BIOGAS PRODUCTION FROM OLIVE RESIDUE

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Approval of the Graduate School of Natural and Applied Scinces

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ABSTRACT

BIOGAS PRODUCTION FROM OLIVE RESIDUE

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Ph.D. in Food Engineering

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Anaerobic digestion is an effective process for the conversion of a solid organic waste into a gaseous fuel (biogas). The carbonaceous matter in the substrate waste is converted into biogas (mainly methane), leaving a digested slurry suitable for reapplication to the land as fertilizer. In this study, the residue remaining after extraction of olives (olive residue) was subjected to anaerobic digestion to generate a gaseous fuel, mostly methane.

The digestive fermentation was carried out in a fermentor of 1.5 L effective volume and in oven digesters of 1 L volume with the temperature maintained at 37 °C throughout the experiments. The runs were conducted as batchwise and semi-continuos and the biogas generation rates were determined by varying the total solid concentration and hydraulic retention time (HRT, in semi-continuous digestion). During batchwise digestion the total solid concentration was maintained at three different values: 5, 10, and 15 % dry solid (DS). In the semi-continuous digestion two sets of experiments were conducted: in the first one, the total solid concentration was held constant (10 % DS) while varying HRT (10,20,30, and 40 days); and in the second one, the total solid concentrations were varied (5, 10, and 15 % DS) at a constant HRT of 30 days. The biogas produced was analyzed daily and the gas mixture was observed to consist mainly of CH_4 and CO_2, the distribution being changed with time.

In the batchwise digestion, the maximum biogas production rate was determined to be 0.47 L (STP) per L digester volume per day at 10 % DS concentration with 80 % CH_4. In the case of semi-continuous digestion, the maximum biogas production rate and yield were determined as 0.69 (L/L digester volume. day) and 0.076 (L/L digester volume.g COD added, chemical oxygen demand), corresponding to a HRT of 20 days and 10 % DS substrate concentration. In these conditions the gas contained 81 % methane by volume and consequently the methane production rate and yield were calculated to be 0.55 (L/L digester volume.day) and 0.06 (L/L digester volume.g COD added) respectively.

The kinetic data obtained in the semi-continuous digestion of olive residue were fitted to an empirical equation obtained by a combination of the Monod and Contois rate expressions with a good correlation. Using this fit, the non-biodegradable matter in the olive residue and the optimum HRT were estimated to be 37 % of total COD and 15 days respectively.

Keywords: Olive residue, anaerobic digestion, methane, biogas production.

ÖZET

ZEYTİN KÜSPESİNDEN BİYOGAZ ÜRETİMİ

DALGIÇ, A. Coşkun

Doktora Tezi

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Anaerobik bozunma, katı atıkların gaz yakıt olan metana dönüştürülmesinde etkili bir işlemdir. Bu işlem, katı atık içindeki karbonlu maddeleri biyogaza (çoğunlukla metan) dönüştürür, geriye kalan kısım ise toprak için gübre olarak kullanılır. Bu çalışmada, yağı alınan zeytin atıkları biyogaz üretimi için anaerobik bozunma işlemine tabi tutulmuştur.

Deneyler, 37 ° 'deki sıvı hacmi 1.5 litre olan fermentör ile sıvı hacmi 1 litre olan inkübatör içerisindeki balonlarda gerçekleştirilmiştir. Çalışmalar kesikli ve yarı-kesikli olarak sürdürülmüş; katı madde miktarı ile alı konma süreleri değiştirilerek biyogaz oluşum hızı belirlenmiştir (HRT, alı konma süresi). Kesikli sistemde katı madde miktarı üç değişik değerde tutulmuştur (% 5, %, 10 ve 15 KM). Yarı kesikli sistemde iki farklı deney seti gerçekleştirilmiştir. Birinci sette, katı madde miktarı sabit tutularak (% 10) alı konma süreleri (10, 20, 30 ve 40 gün) değiştirilmiştir. İkinci sette ise, alı konma süresi (30 gün) sabit tutularak katı madde miktarları (% 5, 10 ve 15 KM) değiştirilmiştir. Üretilen biyogaz günlük olarak analiz edilmiş, ağırlıklı olarak CH_4 ve CO_2 içerdiği ve zamana göre değiştiği gözlemlenmiştir.

Kesikli sistemde en yüksek biyogaz üretim miktarının 0.47 (L (NŞA)/L reaktör.gün) olduğu ve % 80 CH_4 içerdiği belirlenmiştir. Yarı kesikli sistemde

ise, en yüksek günlük biyogaz üretimi ve verimliliği, alı konma süresi 20 gün ve katı madde miktarı % 10 olan deneyde, 0.69 (L/L reaktör. gün) ve 0.076 (L biyogaz/L reaktör.eklenen g KOİ, kimyasal oksijen ihtiyacı) olarak bulumuştur. Bu durumda biyogaz hacimsel olarak % 81 metan içermekte olup, en yüksek günlük metan üretim hızı ve verililiği 0.550 (L/gün) ve 0.06 (L/eklenen g KOİ) olduğu hesaplanmıştır.

