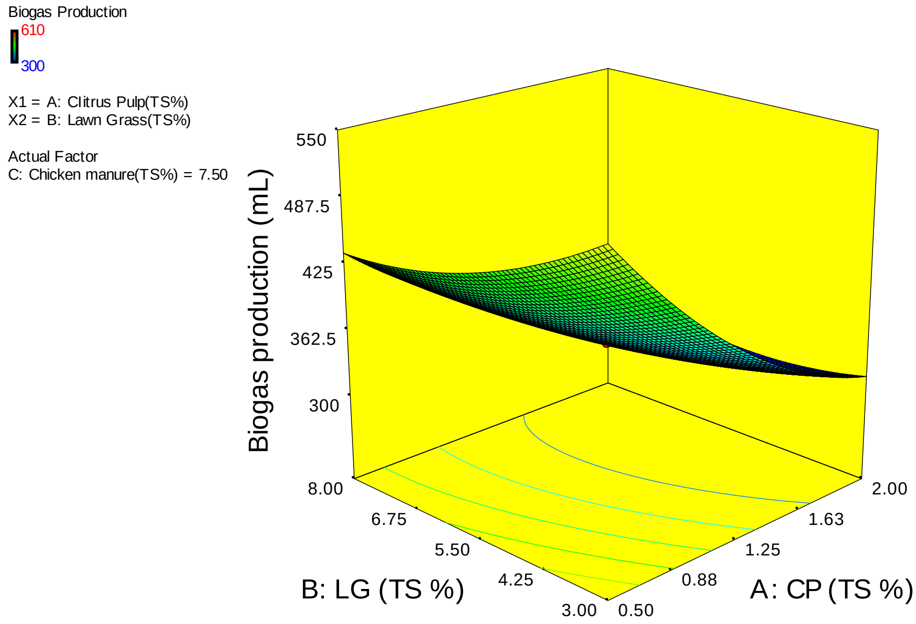

Fig. 5.15. Interactive effect of total solids (TS %) of CP and LG on biogas production (mL)

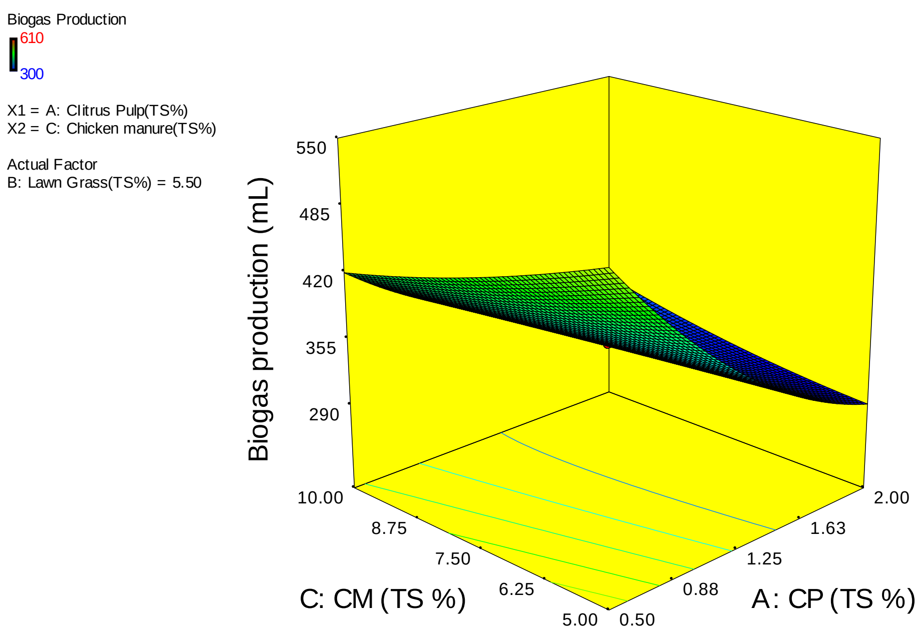

Fig. 5.16. Interactive effect of total solids (TS %) of CP and CM on biogas production (mL)

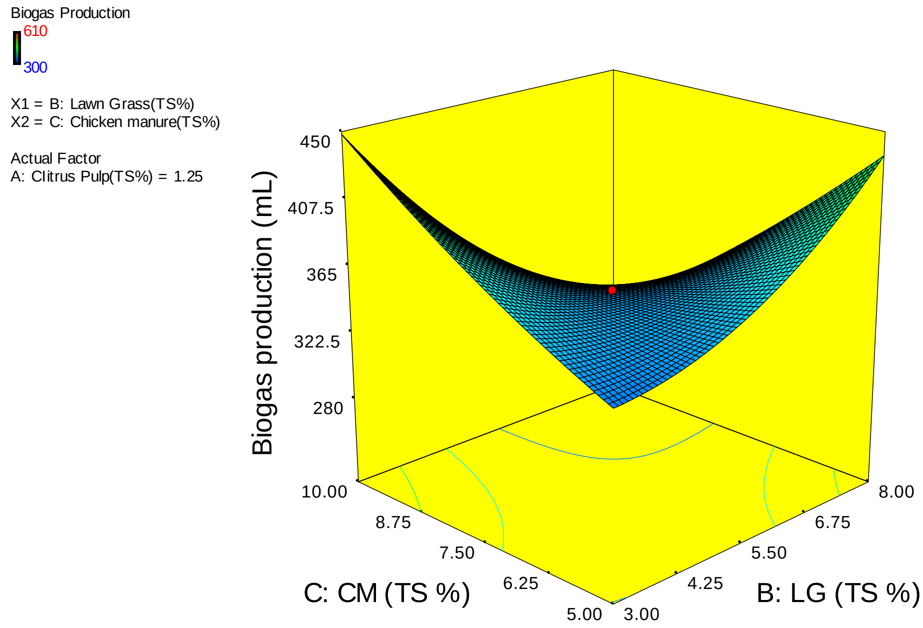

Fig. 5.17. Interactive effect of total solids (TS %) of CM and LG on biogas production (mL)

The optimal points of each factor are evaluated from the quadratic model for maximum biogas production. The optimal points corresponding to the maximum biogas production (705 mL) are: CP of 0.28 (TS %), LG of 9.4 (TS %), and CM of 4 (TS %) . The optimal points from the model are verified through confirmatory experiment. The maximum biogas production obtained from the confirmatory experiment is found to be 688 mL,which closely agrees with the predicted biogas production (705 mL) of the model. It indicates the close fit of the model for biogas production in co-digestion of ternary organic waste mix. Hence, the quadratic model adopted in the present study is validated reasonably and can be used to predict biogas production in anaerobic co-digestion.

From the present Set II study, it can be observed that total solids (TS %) loading of each organic waste influences the AD process and need to be chosen optimally for maximum biogas production. The maximum biogas production can be obtained with total solids (TS %) loading of CP of 0.28 (TS %), LG of 9.4 (TS %), and CM of 4.0 (TS %). In terms of mix proportion in co-digestion mix it can be expressed as CP of 2 %, LG of 68 % and CM of 29 % (based on relative total solids (TS %) loading of organic waste).

5.6 Co-digestion of FW, FVW and DM: Set III

From the previous Set-II, it is observed that co-digestion of ternary organic waste mix improves biogas production. The present set continued the possibilities of improving biogas production further by considering the additional organic wastes viz., FW, FVW, and DM.

5.6.1 Experimental design

SCMD described in Section 3.5.2 is used for the mix proportion design of three organic wastesin co-digestion. SCMD of three component mix consists of 13 experimental runs, presented in Table 5.10.The design points are coded as 0.00, 0.16, 0.33, 0.50, ,0.67,and 1.00, that indicates 0 % , 16%, 33%, 50%, 67%, and 100 % of the corresponding component in co-digestion mix. The organic waste mix in the reactors are prepared as per design based on volume mix proportion at a fixed total solids (TS %) loading of 4 % and I/S ratio of one (Table 5.10).

5.6.2 Biogas production

AD experiments are carried as per the design presented in Table 5.10 and corresponding biogas production (mL) is recorded. Biogas production is recorded for 45 days, thereafter terminated due to negligible biogas production. A lag phase of around 5 days is observed in all the co-digestion mixes (Fig. 5.18). High biogas production observed in run 10 (475 mL), containing equal mix proportion of DM (0.33), FW (0.33), and FVW (0.33). The corresponding biogas production is higher by 61 %, 107 % and 94 % compared to mono-digestion of DM (295 mL), FW (229 mL), and FVW (245 mL) respectively. Low biogas production is observed in run 3 (245mL) and run 4 (229 mL) for mono-digestion of FVW and FW. The C/N ration in corresponding high biogas produced co-digestion mixes is 27.5 (run 10) whereas C/N ratio in low biogas produced mixes are 33 (run 3) and 35 (run 4) respectively. The high biogas production may be due to the improved nutritional characteristics for microorganisms with optimal C/N ratio (27.5). It is in reasonable agreement with the optimal C/N ratio of 30 observed in co-digestion of FW with RS (Kainthola et al., 2020). The methane (CH_4) content in biogas is found to be varying between 53-63%. The methane yield in maximum produced co-digestion mix (run 10) is 188 mL of CH_4/g VS_{added}. The corresponding methane yield is higher compared to the reported (Zheng et al., 2015) methane yield of 158 mL of CH_4/g VS_{added} for co-digestion (0.5:0.5) of switchgrass and DM. From this, it can be observed that co-digestion of ternary organic waste mix with DM, FW and FVW provides conducive environment for the high biogas production.

