

**DETERMINATION OF BIOGAS PRODUCTION POTENTIAL FROM  
VARIOUS SUPERMARKET WASTES**

by

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**Dedicated to my lovely and faithful mother, Oya Alıcı Alkanok.**

**Without her faith, I have never got ahead.**

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## ABSTRACT

Up to date, alternative methods have been investigated to both decrease the environmental effects of wastes and also meet the growing energy demand considering the new technological developments. Then, biogas production through anaerobic digestion comes forward as an alternative method. Biogas and methane production potential of various substrates and waste sources through anaerobic digestion have been carried out in several laboratory and pilot-scale investigations. Through the continued developments of these investigations and applications, using supermarket wastes in biogas plants occurs as a new method to remove wastes in an environmentally way.

The research focused mainly on to investigate the biogas production potential of supermarket wastes. In the concept of research, waste characterizations and suitable total solid (TS, %) ratios of substrates were primarily determined. The objective of this study was to observe the biogas production potentials of every supermarket waste type in the same operation conditions through anaerobic digestion. With this goal, simulated batch-reactors were operated in the laboratory at a constant temperature of 35<sup>0</sup>C. Reactors were filled with shredded and homogenized waste mixtures which were collected from waste storage area of one of the supermarket chain. Substrates were prepared considering TS values which were fixed for every reactor. Also, sludge addition was performed in order to accelerate microbial activity before loading to the reactors.

Consequently, methane-rich biogas production was observed through anaerobic digestion of supermarket wastes. The better performance in gas production and methane concentration was recorded for mixed wastes due to the better nutritional composition. The feasibility study that was calculated in the light of methane and gas production results showed that installing biogas plant could be feasible in an economically manner for supermarkets.

## ÖZET

Günümüze kadar, hem atıklardan kaynaklı çevresel etkilerin azaltılması hem de giderek artan enerji ihtiyacını karşılamak amacıyla alternatif metotlar yeni teknolojik gelişmeler de dikkate alınarak araştırılmaya başlanmış ve anaerobik çürütme yoluyla biyogaz üretimi ön plana çıkmıştır. Bu kapsamda, pek çok farklı hammadde ve atık kaynağının anaerobik çürütme yoluyla biyogaz ve metan üretim potansiyelleri farklı işletme koşullarında laboratuvar ortamında ve pilot ölçekli sahalarda araştırılmıştır. Farklı kaynakların biyogaz tesislerinde kullanımına yönelik çalışmalar ve uygulamalar devam ederken, özellikle çevresel ve ekonomik açıdan bir yük oluşturan süpermarket atıklarının biyogaz tesislerinde değerlendirilmesi atıkların çevresel yolla uzaklaştırılmasını sağlayan uygun bir yöntem olarak ön plana çıkmıştır.

Bu çalışma, süpermarketlerden kaynaklanan atıkların özelliklerine göre anaerobik çürütme yoluyla biyogaz üretim potansiyellerini araştırmayı amaçlamaktadır. Araştırma kapsamında, öncelikle anaerobik çürütme prosesinde değerlendirilebilecek süpermarket atık karakterizasyon tipleri seçilmiş ve bunlar için uygun görülen karışım oranları (%TS) belirlenmiştir. Her bir atık türü için aynı işletme koşullarında anaerobik çürütme yoluyla biyogaz üretim potansiyellerinin gözlemlenmesi hedeflenmiştir. Bu amaç kapsamında laboratuvar ortamında anaerobik çürütücü sistemlerini simule eden batch-reaktörler kurularak 35<sup>0</sup>C sabit sıcaklıkta işletilmiştir. Reaktörler, bir süpermarket zincirine ait atık depolama alanından temin edilen atıklar ile belirlenen TS değerleri ve çamur karışım oranları dikkate alınarak öğütülmüş ve homojen bir karışım halinde doldurulmuştur.

Sonuç olarak, süpermarket atıklarının anaerobik ortamda bozunması ile yüksek metan içerikli biyogaz üretildiği gözlenmiştir. En iyi gaz üretim ve metan konsantrasyon değerleri daha iyi besin kompozisyonuna sahip karışık atıklar için kaydedilmiştir. Laboratuvar çalışmaları sonucunda elde edilen metan ve gaz üretim değerleri ışığında süpermarket zincirleri için biyogaz tesis kurularak enerji ve atık ısı elde edilebileceği ve bu yolla ekonomik fayda sağlanabileceği yapılan fizibilite çalışması ile belirlenmiştir.

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## LIST OF SYMBOLS/ABBREVIATIONS

<b>Symbol</b>	<b>Explanation</b>	<b>Units</b>
MSW	Municipal Solid Waste	
SW	Solid Waste	
ISWM	Integrated Solid Waste Management	
OECD	Organization for Economic Cooperation and Development	
EU	European Union	
BMP	Biochemical Methane Potential	
TL	Turkish Liras	
TUIK	Statistical Agency of Turkey	
MassDEP	Massachusetts Department of Environmental Protection	
	Engineering, Construction, Consulting and Trading	
MIMKO	Coordination Company	
	The New York City Economic Development Corporation	
EDC	Anaerobic Digestion	
	Hydraulic Retention Time	
AD	Organic Dry Matter	
HRT	Organic Loading Rate	
ODM	Gas Production Rate	
OLR		
GPR		
MC	Moisture Content	(%)
CH <sub>4</sub>	Methane	(%)
CO <sub>2</sub>	Carbon Dioxide	(%)
COD	Chemical Oxygen Demand	(mg/L)
TS	Total Solids	(%)
VS	Volatile Solids	(%)
VFA	Volatile Fatty Acids	(mg/L)
TKN	Total Kjeldahl Nitrogen	(g/kg)

NH <sub>3</sub> -N	Ammonia Nitrogen	(mg/L)
TP	Total Phosphorus	(g/kg)
C	Carbon	(%)
N	Nitrogen	(%)
H	Hydrogen	(%)
C/N	Carbon /Nitrogen	
Na	Sodium	(g/kg)
Ca	Calcium	(g/kg)
Mg	Magnesium	(g/kg)
Pb	Lead	(g/kg)
Cd	Cadmium	(g/kg)
Cr	Chromium	(g/kg)
Cu	Copper	(g/kg)
Ni	Nickel	(g/kg)
Zn	Zinc	(g/kg)

## 1. INTRODUCTION

Solid wastes comprise all the wastes arising from human and animal activities that are normally solid and discarded as useless or unwanted. Integrated solid waste management (ISWM) can be defined as the selection and application of suitable techniques, technologies and management programs to achieve specific waste management goals (Tchobanoglous et al., 1993).

The amount of municipal solid waste (MSW) rises constantly in all over the world due to urbanization, rising living standards and changing patterns of social behaviors (higher consumption). The quantity and quality of municipal solid waste (MSW) is important to determine the management strategy and also, appropriate waste disposal method. Wastes are used to be disposed to the raw disposal area without control in Turkey. Promoting ISWM is the primary focus on the supporting a waste economy by promoting sustainability, waste reduction and recycling.

Each year in the European Union, 1.3 billion tons of wastes are produced and approximately 3.5 tons of these wastes are sourced from each person per year. On the other hand, the Organization for Economic Cooperation and Development (OECD) declared that the amount of waste generated in Europe increased by 10% between 1990 and 1995. Most of these wastes were either incinerated or dumped into landfill sites. In order to decrease the amount of landfilled waste, EU determined and set some targets. The EU Landfill Directive imposes a strict target to reduce the biodegradable part of municipal solid waste that is disposed to landfill. In Europe, 35% reduction in biodegradable part of municipal solid waste was achieved in 2004 (Kazmierczyk, 2004).

Turkey's municipal solid waste generation was 428 kg/person-year for the year of 2008. Currently, average amount of daily solid waste generation is 1.21kg/person-day. According to the data of 2010, there were 86 supermarket chains in Turkey and that number is increasing with more than 10% each year. The amount of waste sourced from supermarkets continuously rises depending on the increase in the number of supermarkets. Supermarket wastes are disposed to municipal landfills and removed in the concept of

municipal solid wastes. So, currently general waste management includes both municipal solid wastes and supermarket wastes in Turkey.

In Turkey, major parts of generated wastes are disposed into landfill sites. Today, Turkey faces serious environmental problems because the amount and change in the composition of municipal solid wastes have increased gradually depending on economical, social and technological developments (Ministry of Environment and Forestry, 2008). With increasing amount of these wastes, solid waste management has become an important concern. According to Solid Waste Statistics of Municipalities, approximately 25 million solid wastes were collected by municipalities in 2006 in Turkey. 59.1% of these wastes were taken to the raw disposal areas, and 37.3% to the sanitary landfills. However, there is not any study related to determine the quantity and composition of supermarket wastes in Turkey.

Moreover, the demand for energy has increased enormously depending on the increase in population and economical growth. The energy demand of Turkey increases rapidly due to the high economic development and population grow rate. Today, Turkey's energy necessity is fundamentally dependent on fossil fuel sources (oil, natural gas and coal). Also, its energy production meets only less than half of its total energy consumption. Therefore, Turkey is an energy importing country. At the same time, the reserve for fossil fuels is steadily dwindling. However, Turkey has a large potential for renewable energy sources which are solar, wind, biomass, hydro and geothermal energy (Temiz and Gokmen, 2010).

Among the different nonconventional energy options, conversion of the organic fraction of solid waste into biogas appears to be the best option for solid waste management. Biogas is currently produced by anaerobic degradation of organic waste, arising from municipal, industrial, and agricultural sources (Gunaselen, 1997; Parawira et al., 2008). Supermarket waste contains high amount of biodegradable materials that can be converted into biogas by microbial activities. Biogas contains a mixture of methane, carbon dioxide and trace amounts of other gases. The produced biogas can be used to generate heat and electricity.

The aim of this study is to evaluate and understand the biogas generation potential of food wastes fraction of supermarkets by anaerobic digestion. For this purpose, food waste contents of a supermarket chain were anaerobically digested under mesophilic condition. Food waste fractions that were chosen in this study were meat (chicken, meat, fish and other products), sugar (fructose/glucose containing materials), fruit, vegetable and flower wastes and dairy product wastes.

Considering the need for both energy and integrated waste management of Turkey, utilization of market wastes as renewable energy sources was the main driven force of this research.

## **2. LITERATURE REVIEW**

The literature review has been divided into three main sections: (1) supermarket waste (2) anaerobic digestion and important operational parameters (3) biogas production and the applications for supermarket waste.

### **2.1. Supermarket Waste**

Market products become a waste after a while depending on the shelf-life and other market activities. Wastes are occurred during the opening process of markets. Therefore, supermarkets discard perishable products such as fresh fruits and vegetables, bread, pastries, milk products, meat, fish and chicken products, seafood and other frozen products with or without packing material and other type of products called non-food wastes such as textiles, paper, cardboard, metals, plastics, electronics, qualified household hazardous wastes and others everyday.

Waste potential and waste management of supermarkets are investigated in the following by considering the literatures.

#### **2.1.1. Supermarket Waste Potential in Turkey**

From the earliest years of the Republic, food sector is one of the fastest growing sectors in Turkey. According to report of 2010, food sector provides employment for 977,000,194 people in general. This sector composes 160 billion TL of the gross domestic product by 17,000,391 recorded companies (Uygur et al., 2011).

According to Retailer's and Shopping Center Association, change in the number of supermarkets between the year of 2004 and 2008 were given in Table 2.1 depending on their types. According to the data of 2010, there are 86 supermarket chains in Turkey. This amount is increasing with more than 10 % each year. With increase in the number of

supermarkets, the waste problems sourced from supermarkets become a serious management problem.

Table 2.1. Change in the number of supermarkets between 2004 and 2008 in Turkey (Anatolia Agency, 2011).

The Size of Market	Year				
	2004	2005	2006	2007	2008
<b>Hypermarket</b>	152	160	164	178	183
<b>Big supermarket</b>	396	454	504	568	623
<b>Supermarket</b>	1082	1258	1567	1712	1902
<b>Small Supermarket</b>	3179	3673	4239	4763	5544
<b>Medium Supermarket</b>	15197	15075	14775	14876	15273
<b>Total</b>	20006	20621	21249	22097	23525

The amount and type of supermarket wastes have increased gradually because of economic and social developments and the increase of supermarket numbers. Also, waste sourced from supermarkets is going to increase depending on the developing supermarkets' chains and numbers. Food waste generation sourced from supermarkets varied between 5- 45 tons/month or 1- 10 tons/week according to the food waste generation data (EPA, 2009). 75% of most supermarket waste (after recycling cardboard, paper and plastics) is comprised of non-recyclable biodegradable materials including discarded food, waxed and wet cardboard, paper, renderings, soil and plants.

According to Turkey Statistical Agency, collected municipal solid wastes were determined as 34 million tons in 2004. These wastes are generally disposed to the landfills without any treatment. There are only 16 landfills in Turkey which has 3225 municipality according to the data of Ministry of Environment and Forestry. And also mentioning that 59.1% of wastes are disposed into raw disposal areas and 37.1% of them are disposed to sanitary landfills (Turkish Court of Accounts, 2007).

### 2.1.2. Supermarket Waste Management

Supermarket wastes are important fractions of MSW because they are collected and discarded with MSW. In Turkey, the common practice of solid waste (SW) management for supermarkets is discarded into landfills without any separation. Because supermarket wastes are not collected separately from MSW, Turkey's general waste composition also consists of high amount of supermarket waste. According to the Report that was done by Ministry of Environment and Forestry in 2006, the distribution of solid waste composition was given in Figure 2.1.

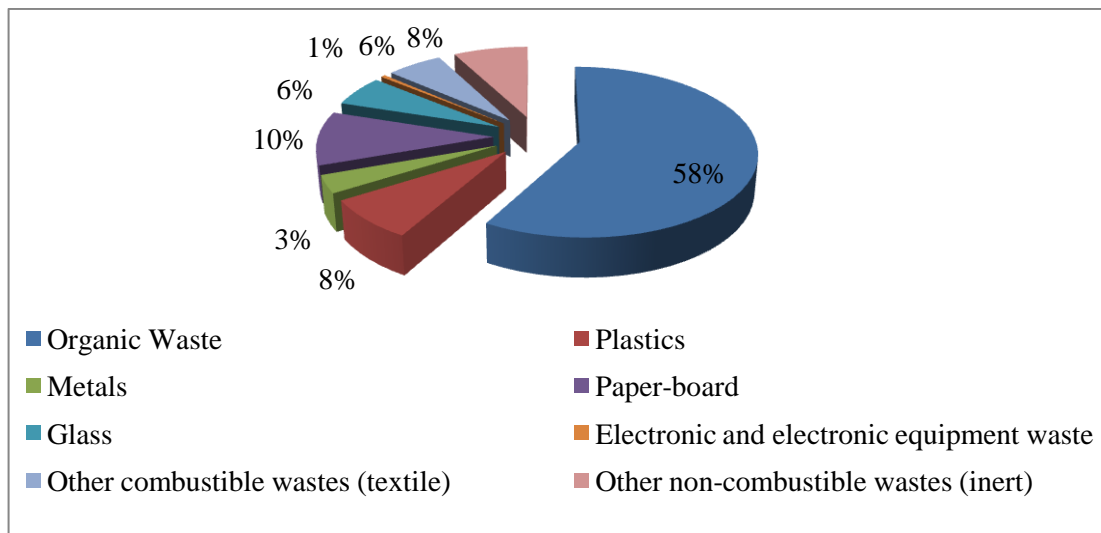


Figure 2.1. Solid waste composition (MIMKO, 2006).

It is reasonable to assume that tipping fees and transportation costs will continue to increase as present landfills become filled. New sites are created at greater distances from population centers (Norrie et al., 1996). Moreover, the concern of these actions is that landfilled wastes involve high amount of valuable materials that can be reused or sold for recycling (Ochoa et al., 2010). So supermarket waste management should be improved and practiced separately. According to the Statistical Agency of Turkey (TUIK), the distribution of applied waste disposal methods in 2004 was given in Figure 2.2.

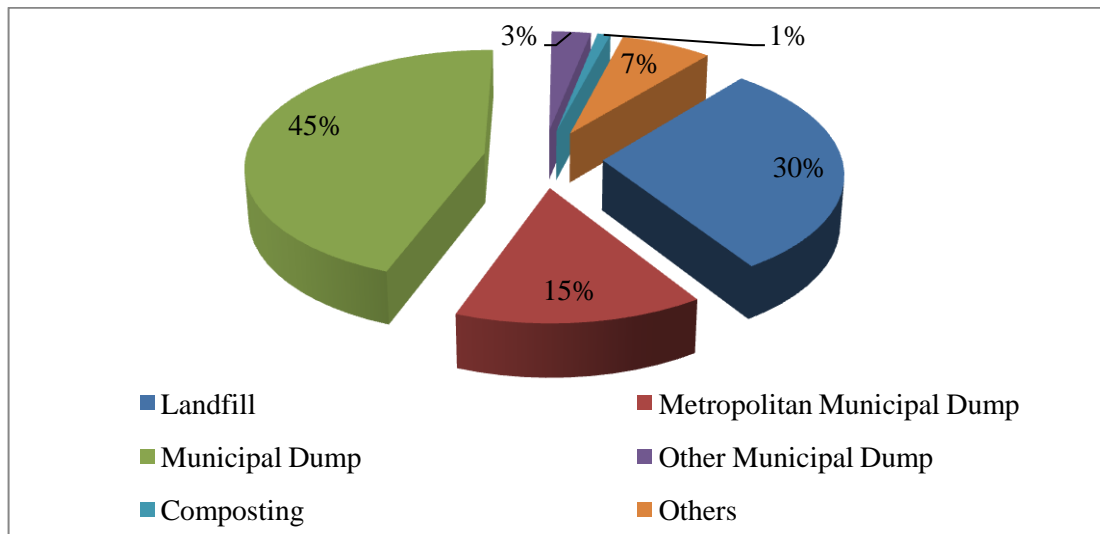


Figure 2.2. The waste disposal methods of Turkey in 2004 (Ministry of Environmental and Forestry, 2008).

According to the European Legislation, biodegradable part of municipal solid waste that is landfilled should be decreased by 50% similarly packaging wastes should be also decreased by 60% for future targets. Currently, recycling of packaging wastes rates in 35-40%, however the reduction of the organic waste in MSW is still a major challenge for municipalities.

Sustainable management of increasing amount of these wastes has become a major social and environmental concern. In order to better manage of waste materials in an environmentally friendly manner and reduce waste disposal costs, supermarket wastes should be characterized depending on the type of discarded materials. In the waste management concept, the waste hierarchy is suggested from Ministry of Environment and Forestry to facilitate determining waste management strategy. Figure 2.3 showed the waste hierarchy. The aim of the waste hierarchy is to extract the maximum practical benefits from products and to generate the minimum amount of waste.