Yarı kesikli sistemde elde edilen kinetik veriler Monod ve Contois eşitliklerinin bir bileşimi olan amprik denkleme uyarlanmıştır. Bu uyarlamada, zeytin küspesindeki biyolojik olarak tüketilemeyen madde miktarı ve en uygun alı konma süresi sırası ile toplam KOİ'nin % 37'si ve 15 gün olduğu bulunmuştur.

Anahtar Kelimeler : Zeytin Küspesi, havasız bozunma, metan, biyogaz üretimi.

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To my sun and wife,
Burak and Demet

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

X	Biomass concentration ($g.dm^{-3}$)
μ	Specific growth rate (day^{-1})
μ_m	Maximum specific growth rate (day^{-1})
S	Biodegradable substrate concentration in the effluent or in the digester ($g.dm^{-3}$)
S_{NB}	Non-biodegradable substrate concentration in the effluent or in the digester ($g.dm^{-3}$)
S_h	Concentration of hydrolyzed substrate ($g.dm^{-3}$)
S_u	Intracellular concentration of hydrolyzed substrate ($g.dm^{-3}$)
S_T	Total substrate concentration in the effluent ($g.dm^{-3}$)
S_{TO}	Total feed substrate concentration ($g.dm^{-3}$)
S_O	Input biodegradable substrate concentration ($g.dm^{-3}$)
k	Hydrolyzed substrate transport rate coefficient (day^{-1})
K_S	Limiting substrate concentration ($g.dm^{-3}$)
K	Kinetic parameter in Chen-Hashimoto equation
K_h	Substrate hydrolysis rate (day^{-1})
B	Empirical constant in Contois equation
A	Kinetic parameter
R	Refractory coefficient
M_v	Volumetric methane production rate (dm^3 of CH_4 $dm^{-3}day^{-1}$)
r_G	Volumetric methane production rate (dm^3 of CH_4 $dm^{-3}day^{-1}$)
γ_v	Volumetric methane production rate (dm^3 of CH_4 $dm^{-3}day^{-1}$)
Θ	Hydraulic retention time (days)
Θ_m	Minimum hydraulic retention time (days)
B	Specific methane yield (dm^3 of CH_4 $g^{-1}$of substrate added)
B_O	Maximum specific methane yield (dm^3 of CH_4 $g^{-1}$of substrate added at infinity Θ)
t	Time
COD	Chemical oxygen demand ($mg\ dm^{-3}$)
TS	Total solids ($g.dm^{-3}$)
VS	Volatile solids ($g.dm^{-3}$)
$-r_s$	Substrate uptake rate ($g\ COD\ dm^{-3}.day^{-1}$)
V_G	Volume of gas produced (dm^3)
K'	Kinetic parameter
K_1	Kinetic parameter
q	Volumetric feeding flow-rate (dm^3day^{-1})
V_r	Culture volume
c_i	Concentration of i^{th} component (moles of i. Unit culture volume^{-1})
r_{fi}	Production rate of I (moles of i formed by reaction . unit culture volume^{-1}.time^{-1})
D	Dilution rate (day^{-1})
F	Feeding rate (volume.time^{-1})
$\dot{F}$	Substrate utilization rate ($g.dm^{-3}.day^{-1}$)
$Y_{X/S}$	Yield factor (g biomass/g substrate)
$Y_{P/S}$	Yield coefficient (dm^3CH_4. g^{-1} substrate)
$Y_{P/X}$	Product yield coefficient (g product/g biomass)

HRT	Hydraulic retention time (day)
i	Asymptotic minimum
f	Asymptotic maximum
b	Coefficient
c	Center point
x_0	Center point for Logistic(4) model
p	Power
d	Time constant for Logistic model
λ	Lag time
TCD	Thermal conductivity detector

CHAPTER I

INTRODUCTION

Rapid industrialization and increase in population have increased the energy requirement in the world over the past decades. Due to the growing demand for energy together with the dwindling sources of fossil fuels, there is increasing interest in the production of fuels from renewable sources. The energy that can be obtained from renewable sources may be solar, biomass, geothermal, wind, and wave energies.

Anaerobic biogas production is a more developed and effective process for the conversion of a broad variety of biomass to methane to substitute natural gas and medium calorific value gases. This process takes place at low temperature and pressure, with relatively inexpensive and simple reactor designs and operating procedures. Anaerobic digestion converts carbon into gas and leaves a digested slurry in form suitable for reapplication to the land as fertilizers.

The digested slurry, obtained as a result of transformations during anaerobic digestion, has the following improved characteristics:

i. Reduced biological oxygen demand.
ii. Reduced problems of contaminating organisms growth on available organic residues.
iii. Favorable change in smell and eventual palatability.
iv. Strongly reduced pathogenic bacterial counts.
v. Increased fertilizer values in terms of nutritional elements.