Table 5.10 Experimental design and biogas production: Set III

Run	DM	FW	FVW	Biogas production(mL)
1	0.16	0.67	0.16	343
2	0.16	0.16	0.67	384
3	0.00	0.00	1.00	245
4	0.00	1.00	0.00	229
5	0.00	1.00	0.00	249
6	0.00	0.00	1.00	263
7	0.50	0.00	0.50	394
8	0.50	0.50	0.00	353
9	0.67	0.16	0.16	363
10	0.33	0.33	0.33	475
11	0.00	0.50	0.50	299
12	1.00	0.00	0.00	295
13	1.00	0.00	0.00	316

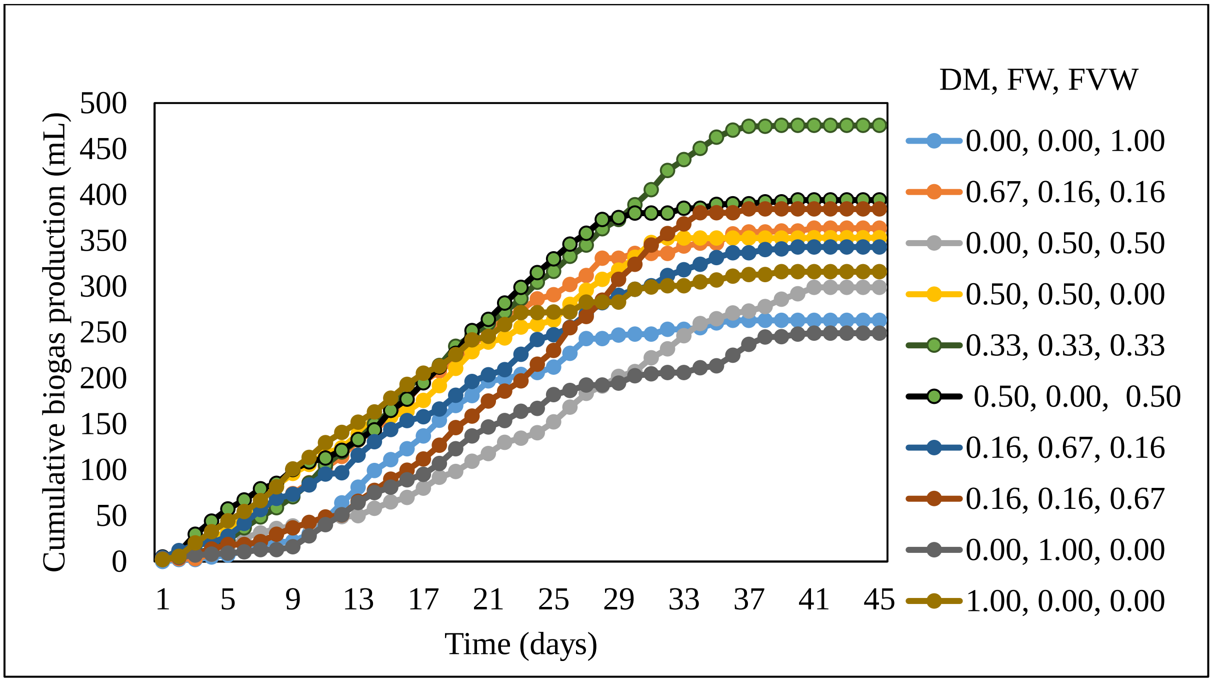

Fig. 5.18. Cumulative biogas production (mL): Set III

5.6.3 Data analysis

The obtained experimental data of biogas production is fitted to linear, quadratic, special cubic and cubic models. Statistical summary of each model is presented in Table 5.11. As mentioned previously, better response can be predicted by the model with lower standard deviation and higher adjusted R^2. In this study, special cubic and cubic models can be selected due to lower standard deviation and higher adjusted R^2 (Table 5.11). Special cubic model is selected to evaluate the influence of mix proportion on biogas production (response). The R^2 and adjusted R^2 of the special cubic model is found to be 0.93 and 0.87 respectively. It indicates that the majority of the data obtained can be explained by using the special cubic model. The AD of three organic wastes of DM, swine manure and RS resulted in R^2 and adjusted R^2 values of 0.98 and 0.97 for special cubic model (Kim et al., 2007), and are comparable to the present study.

Table 5.11 Model suitability check: Set III

Model	**Stand. Deviation**	**R^2**	**Adjusted R^2**
Linear	72.63	0.12	-0.05
Quadratic	34.45	0.86	0.76
Special Cubic	25.45	0.93	0.87
Cubic	25.07	0.95	0.87

After selection of the special cubic model, ANOVA is carried out to evaluate the significance of the model and model terms (Table 5.12). The significance of the model and model terms are verified based on individual P values that are less than 0.05. The F and P value of the special cubic model are 14.48 and <0.05 respectively. It indicates that the model is significant at a confidence level of 95 % ($p<0.05$). The model adequacy is tested through lack of fit F-tests. The lack of fit which had an F-value of 5.67 and p-value of 0.09 which indicates that lack of fit is not significant. Hence, the model is good fit for prediction.

Table 5.12 ANOVA for special cubic model: Set III

Source	Sum of squares	Degrees of freedom	Mean Square	F-value	p-value	
Model	56279	6	9380	14.48	0.00	significant
Mix proportion	7415	2	3707	5.73	0.04	significant
AB: DM*FW	4132	1	4132	6.38	0.04	significant
AC: DM*FVW	9838	1	9838	15.19	0.01	significant
BC: FW*FVW	2450	1	2450	3.78	0.10	
ABC: DM*FW*FVW	4423	1	4423	6.83	0.04	significant
Lack of fit	3303	3	1101	5.67	0.09	not significant

From the ANOVA, it can be observed that the mix proportion, DM*FW (AB), DM*FVW (AC) and DM*FW*FVW (ABC) are found to be significant at $p<0.05$. It means that the mix proportion and interactive effects of DM and FW (AB), DM and FVW (AC), and DM, FW, FVW (ABC) are significantly influencing biogas production at confidence interval of 95 %. The equation (Eq. 5.8) can be used to ascertain the relative impact of each organic waste. The relative impact can be assessed by comparing with its factor coefficients.

$$\text{Biogas production}(\text{mL}) = 299(\text{DM}) + 238(\text{FW}) + 256(\text{FVW}) + 282(\text{DM}*\text{FW}) + 435(\text{DM}*\text{FVW}) + 217(\text{FW}*\text{FVW}) + 2126(\text{DM}*\text{FW}*\text{FVW}) \quad \text{Eq. 5.8}$$

The relative mix proportion of organic waste and interaction between DM and FW (AB), DM and FVW (AC), and DM, FW and FVW (ABC), influenced biogas production possitively. The high coefficient (2126) for mix of three organic waste (ABC) than mix of two organic waste mixes (AB, AC, BC) indicates that ternary organic waste mix performs better than binary organic waste mix for the co-digestion of DM (A), FW (B) and FVW (C). Also as discussed in Section 5.6.2, high biogas production obtained with the three organic waste mix of DM (A) of 33%) , FW(B) of 33% and FVW (C) of 33% that has C/N ratio of 27.5. A low biogas production

production obtained for monodigestion of FW and FVW that has C/N ratio of 35 and 33 respectively. Thus, the positive synergistic effect of three organic waste mix can be attributed to the more balanced nutrient composition for microorganisms with co-digestion. Whereas, the interaction between FW and FVW (BC) has insignifacant effect on biogas production (high p value of > 0.05). It indicates that minimal balance of nutrient composition is achieved with co-digestion of just FW and FVW (without DM). After eliminating the insignificant term (BC) from the above model, it can be re written as the following.

$$\text{Biogas production}(mL) = 299(DM) + 238(FW) + 256(FVW) + 282(DM*FW) + 435(DM*FVW) + 2126(DM*FW*FVW) \quad \text{Eq. 5.9}$$

The influence of mix proportion of organic wastes on biogas production (response variable) presented 3D surface plot over triangle design in Fig. 5.19. The vertices of triangle in the Fig. 5.19 correspond to AD of single organic waste i.e. mono-digestion (100 % of a sole component), whereas side of triangle corresponds to co-digestion of two organic wastes and space of triangle corresponds to co-digestion of three organic wastes. The high biogas production can be observed