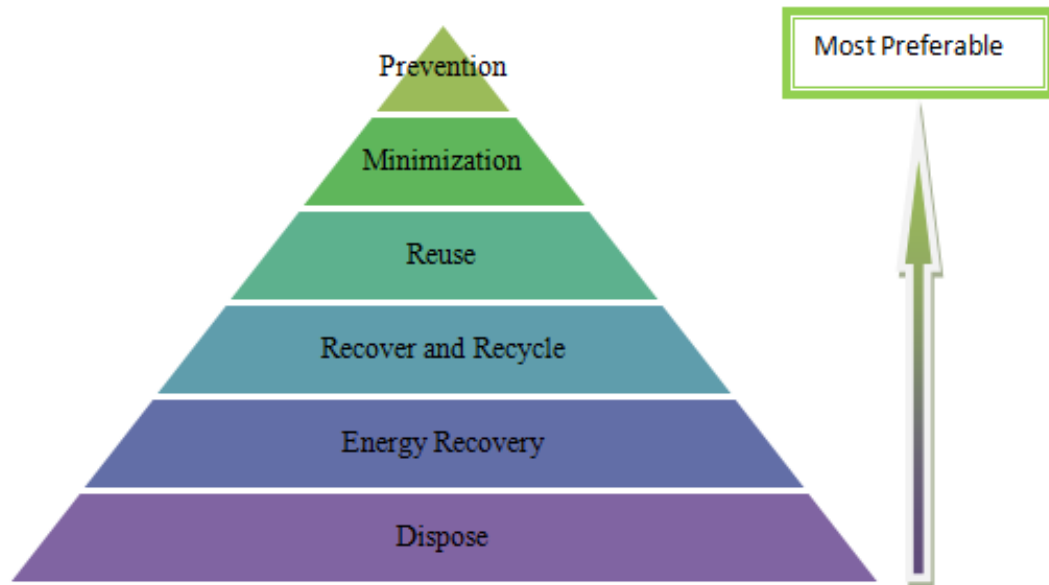


Figure 2.3. The waste hierarchy (EEA, 2012).

### 2.1.3. Supermarket Waste Characterization

There is not any stable supermarket waste characterization in the literature because the quantity and composition of supermarket waste vary depending on the type, size and also the variety of sales products of supermarket. In the view of studies, different supermarket waste characterizations are observed in different type of supermarkets.

Currently, supermarkets generally separate recycling materials such as paper-boards, plastics, glass, PETs. The rest of their wastes are disposed to MSW landfills. Waste composition of supermarkets includes some different properties compared to MSW. This fact is related to the quantitative and qualitative difference of waste materials. The following studies give examples about the market waste properties.

The results of waste characterization studies of Massachusetts Supermarkets in United States of America and Quebec Supermarkets in Canada was given in Table 2.2 and 2.3. Massachusetts Department of Environmental Protection (MassDEP) and Massachusetts Food Association participated for establishing a certification program on recycling of supermarket wastes. This program aims to encourage reuse and recycle of organic and other materials of supermarket wastes in the concept of sustainable programs. For the

certification program, supermarket waste characterization studies were done. In order to join certification program, markets should determine their waste composition. Supermarkets, which participate to the certification program, gain profit and comply with the law about, forbidden the disposal of recyclable wastes in Massachusetts (MassDEP, 2011).

Table 2.2. Waste characterization of Massachusetts Supermarkets (MassDEP, 2011).

<b>Waste Characterization</b>
Solid Waste
Organic Waste
Cardboard
Waxed Cardboard
Office Paper
Bottles and Metals
Fluorescent Lamps
Platforms
Hard plastics (bucket and etc.)
Plastic film
Other Wastes

Norrie et al. (1996) explained in their study that everyday grocery stores discard perishable products such as fruits and vegetables, bread, pastries, milk products, fish, seafood and other frozen products. Discarded packaging materials also represent large volume of waste material. A study was done in the Quebec City area for the characterization of waste materials originating from supermarkets for the assessment of recycling potential. Waste materials that were regularly collected for landfilling on a weekly basis were analyzed on nine separate occasions and included three sampling each from the following stores Heritage, Maxi and Provigo. The proportional analysis of waste materials from these markets was given in Table 2.3. Especially, studies for waste management in Quebec Supermarkets showed that the sizes of supermarkets are not an important parameter affecting supermarket waste composition. No significant changes in the proportional values were observed at the end of the waste characterization study on collected wastes from different-sized supermarkets.

Table 2.3. Waste characterization of Quebec supermarkets  
(Norrie et al., 1996).

Waste Characterization	Supermarket quantity (%)			Average (%)
	Heritage	Maxi	Provigo	
Organic Waste	38.3	48.6	31.1	40.7
Meat	6.1	1,6	3.6	3.6
Paper	3.2	2.9	3.8	3.2
Cardboard	36.1	27.9	37.3	34.0
Plastic	7.8	6.4	8.8	7.2
Glass	0.7	1.3	1.4	1.2
Metal	1,3	2.8	1.3	0.8
Wood	6.0	5.7	8.2	6.4
Others	0.6	3.0	5.0	4.0
<b>Total</b>	100	100	100	100

Cardboard, paper and wood products represented 43% and 74% of waste material, based on weight and volume, respectively while organic matter including fruits, vegetables, baked goods and meat products represented 40 and 10% of waste material based on weight and volume. Plastics, wrapping and bagging materials, represented over 7 and 13% of waste material based on weight and volume, respectively, and other recyclable waste materials such as glass, metal and various miscellaneous objects, represented 4 and 2% of waste material based on weight and volume. Costs associated with supermarket waste disposal may be substantially reduced by source-separation of recyclable and compostable materials. Also, it can reduce pressure on incineration or landfill of wastes. Therefore, the application of recycling and source-separation programs are recommended by determining problems and costs associated with the implementation of such programs (Norrie et al., 1996).

Sri Bala Kameswari et al. (2007) investigated biogas production potential of vegetable market waste and untapped carbon trading opportunities in the concept of energy generation from wastes evaluating Ministry of Renewable Energy Sources in India. He focused on composition and characterization of market waste that would be used in biogas. For this purpose, segregated market wastes were collected from the market complexes

which are the biggest fruit, vegetable and flower markets. Composition and characteristics of market waste was given in Table 2.4.

Table 2.4. Composition and characteristics of market waste  
(Sri Bala Kameswari et al., 2007).

<b>Composition of the Market Waste</b>	<b>(%)</b>
<b>Vegetable wastes</b>	21
<b>Fruit wastes</b>	15
<b>Flower wastes</b>	10
<b>Banana stem and related materials</b>	38
<b>Packaging materials (hay, straw, paper, etc.)</b>	16
<b>Others (plastics, wood, stones, etc.)</b>	1
<b>Characteristics of the Market Waste</b>	<b>(%)</b>
<b>Total solids</b>	25
<b>Volatile solids</b>	73.7
<b>Moisture content</b>	75

Hogan et al. (2004) investigated the supermarket waste characterization in Ireland and the development of an approach to tracking municipal waste composition. Supermarkets represent large section of the retail trade and produce a large fraction of the retail trade waste. The waste of chosen supermarket was analyzed for its composition and weight prior to recycling and disposal for a period of five days. The waste characterization of this market included office paper 4.62%, newspapers/magazines 1.75%, tissue paper 2.88%, paper packaging 0.12%, cardboard packaging 35.75%, plastic film 6.97%, PET 1.77%, other rigid plastic 1.02%, aluminum 0.26%, ferrous metals 0.29%, food waste 38.96%, vegetable oil 1.05%, and returns 4.56%.

The New York City Economic Development Corporation (EDC) contracted with DSM Environmental Services, Inc. (DSM) to assess the feasibility of establishing an organic recovery facility at the Hunts Point Food Distribution Center (Food Center) in the Bronx, New York. The Food Center was located on land owned by the City of New York, and represented parcels leased to over twenty tenants, including the New York City Terminal Market (Produce Market) and the Fulton Fish Market (Fish Market).

Produce Market and Fish Market generated approximately 27,400 tons waste/year (111 tons/day), roughly three-quarters of which was biodegradable. While this material was a valuable feedstock for the recovery operation of organics, the tonnage was at the low end of the range for a facility to be economically feasible. Therefore, DSM determined the quantity and composition of organic wastes generated at the Food Center that could be made available for an organics recovery facility (DSM Environmental Services, Inc., 2005). Table 2.5 provided a summary of the waste estimated to be readily available for an organics recovery facility at the Food Center.

Table 2.5. Daily and annual waste tonnages for organics recovery (DSM Environmental Services, Inc., 2005).

Source of Waste	Daily Tonnage	Annual Tonnage	Percentage (%)
<b>Fish Market</b>	19	4,800	17.5
<b>Produce Market-Common Area</b>	53	13,000	47.5
<b>Produce Market- Dock Waste</b>	39	9,600	35.0
<b>Total</b>	111	27,400	100

More than half (55%) of the material was food waste, and 23% of waste was cardboard. So, 78% of waste was readily degradable, providing valuable feedstock for an organics recovery facility. According to the general waste characterization, degradable materials represent 89% of waste stream. There was also a significant amount of waste wood that would require chipping or shredding before being acceptable to most organics recovery technologies. In addition, there was considerable plastic packaging and other materials that were found throughout the waste stream and would require processing to remove at one or more points in a facility's process.

Therefore, according to the waste characterization studies, supermarket waste compositions consisted of mainly biodegradable organic waste and cardboard packaging wastes. Cardboard packaging wastes could be collected separately at the source and recycled. Biodegradable part of supermarket waste, which covered vegetable/fruit waste, meat (seafood, chicken, meat) waste, milky products and etc., had high biogas production potential.

## 2.2. Anaerobic Digestion of Supermarket Waste

Anaerobic digestion is a biochemical process in which organic matter is degraded to methane through microbiological activities in the absence of oxygen. The process involves four-stages; namely hydrolysis, acidogenesis, acetogenesis and methanogenesis. The process was given in Figure 2.4.

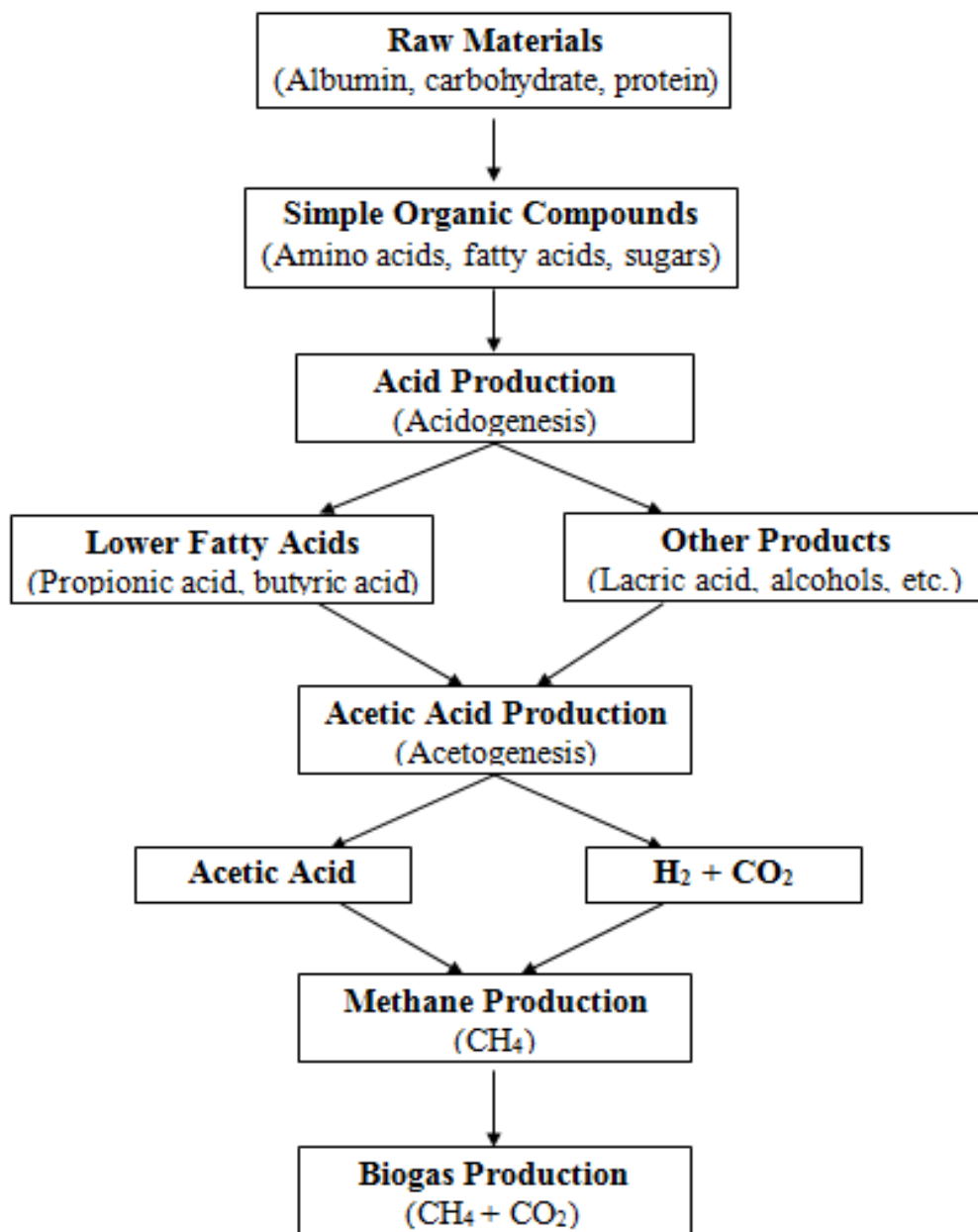


Figure 2.4. Methane production process (German Biomass Research Center, 2010).

Anaerobic biodegradation of organic material proceeds in the absence of oxygen and the presence of anaerobic microorganisms. AD is the consequence of a series of metabolic interactions among various groups of microorganisms. It occurs in three stages, hydrolysis/liquefaction, acidogenesis and methanogenesis.

Fundamentals of anaerobic digestion were used in many researches. In this study, same fundamentals were followed for anaerobic digestion of supermarket wastes. For anaerobic digestion, the two most important parameters in the selection of particular plant feedstock are the economic considerations and the yield of methane for fermentation of that specific feedstock (Smith et al., 1992).

### **2.2.1. Important Parameters in AD Process**

The efficiency of AD is influenced by some critical parameters. Achievement potential of AD is highly dependent on the stability of appropriate conditions. When conditions are changed, microbial activity in the reactor is negatively influenced. The parameters effecting the AD are given in the following section.

2.2.1.1. Temperature. Temperature is an important parameter for microbial system because microorganisms which are processed in reactor show different depending on the change in temperature. Also, it affects the system in several ways including ionization equilibrium, solubility of substrates, substrate removal rate and other constants such as specific growth rate, decay biomass yield, and half saturation constant (Al Seadi et al., 2008). The AD process can take place at different temperatures, divided into three temperature ranges: psychrophilic (below 25<sup>0</sup>C), mesophilic (25<sup>0</sup>C – 45<sup>0</sup>C), and thermophilic (45<sup>0</sup>C – 75<sup>0</sup>C). There is a direct relation between the process temperature and the HRT which was given in Table 2.6.

Table 2.6. Thermal stage and typical retention times (Al Seadi et al., 2008).

<b>Thermal Stage</b>	<b>Process Temperatures</b>	<b>Minimum Retention Time</b>
<b>Psychrophilic</b>	< 20°C	70-80 days
<b>Mesophilic</b>	30-42°C	30-40 days
<b>Thermophilic</b>	43-55°C	15-20 days

The temperature stability is decisive for AD. In practice, the operation temperature is chosen in consideration to the feedstock used. The necessary process temperature is usually provided by floor or wall heating systems, inside the digester.

Operation temperature influences the toxicity of ammonia. Ammonia toxicity increases with increasing temperature and can be relieved by decreasing the process temperature. However, when decreasing the temperature to 50°C or below, the growth rate of the thermophilic microorganisms will drop drastically, and a risk of washout of the microbial population can occur, due to a growth rate lower than the actual HRT (Angelidaki et al., 2004). This means that a well functioning thermophilic digester can be loaded to a higher degree or operated at a lower HRT.

The solubility of various compounds (NH<sub>3</sub>, H<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S and VFA) also depends on the temperature. This can be of great significance for materials which have an inhibiting effect on the process.

It is important to keep a constant temperature during the digestion process, as changes or fluctuations in temperature will affect the biogas production negatively. Thermophilic bacteria are more sensitive to temperature fluctuation of +/-1°C and require longer time to adapt to a new temperature, in order to reach the maximum methane production. Mesophilic bacteria are less sensitive. Temperature fluctuations of +/-3°C can be tolerated, without significant reductions in methane production.

2.2.1.2. pH. The value of pH is a way of measuring acidity/alkalinity of a solution (respectively of substrate mixture, in the case of AD). The value of pH in AD influences the growth of methanogenic microorganisms and affects the dissociation of some compounds of importance for the AD process (ammonia, sulphate, organic acids). Methane formation takes place within a relatively narrow pH interval, from about 5.5 to 8.5, with an optimum interval between 7.0- 8.0 for methanogens. Acidogenic microorganisms usually have lower value of optimum pH (Al Seadi et al., 2008).

The optimum pH interval for mesophilic digestion is between 6.5 and 8.0 and the process is severely inhibited if the pH value decreases below 6.0 or rises above 8.3. The solubility of carbon dioxide in water decreases at increasing temperature (Al Seadi et al., 2008).

The value of pH can be increased by ammonia, produced during degradation of proteins or by the presence of ammonia in the feed stream, while the accumulation of VFA decreases the pH. pH in anaerobic reactors is mainly controlled by the bicarbonate buffer system. Therefore, the pH inside digesters depends on the partial pressure of CO<sub>2</sub> and on the concentration of alkaline and acid components in the liquid phase.

2.2.1.3. Macro and Micronutrients (Trace Elements). Microelements (trace elements) like iron, nickel, cobalt, selenium, molybdenum or tungsten are equally important for the growth and survival of the AD microorganisms as the macronutrients carbon, nitrogen, phosphorus, and sulfur. The optimum ratio of the macronutrients like carbon, nitrogen, phosphorus and sulfur (C:N:P:S) is considered 600:15:5:1. Insufficient provision of nutrients and trace elements, as well as too high digestibility of the substrate can cause inhibition and disturbances in the AD process (Al Seadi et al., 2008).

2.2.1.4. Mixing. The biogas production is highly depending on the digestion of the feedstock by microorganisms. In order to increase the digestion and biogas production, providing contact between the reactor contents and feedstock is taking importance. Mixing allows the complete contact between them. It also reduces the inhibitory effects of local build-up of VFAs and other digestion products. Furthermore, settling could be prevented by mixing not to cause reduction of contact between substrate and microorganism.

2.2.1.5. Alkalinity. Alkalinity is a measure of the buffering or acid-neutralizing capacity of the digester. Since this buffering capacity can be provided by a wide range of substances, total alkalinity is a non-specific measure that is frequently interpreted as a determination of the carbonate, bicarbonate, and hydroxide content of a culture. At pH levels ranging from 6 to 8, the carbon dioxide-bicarbonate system is the major chemical system controlling alkalinity (Chynoweth et al., 1987).

The dissociation of carbonic acid accounts for most of the alkalinity in anaerobic digestion. Bicarbonate alkalinity, pH, and carbon dioxide pressure are interrelated in AD. When the bicarbonate alkalinity falls below 500mg/L, the pH approaches 6.0. Thus, alkalinity destruction results in decreased pH levels (Chynoweth et al., 1987).

2.2.1.6. Toxicity. The presence of toxic compounds influences the activity of anaerobic microorganisms. Toxic compounds can be brought into the AD system together with the feedstock or generated during the process. The application of threshold values for toxic compounds is difficult, on one hand because these kinds of materials are often bound by chemical processes and on the other hand because of the capacity of anaerobic microorganisms to adapt, within some limits, to environmental conditions, herewith to the presence of toxic compounds (Al Seadi et al., 2008).