The product gas from anaerobic digestion process is relatively clean and can be easily upgraded to pipeline quality. Therefore, anaerobic digestion process is an integrated approach that produces energy and fertilizer at the same time.

Common materials used for methane generation are often defined as "waste" materials, e.g., crop residues, animal wastes, and urban wastes

including night soil. Some of these materials are already used in developing countries as fuels and/or fertilizers.

Anaerobic digestion can be carried out in either batch or continuous reactors. Batch reactors, while less efficient, are preferred for smaller farm scale systems, since they are easier to operate, requiring less attention and less opportunity for exposure to oxygen. On the other hand, continuous reactors offer advantages such as lower labour requirements, constant gas output, better quality control, smaller reactors, etc. Frequent start-up and inoculation are also not required. However, the operation of continuous reactors is complex due to the need for continuous pumping of feed and effluent. This disadvantages can be alleviated by using semi-continuous reactors which can be fed only once per day or less frequently if desirable.

1.1. The Aim of This Study

An extensive literature survey showed that, no studies regarding to biogas production from solid olive residues were carried out. Turkey is one of the leading countries in the production of olives (640.000 tons per year). As a result, large quantities of olive residue (≈120.000 ton per year) are produced and this residue might be utilized more efficiently than using it directly as a fuel as it is the case in our country. Also an additional benefit can be obtained by utilizing the remaining waste (after fermentation) as a fertilizer. This study was, therefore, undertaken to fill this gap.

In the present study biogas will be produced from olive residue. Here the term "olive residue" stands for the solid remained after solvent extraction of the cold-pressed olives.

The principal objectives of this study are:

- Investigation of optimum culture source to produce methane from olive residue,
- Determination of optimum substrate concentration in batch reactors,
- Determination of the kinetic models to obtain the biological parameters of biogas production rate in batchwise digestion,

- Determination of the kinetics of methane production from anaerobic digestion of olive residue in semi-batch laboratory scale reactors,

CHAPTER II

RELATED LITERATURE

2.1. The Historical Development of Biogas Production

The fact that organic material, rotting under oxygen-free conditions, will produce methane has been known since the eighteen century when Volta identified methane in marsh gas [1]. The first recorded use of the gas as fuel was in 1895 when the gas collected from a specially designed septic tank was used for street lighting in the city of Exeter, England.

Small scale anaerobic digestion systems were also used to a limited extent on farms during the Second World War, notably in Germany and France. Methane was generated from manure and used to run tractors and other farm equipment. Apart from these relatively isolated cases, the interest in anaerobic digestion for energy production in the developed countries has been a fairly recent phenomenon. A considerable expansion in research activity has occurred in the last decade, covering all aspects of the process.

Interest in anaerobic digestion in the Third World began in India. The Indian Agricultural Research Institute developed the first "Gobar" (cow dung) gas plant in 1939. The Gobar Gas Research Station was formed in 1961 and with the encouragement of the Khadi and Village Industries Commission (KVIC) over 80 000 "biogas" digesters had been built, mostly standardized KVIC designs intended for individual families.

By far the largest current use of anaerobic digestion is in China. Since 1970, as many as 7 million biogas plants have been built, the majority of them in the populated and sparsely forested province of Sichuan (Szechuan) -where a quarter of the population now use biogas. Most of these are family-size unit, although some larger scale facilities also exist for handling waste from schools, hospitals, factories and various other sources.

Korea has also promoted the use of biogas digester, 24 000 digesters having been installed between 1969 and 1973. 7500 units are reported to be operating in Taiwan [1, 2].

2.2. Anaerobic Digestion

Anaerobic digestion is one of the oldest processes used for the stabilization of sludges. It involves the decomposition of organic and inorganic matter in the absence of molecular oxygen.

In the anaerobic digestion process, the organic material in mixture of primary settled and biological sludges is converted biologically, under anaerobic conditions, to variety of end products including methane (CH_4) and carbondioxide (CO_2). The process is carried out in an airtight reactor. Sludge, introduced continuously or intermittently, is retained in the reactor for varying periods of time. The stabilized sludge, withdrawn continuously or intermittently from the reactor, is reduced in organic and pathogen content and is nonputrescible [3, 4].

2.2.1. Process Microbiology

The biological conversion of the organic matter in treatment plant is thought to occur in three steps. (Figure 1.) The first step in the process involves the enzyme-mediated transformation (hydrolysis) of higher-molecular-mass compounds into compounds suitable for use as a source of energy and cell carbon. The second step (acitogenesis) involves the bacterial conversion of the intermediate compounds. The third step (methanogenesis) involves the bacterial conversion of the intermediate compounds into simpler end products, principally methane and carbon dioxide.

In the anaerobic decomposition of wastes, a number of anaerobic organisms work together to bring about the conversion of organic portion of the wastes to a stable end product. One group of organisms is responsible for hydrolyzing organic polymers and lipids to basic structural building blocks such as fatty acids, monosaccharides, amino acids, and related compounds.