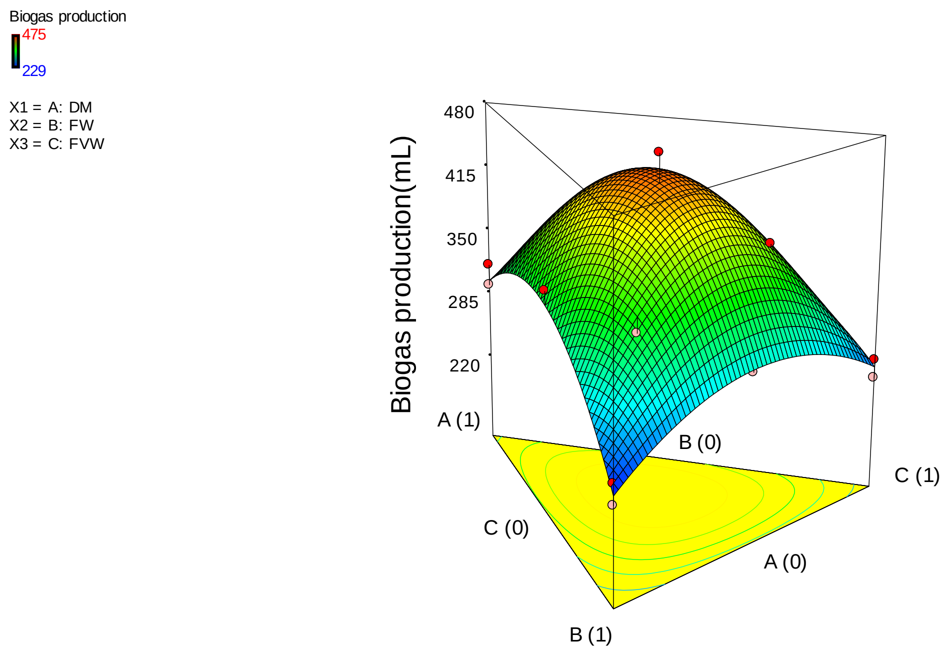

Fig. 5.19 Interactive effect of DM (A), FW (B) and FVW (C) on biogas production (mL)

over triangle space compared to side of triangle and vertices of triangle. It indicates that the synergistic interaction of three organic wastes in co-digestion is higher compared to two organic wastes (side of triangle) and single organic waste (vertices of triangle). Low biogas production at vertices representing mono-digestion of organic wastes, which may be due to imbalanced nutritional composition (Callaghan et al., 2002a; Shen et al., 2013). Thus, the co-digestion of three organic wastes of DM, FW and FVW is favourable to achieve high biogas production.

Optimization is applied to find out the maximum biogas production. The optimal mix proportion of organic waste corresponding to the maximum biogas production (455 mL) is DM of 0.40 (40 %), FW of 0.26 (26 %) and FVW 0.34 (34 %). The optimal mix proportion of each organic waste is verified through confirmatory experiment. The maximum biogas production obtained from the confirmatory experiment is found to be 488 mL,which closely agrees with the predicted biogas production (455 mL) of the model. Hence, special cubic model adopted in the co-digestion study of DM, FW and FVW is validated reasonably. The special cubic model can be used to predict biogas production in anaerobic co-digestion.

From the present Set III, it can be observed that the AD of ternary organic waste mix of DM, FW and FVW yields higher biogas production compared to AD of binary organic waste mix. The maximum biogas production can be obtained with mix proportion of DM of 40 %, FW of 26 % and FVW of 34 %.

5.7 Co-digestion of RS and DM: Set IV

From the previous sets (Set I, Set II, and Set III), it is observed that co-digestion improves biogas production in AD. The adopted quadratic and special cubic models are suitable to evaluate the influence of various factors on biogas production in co-digestion. However, the models have not focussed on the kinetic behaviour of co-digestion. The present set investigated the kinetic behaviour of co-digestion while continuing the possibilities of improving biogas production by considering additional organic wastes viz., RS and DM.

5.7.1 Experimental design

AD experiments are carried out for seven mix proportions of RS and DM. The seven mix proportions of RS and DM are 1:0, 5:1, 3:1, 1:1, 3:1, 5:1 and 0:1. The organic waste mix in the reactors are prepared as per the mix proportions and AD experiments are carried out as per the method described in Section 3.4 The proportions of the organic waste mixes are prepared based on volume at a fixed total solids (TS %) loading of 8% and I/S ratio of 1.3. Biogas production of the different mix proportions are recorded for about 75 days. In order to evaluate the kinetic behaviour the modified Gompertz model is described in section 3.7 is adopted. The kinetic parameters of the model M, R_m and λ are estimated using nonlinear least-square regression method using experimentally obtained methane yield. The kinetic parameters are used to predict the methane yield. The predicted methane yield from the model is plotted with the obtained methane yield in the AD experiments. The goodness of fit for the kinetic parameters is diagnosed using coefficient of determination (R^2).

5.7.2 Biogas production

Significant variations in methane yield have been observed for different mix proportions of RS and DM (Fig. 5.20).A low methane yield of 151.8 mL of CH_4/g of VS is observed for the mono digestion of RS (1:0). It closely coinciding with the reported methane yield for the mono digestion of RS of 127 mL.CH_4/g of VS (Wang et al., 2013) and 171.5 mL CH_4/g of VS (X. Chen et al., 2014a). However, it is relatively higher than reported methane yield of 91.6 mL of CH_4/g of VS (Lianhua et al., 2010). The low methane yield for the mono digestion of RS is may be due to its recalcitrant lignocellulose structure and imbalanced nutrient composition in it (Martínez et al., 2005) (high C/N ratio of 55.4 ±0.1). Whereas, methane yield for mono-digestion of DM is 216.0 mL of CH_4/g of VS and is 42 % higher than the mono-digestion of RS. It is in reasonable agreement with the reported (Morken et al., 2018) methane yield of 218.4 mL of CH_4/g of VS for mono-digestion of DM. However it is slightly lower than the reported (Wang et al., 2013) methane yield of 265 mL of CH_4/g. VS. Slight variations in methane yield of different studies with the same organic matter are may be due to the discrepancies in organic waste characteristics and experimental methodology adopted.

High methane yields of 239.3 mL, 237.9, and 232.0 mL of CH_4/g of VS are obtained for co-digestion mix proportion of 1:1, 1:3 and 1:5 (RS:DM) respectively. The obtained methane yield for co-digestion is higher by 56-57% and 9-10% compared to mono digestion of RS and DM respectively. The average C/N ratios of corresponding organic waste mixes of 1:1, 1:3 and 1:5 are 36.0, 26.3, and 23.1 respectively. The C/N ratios of co-digestion mixes are close to the suggested optimal C/N ratio of 20-35 (Kwietniewska and Tys, 2014). The high methane yield in co-digestion mixes is may be due to the optimal C/N ratio achieved with co-digestion of organic wastes having high and low C/N ratio (Demirel and Scherer, 2011; Morken et al., 2018). The same kind of maximum methane yield is also observed with co-digestion of wheat straw having high C/N ratio with wool textile waste having low C/N ratio (Kabir et al., 2015). The obtained high methane yield of 239.3 mL CH_4/g .VS for mix proportion of 1:1 and C/N ratio of 36 is in reasonable agreement with the reported high methane yields of 215 mL.CH_4/g. VS (El-Shinnawi et al., 1989) and 210 mL of CH_4/g .VS (Yan et al., 2015) at C/N ratio of 30. Thus, high methane yield for co-digestion mixes can be attributed to the synergistic effect with balanced nutritional composition.

5.7.3 Data analysis

The experimentally obtained methane yield for the co-digestion mixes is fitted to the modified Gompertz model and kinetic parameters are evaluated. The high R^2 (0.99) indicating good fitment of the methane yield to the model. It is in consistent with the reported R^2 of 0.94 to 0.99 (Kafle and Kim, 2013) for co-digestion of apple waste with swine manure. The Kinetic parameters are evaluated using nonlinear least-square regression method and detailed as follows:

5.7.3.1 Methane potential (M)

Methane potential (*M*) is the theoretical methane yield that can be generated over infinite digestion time (t). In the present study, methane potentials from the modified Gompertz model are estimated to be 170.9, 164.6, 171.6, 254.0, 244.4, 242.6 and 221.5 mL of CH_4/g of VS for mix proportions of 1:0, 5:1, 3:1, 1:1, 3:1, 5:1 and 1:0 (RS:DM) respectively (Fig.5.20.B). Whereas, the experimentally obtained methane yield (over 75 days of digestion period) is observed to be 151.8, 156.2, 165.1, 239.3,237.9, 232.0 and 216.0 mL of CH_4/g of VS for mix proportions of 1:0, 5:1, 3:1, 1:1, 3:1, 5:1 and 0:1 respectively. The experimentally obtained methane yield is 89-98% of the estimated methane potential from the model. It indicates that the accomplishment of maximum degradation in 75 days of digestion period.