2.2.1.7. Loading. The construction and operation of a biogas plant is a combination of economical and technical considerations. Obtaining the maximum biogas yield would require a long retention time of the substrate inside the digester and correspondingly large digester size by complete digestion of the substrate. In practice, the choice of system design (digester size and type) or of applicable retention time is always based on a compromise between getting the highest possible biogas yield and having justifiable plant economy (Al Seadi et al., 2008). In this respect, the organic load is an important operational parameter, which indicates how much organic dry matter can be fed into the digester, per volume and time unit, according to the equation below:

$$\text{Organic Load (kg/m}^3\text{/d)} = \frac{\text{Mass (kg/d) x Concentration of organic matter (\%)}}{\text{Digester volume (m}^3\text{)}} \quad (2.1)$$

2.2.1.8. Volatile Fatty Acids (VFA). The stability of the AD process is reflected by the concentration of intermediate products (acetate, propionate, butyrate, and lactate) like VFA. In most cases, AD process instability will lead to the accumulation of VFA inside the digester, which can lead furthermore to a drop of pH value. However, the accumulations of VFA will not always be expressed by a drop of pH value, due to the buffer capacity of the digester, through the biomass types contained in it. VFA concentration could show varieties from digester to digester, therefore, it is not recommended as a stand-alone process monitoring parameter (Al Seadi et al., 2008).

2.2.1.9. Ammonia. Ammonia (NH<sub>3</sub>) is an important compound for the AD process. NH<sub>3</sub> is an important nutrient serving as a precursor to foodstuffs and fertilizers and also, is normally encountered as a gas. Proteins are the main source of ammonia in AD.

Very high ammonia concentration inside the digester, especially free ammonia (the unionized form of ammonia), is considered to be responsible for process inhibition. This is common to AD of animal slurries, due to their high ammonia concentration, originating from urine. For its inhibitory effect, ammonia concentration should be kept below 80mg/L. Methanogenic bacteria are especially sensitive to ammonia inhibition. The concentration of free ammonia is direct proportional to temperature, so there is an increased risk of

ammonia inhibition of AD processes operated at thermophilic temperatures, compared to mesophilic ones (Al Seadi et al., 2008).

Moreover, the equilibrium between ammonia and ammonium shifts to the right as it is illustrated with the chemical reaction below in the reactors having high concentrations of ammonium at high pH ranges. As a result of this reaction free ammonia ( $\text{NH}_3$ ), which has toxic effects on the growth and mechanism of the microorganisms responsible for the biogas production, is generated.



For higher pH values, even a relatively low nitrogen concentration may inhibit the process of fermentation. Noticeable inhibition occurs at nitrogen concentration of roughly 1,700 mg/L ammonium-nitrogen ( $\text{NH}_4\text{-N}$ ) in substrate. Nonetheless, given enough time, the methanogens are capable of adapting to  $\text{NH}_4\text{-N}$  concentrations in the range of 5,000-7,000 mg/L substrate, the main prerequisite being that the ammonia level ( $\text{NH}_3$ ) does not exceed 200-300 mg  $\text{NH}_3\text{-N/L}$  substrate. The rate of ammonia dissociation in water depends on the process temperature and pH value of the substrate slurry.

### **2.3. Evaluation of Substrates for Biogas Production**

Biogas is the gaseous product of the anaerobic digestion of organic matter. Biogas consists mainly of methane and carbon dioxide, but also contains several impurities. It is typically made up of 55-70% methane ( $\text{CH}_4$ ), 30-45% carbon dioxide ( $\text{CO}_2$ ), and traces of other gases such as hydrogen, hydrogen sulfide, carbon monoxide, and nitrogen (Deublein and Steinhauser, 2008). Also, it has specific properties which were listed in Table 2.7.

Table 2.7. General features of biogas (Deublein and Steinhauser, 2008).

<b>Energy content</b>	6.0-6.5 kWh/m <sup>3</sup>
<b>Fuel equivalent</b>	0.60-0.65 L oil/m <sup>3</sup> biogas
<b>Explosion limits</b>	6-12% biogas in air
<b>Ignition temperature</b>	650-750°C
<b>Critical pressure</b>	75-89 bar
<b>Critical temperature</b>	-82.5°C
<b>Normal density</b>	1.2 kg/m <sup>3</sup>
<b>Smell</b>	Bad eggs (the smell of desulphurized biogas is hardly noticeable)
<b>Molar Mass</b>	16,043kg/kmol

The practically attainable methane yield depends on many factors like composition, grain size, and proportions of the assigned substrates, and the microbial degradability of the biomass, the content of dry matter and organic dry matter (ODM), and finally the relationship of the nutrients to each other. Also, the parameters of the technology of fermentation are of importance such as the number of stages, the temperature, the residence time of the substrate in the reactor, the kind and frequency of the mixing of the substrate, and the quantity and frequency of the substrate addition.

The gas components are specific to the plant and substrate and should be checked regularly on a long-term basis. Typical components and impurities in biogas were given in Table 2.8.

Table 2.8. Typical components and impurities in biogas (Deublein and Steinhauser, 2008).

Component	Content	Effect
<b>CO<sub>2</sub></b>	25-50% by volume	<ul style="list-style-type: none"> <li>– Lowers the calorific value</li> <li>– Increases the methane number and the anti-knock properties of engines</li> <li>– Causes corrosion if the gas is wet</li> </ul>
<b>H<sub>2</sub>S</b>	0-0.05% by volume	<ul style="list-style-type: none"> <li>– Corrosive effect in equipment and piping systems</li> <li>– SO<sub>2</sub> emissions after burners or H<sub>2</sub>S emissions with imperfect combustion – upper limit 0.1 by vol.%</li> <li>– Spoils catalysts</li> </ul>
<b>NH<sub>3</sub></b>	0-0.05% by volume	<ul style="list-style-type: none"> <li>– NO<sub>x</sub> emissions after burners damage fuel cells</li> <li>– Increases the anti - knock properties of engines</li> </ul>
<b>Water vapor</b>	1-5% by volume	<ul style="list-style-type: none"> <li>– Causes corrosion of equipment and piping systems</li> <li>– Condensates damage instruments and plants</li> <li>– Risk of freezing of piping systems and nozzles</li> </ul>
<b>Dust</b>	>5 μm	<ul style="list-style-type: none"> <li>– Blocks nozzles and fuel cells</li> </ul>
<b>N<sub>2</sub></b>	0-5% by volume	<ul style="list-style-type: none"> <li>– Lowers the calorific value</li> <li>– Increases the anti - knock properties of engines</li> </ul>
<b>Siloxanes</b>	0-50 mg/m <sup>3</sup>	<ul style="list-style-type: none"> <li>- Act like an abrasive and damages engines</li> </ul>

These parameters must be analyzed in a laboratory test and in a pilot plant as well before the construction of a production plant. A test can be in principle continuous or batch wise. First, the biomass samples must be homogenized, cut up, and diluted. Then, they are loaded into the laboratory reactor. After that, temperature and the value of pH are adjusted. For the tests in the laboratory or in the pilot plant, the following measurements are recommended. The appropriate measuring devices can be fixed to the reactor or installed separately (Deublein and Steinhauser, 2008).

- Temperature
- pH value and redox potential
- Dry matter and water content

- Content of organic dry matter (ignition loss)
- Degradability as total content of organic acids/acetic acid equivalent and inhibitors
- Salt content
- Total content of nitrogen (N), phosphorus (P), potassium(K), magnesium (Mg), sulfur (S), pH-decreasing components
- Availability of plant nutrients such as nitrate nitrogen ( $\text{NO}_3$ ), ammonium nitrogen ( $\text{NH}_4$ ), phosphate ( $\text{P}_2\text{O}_5$ ), potassium oxide ( $\text{K}_2\text{O}$ ), and magnesium (Mg)
- Granulation (maximum grain size), gross density
- Heavy metals like lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), mercury (Hg)
- Content of short - chain fatty acids, principally acetic acid, propionic acid, butyric acid, and *iso*- butyric acid
- C/N ratio

The measurements give information on the biogas yield, the expected nutrients, the extent of decomposition of the biomass which can be provided during the fermentation, the fertilization value of the residue, and also the preferable type, dimensions, and the operation mode of the production plant.

Potential feedstocks that are used for biogas production were given with an example schema in Figure 2.5.

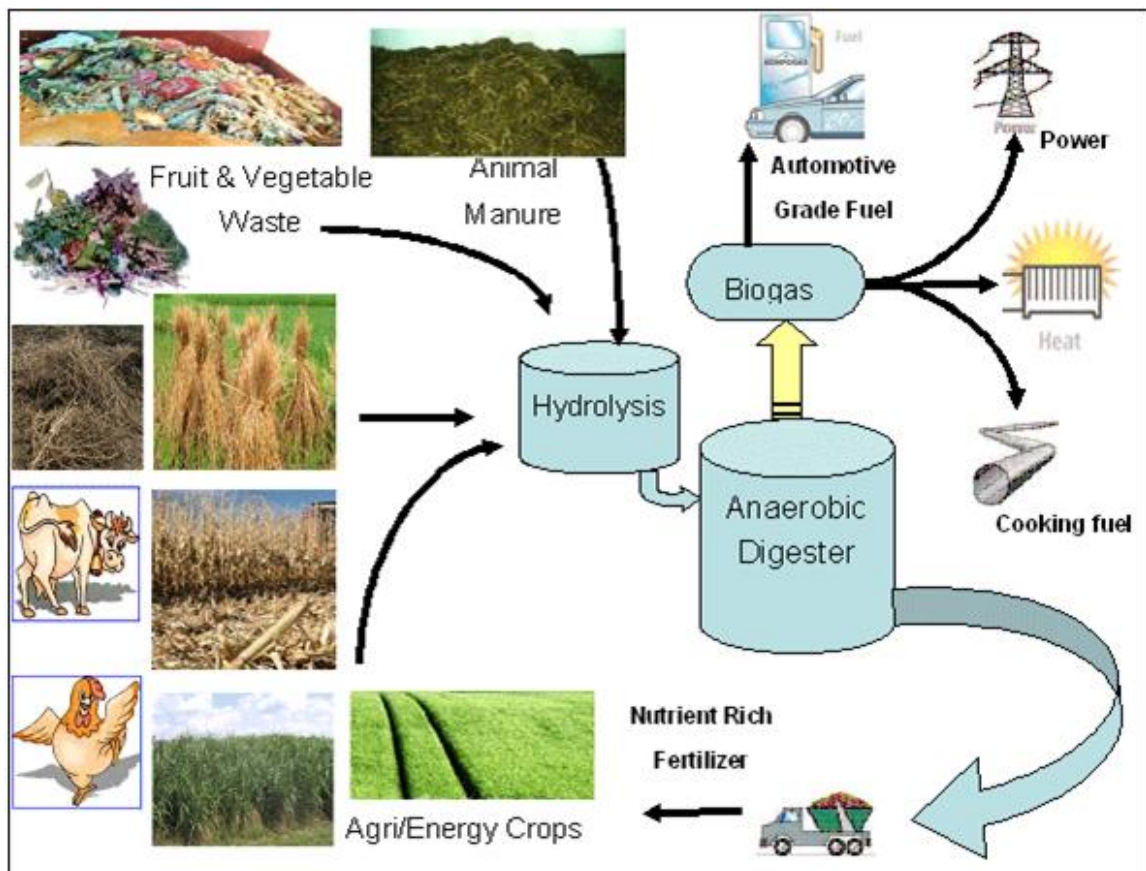


Figure 2.5. Biowaste sources (Tespl, 2010).

Demirel and Scherer (2009) studied that the sugar beet silage was used as the mono-substrate in bio-methanization of energy crops through mono-digestion for continuous production of renewable biogas study. The sugar beet silage had a low pH of around 3.3–3.4, without the addition of manure. The mesophilic biogas digester was operated in a hydraulic retention time (HRT) range between 15 and 9.5 days. The highest specific gas production rate (spec. GPR) and CH<sub>4</sub> content were 0.67 L/gVS/d and 74%, respectively, obtained at an HRT of 9.5 days. The digester worked within the neutral pH range as well. Since this substrate lacked the availability of macro and micro nutrients, and the buffering capacity as well, external supplementation was definitely required to provide a stable and efficient operation, as provided using NH<sub>4</sub>Cl and KHCO<sub>3</sub> in this case (Demirel and Scherer, 2009).

Qiao et al. (2011) stated that raw materials of fruit/vegetable and food waste show higher methane production than that of cow manure, pig manure, and municipal sewage sludge in the study. After hydrothermal pretreatment at typical condition (170°C at 1 h),

the biogas production of pig manure, cow manure, fruit/vegetable waste, and municipal sewage sludge increased by 7.8%, 13.3%, 18.5%, and 67.8% respectively. Biogas decreases generally by 3.4% after the treatment of food wastes. The methane yield of pig manure, fruit/vegetable waste and municipal sewage sludge increased respectively as 14.6%, 16.1% and 65.8%. After the treatment of cow manure and food waste, the methane decreased by 6.9% and 7.5%. The general characteristics of the study were given in Table 2.9 (Qiao et al., 2011). As tested in this study, for per gram VS of raw biomass waste, the order of biogas production potential were as follows: food waste > fruit/vegetable waste > sludge.

Table 2.9. The general characteristics of raw and treated biomass (Qiao et al., 2011).

<b>Substrate</b>	<b>pH</b>	<b>TS (%)</b>	<b>VS (%)</b>	<b>TN (g/L)</b>	<b>TP (g/L)</b>	<b>COD (g/L)</b>	<b>Biogas (mL/gVS)</b>
<b>Sludge</b>	7.15	14.58	10.63	-	-	-	202
<b>Treated Sludge</b>	6.47	-	-	1.74	0.219	30	339
<b>Fruit/Vegetable Waste</b>	4.06	9.15	7.72	1.69	0.307	-	443
<b>Treated Fruit/Vegetable Waste</b>	4.17	-	-	1.77	0.249	48.6	525
<b>Food Waste</b>	4.41	19.71	17.04	1.48	0.783	-	781
<b>Treated Food Waste</b>	4.30	-	-	3.08	0.537	134	754

Another study was carried out by El-Mashad and Zhang (2010). They studied biogas production from co-digestion of dairy manure and food waste. All the tests were carried out in duplicate using 1L anaerobic reactors at mesophilic temperature ( $35\pm 1^\circ\text{C}$ ) for 30 days. In each digestion test, 100mL of inoculums (seed bacterial culture) was mixed with the substrate (manure, food waste or mixture) in the reactors; tap water was added to fill the liquid volumes up to effective volumes of 500mL. Methane yield and average methane

content of the biogas produced from food waste after 20 and 30 days was given in Table 2.10.

Table 2.10. Methane yield and average methane content from food waste (El-Mashad and Zhang, 2010).

Parameter	Food waste		32% food waste + 68% manure		48% food waste + 52% manure	
	20 days	30 days	20 days	30 days	20 days	30 days
<b>Biogas Yield (L/kg VS)</b>	520	657	411	455	504	531
<b>Methane Yield (L/kg VS)</b>	256	353	251	282	293	311
<b>CH<sub>4</sub> content of biogas (%)</b>	49	54	61	62	58	59
<b>pH</b>	ND	7.1	ND	7.2	ND	7.2

ND: Not determined

Moreover, one of the studies was done to determine biogas production potential of market waste called Application of biogas technology as a renewable energy source and environmental friendly technique to manage solid waste. The objectives of the study were to (1) analyze the chemical composition of market garbage and paddy straw, (2) find the composition of market garbage and (3) assess the gas production pattern in biomethanation of market garbage and paddy straw. A Sri Lankan batch type digester was used with a volume of 5m<sup>3</sup> and total weight of the market garbage filled in to the digester was 3580 kg. Therefore, total gas production from market garbage was 164.20m<sup>3</sup> during the 228 days and average biogas volume per day was around 0.72m<sup>3</sup> in digester (Bandara et al., 2003).

According to the studies that investigate the biogas production potential of wastes, alternative feedstock and their biogas production potential were given in Table 2.11.

Table 2.11. Alternate feedstock and their potential for biogas production.

Feedstock	Reactor Size	Temperature/ Retention Time/ TS content	Biogas Production	Methane fraction	Reference
<b>Raw fruit &amp; vegetable waste (shredded)</b>	18L	Mesophilic	0.83-2.34L/L/d	54-65%	Bouallagui et al., 2005
		Thermophilic	1.7-3.17L/L/d	58-62%	
<b>Fruit &amp; vegetable waste</b>	10L	5% TS HRT=47days	0.16L/kg TS	-	Bouallagui et al., 2005
<b>Bananas (fruit &amp; stem) Potatoes (peelings rejects) Oats</b>	20L	Mesophilic	497L/kg TS	53%	Stewart et al., 1984
			350-410L/kg TS	44-50%	
			227-257L/kg TS	51-54%	
<b>Biscuit and chocolate</b>	180L	10% TS HRT = 40 days	466L/kg waste added	57%	Ranade et al., 1989
<b>Meat and bone meal</b>	1175mL	5% TS	482mL CH <sub>4</sub> /g removed VS	-	Wu et al., 2009

### 3. MATERIALS AND METHODS

#### 3.1. Design of Simulated Batch Reactor

In this study, bench-scale digesters were used in laboratory. 1L borosilicate glass bottles were used as batch reactors. They were placed in hot room at an average temperature with 35-37<sup>0</sup>C to satisfy mesophilic conditions. The temperature was kept constant by an automatic heat controller. Each glass bottle was sealed to prevent leak. Gas outlets of each reactor were connected to the glass tubes. Glass tubes were connected to two measuring cylinders. One of the cylinders was plastic and the other one was glass. Daily gas production was measured by using the water displacement method of these cylinders. The detailed experimental setup was determined and drawn in Figure 3.1 depending on this study.

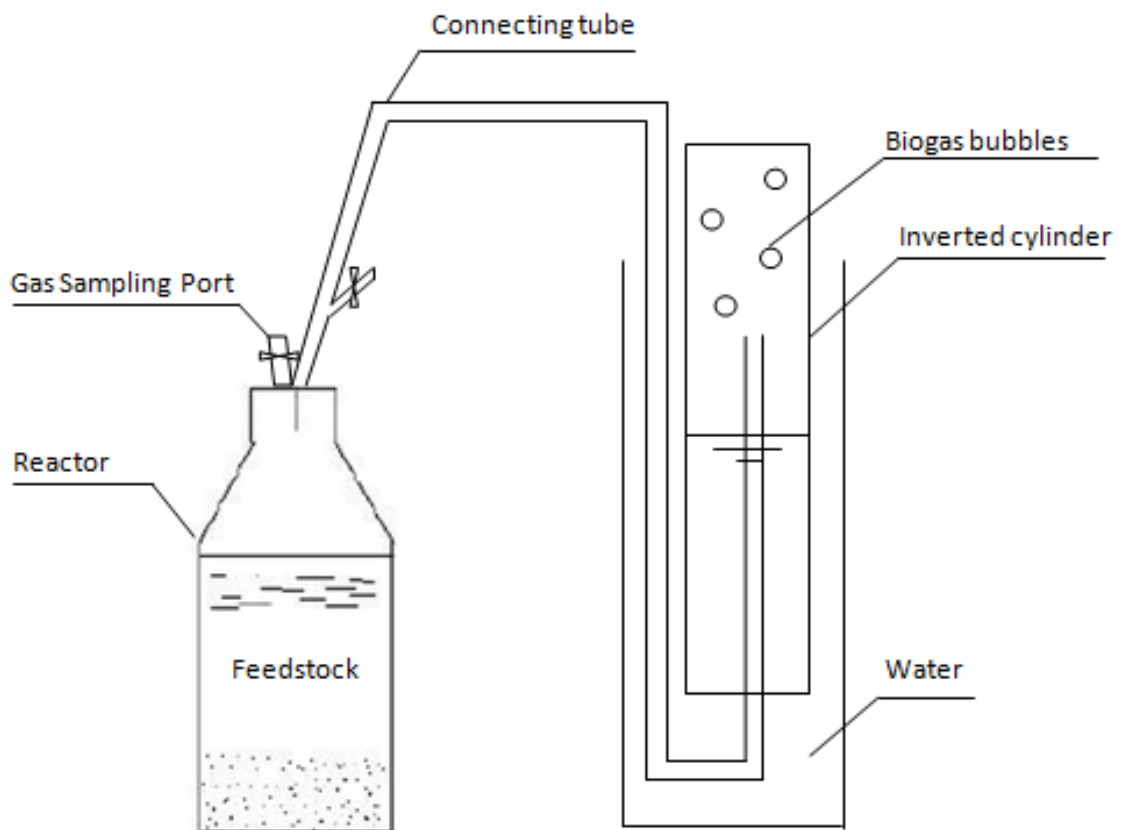


Figure 3.1. Configuration of the gas measuring system.