A second group of anaerobic bacteria ferments the breakdown products from the first group to simple organic acids, the most common of which in anaerobic digestion is acetic acid. The second group of microorganisms, described as

nonmethanogenic, consist of facultative and obligate anaerobic bacteria that are often identified in the literature as acidogens or acid formers [5,6,7,8,9].

A third group of microorganisms converts the hydrogen and acetic acid formed by acid formers to methane and carbon dioxide. The bacteria responsible for this conversion are strict anaerobes, called methanogenic, and are identified in the literature as methanogens or methane formers. [3,4]

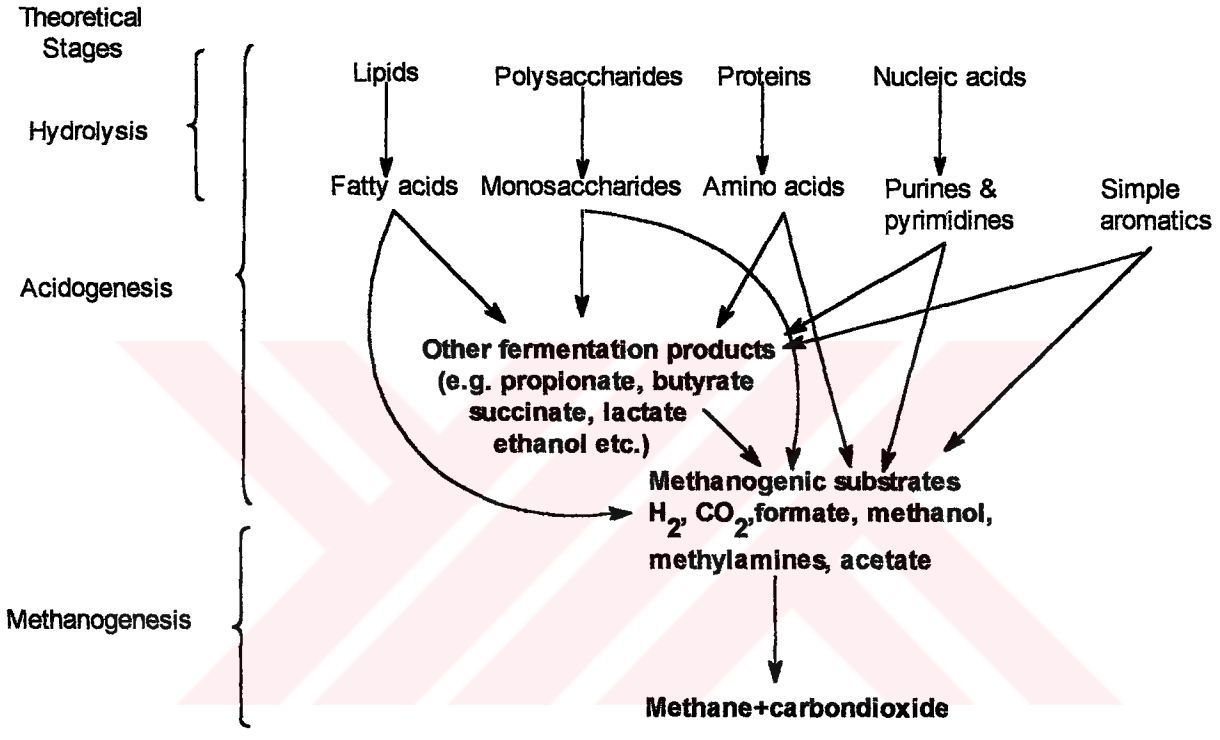

Figure 1. Pathways leading to the production of methane and carbon dioxide from the anaerobic digestion of the organic fraction of solid wastes [4].

2.2.1.1. Methane producing bacteria

Methane production is carried out by methanogenic bacteria which are anaerobes. A variety of morphological types of methanogenic bacteria have been isolated and studies of their physiology and molecular properties have served to classify methanogens into eight major groups containing a total of eighteen genera as shown in Table 1 [10,11].

Ten substrates have been shown to be able to produce methane by one or another methanogenic bacterium. Carbondioxide, CO_2, is a nearly universal substrate for methanogens, the needed electrons usually being derived from H_2. When growing on H_2+CO_2, the methanogens are autotrophic, with CO_2 serving as both carbon source and electron acceptor. In addition to CO_2, a variety of other compounds can be converted to methane by certain methanogenic species.