5.7.3.2 Lag phase (λ)

Lag phase (λ) is the initial time needed for hydrolysis, acidogenesis, and acetogenesis in producing acids, alcohols, and H_2/CO_2 from the organic matter (Lianhua et al., 2010). Lag phase indicates the delay in consistent methane production at the beginning of the AD process. Lag phase is found to be varied among different co-digestion mixtures considered in the present study

(Fig.5.20.C). The longer lag phase (λ) of 21.7-24.4 days is observed for mix proportions containing pure and high amount of RS (1:0, 5:1, and 3:1). The reason for the longer lag phase may due to the time requirement of microbial communities in AD system to adopt to new environment (Cho et al., 2013). It can be due to the recalcitrant lignin structure in RS resisting the hydrolysis which is the first step in AD (Martínez et al., 2005). Shorter lag phase (5.7 to 10.2 days) are observed for the co-digestion mixes primarily containing high amount of microbial rich DM (1:1, 1:3 and 1:5 mixtures). The shorter lag phase is may be due to the conducive environment provided by co-digestion with microbial rich, easily degradable DM.

5.7.3.3 Maximum methane production rate (R_m)

Maximum methane production rate (R_m) is the rate at which methane is produced in exponential phase of digestion. It is found to be in the range of 4.5 to 5.9 mL of CH_4/g of VS.day for all the studied co-digestion mix proportions (Fig. 5.20.D). The mono-digestion of RS (1:0) and mix proportion containing high amount of RS (5:1) had shown lower R_m values compared to other mix proportions. The highest R_m values are observed for co-digestion mix proportion of 1:1 (5.8 mL of CH_4/g of VS. day) and 1:3 (5.9 mL of CH_4/g of VS. day). The high R_m is may be due to the synergism in co-digestion mix proportions for quick rate of methane production. The same kind of high R_m value is observed in co-digestion of pre-treated RS with OFMSW and pre-treated thickened waste activated sludge (Abudi et al., 2016a). The slow rate is observed for mix proportions containing high amount of RS may be due to slowly degradable lignocellulose matter and is in agreement with the study of (J. Li et al., 2014b). Hence, co-digestion promotes the rate of methane production in addition to maximising the methane yield.

5.7.3.4 Digestion time (T_{90}, T_{80} and T_{eff})

Digestion time indicates the organic matter utilization rate in biodegradation. T_{90} and T_{80} are the time taken for the accumulation of 90% and 80% of methane yield. The parameter T_{eff} is the effective time taken for digestion, obtained with the exclusion of lag phase (λ) from T_{80} (T_{80}-λ) (S Xie et al., 2011). The T_{90}, T_{80} and T_{eff} of mix proportions are shown in Fig. 5.21. It can be observed that T_{90} and T_{80} are in the range of 55-60 days and 45-50 days, respectively. The parameters are in close agreement with the reported T_{90} of 52 days (Yuan et al., 2015)and T_{80} of 50 days(X. Chen et al., 2014a) in AD of corn stover and RS respectively. From the Fig. 5.21, it can also be observed that the parameters T_{90}, T_{80}, are slightly low for mix proportions containing high DM. It may be

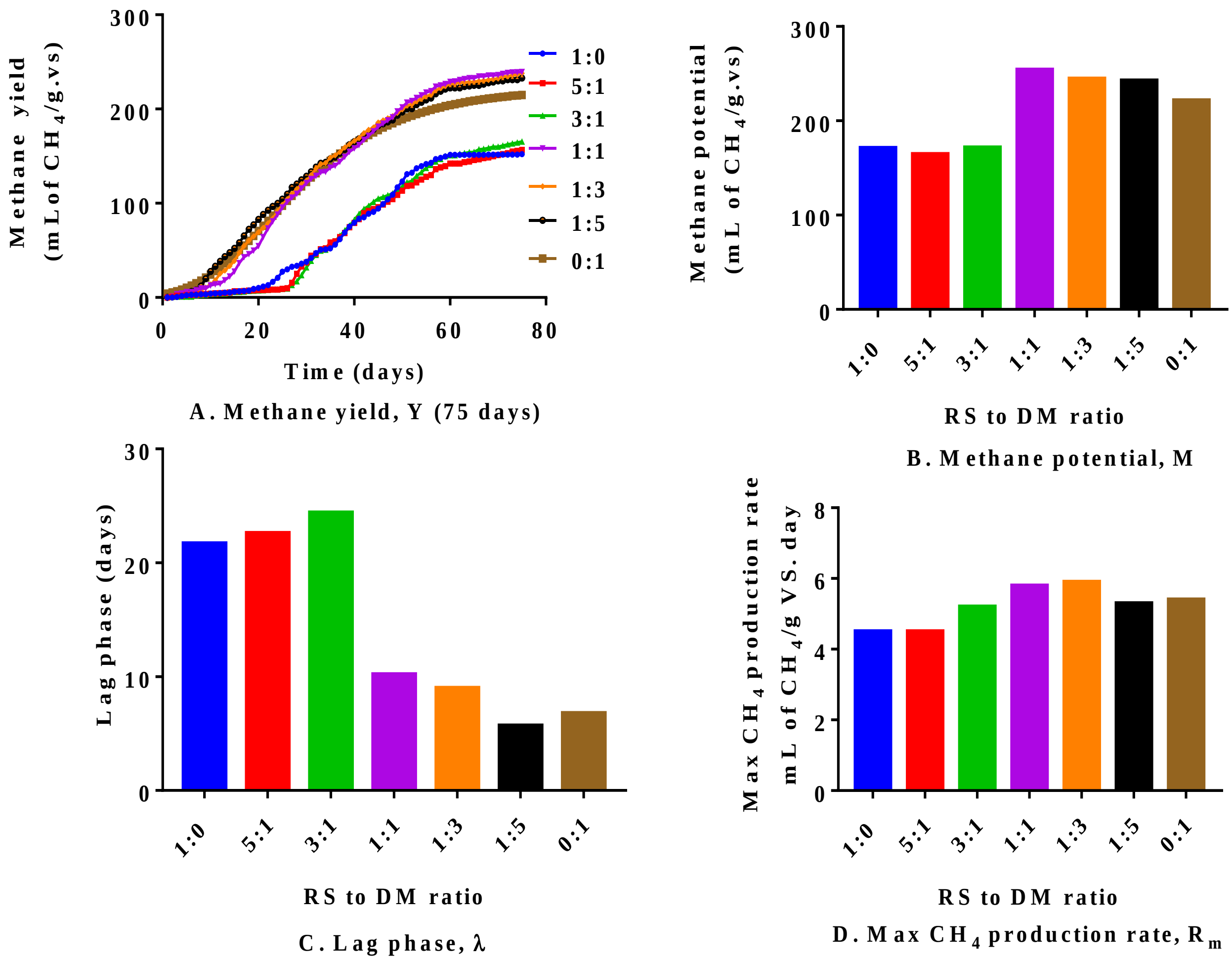

Fig. 5.20 Effect of mix proportion of RS and DM on the kinetic behavior

due to the presence of easily biodegradable organic matter in DM compared to RS, which is slowly biodegradable organic matter. Whereas, effective digestion time (T_{eff}) is found to be high (30-40 days) for the proportions containing high DM (1:1, 1:3, 1:5 and 0:1) due to shorter lag phases. It is necessary to maintain the organic matter throughout the effective digestion time for efficient degradation (S Xie et al., 2011). Hence, retention time of about 30 - 40 days in the digester is recommendatory for effective digestion.

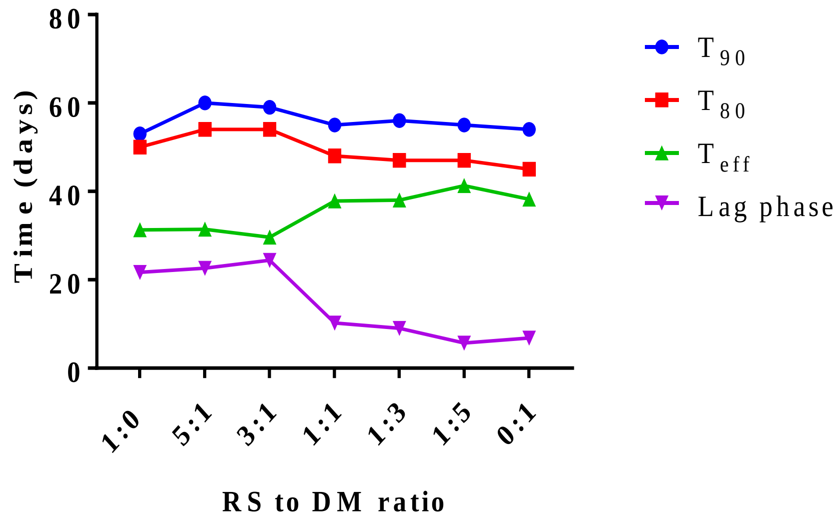

Fig. 5.21 Digestion time (T_{90}, T_{80} and T_{eff}) in different mix proportion of RS and DM

From the present Set-IV, it can be observed that co-digestion favoured the kinetic behaviour in terms of reduced lag phase , improved rate of methane production and methane yield. It is recommendatory to adopt the co-digestion mix proportions of 1:1, 1:3 and 1:5 in field level application for RS and DM. In the case abundant availability of RS, the co-digestion mix of 1:1 can be adopted that utilises high amount of RS with maximum methane yield. Whereas, in case of abundant DM, the co-digestion mix proportions of 1:3, 1:5 can be adopted for the effective utilisation.