### 3.1.1. Reactor Loading

In this study, biogas production potential of different type of supermarket wastes was observed. In order to determine their biogas generation potential, organic wastes were chosen. Selected wastes were fruit, vegetable and flower waste (FVFW), meat waste (MW), sugar waste (SW) and dairy product waste (DPW). Wastes were studied in batch system separately to observe biogas production potential. Moreover, mixed supermarket waste (FVFW, MW, SW and DPW) were fed in batch reactors to determine biogas production potential together.

Wastes were taken from Waste Storage Facility of one of the leading supermarket chain waste storage area. They were shredded to provide homogeneous environment and enhance the digestibility of wastes in reactors. Composition of supermarket waste could include different type of waste categories due to supermarket's various products. In this study, used fractions were as follows;

- *Fruit, Vegetable and Flower Waste (FVFW)*: Fruits, vegetables and flowers that were discarded as a waste from supermarkets were collected from the storage area. They were shredded and mixed equally before feeding to the reactor.
- *Meat Waste (MW)*: It included fish, chicken and meat wastes that were both packaged and delicatessen products. They were shredded before feeding the reactor.
- *Dairy Product Waste (DPW)*: It was consist of waste from dairy products such as yogurt, cheese, milk and milk puddings and other dairy products.
- *Sugar Waste (SW)*: It included sugary products such as chocolate, chocolate wafers, candy and sugars.
- *Mixed Waste (Mix.W)*: It was consist of the equal mixtures of FVFW, DPW, MW and SW with sludge.

Anaerobic digestion experiments were conducted in two sets using laboratory-scale batch reactors. The experimental protocol was given in Table 3.1. All experiments were

performed according to the procedures given in Standard Methods. All batch reactors were operated in parallel to each other for quality assurance purposes.

Table 3.1. Experimental protocol.

Reactors	Substrates	TS Content (%)
<b>Set- 1</b>		
<b>R1-R2</b>	Fruit, vegetable and flower waste + Sludge	5 %
<b>R3-R4</b>	Dairy product waste + Sludge	
<b>R5-R6</b>	Mixed waste + Sludge	
<b>R7</b>	Control (Sludge)	
<b>Set- 2</b>		
<b>R1-R2</b>	Sugar Waste + Sludge	5 %
<b>R3-R4</b>	Meat Waste + Sludge	
<b>R5-R6</b>	Mixed Waste + Sludge	8 %
<b>R8-R9</b>	Mixed Waste + Sludge	10 %
<b>R7</b>	Control (Sludge)	5 %

In the first set, seven reactors were used for feedstock that are fruit, vegetable and flower waste (FVFW), dairy product waste (DPW) and mixed waste (Mix.W) and one was used for sludge control at 5% Total Solids (TS) content. Moreover, nine reactors were used for sugar waste (SW), meat waste (MW), mixed waste and sludge. Reactors loaded with SW and MW were operated with 5% TS ratios to determine their individual biogas production. Mixed wastes were also operated with 8% and 10% TS ratios in order to determine the maximum biogas production depending on the TS contents. Those feedstock were mixed and digested in anaerobic batch reactors under mesophilic conditions at 35-37°C. Batch reactors were loaded with supermarket wastes mixed with seed sludge to commence and enhance the rate of anaerobic degradation with methane production. The substrate to inoculum ratio (S/I) was 9/1.

### 3.1.2. Analytical Techniques

Before feeding into the reactors, the substrate and sludge were analyzed to determine their properties. The analytical protocol of the proposed study was given in Table 3.2.

Table 3.2. Analytical protocol.

<b>Parameter</b>	<b>Method</b>	<b>Instruments</b>
<b>pH</b>	Online pH meter	pH meter
<b>Alkalinity</b>	2320 B Method Titration (APHA,AWWA-WEF-1998)	-
<b>ORP</b>	Online pH meter	pH meter
<b>COD</b>	5220C Closed Reflux Titrimetric Method	Spectrophotometer
<b>VFA</b>	5560C Distillation Method	-
<b>Total solids (TS), Volatile solids (VS)</b>	2540 Method (APHA, AWWA, WEF, 1998)	-
<b>Total kjeldahl nitrogen (TKN)</b>	4500 Method (APHA, AWWA, WEF, 1998)	HACH Digester
<b>Ammonia-nitrogen (NH<sub>3</sub>-N)</b>	Nessler Method	Spectrophotometer
<b>C/N</b>	-	Costech Elemental Analyzer (ECS 4010 CHNSO Analyzer)
<b>Total phosphorus (TP)</b>	8190 Method – PhosVer 3 with Acid Persulfate Digestion	HACH Digester
<b>Calcium (Ca), magnesium (Mg), sodium (Na)</b>	Direct Aspiration and Extracted Metals (ASTM Standards,1986)	Atomic absorption spectroscopy
<b>Heavy Metals</b>	Direct Aspiration and Extracted Metals (ASTM Standards,1986)	Atomic absorption spectroscopy
<b>Gas production</b>	Water displacement method with cylinders	Water displacement method with cylinders
<b>Gas composition (CH<sub>4</sub>, CO<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>)</b>	Gas Chromatograph	Gas Chromatograph HP 6850

The pH and ORP were measured online by a pH meter. Procedure of alkalinity was done by sulfuric acid titration of sample observing pH 4.5 and 8.3, respectively.

A well-mixed sample was evaporated in a weighted dish and dried to constant weight in an oven at 103<sup>0</sup>C for TS concentration. Also, a well-mixed sample was filtered through a Standard glass fiber filter and the residue retained on the filter was dried to a constant weight at 103<sup>0</sup>C for TSS concentration. The residue from TS and TSS procedure was ignited to constant weight at 550<sup>0</sup>C. The remaining solids represented the fixed total or suspended solids while the weight lost on ignition was the volatile solids.

For COD analysis, volumetric measurements of sample and reagents were made. Standard potassium dichromate digestion solution and ferroin indicator solution were added after 2mL sample was filled in borosilicate culture tubes. Then sulfuric acid reagent was added into each tube. Tubes were tightly cap and each one inverted several times to mix completely. Then, tubes were placed in block digester preheated to 150<sup>0</sup>C and reflux for 2 hours. When they cooled to room temperature, they were read in spectrometer at 600nm.

Solid samples were digested in digester at 440<sup>0</sup>C with concentrated sulfuric acid. Peroxide was added onto sample when observing formation of steam. After digestion procedure, TKN indicator, potassium hydroxide, mineral stabilizer, polyvinyl alcohol and finally deionized water were added. Mixing is necessary after each indicator addition. Then every sample was read in spectrometer at 460nm.

TP was read by using PhosVer 3 with Acid Persulfate Digestion in spectrometer. Results were recorded as mg/L PO<sub>4</sub><sup>-3</sup>.

Distillation method was used to determine VFA concentrations. Centrifuged samples combined with supernatant liquors. Then, flask was connecting to a condenser and distillation was started. After distillation, 0.1N NaOH was used for titration using phenolphthalein indicator and a pH meter until to the stable end point. Then VFA concentration was calculated depending on the titrated NaOH and sample concentration.

Calcium (Ca), magnesium (Mg), sodium (Na), potassium (P) and heavy metals were measured by direct aspiration and extracted metals in Atomic Absorption Spectroscopy. In order to determine the concentrations, every sample was diluted in different proportions.

Gas production was measured due to the rise of cylinder through water displacement for each reactor. The amount of increase in cylinder was recorded and then accumulated gas was released by reset the system. Also, the composition of the produced biogas was analyzed by Gas Chromatograph (GC) HP Agilent 6850 (Carboxen 1010 plot column 30m x 0.53mm) using thermal conductivity detector (TCD). The instrument calculated the composition of each gas in terms of percentage by plotting the areas under the peaks to the calibration curves. Air tight syringe (2.5mL) was used to collect the sample accumulated in the headspace and only 0.5mL was given to the instrument according to the calibration method.

### **3.1.3. Experimental Studies**

Substrates and sludge were analyzed for pH, total solids (TS, %), volatile solids (VS, %), alkalinity, COD, C/N, TKN, TP, ammonia, elemental analysis with carbon, nitrogen, sodium, calcium and manganese and also heavy metals. According to results of analysis, determined TS values were fixed for each reactor.

Set 1 was prepared and started to run in mentioned conditions which were adjusted pH at 7.0-7.2. However, a decrease in pH was observed during the first week of digestion due to high volatile fatty acids formation. Because of the decrease in pH, methane production could not observe during the digestion period. Eventually, first set was cancelled and repeated. Demirel and Scherer (2009) reported that if substrate is poor in terms of nutrients availability and the buffering capacity, ammonium chloride ( $\text{NH}_4\text{Cl}$ ) and potassium hydrogen carbonate ( $\text{KHCO}_3$ ) are both regularly used, in order to provide ammonium ( $\text{NH}_4^+$ ) and adequate buffering capacity by keeping the pH of the digester stable and maintaining sufficient concentrations of  $\text{NH}_4^+$  in the digester (Demirel and Scherer, 2009). Also, it was reported that pH could be adjusted to optimum pH range for methane production using  $\text{NaHCO}_3$  solution (Rao and Singh, 2003). Hence, Set 1 was re-established after the pH adjusted with  $\text{KHCO}_3$  solution.

During the digestion period, reactors were mixed each day prior to gas measurement to maintain intimate contact between the microorganisms and the substrate. Daily gas production was recorded and gas composition was measured once a week during the digestion period. The picture of the reactor system was given in Figure 3.2.



Figure 3.2. The reactor system.

After the end of the digestion period, pH, TS, VS, alkalinity, COD, C/N, TKN, TP, ammonia, elemental analysis with carbon, nitrogen, sodium, calcium and manganese and also heavy metals were measured for each reactor.

#### 4. RESULTS AND DISCUSSION

Parameters such as VS, pH, ORP, alkalinity, TKN, ammonia and TP were monitored before and after digestion process because of their importance for anaerobic digestion. Except those parameters, COD, TS, elemental and heavy metal analysis were conducted to determine the characteristics of feedstock. Moreover, VFA analysis was also conducted to determine the impacts of acid accumulation on gas production.

The initial characteristics of food fractions and seed sludge used in the study were given in Table 4.1.

Table 4.1. Initial characteristics of food fractions and seed sludge.

Parameters	FVFW	DPW	SW	MW	Sludge
<b>TS (%)</b>	31.58	42.25	35.2	41.0	7.2
<b>VS (% of TS)</b>	85.0	63.1	93.38	48.61	57.4
<b>Carbon (%)</b>	47.02	78.92	39.06	63.71	41.16
<b>Nitrogen (%)</b>	2.46	3.86	1.5	7.5	2.31
<b>Hydrogen (%)</b>	5.37	9.13	8.6	7.34	4.44
<b>C/N</b>	19.11	20.45	26.04	8.49	17.82

In order to assess the performance of an anaerobic digester, it is important to analyze the characteristics of wastes. The C/N ratio is the indicator of the nutrient balance in the waste matrix showing available carbon and nitrogen for the microbial activity. Table 4.2 gave the results of elemental and heavy metal analysis only for substrates that were prepared in laboratory after obtaining from supermarket waste storage area. Results of elemental and heavy metal analysis were given in Table 4.2.

Table 4.2. Initial elemental and heavy metal concentrations.

<b>Unit</b>	<b>Metals (g/kg)</b>								
<b>Substrates</b>	<b>Na</b>	<b>Ca</b>	<b>Mg</b>	<b>Cd</b>	<b>Ni</b>	<b>Zn</b>	<b>Cr</b>	<b>Pb</b>	<b>Cu</b>
<b>FVFW</b>	0.05	12.35	0.97	n.d.	n.d.	0.03	n.d.	n.d.	0.01
<b>DPW</b>	15.0	22.50	1.23	n.d.	n.d.	0.04	n.d.	n.d.	0.01
<b>MW</b>	9.58	5.75	0.78	n.d.	n.d.	0.04	n.d.	n.d.	0.01
<b>SW</b>	4.15	0.24	2.5	n.d.	n.d.	0.02	n.d.	n.d.	n.d.
<b>Mixed W.</b>	5.64	9.21	1.31	n.d.	n.d.	0.09	n.d.	n.d.	0.01
<b>Sludge</b>	0.4	2.50	0.08	0.01	0.02	0.03	0.02	n.d.	n.d.

\*n.d.: not determined

Calcium, sodium and magnesium are required for microbial activity and specific growth rate. While moderate concentrations stimulate microbial growth, excessive amounts slow down the growth. Also higher concentrations can cause inhibition. Heavy metal concentrations of reactors were low except zinc concentrations, so lower concentrations could be negligible. Zinc is an essential mineral that is naturally present in some foods, added to others, and available as a dietary supplement. Daily level of intake sufficient nutrient is nearly 97–98% for healthy individuals. Therefore, zinc concentrations were normal for the process related to the food.

Materials with different C/N ratios differ widely in their yield of biogas. The optimum C/N ratio is between 20 and 30 for anaerobic digesters (Dennis and Burke, 2001). A high C/N ratio is an indication of rapid consumption of nitrogen by methanogens and results in lower gas production. On the other hand, a lower C/N ratio causes ammonia accumulation and pH values exceeding 8.5, which is toxic to methanogenic bacteria. C/N ratios of reactors were under the range that could inhibit the system according to the results of analysis (Table 4.2).

Type of supermarket wastes were operated with 5% TS ratio in batch reactors for determining biogas production potential. Mixed Wastes were also operated with 8% and 10% TS ratios in Set-2 after high methane production was observed with 5% TS ratio of Mixed Wastes in Set-1. In the following chapters laboratory analysis for Set-1 and Set-2 were explained separately.

## 4.1. Results of Set-1

### 4.1.1. Substrate Analysis for Set-1

In the first set, substrates such as FVFW, DPW and Mixed Waste were loaded to the reactors with an adjusted TS content of 5%. Also, control reactor was carried out with the same TS ratio. The COD concentrations of the solutions were measured before loading to the reactors. The COD concentrations showed difference depending on the type of substrates. The COD concentrations of FVFW, DPW, Mixed Wastes and sludge were recorded as approximately 18,000 mg/L, 13,000 mg/L, 27,000 mg/L and 2,484 mg/L. Also, the results of the initial analysis for each reactor were given in Table 4.3. Analyses were conducted both before and after digestion in order to observe the changes in the reactors.

Table 4.3. Loading analysis of reactors.

Reactors	Substrates	TS (%)	VS (% of TS)	
		Before Digestion	Before Digestion	After Digestion
<b>Set – 1</b>				
<b>R1</b>	FVFW+Sludge	5	85.0	44.7
<b>R2</b>	FVFW+Sludge			40.2
<b>R3</b>	DPW+Sludge	5	63.1	37.5
<b>R4</b>	DPW+Sludge			32.5
<b>R5</b>	Mixed Waste+Sludge	5	72.3	37.5
<b>R6</b>	Mixed Waste+Sludge			39.2
<b>R7</b>	Sludge	5	57.4	31.0

Given TS contents represented the solid contents placed into the reactor before digestion. VS contents of the reactors decreased through to the end of the experiment. The VS removal showed variability in substrates. After digestion, nearly 45% VS degradation was achieved for reactors in Set-1. Highest VS removal was performed in R2 with 52.7% VS conversion rate. R5 and R6 were also showed sustainable VS degradation during the digestion.

Substrates used in the study had low pH values. Since, low pH values are not suitable for the anaerobic digestion process; pH of reactors should be neutralized by buffer solutions ( $\text{KHCO}_3$ ). Laboratory studies showed that drastic decrease in pH was recorded during the anaerobic digestion process. The pH remained at low values because of the excessive production of volatile fatty acids and their accumulation. Since substrates were poor in terms of buffering capacity, potassium hydrogen carbonate ( $\text{KHCO}_3$ ) was used in order to keep the pH of the digester stable. Original pH and ORP values of substrates and their stabilized values after solution addition were given in Table 4.4.

Table 4.4. pH and ORP analyses before and after digestion.

Parameters		Original		After Buffer Addition			
		pH	ORP (mV)	pH		ORP (mV)	
Reactors	Substrates			Before Digestion	After Digestion	Before Digestion	After Digestion
<b>Set – 1</b>							
<b>R1</b>	FVFW+Sludge	5.93	61.0	7.46	7.0	-32.6	8.3
<b>R2</b>	FVFW+Sludge				6.8		10.2
<b>R3</b>	DPW+Sludge	4.95	53	7.2	6.3	-18.1	22
<b>R4</b>	DPW+Sludge				6.5		20.1
<b>R5</b>	Mixed Waste+Sludge	6.04	109.9	7.26	7.2	-21.8	10.5
<b>R6</b>	Mixed Waste+Sludge				7.0		7.2
<b>R7</b>	Sludge	7.11	-15.6	7.36	7.0	-27.4	5.7

Since the parameters of pH and alkalinity is related to each other, alkalinity values change after addition of buffer solution. The measured alkalinity concentrations were given in Table 4.5.

Table 4.5. Alkalinity concentrations.

Before Buffer Solution		
Substrates	TS (%)	Alkalinity (mg CaCO <sub>3</sub> /L)
<b>Set – 1</b>		
FVFW+Sludge	5	270
DPW+Sludge	5	135
Mixed Waste+Sludge	5	150
Sludge	5	1440

Alkalinity values of the substrates that were used in this study were low. Also, drastic decreases in pH values were seen in reactors during the laboratory studies. However, pH values and alkalinity concentration should be suitable for biogas production. So, optimum pH and alkalinity for anaerobic digestion were provided with the addition of buffer solution. Obtained alkalinity after buffer solution addition and VFA concentrations were given in Table 4.6 due to the period of digestion.

Table 4.6. Alkalinity and VFA analysis for Set-1.

After Buffer Solution Addition (KHCO <sub>3</sub> )				
Reactors	Substrates	Alkalinity (mg CaCO <sub>3</sub> /L)		VFA (mg CH <sub>3</sub> COOH/L)
		Before Digestion	After Digestion	After Digestion
<b>Set – 1</b>				
R1	FVFW+Sludge	3125	4025	1250
R2	FVFW+Sludge		4425	1050
R3	DPW+Sludge	4800	5918	3263
R4	DPW+Sludge		5675	3025
R5	Mixed Waste+Sludge	2350	2465	947
R6	Mixed Waste+Sludge		2950	1050
R7	Sludge	2500	3370	1575

A few increases in alkalinity concentrations were observed after digestion period. Anaerobic degradation processes consume hydrogen ions and releases gases in the absence of oxygen. This consumption of hydrogen ions increases the alkalinity. In general, increase in alkalinity concentration could cause the decrease in pH. However, decomposition of used substrates which had a large amount of proteins caused the release of ammonia. Therefore, releasing ammonia into solutions could be able to increase in pH while alkalinity concentrations were also high.

Also, VFA concentrations were higher in solutions after anaerobic digestion period. Substrates that were used in this study were highly degradable organic matters. So they were easily converted into VFA. The production of a large amount of VFA leads to the decrease in pH, however, a slight decrease in pH was observed in solutions which could be negligible (Table 4.4).

Adequate amounts of nutrients are essential for supporting the growth and maintenance of microbial population as well as for the efficient operation of anaerobic processes. One of those nutrients is nitrogen compounds. The TKN and Ammonia concentrations were given in Table 4.7. However, TKN concentration showed a decrease after digestion depending on the removal process. The highest removal in the TKN concentration was observed in DPW (R3 and R4). Except inoculums, ammonia-N concentrations showed an increase in the reactors. An increase in ammonia-N concentration was attributed to the biodegradation of organic nitrogen in waste. The highest increase in ammonia-N concentration was observed in DPW.