Table 1. Some Methanogenic bacteria and their substrates

Microorganisms	Substrates
Methanobacterium formicicium	H_2+CO_2, formate
Methanobrevibacter ruminantium	H_2+CO_2, formate
Methanosarcina barkeri	H_2+CO_2, formate, methanol, methylamines, acetate
Methanothrix soehgenii	acetate

Three classes of methanogenic substrates are known (Table 2.) and as expected, all are used with the release of free energy suitable for ATP synthesis [11,12]. The first involves the use of CO_2-type substrates:

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

$$4HCOOH \rightarrow CH_4 + 3CO_2 + 2H_2O$$

$$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$$

The second class of reaction involves reduction of the methyl group of methyl-containing compounds to methane. In the case of methanol or methylamine. The overall reaction to methane has the following stoichiometry:

$$4CH_3OH \rightarrow 3CH_4 + CO_2 + 2H_2O$$

$$4CH_3NH_3Cl + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4Cl$$

In these reactions some molecules of the substrate serve as electron donor and are oxidized to CO_2, whereas other molecules are reduced and serve as electron acceptor. In growth on methyl compounds the reducing power for methanogenesis

can also come from H_2. In fact, one species of methanogen, *Methanosphaera statmanae*, can grow only in the presence of H_2. In this case:

$$CH_3OH + H_2 \rightarrow CH_4 + H_2O$$

The final methanogenic reaction is acetoclastic, the cleavage of acetate to CH_4 plus CO_2 ;

$$CH_3COOH \rightarrow CH_4 + CO_2$$

Only three genera of mathanogens, *Methanosarcina, Methanosaeta,* and *Mathanothrix,* have representatives able to carry out the acetoclastic reaction.

Table 2. Substrate classification

CO_2-type substrates	CO_2+H_2 formate (HCOOH) CO
Methyl substrates	methanol CH_3OH methylamine $CH_3NH_3^+$ dimethylamine $(CH_3)_2NH_2^+$ trimethylamine $(CH_3)_3NH^+$ methylmercaptan CH_3SH dimethylsulfide $(CH_3)_2S$
Acetoclastic substrate	acetate CH_3COOH

2.2.1.2. Biochemistry of CO_2, reduction to CH_4

The reduction of CO_2 to CH_4 is generally H_2-dependent but formate, carbon monoxide, and even elemental iron (Fe^0) can serve as electron donors for methanogenesis. The reduction of CO_2 to CH_4 occurs via several intermediates. The steps in CO_2 reduction, shown in Figure 2. CO_2 is activated by methanofuran and subsequently reduced to the formyl level. The formyl group is transferred from methanofuran to tetrahydromethanopterin (MP) and subsequently dehydrated and reduced in two separate steps to methylene and methyl levels. The methyl group is transferred from methanopterin to coenzyme M. Methyl-coenzyme M is reduced toe

methane by methyl reductase system in which F_{430} and HS-HTP and the product of the reaction, beside CH_4, is disulfide of CoM and HTP (CoM-S-S-HTP). Free CoM and HS-HTP are regenerated by reduction with H_2.[11]