5.8 Comparison of co-digestion scenarios

Methane yield is determined by dividing the amount of methane produced for four optimal mix proportions of co-digestion sets with the amount of VS $_{added}$. Methane yield per gram of VS $_{added}$ for the four sets that yielded maximum biogas production is shown in Fig. 5.22. The methane yields are 94 mL CH_4/g VS, 196 mL CH_4/g VS, 188 mL CH_4/g VS and 239 mL CH_4/g VS for Set I (FW +CM), Set II (CP + LG + CM), Set III (DM + FW + FVW), and Set IV (DM + RS) respectively. It can be observed that the co-digestion of Set IV (DM + RS) registered high methane yield followed by Set II (CP + LG + CM), Set III (DM + FW + FVW), and Set I (FW +CM). The low performance in Set I compared to other mixes may be due to the low biodegradable fraction of CM (VS content of 60%). Different methane yields in four sets can be attributed to diverse feedstock characteristics considered in the present study.

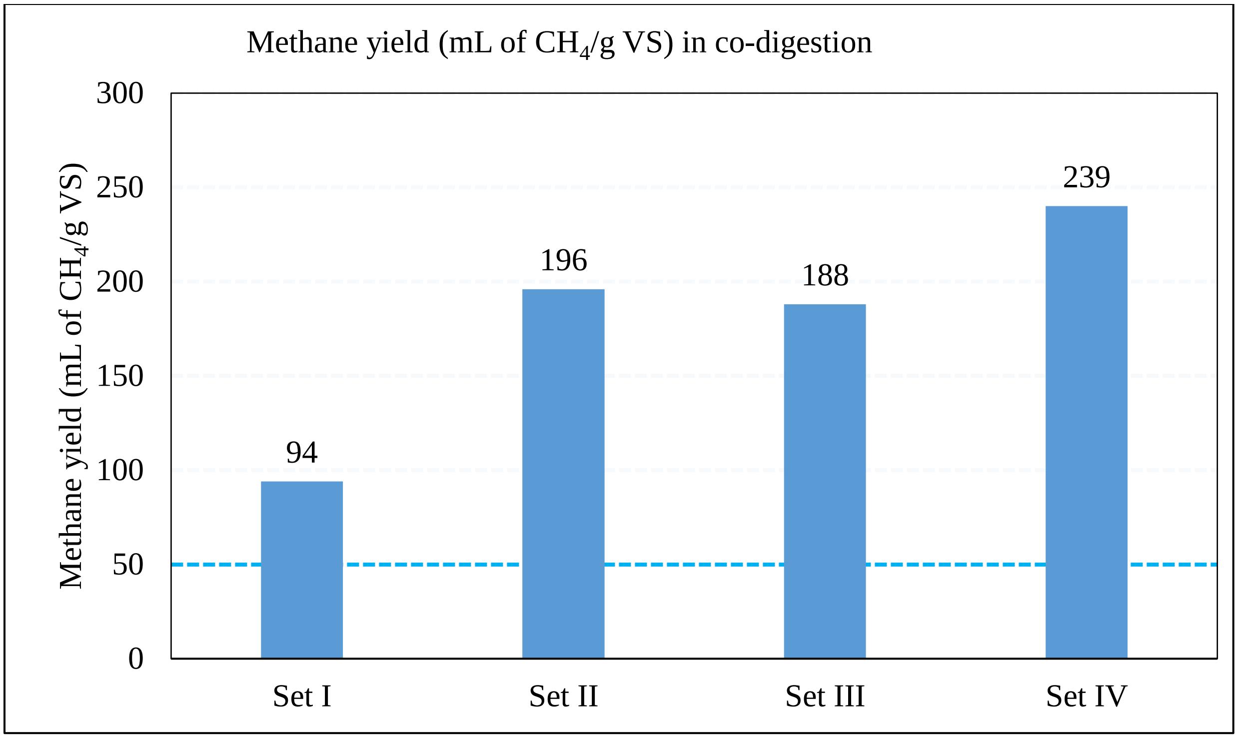

Fig. 5.22. Methane yield (mL of CH_4/g VS) for four co-digestion scenarios

5.9 Summary

From the present chapter, it can be observed that

- Single organic waste as a feedstock for AD may not be a wise option for maximum biogas production due to inconsistent characteristics. The characteristics of feedstock can be improved with co-digestion for maximum biogas production.
- Co-digestion mix proportion and total solids (TS%) in AD influences the process and are to be chosen optimally for maximum biogas production.
- The optimal proportion of organic waste mixes for maximum biogas generation are as follows.
  - Set-I : FVW of 42 %, CM (58 %)
  - Set-II CP of 2 %, LG of 68 % and CM of 29 %
  - Set-III: DM of 34 %, FW of 24 % and FVW of 42 %.
  - Set-IV: RS and DM are 50% and 50 %, or 25 % and 75 %, or 16.3 % and 83.7 %
- RSM is a suitable approach for evaluation and optimization of biogas production in co-digestion of binary and ternary organic waste mixes.
- Modified Gompertz model accounted well for studying the kinetic behaviour in co-digestion of the organic wastes.

Chapter 6 Energy- Economic Analysis

From Chapter 5, it is observed that co-digestion enhances biogas production from organic wastes. Use of these wastes commercially for biogas production involve several unit operations and its benefits need to be quantified. In order to evaluate the benefits, the internal consumption of energy and various costs involved are estimated and detailed as follows. Summary is presented at the end of the chapter.

6.1 Design parameters

The energy and economic benefits are estimated based on optimal organic waste mix proportions, obtained for the four sets in Chapter 5. Several design parameters are considered in the installation and maintenance of a large scale AD plant in bio-energy generation. The size of the AD plant is 200 m^3 with working volume of 160 m^3, leaving some headspace (40 m^3) for biogas collection. The combined heat and power generation (CHP) system converts the biogas produced from optimal organic waste mix proportions to heat and electricity. The CHP system is based on internal combustion engine with a heat recovery facility (Fig. 6.1). The plant at large scale is considered to produce 80% of biogas obtained at laboratory scale due to scale up factor (Ruffino et al., 2015). The electrical and thermal energy efficiencies of CHP system are 35% and 50% respectively (Scano et al., 2014). The lower heating value (LHV) of methane in biogas is 39.62 MJ (Scano et al., 2014). The design parameters of AD plant is summarised in Table 6.1.

Table 6.1 Design parameters of large scale AD plant

	Set-I (CM + FVW)	**Set-II (CM+LG+ CP)**	**Set-III (DM+FW+FVW)**	**Set-IV (DM + RS)**
Feedstock composition (based on dry matter)	FVW-42 %, CM -58 %	CP -2 %, LG-68 % ,CM -29 %	FVW-42%, FW-24 %, DM -34 %,	RS-50%, DM-50 %
Feedstock loading rate (fresh matter), (t/day)	4.4	1.8	4.5	2.3
Water requirement (m^3/day)	0.9	3.5	0.8	3
Feedstock volumetric loading (m^3/day)	5.3	5.3	5.3	5.3

HRT (days)	30	30	30	30
Specific methane production (mL CH_4/g VS)	94	196	188	239
Digester filling co-efficient	0.8	0.8	0.8	0.8
CHP electrical efficiency (%)	35	35	35	35
CHP thermal efficiency (%)	50	50	50	50