Total phosphorus (TP) was monitored as one of the major nutrient in anaerobic digestion. TP concentrations of waste mixtures were also given in Table 4.7.

Table 4.7. TKN, ammonia and TP analyses.

Reactors	Substrates	TKN (g/kg dry matter)		Ammonia (mg/L NH <sub>3</sub> -N)		TP (g/kg dry matter)	
		Before Digestion	After Digestion	Before Digestion	After Digestion	Before Digestion	After Digestion
<b>Set – 1</b>							
<b>R1</b>	FVFW+Sludge	84	48	137	350	11	7
<b>R2</b>	FVFW+Sludge		50		476		6
<b>R3</b>	DPW+Sludge	138	8	40	860	2	0
<b>R4</b>	DPW+Sludge		7		920		0
<b>R5</b>	Mixed Waste+Sludge	111	66	106	76.5	38	8
<b>R6</b>	Mixed Waste+Sludge		61		87		7
<b>R7</b>	Sludge	44	47	244	144	28	18

TKN concentrations of supermarket wastes that were digested in reactors decreased after digestion period. However, ammonia concentrations of these wastes showed different characteristics. While ammonia concentrations of FVFW and DPW increased, concentrations of Mixed W. and sludge decreased after the digestion period. According to the data in above table, ammonia concentrations of FVFW and DPW increased during the degradation of TKN concentrations. Because of the high protein content of substrates, high amount of ammonia released to the solution which caused the increase in alkalinity concentration. As a result, there was no statistically trend between TKN and ammonia concentrations after digestion period.

Elemental and heavy metal concentrations of substrates were given in Table 4.8. The result of analysis gave information about the chemical properties of substrates after digestion. C/N ratios of fresh substrates were given in Table 4.2. C/N ratio, elemental and heavy metal concentrations of substrates were measured after digestion and given in Table 4.8.

Table 4.8. Results of elemental and heavy metal concentrations.

Unit	-	Metals (g/kg)								
Reactors	C/N	Na	Ca	Mg	Cd	Ni	Zn	Cr	Pb	Cu
<b>Set-1</b>										
<b>R1</b>	11	0.1	0.31	0.01	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R2</b>	10	0.1	0.29	0.01	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R3</b>	19	5.8	0.08	0.02	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R4</b>	15	5.5	0.08	0.02	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R5</b>	13	5.4	0.06	0.05	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R6</b>	11	4.3	0.06	0.06	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R7</b>	20	0.3	0.03	0.02	0.01	0.01	0.01	<0.01	n.d.	n.d.

\*n.d.: not determined

C/N concentrations of FVFW, DPW and Mixed Waste decreased after digestion period. Also, light metal ions and heavy metal concentrations generally decreased after digestion.

#### **4.1.2. Gas Analyses for Set-1**

Biogas production was monitored by measuring daily gas production. The daily gas productions and cumulative gas productions of reactors were presented respectively in Figures 4.1 and 4.2 for Set-1.

Highest gas production was observed in R1 and R2 at the beginning of the laboratory tests. Daily gas production of about 100- 1,350mL was obtained during the first 16 days. Highest gas productions were recorded for FVFW and DPW with 1,350mL and 900mL, respectively. Decrease in daily gas productions started in the same time duration for all reactors.

Cumulative gas productions of reactors which showed the total gas production during the digestion period were given in Figure 4.2 for Set-1.

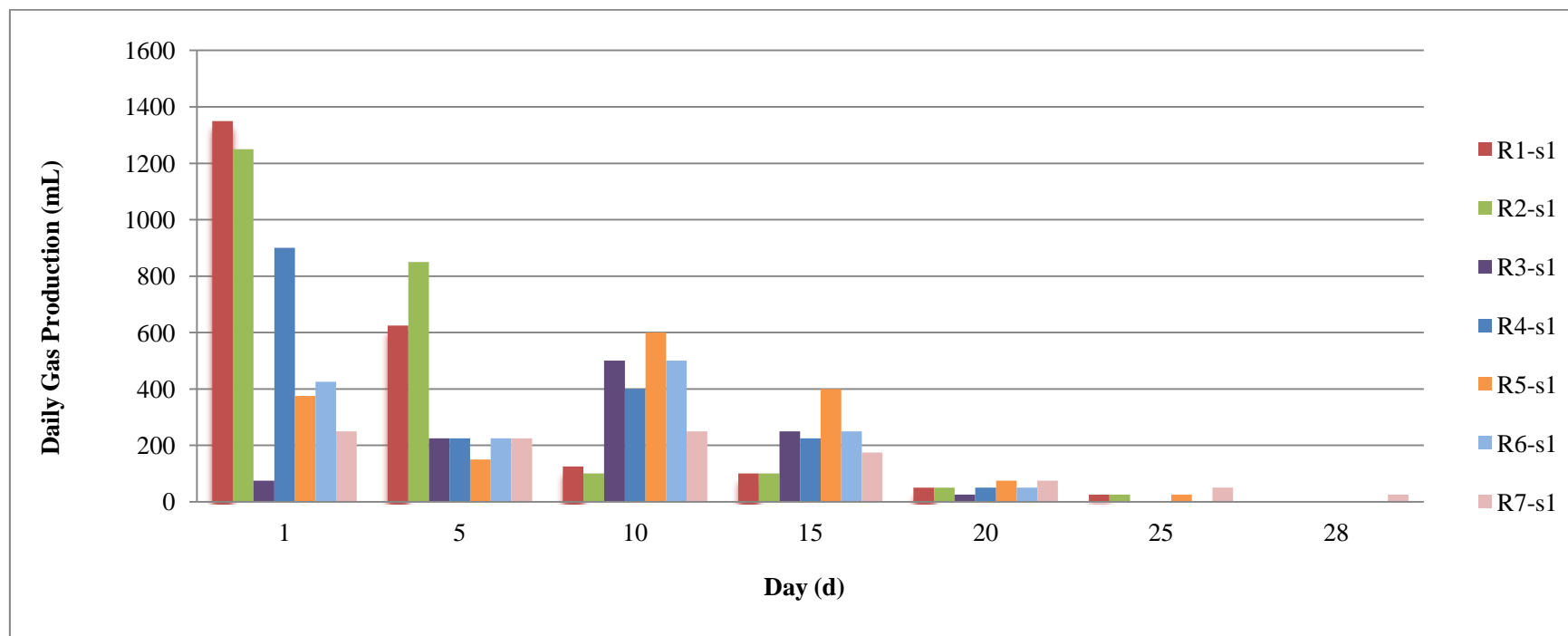


Figure 4.1. Daily gas production – Set 1.

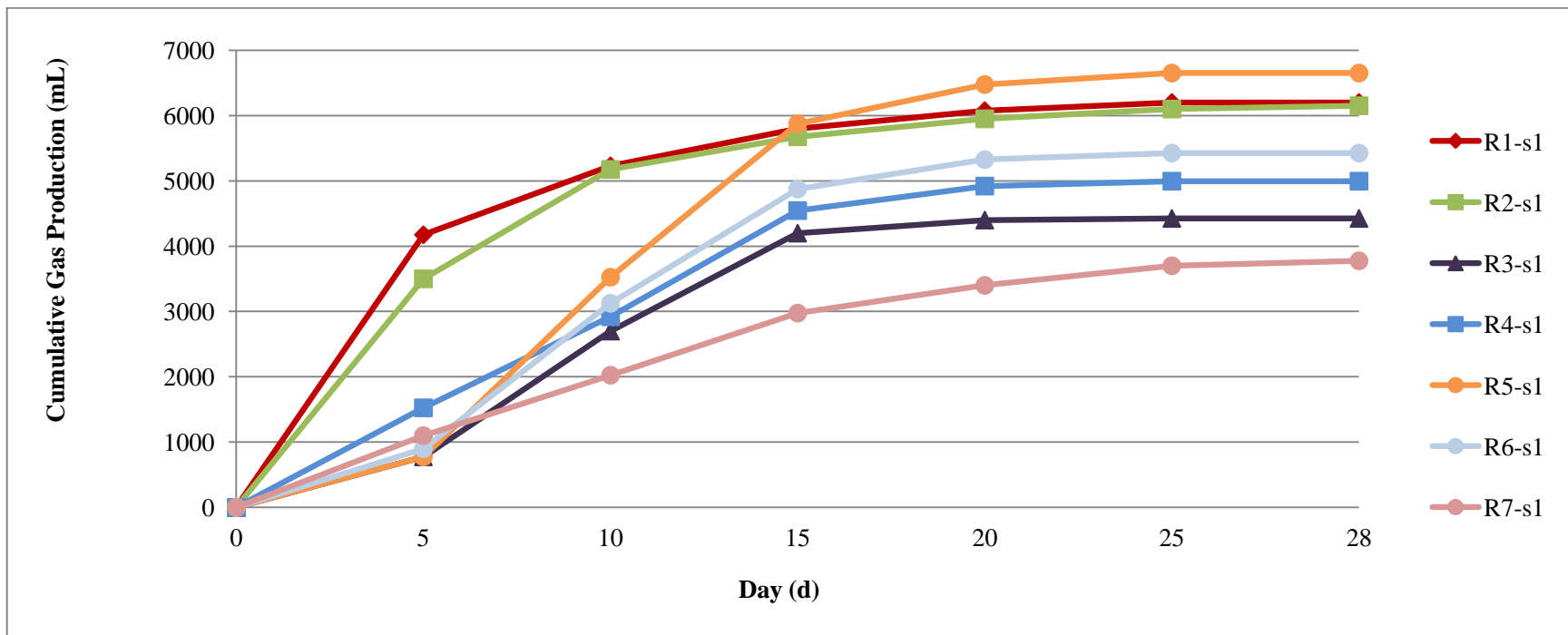


Figure 4.2. Cumulative gas production– Set-1.

General trend in gas production was to increase up to the maximum point for every substrates and then gradually decrease in the amount of gas production during the digestion period. Cumulative gas production showed continuously increase during the digestion. The highest cumulative gas production was observed in R5 with 6,650mL for mixed waste and R1 and R2 with 6,175mL on average for FVFW. The lowest cumulative gas production was observed in R7 which is control reactor of Set-1.

Biogas which mainly consists of methane ( $\text{CH}_4$ ) and carbon dioxide ( $\text{CO}_2$ ) is the gaseous product of the anaerobic digestion of organic matter. Thus, determining gas composition is an important point for anaerobic digestion process. Biogas composition for the batch reactors was analyzed once in a week. Methane concentrations of reactors during the digestion period are given in Figure 4.3 for Set-1.

Methane productions of different substrates which were FVFW, DPW and mixed wastes showed similar fluctuations during the digestion process. Maximum methane productions were observed on the 16<sup>th</sup> day as a general trend except control reactor. The highest methane percentages were recorded as 55.4% and 59.2% in R3 and R4 which were loaded with dairy product wastes in Set-1.

Cumulative methane production of all reactors was close to each other in terms of percentage. Mixed wastes, which were loaded in parallel reactors as R5 and R6, produced maximum methane production. Also, laboratory tests showed that parallel reactors produced methane similar to each other. So this fact explained that digestion processes were actualized in the same way and time duration in parallel reactors. Only control reactor (R7) was shown sudden increase in the beginning of the digestion period depending on the rapid degradation. Also, Cumulative methane production in terms of mL was given in Figure 4.4 depending on methane concentration.

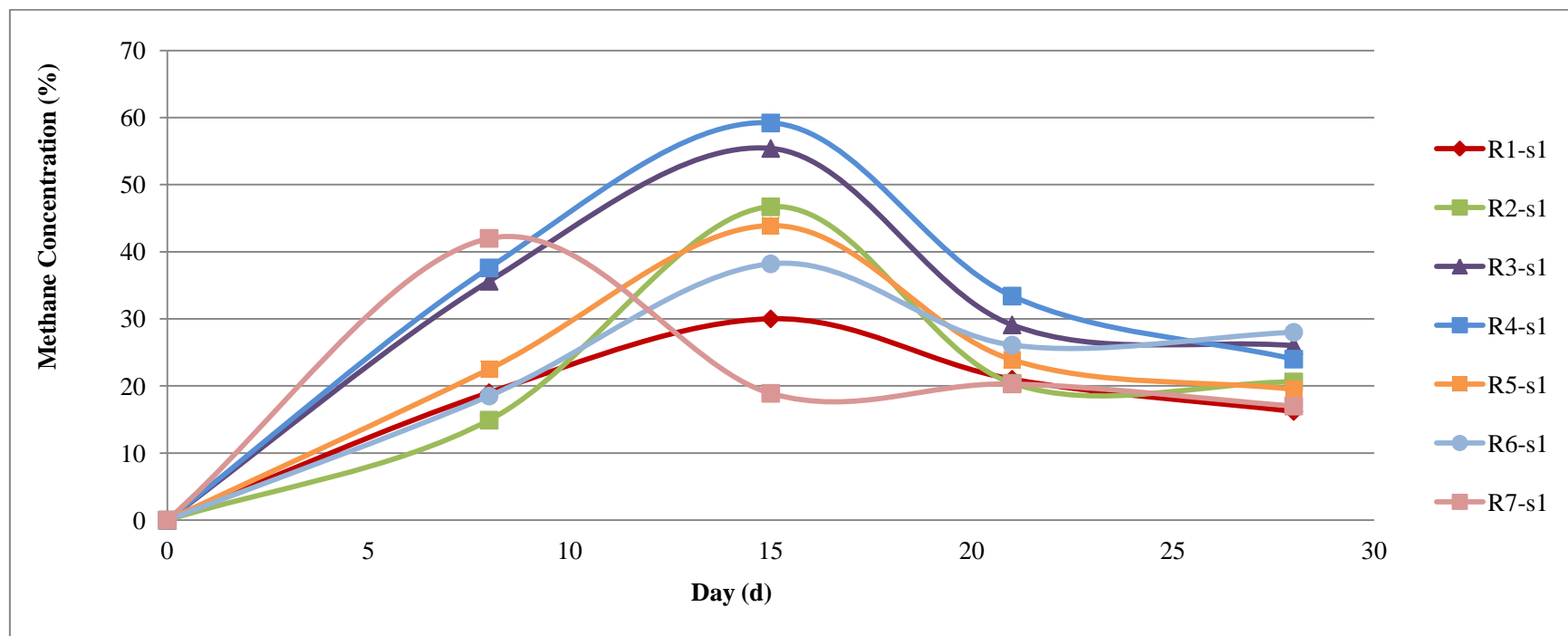


Figure 4.3. Methane concentrations of reactors– Set-1.

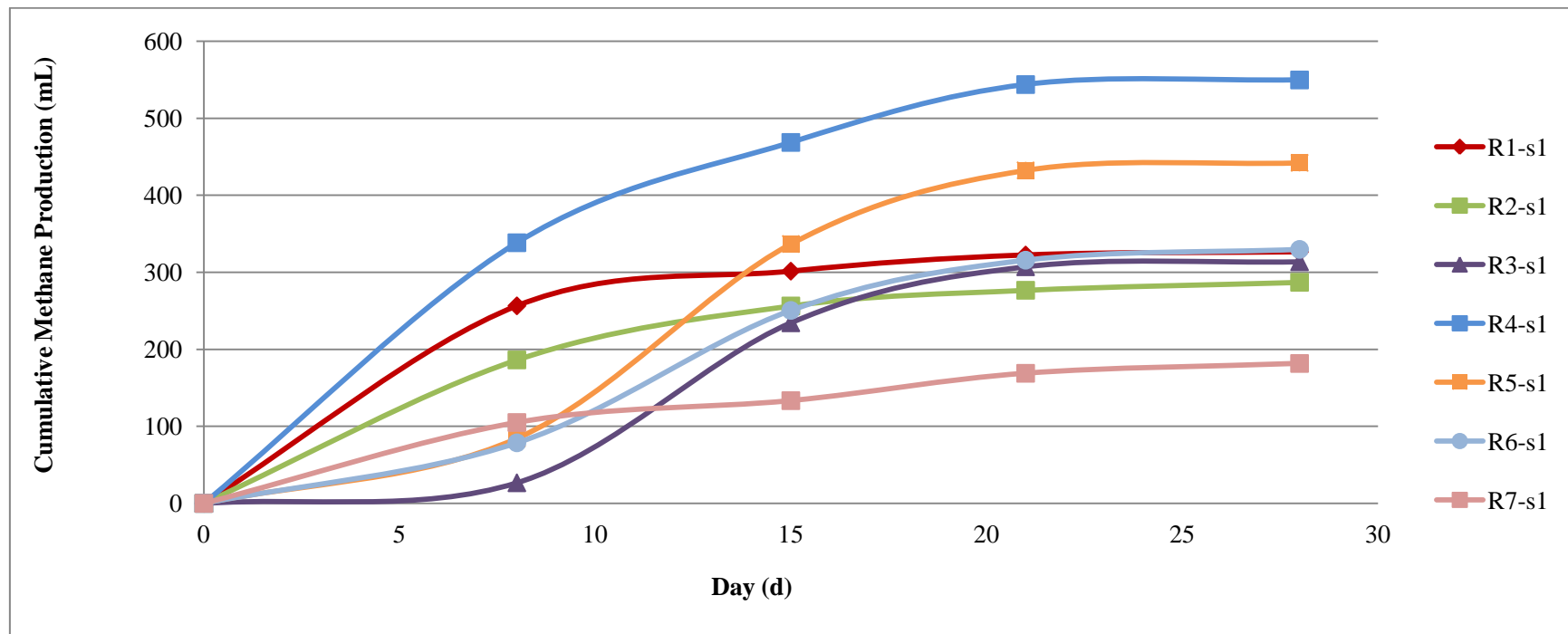


Figure 4.4. Cumulative methane production– Set-1.

There was not a general trend in cumulative methane production. Highest cumulative methane production was observed in R4 which was loaded with DPW. However, the parallel of this one did not show a similar methane production because their gas productions were different from each other. R5 including Mixed Wastes was the second in cumulative methane production. R1 and R2 loaded with FVFW showed similar methane production during the digestion process.

Consequently, the study was showed that the methane production potential of supermarket wastes was high in anaerobic digestion. High methane content was obtained from the highly biodegradable supermarket waste contents which were FVFW, DPW and Mixed W. in Set-1. High methane content was provided by the degradation of DPW which had more protein comparing to other waste contents despite less cumulative gas production from others. This fact displayed that decomposition of protein rich substrates in anaerobic reactors could provide more methane production. However, FVFW which included fructose produced more gas with less methane content during the digestion period. So, protein rich substrates produce less gas with high methane content whereas substrates containing fructose produce more gas production. Furthermore, Mixed W. which included mixing of FVFW, DPW, MW and SW showed high gas production that could be seen in Figure 4.2, but its methane concentration stayed under the DPW's methane concentration depending on the interaction of different substances.

## **4.2. Results of Set- 2**

### **4.2.1. Substrate Analysis for Set- 2**

In the second set, nine batch reactors loaded with SW, MW and mixed waste was used for the digestion processes. Also, control reactor loading with sludge was carried out like the first set. In this set, SW, MW and sludge were operated at 5% TS ratio similar to Set-1 to determine their biogas production potential. Moreover, mixed wastes with 8% and 10% TS ratio were operated. Studying the different TS ratios of mixed wastes in anaerobic digestion had two reasons. One was related to the supermarket waste management system. Separating wastes into categories would not be suitable for supermarkets because of the

limiting areas. Another one was obtaining more sustainable gas and methane productions because of the better nutritional composition. Hence, waste management system for biogas production would be needed to apply waste content in a mixture in the practice.