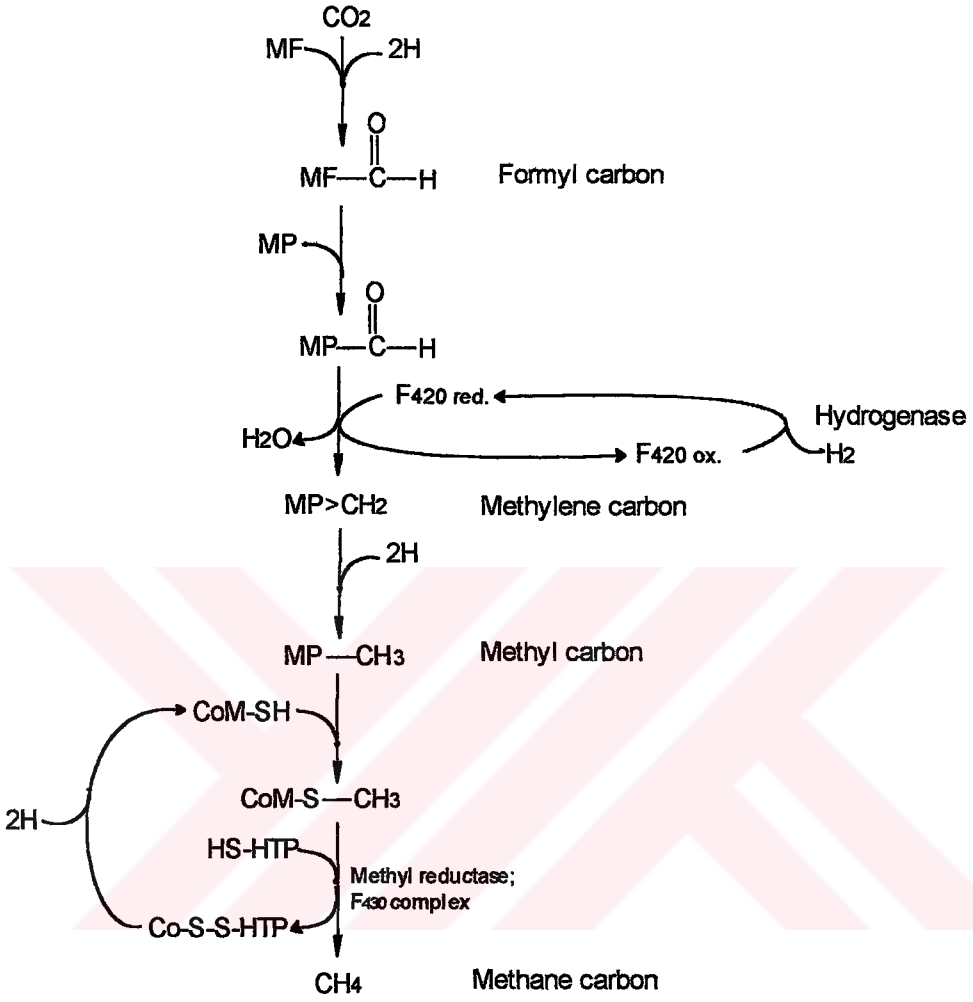

Figure 2. Pathway of methanogenesis from CO_2. Abbreviations: MF, methanofuran; MP, tetrahydromethanopterin; CoM, coenzyme M; F_{420}, coenzyme F_{420}; F_{430},coenzyme F_{430}; HS-HPT, 7-mercaptoheptanoylthreonine phosphate [11].

2.2.1.3. Methanogenesis from methyl compounds and acetate

Biochemical evidence suggests that methyl compounds such as methanol are catabolized by donating methyl groups to a vitamin B_{12} protein to form CH_3-B_{12}. The later donates the form of CH_3-CoM from which methane is obtained by reduction

with electrons derived from oxidation of other molecules of methanol to CO_2(Figure 3). Carbon for biosynthesis originates by formation of CO from the oxidation of a methyl group from methanol and the combination of CO and methyl group by carbon monoxide dehydrogenase to give acetate [11].

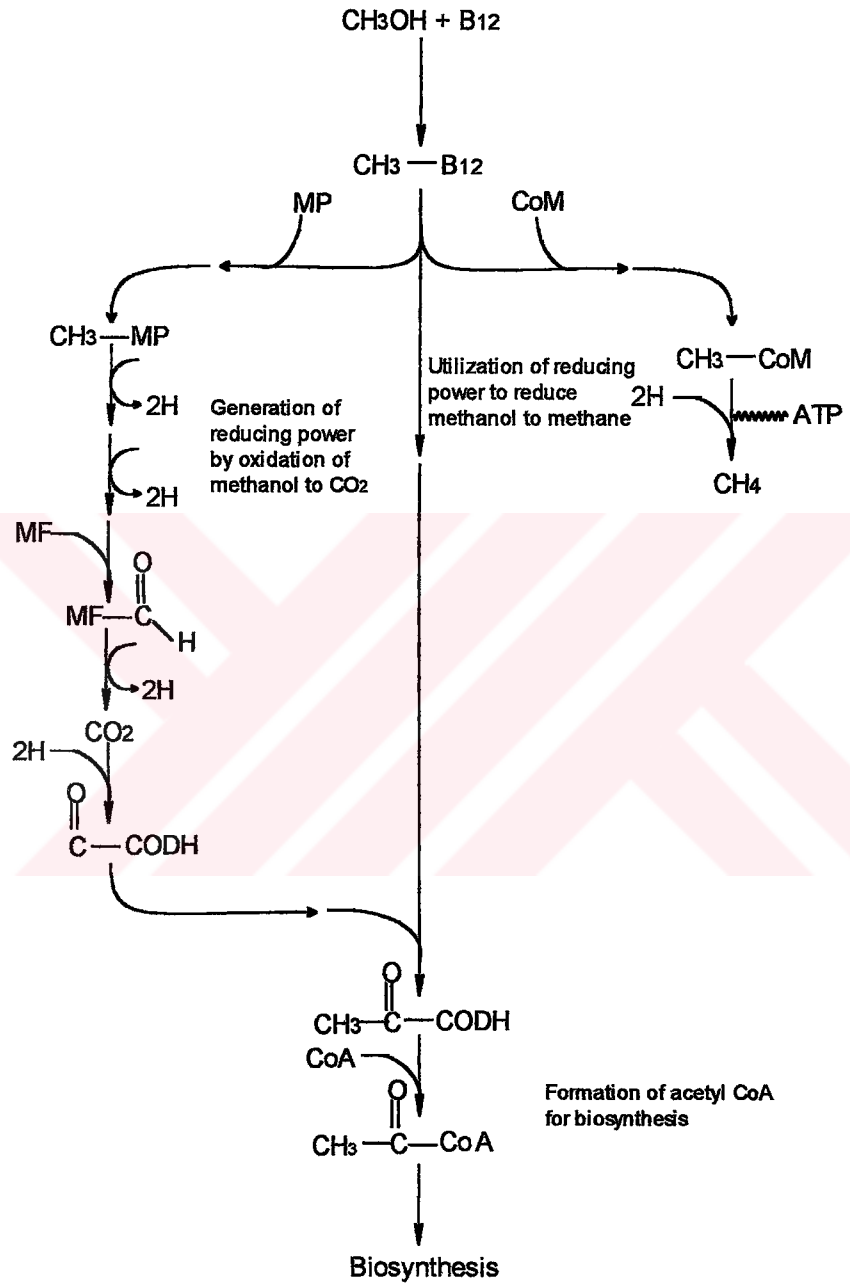

Figure 3. Utilization of reaction of the acetyl-CoA pathway during growth on methanol by methanogenic bacteria [11].