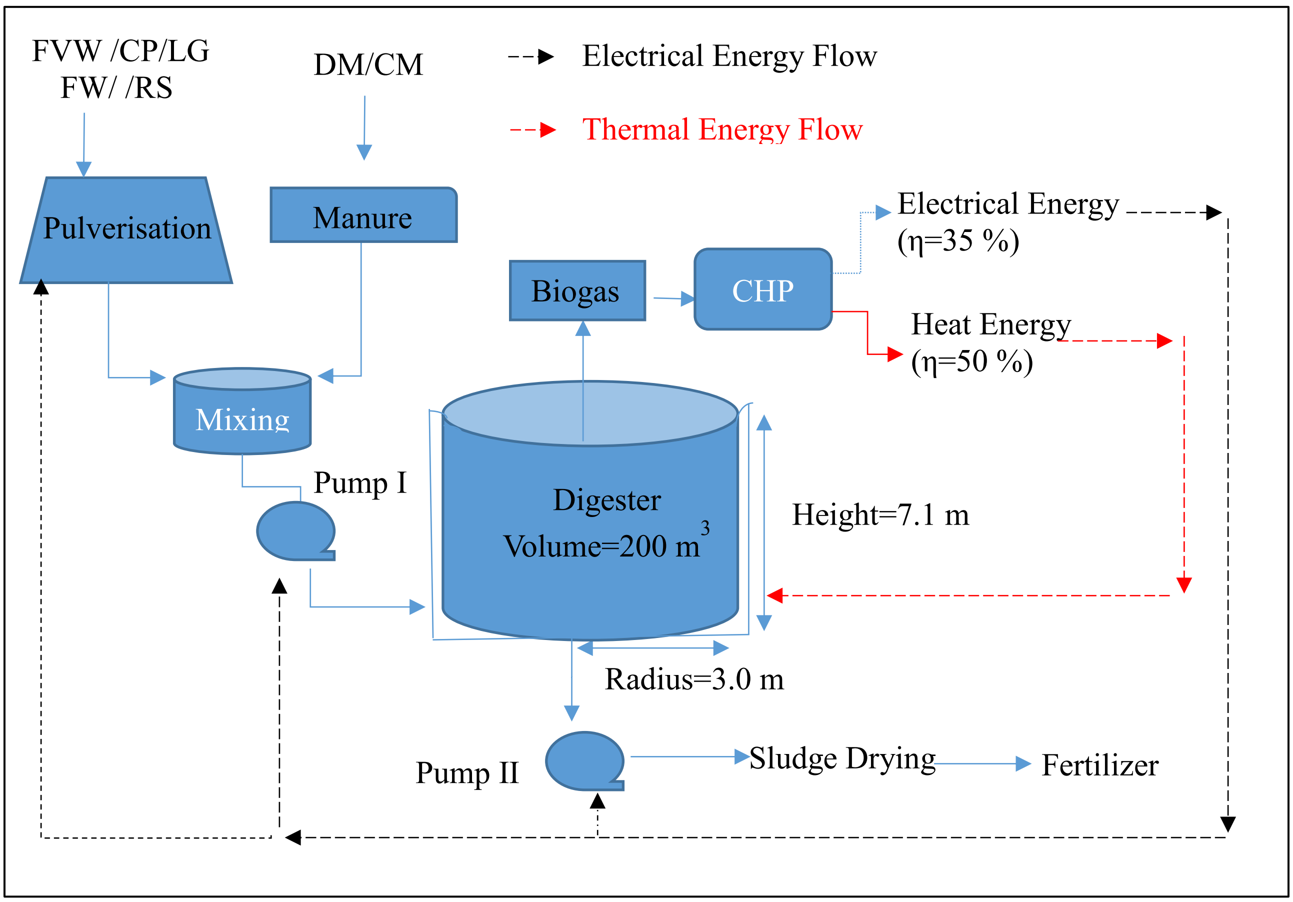

Fig. 6.1 Schematic diagram and energy flow of large scale AD plant

6.2 Energy analysis

Energy production for optimal co-digestion mix combinations is evaluated based on specific methane production and feedstock loading rate (Table 6.2). The net electrical and thermal energy production is estimated as per methods presented in Section 3.8 and detailed as follows:

6.2.1 Net electrical energy production

The net electrical energy is estimated by subtracting electrical energy consumption from electrical energy production. Electrical energy consumption is assessed for pulverisation, pumping, conveyance of the feed material in AD plant. Among the organic waste mix combinations , the co-digestion of Set IV (DM + RS) registered high net electrical energy production (616 kWh-e/day) and co-digestion of Set I (CM + FVW) registered low net energy production (172 kWh-e/day) (Fig. 6.2). The net electrical energy production of Set IV (DM & RS) is 260 % higher compared to co-digestion mix of Set I (CM + FVW) respectively. The co-digestion of Set I (CM+FVW) resulted in low net energy production due to its low methane production. The auxiliary equipment of plant consumes an electrical energy of 10%, 8%, 7%, and 4% that is produced for organic waste mix of Set I (CM + FVW), Set II (CM + CP + LG), Set III (DM + FW + FVW), Set IV (DM + RS). The variations in percentage (%) of consumption are due to the differences in energy production in the form of biogas from the co-digestion mixes. The annual net electrical energy that can be produced for co-digestion of Set IV is 224 MWh-e/year. If the electrical energy produced is used for domestic purpose, it can supply the power requirement of 560 families in a year (Each family in rural India consumes approximately 400 kWh-e/year). The produced electrical energy can also be used for street lighting, agricultural purposes or can be supplied to national electric grid.

6.2.2 Net thermal energy production

The net thermal energy is estimated by subtracting thermal energy consumption from thermal energy production. Thermal energy consumption is assessed based on heat energy requirements of the AD plant to maintain constant mesophilic temperature (35^{O} C). Among organic waste mixes , the co-digestion of Set IV (DM + RS) registered high net thermal energy production (883 kWh-t/day) and co-digestion of Set I (CM + FVW) registered low net energy production (240 kWh-t/day) (Fig. 6.2). The net thermal energy production of Set IV (DM + RS) is 270 % higher compared to Set I (CM + FVW). The co-digestion of Set I resulted in low net thermal energy production due to its low methane production. The heating system of the plant consumes thermal energy of about 12 %, 9% , 9%, and 4 % that is produced for organic waste mix of Set I (CM + FVW), Set II (CM+CP+LG), Set III (DM+FW+FVW), and Set IV (DM+RS) respectively. The remaining thermal energy can be used either for thermal pre-treatment of organic wastes to further enhance the AD performance or any industrial use that has heat requirement in the vicinity.

The performance of the plant for four sets is presented in Table 6.2. From the table, it can be observed the Set IV (DM + RS) yielding high net energy production followed by Set II (CM + CP +LG) and Set III (DM + FW + FVW). The least performance is observed for co-digestion of Set I (CM + FVW).The least performance for Set I is due to low energy production (biogas) obtained in the present study compared to other set of combinations.

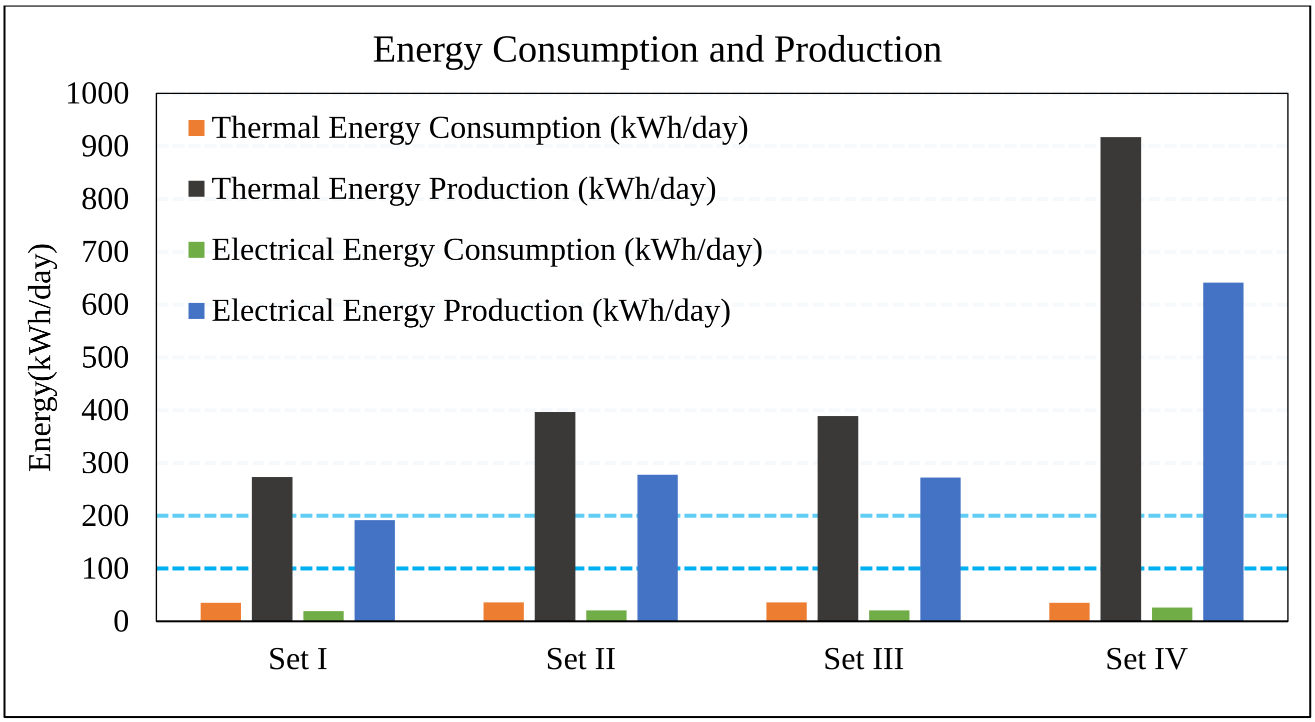

Fig. 6.2 Energy consumption and production in co-digestion

Table 6.2 Performance of the large scale AD plant

	Set-I (CM + FVW)	**Set-II (CM+LG+ CP)**	**Set-III (DM+FW+FVW)**	**Set-IV (DM + RS)**
Electrical energy production (kWh/day)	192	278	272	642
Electrical energy consumption (kWh/day)	19	21	20	26
Net electrical energy production (kWh/day)	173	257	252	616
Thermal energy production (kWh/day)	274	396	389	917
Thermal energy consumption (kWh/day)	35	35	35	35
Net thermal energy production (kWh/day)	239	361	354	882

6.3 Economic analysis

Economic analysis is carried for the four sets based on costs that can be incurred (capital, and O&M costs) and financial benefits over plant life of 20 years. The costs and financial benefits are detailed as follows.