Substrates such as FVFW, DPW, MW and SW which were singly operated were studied to determine the individual biogas production potentials. Moreover, mixture of supermarket wastes also was operated at 8% and 10% TS ratio in Set-2 like operating at 5% TS ratio in Set-1. Biogas production of mixed supermarket wastes was searched continuously in Set-2 because its high biogas production potential was observed in Set- 1. Generally, the COD range showed difference depending on the type of substrate. Therefore, each type of substrates was analyzed for COD concentration to determine the COD concentration before digestion. Concentrations were given for SW, MW, Sludge, and Mixed Wastes with 8% and 10% TS ratio as respectively 10,858 mg/L, 13,959 mg/L, 12,462 mg/L and 27,430 mg/L.

TS and VS analyses were conducted for substrates before and after digestion period and the results were given in the Table 4.9. TS concentrations of substrates were determined to fix the TS ratio in reactors before digestion.

Table 4.9. Loading analysis of reactors.

Reactors	Substrates	TS (%)	VS (% of TS)	
		Before Digestion	Before Digestion	After Digestion
<b>Set – 2</b>				
<b>R1</b>	SW+Sludge	5	35.2	22.3
<b>R2</b>	SW+Sludge			19.8
<b>R3</b>	MW+Sludge	5	41.0	29.1
<b>R4</b>	MW+Sludge			30.6
<b>R5</b>	Mixed Waste+Sludge	8	74.2	35.7
<b>R6</b>	Mixed Waste+Sludge			30.1
<b>R7</b>	Sludge	5	55.0	31.6
<b>R8</b>	Mixed Waste+Sludge	10	73.5	35.8
<b>R9</b>	Mixed Waste+Sludge			34.4

Initial and final VS of reactors were also measured for Set- 2. Highest VS removal was recorded for mixed wastes with 8% and 10% TS ratio. Minimum VS degradations were measured as over 27% and 40% for MW and SW, respectively. So, FVFW and DPW were decomposed more easily than MW and SW. Therefore, increasing the amount of FVFW and DPW in the mixture would accelerate the biodegradation process.

Decrease in the pH value of reactors causes a reduction in the gas production, so this parameter is considered as one of the most significant parameters because of its impacts on the anaerobic digestion. Methane bacteria could grow at all pH values between 6.0 and 8.5 with an optimum slightly above pH 7.0. However, buffering capacity of substrates was not enough to stabilize the pH at the desired value that was observed in the beginning of the laboratory studies. So, potassium hydrogen carbonate ( $\text{KHCO}_3$ ) was used in order to keep the pH in optimum values. The pH and ORP values were given in Table 4.10.

Table 4.10. pH and ORP analyses before and after digestion.

Parameters		Original		After pH Stabilization			
		pH	ORP (mV)	pH		ORP (mV)	
Reactors	Substrates			Before Digestion	After Digestion	Before Digestion	After Digestion
<b>Set – 2</b>							
<b>R1</b>	SW+Sludge	7.15	-15.4	7.75	6.8	-49.1	-15
<b>R2</b>	SW+Sludge				6.2		-8
<b>R3</b>	MW+Sludge	6.71	8.5	7.60	6.8	-40.0	-53.5
<b>R4</b>	MW+Sludge				6.3		-44.5
<b>R5</b>	Mixed Waste+Sludge	6.5	21.8	7.56	7.0	-38.6	25
<b>R6</b>	Mixed Waste+Sludge				6.5		21
<b>R7</b>	Sludge	6.86	0.8	7.50	7.1	-34.1	-11.6
<b>R8</b>	Mixed Waste+Sludge	6.07	45.4	7.49	7.1	-33.5	20.1
<b>R9</b>	Mixed Waste+Sludge				7.0		18.5

Original pH values of substrates in Set-2 were not a low as in Set-1. pH was stabilized between 7.0 and 8.0 in order to provide suitable conditions for bacterial activity and also gas production by the addition of buffer solution. Despite buffer solution addition, decrease in the pH values was observed after digestion.

Fresh and uncooked foods had negative ORP while cooked and processed foods had positive ORP because reduction potential of processed foods decreases. In the light of that, R5, R6, R8 and R9 which were loaded with mixed wastes showed positive ORP solutions in contrast to other reactors. While ORP of mixed wastes was positive charge after digestion, ORP of reactors loaded with SW, MW and sludge were measured as a negative charged. Negative charged ORP presented that there were greater concentrations of electrons in the substance. However, increased ORP reduced digestion performance and biogas production.

Alkalinity analysis of Set-2 were carried out before buffer solution addition same as Set-1. Also, alkalinity of substrates was lower than the threshold level for ideal gas production. The measured alkalinity concentrations are given in Table 4.11.

Table 4.11. Alkalinity concentration.

<b>Before Buffer Solution</b>		
<b>Substrates</b>	<b>TS (%)</b>	<b>Alkalinity (mg CaCO<sub>3</sub>/L)</b>
<b>Set - 2</b>		
<b>SW+Sludge</b>	5	720
<b>MW+Sludge</b>	5	830
<b>Mixed Waste+Sludge</b>	8	630
<b>Mixed Waste+ Sludge</b>	10	510
<b>Sludge</b>	5	1455

The necessary threshold level for anaerobic digestion was provided after buffer solution addition. After that, substrates were loaded to the reactors for the digestion process like Set-1. Results of alkalinity and VFA analysis were given in Table 4.12.

Alkalinity and VFA of all reactors were higher in Set- 2 than Set- 1 depending on different substrates. Increase in alkalinity concentrations were recorded after digestion because of the high amount of ammonia concentration in the solutions due to the decomposition of substrates with high protein content. Obtaining substrates from supermarket waste storage area were highly degradable organic materials, so they were easily converted to soluble compounds that cause the production of a large amount of VFA after digestion.

Table 4.12. Alkalinity and VFA analysis for Set-2.

After Buffer Solution Addition (KHCO <sub>3</sub> )				
Reactors	Substrates	Alkalinity (mg CaCO <sub>3</sub> /L)		VFA (mg CH <sub>3</sub> COOH/L)
		Before Digestion	After Digestion	After Digestion
<b>Set – 2</b>				
<b>R1</b>	SW+Sludge	3250	4350	3085
<b>R2</b>	SW+Sludge		4000	3125
<b>R3</b>	MW+Sludge	7000	10200	2022
<b>R4</b>	MW+Sludge		12120	2126
<b>R5</b>	Mixed Waste+Sludge	6500	6750	2350
<b>R6</b>	Mixed Waste+Sludge		6565	2075
<b>R7</b>	Sludge	2350	3200	1750
<b>R8</b>	Mixed Waste+Sludge	6400	6500	2402
<b>R9</b>	Mixed Waste+Sludge		6700	2586

TKN, ammonia-N and TP concentrations of Set- 2 were given in Table 4.13 before and after digestion process. According to the results of analyses, TKN concentrations showed a decrease after digestion. The highest removal in the TKN concentration was observed in MW (R3 and R4) and also mixed waste (R8 and R9). Furthermore, ammonia-N concentrations showed an increase in the reactors. On the other hand, TP concentrations decreased except SW (R1 and R2). TP concentrations of SW could be negligible.

Table 4.13. TKN, ammonia and TP analyses.

Reactors	Substrates	TKN (g/kg dry matter)		Ammonia (mg/L NH <sub>3</sub> -N)		TP (g/kg dry matter)	
		Before Digestion	After Digestion	Before Digestion	After Digestion	Before Digestion	After Digestion
<b>Set – 2</b>							
<b>R1</b>	SW+Sludge	38	12	90	188	0	0
<b>R2</b>	SW+Sludge		15		388		0
<b>R3</b>	MW+Sludge	74	16	280	360	22	13
<b>R4</b>	MW+Sludge		16		345		12
<b>R5</b>	Mixed Waste+Sludge	115	66	98	406	36	5
<b>R6</b>	Mixed Waste+Sludge		70		460		6
<b>R7</b>	Sludge	50	46	208	136	25	18
<b>R8</b>	Mixed Waste+Sludge	118	67	180	248	45	10
<b>R9</b>	Mixed Waste+Sludge		68		334		11

According to Table 4.13, TKN concentrations of substrates decreased after digestion period while ammonia concentrations showed a drastic increase in the outlet of reactors except control reactor. High organic fraction of substrates which had high protein content released large quantity of ammonia concentration during the digestion process. Increase in ammonia concentrations also caused increase in alkalinity concentrations while pH stayed in nearly neutral like Set-1. Moreover, TP concentrations of reactors declined observing that SW had not phosphate concentrations in the both inlet and outlet because of its elemental structure.

Substrates showed similar degradation in TKN, Ammonia and TP concentrations comparing to Set- 1 and Set- 2.

Elemental and heavy metal analysis were also measured to determine the content of supermarket waste before and after digestion. Carbon and nitrogen content was determined because carbon/nitrogen ratio was an important factor to use wastes in anaerobic digestion process. Also, heavy metal content was an important parameter for using digestate as fertilizer. The results of elemental and heavy metal analysis were given in Table 4.14.

Table 4.14. Results of elemental and heavy metal concentrations.

Unit	-	Metals (g/kg)								
Reactors	C/N	Na	Ca	Mg	Cd	Ni	Zn	Cr	Pb	Cu
<b>Set-2</b>										
<b>R1</b>	20	2.13	0.21	0.01	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R2</b>	18	2.10	0.21	0.01	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R3</b>	9	5.41	2.55	0.01	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R4</b>	7	4.38	2.18	0.01	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R5</b>	16	1.12	5.05	0.03	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R6</b>	15	1.11	4.78	0.03	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R7</b>	20	0.4	1.25	0.04	0.01	0.01	0.01	0.01	n.d.	n.d.
<b>R8</b>	18	1.12	5.12	0.04	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R9</b>	17	1.15	5.23	0.03	<0.01	<0.01	0.04	<0.01	n.d.	n.d.

\*n.d.: not determined.

Calcium, sodium and magnesium were essential for the growth of certain strains of methanogens. Light metal concentrations of reactors were higher than heavy metal concentrations because food fractions have different nutrient compositions. Heavy metal concentrations of reactors were negligible except zinc concentrations. Heavy metal concentrations could cause inhibition of methanogenesis when their concentration reached to the toxicity level. Materials with different C/N ratios differ widely in their yield of biogas. If C/N ratio is higher than the optimum range (20-30), biogas production will be low. C/N ratios of reactors were under the range that could inhibit the system in Set-2.

When comparing the results of elemental and heavy metal analysis of Set-1 and Set-2, it was observed that different substrates had different concentrations (Table 4.8 and Table 4.14). C/N ratios were generally close to each other in all reactors. Elemental concentrations showed differ depending on the characterization of substrates such as FVFW, DPW, SW, MW and Mixed W. But it could be seen that elemental concentrations of Mixed W. with different TS ratios were similar to each other. Heavy metal concentrations could be negligible in both Set- 1 and Set- 2.

#### **4.2.2. Gas Analyses for Set- 2**

Daily gas production of Set- 2 was observed and recorded during the digestion process (Figure 4.5). The degradation time of reactors was similar with Set- 1. Both sets were operated for 28 days.

R6 and R9 which had Mixed Wastes with different TS ratios (8% and 10%) showed higher gas production at the beginning of the laboratory tests and then a drastic decrease was observed in both reactors. On 4<sup>th</sup> day, gas productions of all reactors started to increase in parallel to each other. Gas production of SW (R1-s2 and R2-s2) was also high during the first 2 days, but its gas production consumed quickly. However, gas productions in R3 and R4 loaded with MW were decreased quickly and stopped by day 20. Furthermore, each of R5, R6, R8 and R9 showed similar fluctuations in gas production during the digestion.

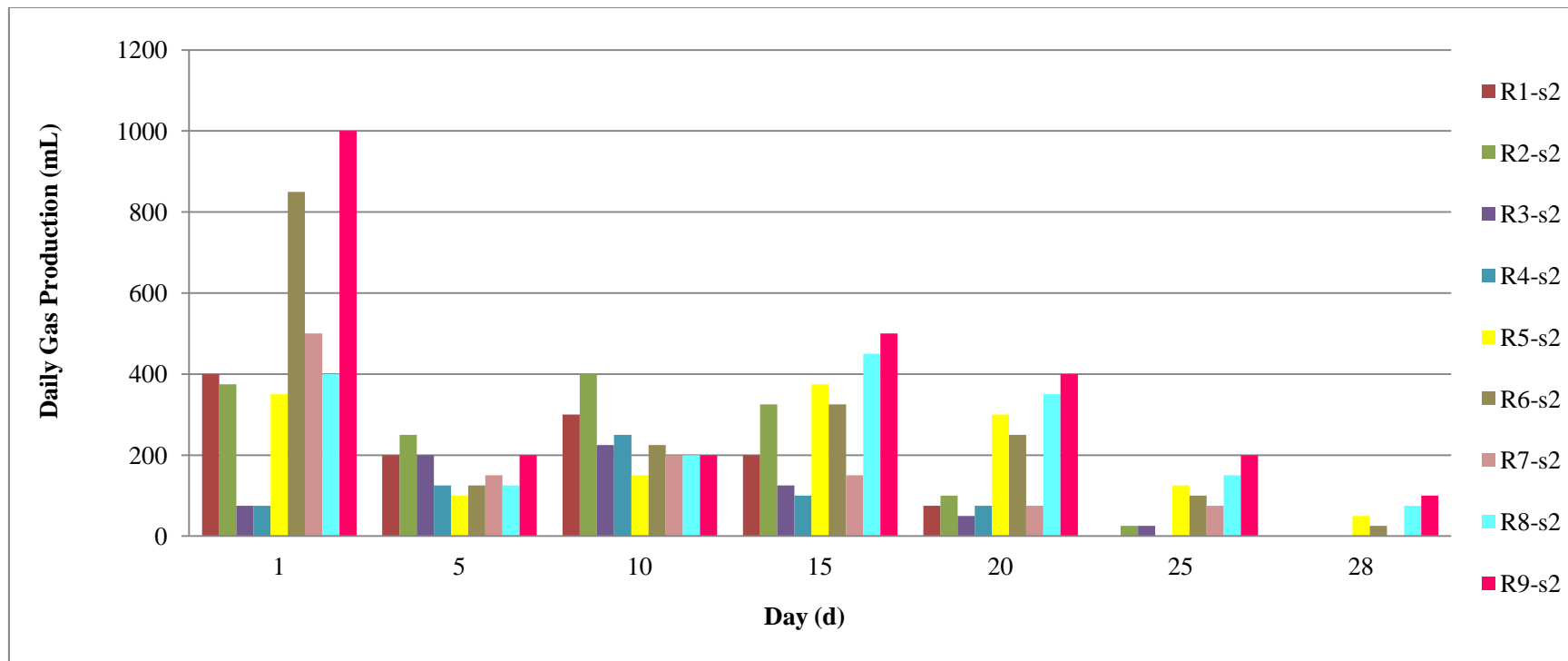


Figure 4.5. Daily gas production– Set- 2.

It was observed that daily gas productions were changed depending on the different substrates in the study. SW (R1-s2 and R2-s2) produced high amount of gases in the beginning while MW (R3-s2 and R4-s2) produced it more slowly because the degradability of glucose were higher than fats. Also, total gas production of MW was considerably lower than other substrates. The difference in gas production rates was caused from the differences in elemental structure of substrates. Obtained daily gas productions showed difference between the values of 25mL to 1,000mL in this set. The better gas productions were performed with the values of 850mL and 1,000mL for mixed wastes with 8% and 10% TS content, respectively at the first week of digestion. Daily gas productions were consumed for SW and MW on the 25<sup>th</sup> day of digestion. Furthermore, parallel reactors of mixed waste (R5-s2, R6-s2 and R8-s2, R9-s2 with 8% and 10% TS ratios) showed difference in gas production during the digestion process in Set- 2 while they (R5-s1, R6-s1 with 5% TS ratios) showed similar gas production rates in Set- 1.

Cumulative gas production of Set- 2 was calculated depending on the daily gas productions after 28 days of digestion. The cumulative productions of each reactor were given in Figure 4.6.

The highest gas production was achieved with the value of 9,000 mL by mixed waste with 10% TS ratios during the digestion process. Mixed Wastes with 8% TS ratios followed with approximately 6,000 mL cumulative gas production in Set- 2. The lowest gas production was observed in reactors fed with MW (R3-s2 and R4-s2). The amount of gas production of SW was higher than MW during process.

Comparing Set- 1 and Set- 2, it was observed that control reactors showed similar gas production rates and produced approximately 4,000 mL gases. MW produced the lowest gas production in all reactors both in SET-1 and Set- 2. Cumulative gas productions of DPW in Set- 1 and SW in Set- 2 were similar to each other. When comparing all the results of Mixed Wastes with different TS ratios in Set- 1 and Set- 2, it was observed that cumulative gas productions had increased due to the increase in TS ratio.

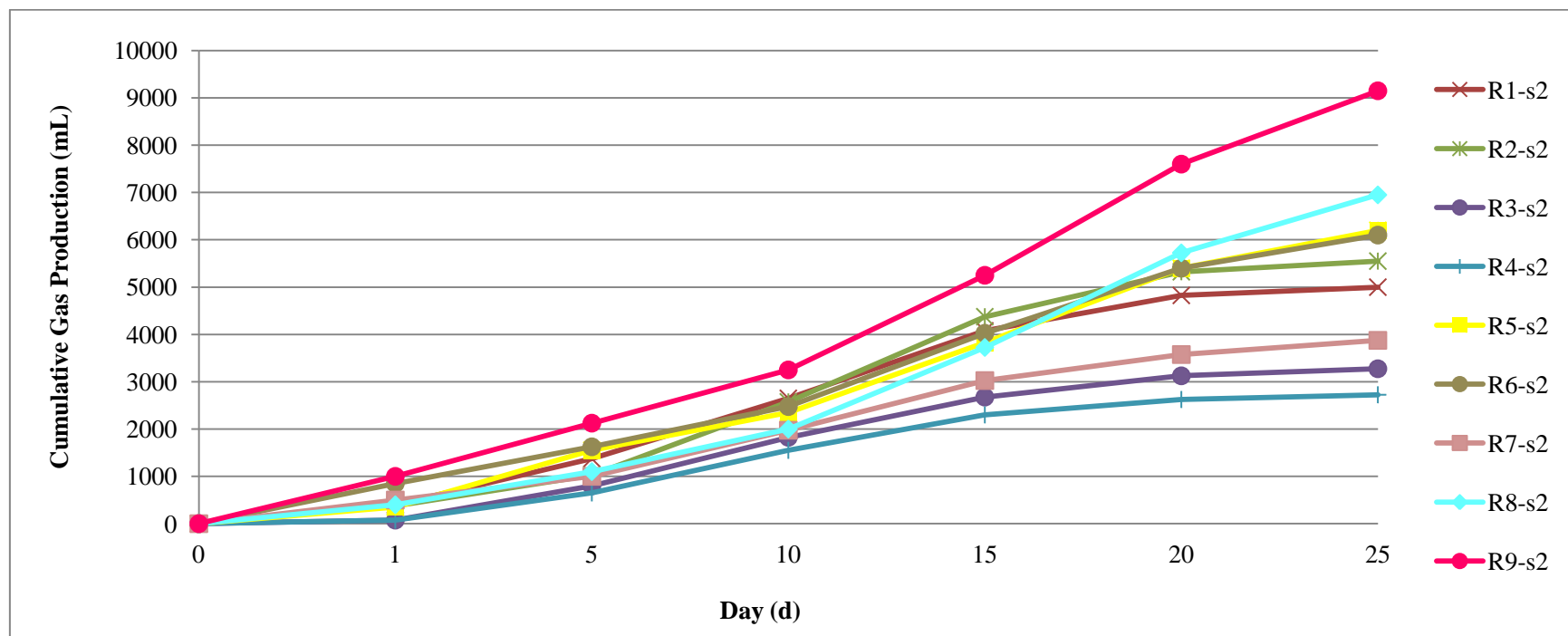


Figure 4.6. Cumulative gas production– Set- 2.