Growth of acetoclastic methanogens is also tied to reactions of the acetyl-CoA pathway. In acetoclastic methanogens acetate is used directly for biosynthesis. For energy purposes, acetate is also the energy source. Acetate is thought to be activated to acetyl-CoA which can interact with carbon monoxide dehydrogenase following which the methyl group of acetate is transferred to the vitamin-B_{12} enzyme of the acetyl-CoA pathway to yield CH_3-B_{12}(Figure 4.). From here the methyl group is transferred to tetrahydromethanopterin and then to coenzyme M to yield CH_3-CoM. The latter is then reduced to CH_4 using electrons generated from the oxidation of CO to CO_2 by CO dehydrogenase.

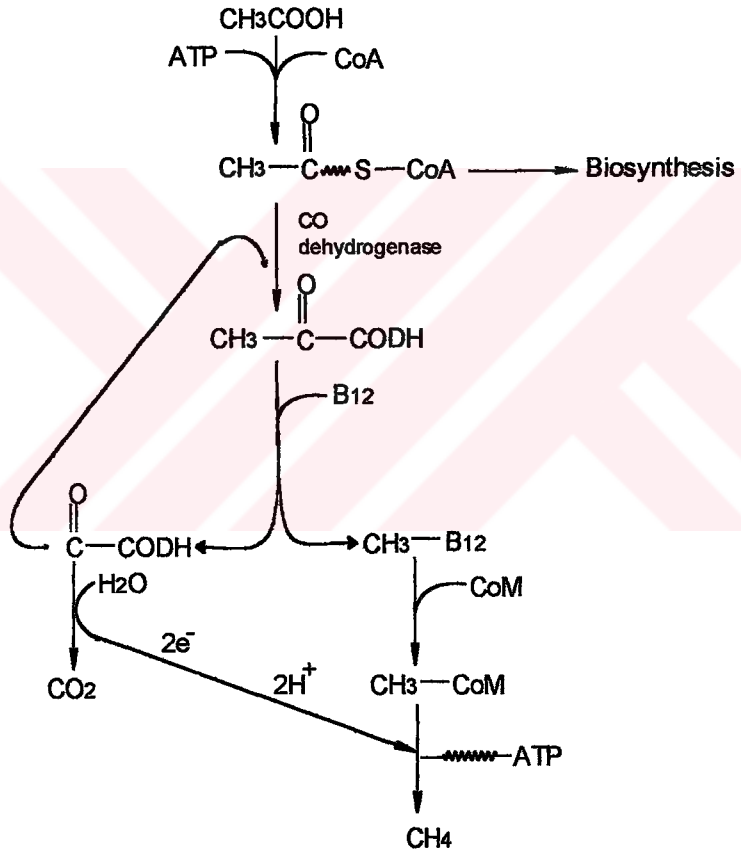

Figure 4. Utilization of reaction of the acetyl-CoA pathway during growth on acetate by methanogenic bacteria [11].

2.2.2. Parameters and process optimization

The metabolic activity involved in microbiological methanation is dependent on the following factors:

- Substrate temperature
- Available nutrients
- Retention time (flow-through time)
- pH level
- Nitrogen inhibition and C/N ratio
- Substrate solid content and agitation
- Inhibitory factors

Due to the fact that each of the various types of bacteria responsible for the three stages of the methanogenesis is affected differently by those parameters, and since interactive effects between the various determining factors are likely, no precise quantitative data on gas production as a function of those factors can be offered. Thus, discussion of the various factors is more or less limited to their respective qualitative effects on the process of fermentation.

2.2.2.1. Substrate temperature

Temperature range of anaerobic fermentation

Anaerobic fermentation requires an ambient temperature between 3°C and approximately 70°C. Differentiation is generally made between three temperature ranges. The psychrophilic temperature range lies below 20°C, the mesophilic between 20°C and 40°C and the thermophilic one above 40°C. [13,14,15]

Minimal average temperature

The biodigestive performance, i.e. the metabolic activity, of the bacteria, normally increases with temperature. Since, however, the amount of free ammonia also increases with temperature, the biodigestive performance could be inhibited or even reduced as a result. In general, a biogas dissemination is only feasible where mean annual temperatures amount to around 20°C or where the average daily temperature is at least 18°C. Within the range of 20-28°C gas production increases over-proportionately. If the temperatures are low, methanogenesis will slow down. If

the temperature of the biomass is below 15°C gas production will be so low that biogas plants are no longer worthwhile [16].