6.3.1 Capital cost

Capital cost is the investment required for the installation of the digestion tank and auxiliary equipment such as pulveriser, conveyor, and other miscellaneous items at the time of installation. The cost HDPE material for digestion tank, pulveriser, conveyor and other miscellaneous items are obtained based on the market enquiries. The cost of HDPE material for 200 m^3 volume of digestion tank is about Rs 13, 00,000 /- (Rs 6.5 /-litre based on present market enquiries-2020). The costs of pulveriser, conveyor and other miscellaneous items are about Rs 2, 00,000 /-. The cost of CHP unit with heat recovery facility is Rs 5, 00,000/-. The total cost of the plant is about Rs 20,00,000 /- (Table 6.3). Land costs are not considered, assuming sufficient land is available and provided by the waste management authorities free of cost (land costs vary from rural to urban areas in India).

Table 6.3 Capital cost of AD plant

Item	**Approximate Cost (Rs/-)**
Digestion tank	13,00,000
CHP unit	5,00,000
Pulveriser, conveyor and miscellaneous units	2,00,000
Total	20,00,000

6.3.2 Operational & maintenance (O & M) cost

O&M cost is the cost required for operating and maintenance of the plant for bio-energy generation. The annual O & M cost about 10 % of the capital cost of plant (Ruffino et al., 2015; Scano et al., 2014). It includes labour cost and other unforeseen costs.The O&M cost of the large scale digester is Rs 2,00,000 /-

Two different scenarios are considered that use the electrical energy to estimate the economic benefits. Scenario I pertains to direct use of the electrical energy internally for domestic consumption (household community level) and corresponding cost of energy (Rs/kWh) is estimated. Scenario II pertains to sale of the electrical energy to national electric grid and corresponding payback period and net present value are estimated. Thermal energy produced is not considered as its sale may not be guaranteed in the vicinity. The digested sludge, which is one of the by-products from the process, is considered for “return policy”. The “return policy” is the delivery of fertiliser free of cost to entities (households, restaurants, village level communities) that supplied segregated solid waste. The return policy encourages the segregation of waste at source generation itself.

6.3.3 Scenario I (Direct use of energy)

Scenario I is the use of electrical energy generated (after the internal consumption) for domestic purpose. The cost of electrical energy is estimated based on the method described in

Section 3.8.1. The cost of energy for organic waste mix of Set I (CM + FVW), Set II (CM + CP + LG), Set III (DM+FW+FVW), and Set IV (DM + RS) is estimated to be Rs.6.9/-, Rs.4.6/-, Rs.4.7/-, and Rs.1.9/ respectively (Fig. 6.3). Among organic waste mixes, co-digestion of Set IV (DM + RS) registered low cost of energy (Rs.1.9/-) and co-digestion of Set I (CM + FVW) registered high cost (Rs.6.9/-). The cost of energy for Set IV (DM + RS) is 263 % lower compared to Set I (CM + FVW) respectively. The low cost of energy for the co-digestion of Set IV (DM + RS) is due to the higher energy (biogas) production. In India, the domestic market price of electrical energy is about Rs 6.25 /-. It can be observed that the cost of energy is lower compared to the domestic market price (Rs 6.25 /-) except for Set I (CM + FVW). It means that AD of these co-digestion mixes provides energy to plant operators at lower price than market price and are feasible in terms of costs incurred towards production and generation.

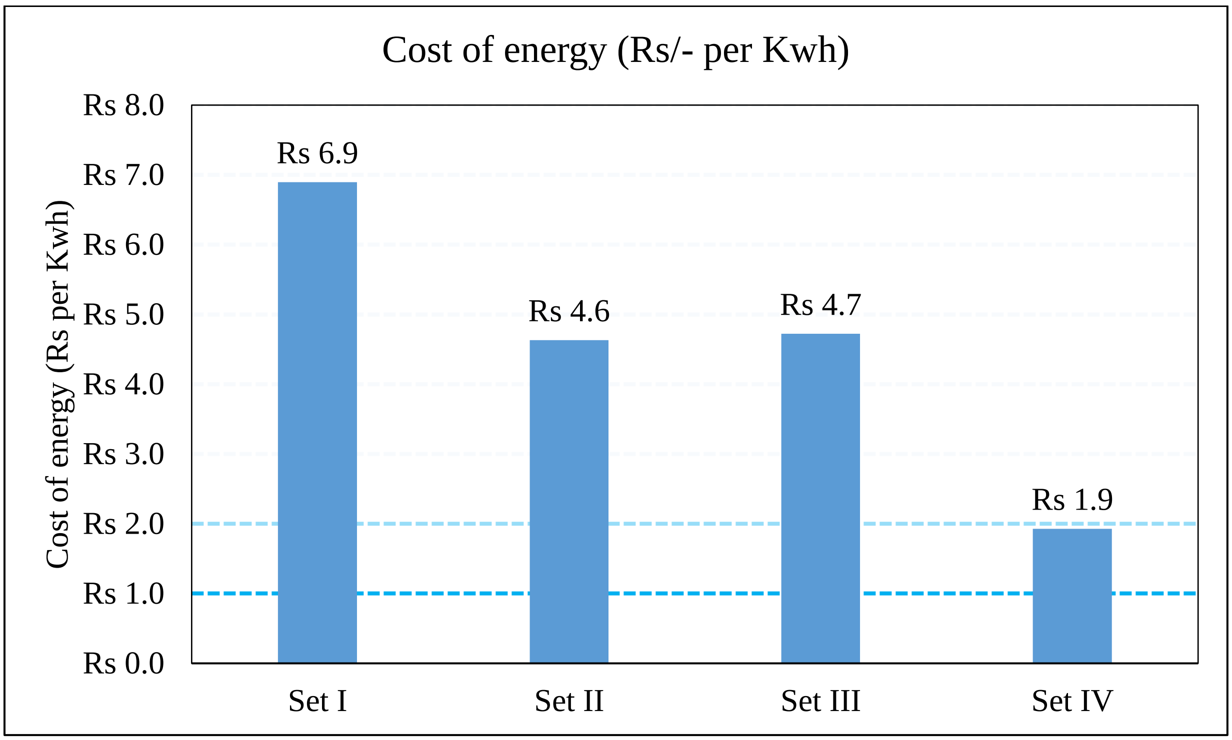

Fig. 6.3 Cost of energy for the four co-digestion sets

6.3.4 Scenario II (Supplying to electric grid)

Scenario II is the sale of the electrical energy to the national electric grid, after internal consumption of energy for plant. The revenues are estimated by multiplying the produced electrical energy with the current domestic market price (≈Rs 6.25/kWh). Subsequently, the pay back period and net present value (NPV) are estimated and summarised in Table 6.4.