Determining gas composition was an important point for anaerobic digestion process because produced gases consisted mainly of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). Methane concentrations of Set- 2 were given in Figure 4.7 during the digestion process.

Methane concentrations showed different fluctuations depending on the type of substrates. SW and MW produced lower methane than other substrates in Set-2. Maximum methane production was observed in the 16<sup>th</sup> day except reactors loaded with MW (R3-s2 and R4-s2). On 16<sup>th</sup> day, methane concentrations of R3-s2 and R4-s2 closed to the zero point, but then their methane concentration showed a little bit increase. The highest methane production was recorded as 63% in R8-s2 and 69.5% in R9-s2 which constituted mixed waste with the 10% TS loading ratio.

Methane concentrations of reactors both in Set- 1 and Set- 2 also showed difference depending on the type of substrates. Highest methane concentrations were observed in DPW (R3-s2 and R4-s2) in Set- 1 due to the high degradation of milky products. However, highest methane production was observed in Mixed Wastes with different TS ratios (8% and 10%) in Set- 2. There was a slight difference in methane concentration of control reactors between Set- 1 and Set- 2.

Methane concentrations and cumulative methane concentrations of reactors were given in Figure 4.7 and 4.8, respectively.

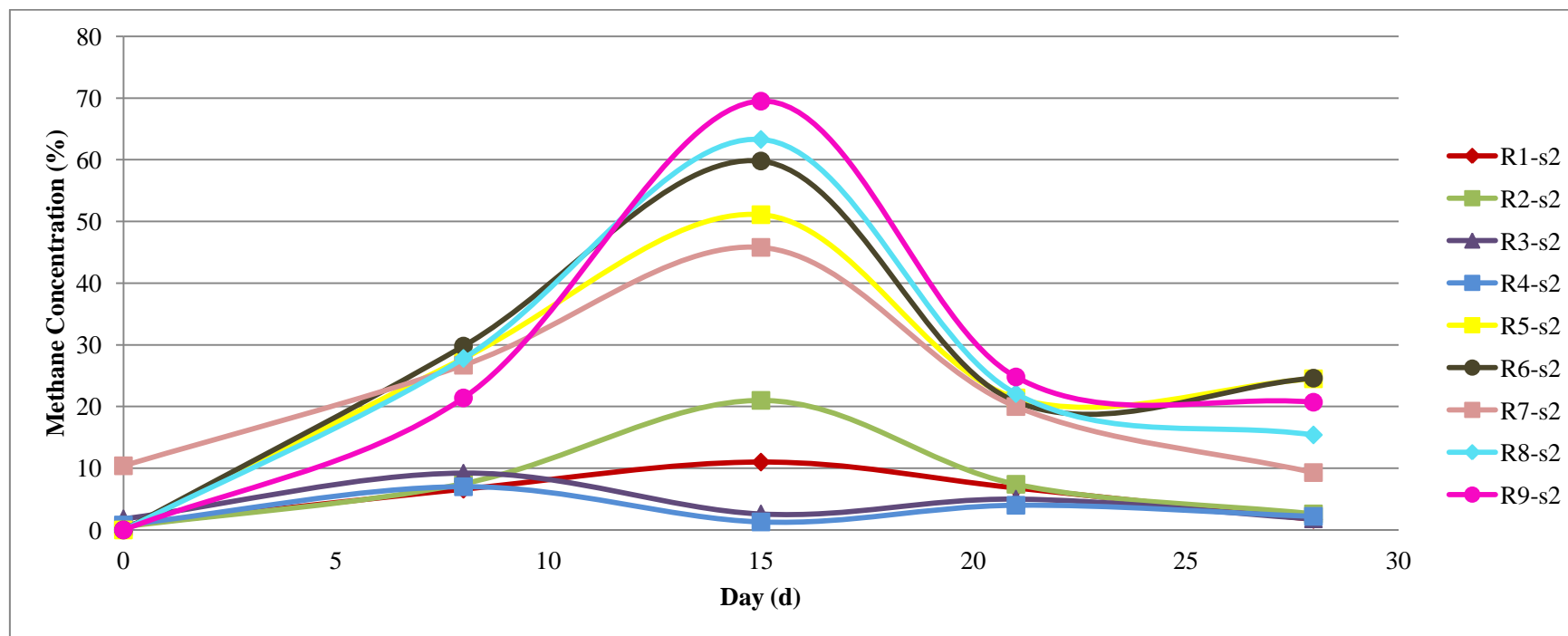


Figure 4.7. Methane concentrations of reactors– Set- 2.

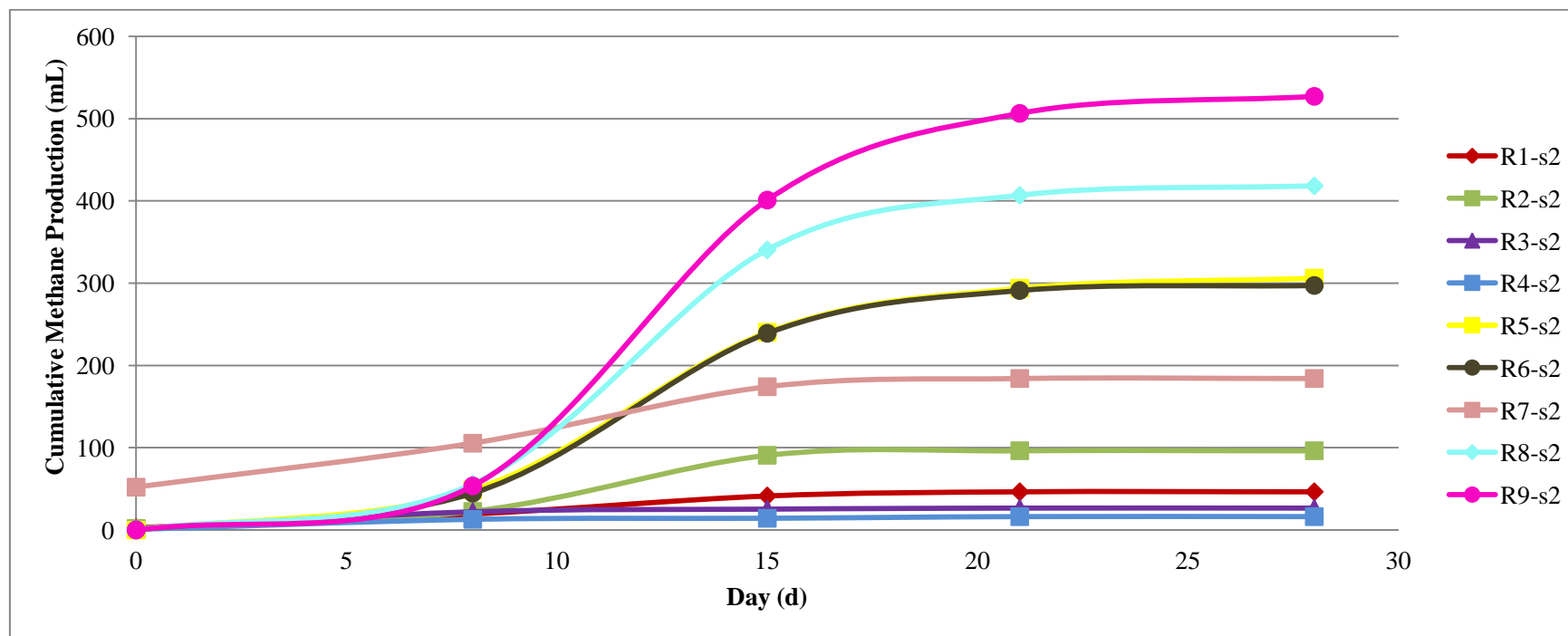


Figure 4.8. Cumulative methane production– Set- 2.

The highest cumulative methane productions were observed respectively in R9, R8, R5 and R6 loaded with different TS ratios of mixed wastes. Production and depletion of methane content was similar to each other for reactors loaded with mixed wastes as seen in Figure 4.10. However, other reactors loaded with SW and MW failed to produce more methane because of their low biodegradability content contrast to mixed wastes.

Mixed Wastes with different TS ratios produced highest methane concentration during the digestion process in both Set- 1 and Set- 2. Whereas the operational conditions were same for all reactors, R1-s2, R2-s2, R3-s2 and R4-s2 was not showed a good performance in both gas and methane production depending on the characteristics of substrates. This difference in both gas and methane production was attributed to the characteristics of the substrates which was analyzed in the laboratory tests. While mixed wastes produced gas with higher methane content, sugar and meat wastes could not achieved higher gas productions and methane concentrations.

### **4.3. Comparing the Gas Production of Mixed Wastes**

Utilizing supermarket wastes in a mixture form was more suitable than using them separately in biogas plants. Using wastes in a mixture form could provide cheaper and easier method for supermarket managers. Also, laboratory studies showed that mixed wastes could produce good amount of gas with high methane content during the digestion process. Therefore, studying the different TS ratios of mixed wastes in anaerobic digestion had generally two reasons.

1. One was related to the supermarket waste management system. Separating wastes into categories would not be suitable for supermarkets because of the limiting areas.
2. Another one was obtaining more sustainable gas and methane productions because of the better nutritional composition.

In order to compare the gas production potential of mixed wastes with different TS ratios, cumulative gas productions of mixed wastes were given in Figure 4.9.

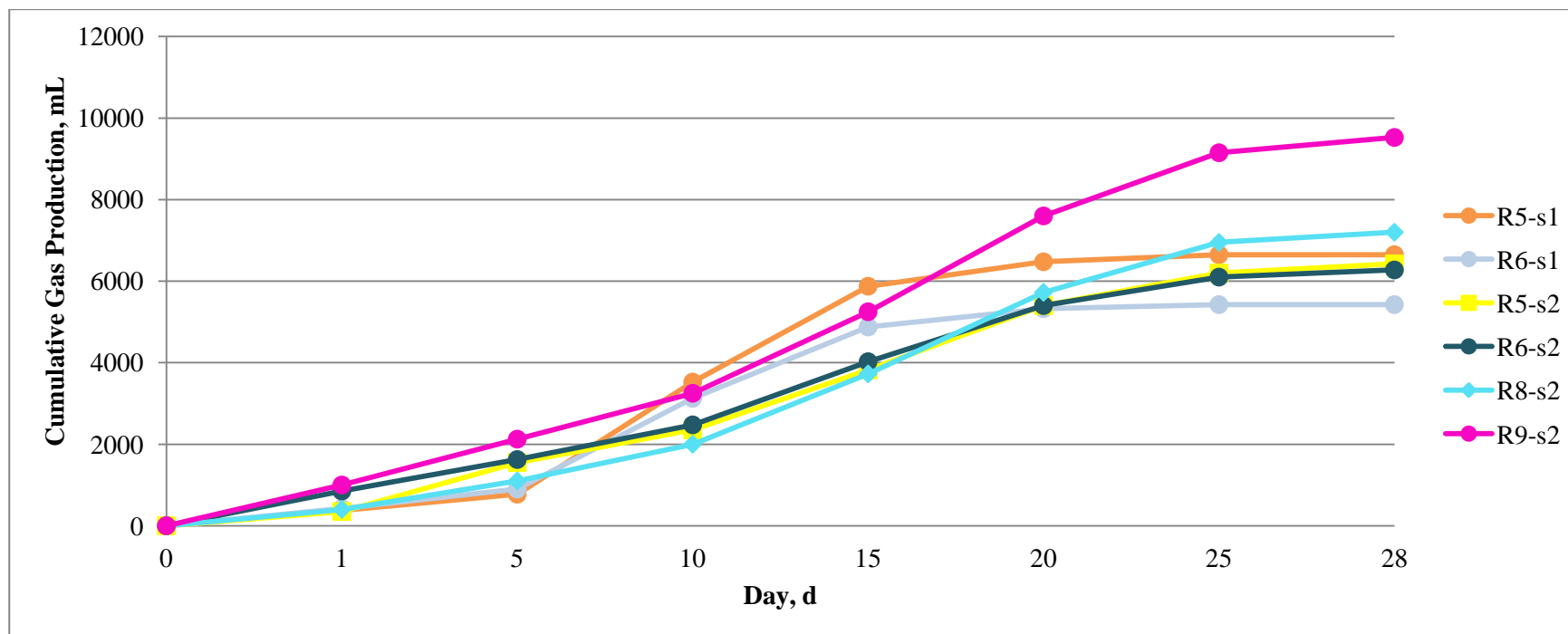


Figure 4.9. Cumulative gas production of mixed wastes.

Mixed wastes with 10% TS ratio (R9-s2) produced the highest amount of gas (approximately 10,000mL) during the digestion process. Also, its parallel reactor (R8-s2) followed it in gas production with approximately 7,000mL. Cumulative gas productions of mixed wastes with 5% TS ratio (R5-s1) was higher than Mixed Wastes with 8% TS ratio (R5-s2 and R6-s2) whereas parallel reactor of R5-s1 (R6-s1) produced the lowest gas production in all mixed wastes during the digestion process. Therefore, study showed that wastes with same TS ratio would not always give the same results in anaerobic digestion. There could be some inhibitory effects depending on the degradation phases.

Because the energy production potential was related to the methane content in gases, methane concentrations were recorded once in a week. Methane concentrations of mixed wastes with different TS ratios were given in Figure 4.10.

Methane concentration of mixed wastes which had higher solid content was more than the other wastes. As it can be seen from the Figure 4.10, highest methane concentration was recorded in mixed wastes with the TS ratios as 10%, 8% and 5%, respectively. Because of the rapid biodegradability of these wastes, higher solid content showed better results in both gas and methane production. Also, cumulative methane productions of parallel reactors were given in Figure 4.11.

Methane concentrations and cumulative methane productions of mixed wastes with different TS contents were given in the following figures numbered as Figure 4.10 and 4.11, respectively.

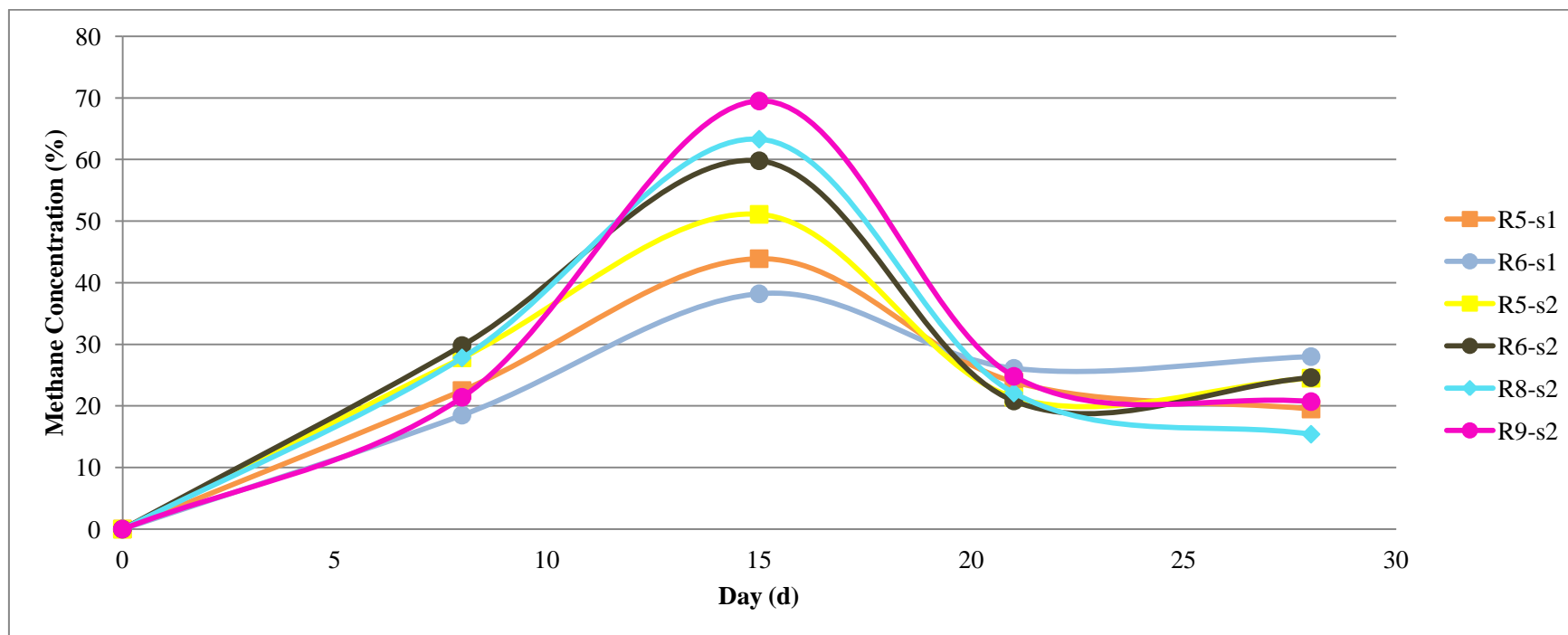


Figure 4.10. Methane concentration of mixed wastes.

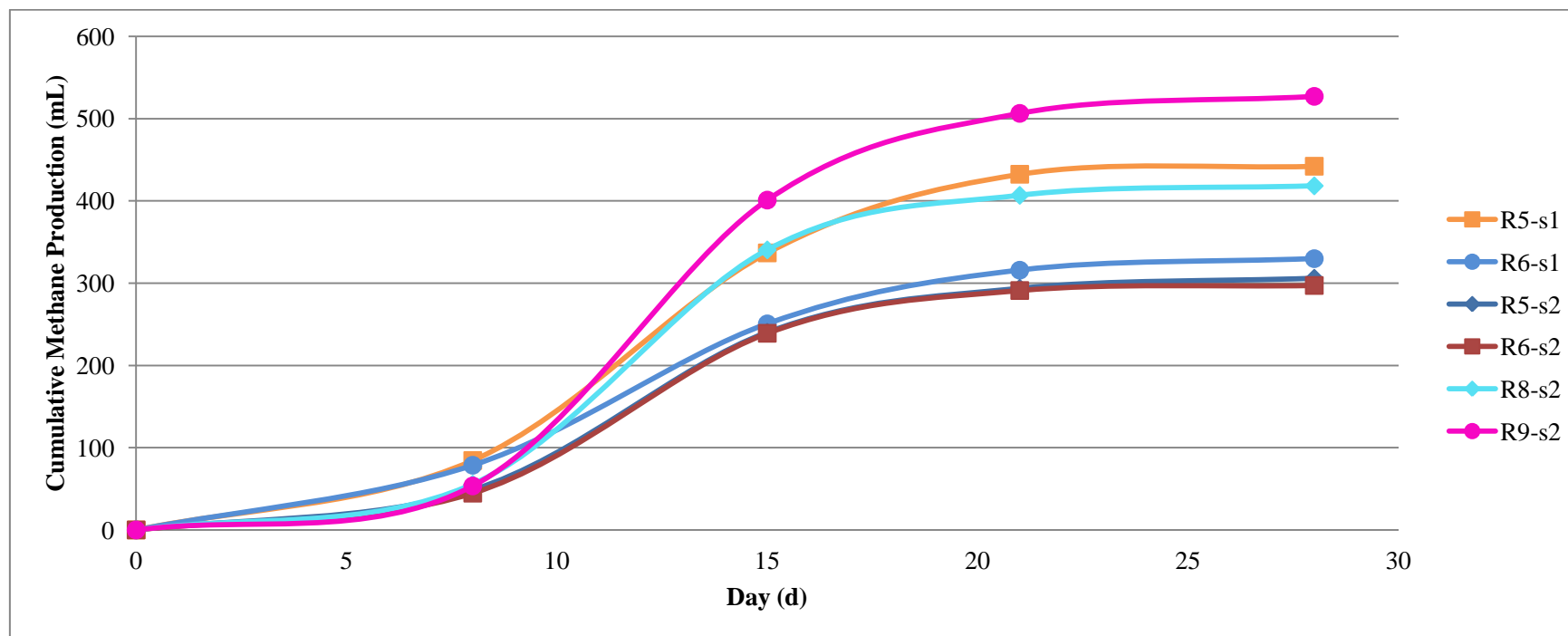


Figure 4.11. Cumulative methane production of mixed wastes.