Table 6.4 Economic analysis of the four co-digestion sets

Scenario I (Direct use of energy)				
	Set-I (CM +FVW)	**Set-II (CM+LG+ CP)**	**Set-III (DM+FW+FVW)**	**Set-IV (DM+RS)**
Total capital cost (lakhs)	20.00	20.00	20.00	20.00
Annual capital charge (lakhs) (@11.7 %)	2.34	2.34	2.34	2.34
Annual O& M costs, lakhs (@10%)	2.00	2.00	2.00	2.00
Total annual cost	4.34	4.34	4.34	4.34
Annual Net electrical energy production (MWh/year)	62	93	91	224
Cost of energy (Rs/kWh)	6.9	4.6	4.7	1.9
Scenario II (Supplying to electric grid)				
Electrical Energy Revenues (Lakhs/year), EER	3.93	5.85	5.74	14.04
Net cash flow ,NCF (Lakhs/year) (EER- O& M costs)	1.93	3.85	3.74	12.04
Pay back period (Discount rate @10 %)	--	7.0 years	7.0 years	2.0 years
Net present value (NPV), lakhs (Discount rate @10 %)	--	12.7	11.8	82.50
Net present value/Capital cost	--	0.63	0.59	4.12

The payback period indicates the amount of time it takes to recover the cost of an investment. The payback periods for organic waste mixes of Set II (CM + CP + LG), Set III (DM + FW + FVW), and Set IV (DM + RS) are 7.0, 7.0, and 2.0 years respectively. (Menind, 2009) reported payback period about 8 years for DM based AD plants. This means that investment on AD plant can be fully recovered at the end of payback period. Among organic waste mixes, the Set IV (DM + RS) registered low payback period (2.0 years). The obtained pay back periods in the present study are reasonably encouraging for organic waste management in study area. However, co-digestion mix of Set I (CM + FVW) cannot be paid back due to low electrical energy revenues compared to annual costs. It means that investment costs cannot be recovered with the present energy generation and current price of electricity for Set IV. Research can be carried out for further improvement in energy production with other possible strategies and provision of subsidies to reduce capital cost.

Net present value (NPV) is used in capital budgeting to analyse the profitability of an investment in present value. It is calculated by taking the difference between the present value of cash inflows and present value of cash outflows over a plant life (20 years). The NPVs are 12.7, 11.8, and 82.5 lakhs (at discount rate of 10%) for AD plants based on feedstock of Set II (CM + CP + LG), Set III (DM + FW + FVW), and Set IV (DM + RS) respectively. It means that a profit of 12.7, 11.8, and 82.5 lakhs can be obtained at the end of plant life span (20 years). The ratio between NPV and capital cost indicates contribution of profit for capital investment in setting of new plant, at the end of life span of 20 years. The ratio are 0.63, 0.59 and 4.12 is for AD plants based on Set II (CM + CP + LG), Set III (DM + FW + FVW), and Set IV (DM + RS) respectively. This means that the profits from the sale of electricity likely to earn 63 %, 59 %, and 412 % of the capital investment for the implementation of new plant (at the end of the useful life span of 20 years). Based on this project data, the AD plants are preferable in the order of Set IV (DM + RS) > Set II (CM + CP + LG) > Set III (DM + FW + FVW).

From the above discussion, it can be observed that co-digestion of organic waste mixes is economically viable and preferable for field scale implementation in the order of Set IV (DM + RS) > Set II (CM + CP + LG) > Set III (DM + FW + FVW). However, co-digestion CM & FVW may not be economically viable at the present energy production rate. In the present analysis, social benefits such as reduced GHG emissions and improved hygiene conditions are not considered as they cannot be financially quantified. If the social benefits are also taken into account, the AD could become the technology that is highly attractive for energy production in India.

6.4 Summary

From the present study, it can be observed that

- AD of organic wastes with co-digestion is a profitable technology to augment the energy supply.
- Auxiliary equipment of the AD plant consumes an electrical energy which is of 4-10 % of the energy produced by plant while the remaining electrical energy can be used for alternative purposes.
- The heating system of the AD plant consumes thermal energy which is of 4-12 % of the energy produced by plant while the remaining thermal energy can be used for alternative purposes.
- The cost of energy for organic waste mixes of Set I (CM + FVW), Set II (CM + CP + LG), Set III (DM + FW + FVW), and Set IV (DM + RS) are Rs.6.9/-, Rs.4.6/-, Rs.4.7/-, and Rs.1.9/-respectively.
- Among the organic waste mix combinations investigated, the co-digestion of Set IV (DM + RS) registered low payback period (2.0 years) compared to other co-digestion mixes.
- The organic waste mixes are financially feasible in the order of Set IV (DM + RS) > Set II (CM + CP + LG) > Set III (DM + FW + FVW), and are recommended for field scale implementation in study area.

Chapter 7 Conclusions and Scope for Further Study

Increase in urbanization and consumption standards leading to the generation of different kinds of organic wastes from municipalities, agricultural processes and food based industries. The present work is aimed to utilize the available, widely generated organic wastes for AD in Warangal district as well as other parts of the country. Following are the significant conclusions based on the present work.

Crop residues are widely generated in India and can be used as feedstock for AD. Major crop residues generated in India are rice, wheat and maize which have bio-energy potential of about 653×10^9 MJ/year. The bio-energy potential of residues could substitute an equivalent coal consumption of 52 Mt/year. The coal substitution could avoid 46 Mt of GHG (CO_2) emissions/year from being released into the atmosphere. However, the collection and transportation of these residues to the centralized AD facility remains challenge and it can be feasible only if the governing states adopt an appropriate policy for their utilization.

Single organic waste as a feedstock for AD may not be a wise option due to imbalanced nutritional characteristics and its non-availability in all seasons. The feedstock characteristics can be improved with co-digestion of available and suitable organic wastes for maximising biogas production. In the present study four combinations of organic wastes are studied to identify the optimal mix proportions of the organic wastes for maximum biogas generation and are as follows.

- Set-I: Fruit vegetable waste (FVW) of 42 % and chicken manure (CM) of 58 %.
- Set-II: Citrus pulp (CP) of 3 %, lawn grass (LG) of 68 % and chicken manure (CM) of 29 %.
- Set-III: Dairy manure (DM) of 34 %, food waste (FW) of 24 % and fruit vegetable waste (FVW) of 42 %.
- Set-IV: Rice straw (RS) and dairy manure (DM) of 50% and 50 %, or 25 % and 75 %, or 16.3 % and 87.7 %.

Response surface methodology (RSM) is a suitable approach for modelling the co-digestion behaviour and optimizing biogas production in AD of two or three organic wastes. In addition, modified Gompertz model accounted well for understanding the kinetic behaviour in co-digestion.

The AD of above organic waste combinations is energetically & economically feasible except for the co-digestion of CM & FVW (Set I). The auxiliary equipment of large scale plant consumes an electrical energy about 4-10 % and thermal energy about 4-12 % that produced from AD plant. Among the organic waste mix combinations investigated, the co-digestion of DM & RS (Set IV) registered low pay-back period (2.0 years) compared to other co-digestion mixes. The organic waste combinations of CM, CP & LG (Set II), DM, FW & FVW (Set III), DM&RS (Set IV) are energetically & economically feasible and are recommended for field scale implementation.

The key findings of the research are as follows.

i. The AD of surplus crop residues from rice, wheat, and maize has significant bio-energy potential to meet the energy demand of the nation and need to be seriously considered as an alternate source of renewable energy.

ii. The bio-energy potential from the AD of crop residues could significantly avoid GHGs from being released into the atmosphere.

iii. The organic wastes which do not have suitable composition individually for AD (FW, FVW, LG, DM, RS, CP, CM) can translate into superior quality of feedstock when co-digested.

iv. The co-digestion of FVW (42%) with relatively low proportion of FW (24%) and slightly higher proportion of DM (34%) is recommended for maximum biogas production.

v. The presence of CP even at moderate proportion is found to inhibit biogas production. The co-digestion of low proportion of CP (2%), high proportion of LG (68%) and moderate proportion of CM (29%) is recommended for maximum biogas production

vi. The co-digestion of RS with equal or higher amount of DM (≥50%) is recommended for maximum biogas production.

vii. The co-digestion also enhanced the process performance in terms of improved rate of methane production (R_m) and reduced lag phase (λ).

viii. The co-digestion of RS and DM yielded high-energy production among four co-digestion scenarios investigated.

ix. The enhanced biogas production with co-digestion is sufficient to operate auxiliary equipment and heating system that consumes about 4- 12% of energy produced. The remaining energy can be used for domestic/industrial purposes.

x. The organic waste mixes are financially preferable in the order of DM & RS (Set IV) > CM, CP & LG (Set II) > DM, FW & FVW (Set III) and are recommended for field scale implementation.

The results of the thesis could act as base line data for rural and municipal solid waste management authorities. The management authorities can adopt an appropriate policy for the collection and transportation of the organic waste to generate bio-energy and effective management of organic wastes.

7.1 Specific Contributions

The main contributions of the research are as follows:

i. The bio-energy potential and environmental impact for AD of surplus crop residues was evaluated.

ii. The co-digestion behaviour of the locally available organic wastes was investigated for biogas production with a focus on feasibility.

iii. The optimal organic waste mix proportions for maximum biogas production that can be used for large scale AD process were proposed.

iv. The energy production and the cost of the electrical energy production for co-digestion of different scenarios were evaluated.

7.2 Scope for further study

The following future work is recommended:

i. The feasibility of conducting other pre-treatment studies in addition to co-digestion for further enhancement of biogas production can be explored.

ii. The suggested mix proportions of organic wastes in the present study can be tested at large scale to assess the uncertainties and assumptions associated with costs, funding, price of feedstock, and digestate sale etc.

iii. It would be also interesting if life cycle analysis (LCA) is carried out for biogas production of the mix proportions.

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