Highest cumulative methane production was achieved by mixed waste with 10% TS concentration. Cumulative methane productions showed difference in parallel reactors. Moreover, cumulative methane productions of all Mixed Wastes with different TS ratios closed to each other (approximately 35-40%) although there were differences in gas and methane production.

Therefore, it would be wrong to say that gas and methane production would increase depending on the increase in TS concentration. Increase in TS concentration could accelerate the production of gas and methane, as it also could cause an inhibitory effect on AD above a certain value. High TS concentration could cause an inhibition effect on digestion process.

#### **4.4. Evaluation of the Study**

Supermarket waste types were operated in batch reactors to determine the individual biogas production potential. Also, different TS ratios (5%, 8% and 10%) of mixed wastes were operated for specifying the optimum biogas production. Ranade et al. (1990) studied the influence of different TS content of biogas production and reported that the optimum production was observed at 8% TS. Moreover, anaerobic batch digestion of mixed vegetable waste was also carried out successfully at 5 % TS concentration with 0.26 L/g VS according to Bouallagui et al. (2005). Therefore, this study was performed to obtain high biogas production from supermarket wastes with suitable TS ratios which were determined due to the performed studies.

Methane yield defines as the amount of methane produced for a given quantity of organic matter removed. The methane yields of anaerobic digestion were calculated by using the methane production and initial loading. The methane yield of reactors was given in Table 4.15.

Table 4.15. Cumulative methane yield.

SET -1			SET -2		
Reactor	VS added (g VS/L)	Methane Yield (L CH <sub>4</sub> /g VS)	Reactor	VS added (g VS/L)	Methane Yield (L CH <sub>4</sub> /g VS)
R1-s1	6.2	0.41	R1-s2	2.0	0.19
R2-s1		0.39	R2-s2		0.21
R3-s1	5.5	0.35	R3-s2	3.1	0.25
R4-s1		0.34	R4-s2		0.25
R5-s1	5.8	0.41	R5-s2	6.2	0.40
R6-s1		0.41	R6-s2		0.40
R7-s1	4.0	0.33	R7-s2	4.2	0.33
			R8-s2	6.2	0.42
			R9-s2		0.45

DPW and FVFW which were the raw substrates in supermarket wastes had the highest methane yield production potential. The lowest methane yield was recorded with 0.19 L CH<sub>4</sub>/g VS and 0.21 L CH<sub>4</sub>/g VS by SW. Mixed wastes yielded 0.41 L CH<sub>4</sub>/g VS on average after 28 days of digestion. The better performance of the mixture can partly be explained by a better nutritional composition. Obtained methane yield could be accelerated by increasing the amount of FVFW and DPW which yielded 0.40 and 0.34 L CH<sub>4</sub>/g VS on average, respectively.

The methane yield obtained in this study was comparable to the values reported in the literature. A methane yield of 0.47 L CH<sub>4</sub>/g VS was reported by Cho et al. (1995) during the digestion of municipal food waste at 37<sup>0</sup>C and 25 days. Also, Nordberg and Edström (2005) reported that a mixture of energy crops and organic waste reached a methane yield of 0.33-0.38 L/g VS with the loading rate of 6.0 g VS/L/d. Moreover, California Energy Commission reported that 0.42 and 0.44 L/g VS methane yields were obtained with a initial loading of 6.8 and 10.5 g VS/L of food waste (El-Mashad et al., 2005).

Furthermore, important observations which could affect the digestibility of substrates in the reactor carried out during the study. Foam forming on the surface of the batch reactors was recorded especially in R3-s2, R4-s1, R5-s1 and R6-s1 in Set 1 and R3-s2, R4-s2, R5-s2, R6-s2 and R9-s2 in Set 2. Also, there was the waste settlement in the bottom of the reactors which indicated the un-decomposed part of the substrates. Additionally, supermarket wastes had low pH values (acidic form). If buffer solution was not added to the reactors to stabilize the pH, biogas production could not be recorded because of the acid accumulation.

## 5. FEASIBILITY STUDY

Supermarket waste generation is rapidly increasing in Turkey and all over the world. This is going to start creating enormous waste disposal problems. On the other hand, an energy need of Turkey is becoming a serious problem similar to the rest of the world. Anaerobic digestion of supermarket wastes should be taking into consideration as an alternative renewable energy source since a substantial amount of supermarket waste is produced each year.

### 5.1. Studying the Biogas Plant Potential for Supermarket Waste

According to Turkey Statistical Agency, collected municipal solid wastes were determined as 34 million tons in 2004 (Turkish Court of Accounts, 2007). Any research that determines the quantity of waste sourced from supermarkets has not been operated in Turkey yet. Unfortunately, assumption is necessary for determining the biogas production potential of supermarket wastes. So, assuming that a supermarket chain produced approximately 10,000 ton waste/year according to the literature related to supermarket waste management, following feasibility study was calculated. Dry matter (DM), organic dry matter (ODM) and biogas potential of food wastes that were given in Biogas Guide were accepted for supermarket wastes in this study. Accepted values were given in Table 5.1 (DBFZ, 2010).

Table 5.1. Accepted supermarket waste properties (DBFZ, 2010).

Material	DM	ODM	Biogas Potential (Nm <sup>3</sup> /t ODM)
Supermarket Waste	16%	87%	680

Because using mixed wastes was more suitable in case of waste management for supermarkets, average methane content was calculated by considering the recorded methane contents of mixed waste with different TS ratios during the study. In order to

calculate the energy production of biogas plant, accepted parameters were given in Table 5.2.

Table 5.2. Energy values for biogas plants.

Parameter	Value	Unit
1 m <sup>3</sup> Biogas	0.65	m <sup>3</sup> methane
1 m <sup>3</sup> Methane	9.97	kW energy
1 Kw	860	kcal
1 year	8,760	hour
Annually Activating Ratio	92%	percentage
Electricity Production Efficiency of Cogeneration	42%	percentage
Thermal Efficiency of Cogeneration	46%	percentage
The Unit Price of Electricity	0.24	TL/kWh electric

Calculated biogas and methane production potential and electricity and heat production were given in Table 5.3 according to the accepted parameters and waste assumptions that were mentioned above.

Table 5.3. Feasibility study for supermarket wastes.

Feasibility Study for Supermarket Waste Biogas Plant	
Supermarket Waste	10,000 ton/year
Biogas Potential	946,560 m <sup>3</sup> /year
Methane Potential	615,264 m <sup>3</sup> /year
Electricity Production	2,370,248 kWh/year
Heat Production	2,426,682,431 kcal/year
Installed Power	294 kWe

Biogas and methane production potentials were calculated as 946,560 m<sup>3</sup>/year and 615,264 m<sup>3</sup>/year for a supermarket chain according to the results of methane production obtained from this study. Minimum 2,370,248 kWh/year electricity production could be obtained from biogas plant which digested 10,000 ton waste/year. Also, digestate that was obtained from biogas plant could be sold for fertilizer applications. Consequently, estimated installed power of that plant was determined as 294 kWe for Turkey.

The production of electricity, heat and natural gas from biomass was an environmentally and economically attractive option. A comprehensive biogas plant would provide these options. However, a biogas plant was a complex installation, consisting of a variety of elements. The layout of such a plant would depend on a large extent of the types and amounts of feedstock. Therefore, substrates which would be planning to use in biogas plants, should be analyzed and evaluated by the experts.

## **5.2. Using Digestate as a Fertilizer**

There has been a rapid development in the evaluation of biogas production after refreshing the Renewable Energy Law (EEG). Various regulations should be considered related to the production, processing and implementing on agricultural lands of fermentation waste in biogas plant. Because of the importance to evaluate these wastes, Germany has made some innovations in the Renewable Energy Law. According to these innovations, fermentation residues can be classified as organic-chemical fertilizers and farm manure depending on the used main materials (Dittrich, 2011).

In Turkey, current regulations and laws are not suitable for the application of digestate from biogas plant (Al Seadi et al., 2012). Regarding the solid manure management, the organic agriculture regulation could be applied to until it was revoked in 2004. It was indicated that total organic fertilizer amount must not exceed 170 kg/N/ha/year for organic herbal production. Also, there were tightness standards for the supply of manure storage areas. Unfortunately, the storage of digestate was not included in this regulation either.

Regulation regarding the production, importation and placing on the market of agricultural organic, organomineral fertilizers, soil regulators and other microbial product with enzyme content was officially announced in official Gazette with the number of 27601 on the 4<sup>th</sup> of June, 2010. Within this regulation some limitations were put regarding heavy metals and microorganisms as shown in Table 5.4. If the manure fulfills the limitations, it can be used as fertilizer directly (DBFZ, 2011).

Table 5.4. Limitations of parameters regarding to the regulation (Ministry of Agriculture and Rural Affairs, 2011).

<b>Limits of Heavy Metal</b>	<b>Unit</b>	<b>Value</b>
Cadmium, (Cd)	mg/kg or ppm	3
Copper, (Cu)	mg/kg or ppm	450
Nickel, (Ni)	mg/kg or ppm	120
Lead, (Pb)	mg/kg or ppm	150
Zinc, (Zn)	mg/kg or ppm	1100
Mercury, (Hg)	mg/kg or ppm	5
Chromium, (Cr)	mg/kg or ppm	270
<b>Health Parameters</b>	<b>Unit</b>	<b>Value</b>
Total coliform	kob/g or kob/ml	1.0x10 <sup>3</sup>
Total bacteria (Anaerobic, microaerophile)	cell/g	1.0x10 <sup>3</sup>
Total aerobic microorganisms	5cfu/ml	None
Enterobactericea	cfu/ml	< 3
Total lactose-positive bacteria	cfu/ml	< 1
Escherichia coli	-	None
Clostridium spp	5cfu/ml	< 2
Salmonella spp	-	None
Mycobacterium spp	-	None
Staphylococcus surcus	-	None
Bacillus anthracis	-	None
Bacillus cereus	-	None
Total fungi and yeast	cfu/ml	< 3

According to the results obtained in this study, observing that remaining materials after digestion had not included any harmful elements for fertilizer applications. Because the substrates were the type of food wastes, remaining wastes (digestate) had not contained heavy metals. Heavy metal analyses of digestate were given in the Table 5.5 for Set- 1 and Table 5.6 for Set- 2.

Table 5.5. The properties of digestate for Set- 1.

Reactors	Concentration (g/kg)					
	Cd	Ni	Zn	Cr	Pb	Cu
<b>Set-1</b>						
<b>R1</b>	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R2</b>	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R3</b>	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R4</b>	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R5</b>	<0.01	<0.01.	0.04	<0.01	n.d.	n.d.
<b>R6</b>	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R7</b>	0.01	0.01	0.01	<0.01	n.d.	n.d.

\*n.d.: not determined

Table 5.6. The properties of digestate for Set- 2.

Reactors	Concentration (g/kg)					
	Cd	Ni	Zn	Cr	Pb	Cu
<b>Set-2</b>						
<b>R1</b>	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R2</b>	<0.01	<0.01	0.01	<0.01	n.d.	n.d.
<b>R3</b>	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R4</b>	<0.01	<0.01	0.02	<0.01	n.d.	n.d.
<b>R5</b>	<0.01	<0.01.	0.04	<0.01.	n.d.	n.d.
<b>R6</b>	<0.01	<0.01	0.04	<0.01	n.d.	n.d.
<b>R7</b>	0.01	0.01	0.01	0.01	n.d.	n.d.
<b>R8</b>	<0.01	<0.01.	0.04	<0.01.	n.d.	n.d.
<b>R9</b>	<0.01	<0.01	0.04	<0.01	n.d.	n.d.

\*n.d.: not determined

When comparing the results of heavy metals both Set- 1 and Set- 2 with the given limits in Table 5.4, digestate had not contained any harmful effect for utilizing as a organic fertilizer according to the current regulations.

Since the regulation about the digestate is not enough, this poses a problem in terms of application in Turkey. As a result, the scope of the Fertilizer Regulation in EU should be designated under the regulations in Turkey. Because of the absence of Fertilizer Regulation in Turkey, the principles of EU directive should be considered in the fertilizer application. According to the regulation, some properties of digestate should be determined for evaluating as organic-chemical fertilizers and farm manure. These properties were listed in the following (Dittrich, 2011):

- Total solids
- Bacteria and microorganisms
- Total nitrogen (N)
- Ammonia nitrogen (NH<sub>4</sub>-N)
- Total phosphate (P<sub>2</sub>O<sub>5</sub>)
- Total potassium dioxide (K<sub>2</sub>O)
- Arsenic (Ar), lead (Pb), cadmium (Cd), zinc (Zn), copper (Cu), nickel (Ni), mercury (Hg)

## 6. CONCLUSIONS

Laboratory studies showed that anaerobic digestion of supermarket waste was a viable management option with its high biogas production potential. Also, anaerobic digestion was a feasible way to remove wastes. It would decrease the disposal costs and the environmental damages comparing the other disposal alternatives. According to European Union Waste Directive, disposal of organic wastes into landfills should be decreased and end until 2020 for European Union members. Therefore, Turkey defined annual targets related to the amount of landfilled organic waste in 2005. Goals, which were determined to decrease the total organic wastes to be landfilled, were gradually 75%, 50% and 35% decrease as weight of total organic wastes within 5, 8 and 15 years according to the waste amounts in 2005. Evaluating supermarket wastes in biogas plants would provide both reaching the goals related to the regulation, and also creating an energy source for Turkey. Studying biogas production potential of these wastes gains importance based on that information.

This study was shown that supermarket wastes had high biogas production potential. Waste types could be listed as follows FVFW, DPW, MW and SW depending on their digestibility. Also, cumulative gas production of mixture of those wastes was higher than each other's. Especially, the mixture of supermarket wastes presented more sustainable anaerobic digestion process depending on the better nutritional composition. In addition to those benefits of using supermarket wastes in a mixture form, that was also more suitable for supermarkets because it was hard to separate these wastes from each other at the source. Supermarkets would prefer to send these wastes to biogas plant in case of a mixture because this would provide cheaper and easier method for supermarket managers. Therefore, studying and determining the biogas production potential of supermarket wastes in a mixture form was very important in order to shed light on activities related to establishing biogas plant.

The batch reactors were designed and operated to simulate biogas process as controlled anaerobic reactors with sludge addition accelerating the microbial activity.

Based upon the experimental results during the study, the following conclusions were obtained.

1. The better gas production and methane yield was performed by mixed wastes depending on a better nutritional composition.
2. More than 55% methane produced from mixed wastes in anaerobic digestion.
3. Cumulative methane production of mixed wastes increased with increasing solid contents in reactors.
4. The highest cumulative biogas production was recorded as 9,525mL and 7,200mL for mixed wastes with the loading rate of 10% TS.
5. Substrates could be listed as Mixed Wastes, FVFW, DPW, SW and MW from the highest to the lowest in cumulative gas production.
6. Highest methane contents in biogas were recorded as 44%, 60% and 70% on average for mixed wastes with 5%, 8% and 10% TS ratios, respectively.
7. The better performance in methane yield was obtained from mixed wastes with 0.41, 0.40 and 0.43 L CH<sub>4</sub>/ g VS on average for 5%, 8% and 10% TS loading rates, respectively.
8. DPW and FVFW yielded the highest methane with 0.34 and 0.40 L CH<sub>4</sub>/ g VS on average in substrates not to consider the mixture form.
9. The lowest cumulative gas production was recorded approximately as 3,000mL for MW while the lowest methane yields were obtained from SW and MW with 0.20 L CH<sub>4</sub>/g VS and 0.25 L CH<sub>4</sub>/g VS on average, respectively.
10. The digestibility of substrates was determined as follows FVFW, DPW, MW and SW.
11. Daily gas production increased until day 16, and then began to decline slowly.
12. High ammonia concentrations were recorded in reactors in both Set-1 and Set-2 depending on the high protein content of supermarket wastes.
13. Zn concentrations were high in all reactors because it was naturally present in foods. However, Zn concentrations of reactors had not any inhibitory effect on digestion process.
14. The number of supermarket chains is increasing with more than 10% each year, so wastes sourced from supermarkets increases continuously. According to the results

of study, anaerobic digestion of supermarket wastes would be the best practice with energy production feature.

15. The results of the study proved that anaerobic digestion of these wastes could be the solution for the need of bioenergy and also the disposal in environmentally friendly way.

Consequently, supermarket wastes were landfilled into Municipal Solid Landfills in current situation. However, landfilling of these wastes was a waste of energy, so an alternative method should be submitted for the disposal of organic materials like supermarket wastes. Therefore, anaerobic digestion of supermarket wastes becomes an alternative method with features as obtaining feasible energy by enhancement of methane generation and reducing possible adverse effects of landfills. Moreover, using anaerobic digestion for supermarket waste reduces the need for landfill area and cost of it. Also, anaerobic digestion of supermarket waste produces waste heat and digestate which are marketable products. If sustainable management is adopted related to anaerobic digestion of supermarket waste, national energy sources would not be wasted.

## 7. RECOMMENDATIONS

The amount and type of supermarket wastes have increased gradually because of economic and social developments. Also, waste sourced from supermarkets is going to increase depending on the developing supermarkets' chains and numbers. So, sustainable management has become a major social and environmental concern in order to protect natural resources and ecology in the concept of waste management strategy. Supermarkets should be determined waste management strategies. Supermarket enterprises could benefit from energy production and digestate sales with the use of sustainable management.

After studying the biogas production potential of supermarket wastes, it seems necessary to improve and elaborate the anaerobic digestion process of various food fractions of supermarket wastes. Microbiological compositions of substrates could be searched in order to obtain better gas and methane concentrations by determining the bacterial content during the digestion period.

The study was also enlightened whether establishing biogas plant for supermarkets would be feasible from a financial, technical and environmental perspective to process organic waste. The necessity to build up a biogas plant for supermarket wastes could be observed especially considering the lack of waste disposal capacity, and potential increases in waste disposal costs, as well as the environmental impacts associated with transporting waste. Therefore, a feasibility study should be operated for determining the potential of supermarket wastes in Turkey.

The feasibility study could contain the following principle tasks:

1. Conduct a waste characterization analysis to determine the quantity and composition of material in the waste stream obtained from supermarkets.
2. Conduct a technology evaluation to determine which technologies would be best suited to recover organics in a technical and community perspective.

3. Conduct a financial assessment of the most promising technologies, and compare estimated costs to current disposal costs, or other off-site alternatives for composting waste.
4. Evaluate potential sites for locating a facility.

Also, there is a lack of regulations related to the use of biomass in energy producing plants and the implementation of by-products from these plants. This gap causes the inhibition of biogas technology developments in Turkey. Consequently, regarding the implementation of biogas in Turkey, following framework is necessary:

- manure management regulation
- energy targets regarding the biogas within an energy action plan
- favorable feed in tariffs (FiT) for biogas
- biowaste management with targets and/or with given utilization pathways

This study showed that there was a high energy production potential of supermarket wastes, so there was a need to accelerate studies and applications related to use of supermarket wastes in the concept of waste management strategy. Until a waste management strategy is adopted for supermarkets, highly biodegradable wastes will continue to be landfilled in a manner of energy loss.

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