Changes in temperature

The process of biomethanation is very sensitive to changes in temperature. The degree of sensitivity, in turn, is dependent on the temperature range. Brief fluctuations not exceeding the following limits may be regarded as still uninhibitory with respect to the process of fermentation:

- psychrophilic: ± 2°C/h
- mesophilic: ± 1°C/h
- thermophilic: ± 0,5°C/h

The temperature fluctuations between day and night are no great problem for plants built underground since the temperature of the earth below a depth of one meter is practically constant. [17]

2.2.2.2. Available nutrients

In order to grow, bacteria need more than just a supply of organic substances as a source of carbon and energy. They also require certain nutrient salts (mineral nutrients). In addition to carbon, oxygen and hydrogen, the generation of biomass requires an adequate supply of nitrogen, sulfur, phosphorous, potassium, calcium, magnesium and a number of trace elements such as iron, manganese, molybdenum, zinc, cobalt, selenium, tungsten, nickel etc. "Normal" substrates such as agricultural residue or municipal sewage usually contain adequate amounts of the afore-mentioned elements. On the other hand, an excessive concentration of any individual substance usually has an inhibitory effect, so that tests or careful analyses are indicated on a case-by-case basis in order to determine which amount of which nutrients, if any, still need to be added. [6,17,18]

2.2.2.3. Retention time

Batch-type and continuous plants: The retention time can only be accurately defined in batch-type facilities. For continuous systems, the calculations are based on a mean retention time arrived at by dividing the digester volume by the daily influent rate. Depending on the vessel geometry, the means of mixing, etc., the effective

retention time may vary widely for the individual substrate constituents. Selection of a suitable retention time thus depends not only on the process temperature, but also on the type of substrate used.

Cost efficiency: Cost efficiency is normally the determining factor in the selection of a particular operating point within the context of the process parameters retention time - process temperature - substrate quality - volumetric load.

Substrate: For liquid manure undergoing fermentation in the mesophilic temperature range, the following approximate retention time values apply:

liquid cow manure: 20-30 days

liquid pig manure: 15-25 days

liquid chicken manure: 20-40 days

If the retention time is too short, the bacteria in the digester are "washed out" faster than they can reproduce, so that the fermentation practically comes to a standstill. This problem rarely occurs in agricultural biogas systems. [17,19]

Table 3 shows the effect of HRT on the methane production and effluent characteristics for some food wastes.

2.2.2.4. pH value

The methane-producing bacteria live best under neutral to slightly alkaline conditions. Once the process of fermentation has stabilized under anaerobic conditions, the pH will normally take on a value of between 7 and 8.5. Due to the buffer effect of carbon dioxide-bicarbonate (CO_2 - HCO_3-) and ammonia-ammonium (NH_3 - NH_4^+), the pH level is rarely taken as a measure of substrate acids and/or potential biogas yield. A digester containing a high volatile-acid concentration requires a somewhat higher-than-normal pH value. If the pH value drops below 6.2, the medium will have a toxic effect on the methanogenic bacteria. [6,18,27,28,29]

2.2.2.5. Nitrogen inhibition and C/N ratio

Nitrogen inhibition: All substrates contain nitrogen. For higher pH values, even a relatively low nitrogen concentration may inhibit the process of fermentation. Noticeable inhibition occurs at a nitrogen concentration of roughly 1700 mg

Table 3. The effect of HRT, on the methane production under anaerobic conditions for some food wastes

Food Waste	HRT (day)	T (°C)	Influent				Effluent				Methane		Ref.
			pH	TS	COD	VS	pH	TS	COD	VS	%	Yield	
Straw and manure	15	35	5.72	78	102.8	66	6.98	53.2	30.2	44.4	31.1	0.42	[13]
	10						6.72	45.9	32.1	38.5	37.4	0.73	
	8						6.98	52.6	28.8	40.8	40.0	0.88	
Manure	15	35	5.07	73.3	73.4	63.2	7.36	34.1	35.8	26.5	57.3	1.47	[13]
	10						7.29	35.9	36.8	28.4	54.6	1.81	
	8						6.99	39.3	46.3	31.9	48.5	1.56	
Palm oil	6-7	50						62.0	57.0		70.0		[20]
Wheat straw	15	55	7.2	50	59.33	35.32	7.3	48	20.0	21.0	31.2	0.49	[21]
	10						7.3	49.1	26.0	21.3	33.7	0.42	
	8						7.3	48.7	29.8	21.8	25	0.45	
Sun flower heads	15	55	6.8	20	21.32	13.54	7.0	18.48	17.08	10.54	62	0.18	[22]
	10						6.9	18.34	17.25	9.10	58	0.28	
	8						6.9	17.29	16.9	10.24	48	0.37	
Fruits and Vegetable	24	30	-	40	-	94.3	7.1	-	-	341*	61.2	0.82	[23]
	16						7.1	-	-	610*	51.1	1.09	
	8						4.6	-	-	6430*	22	0.62	
Biscuit and Chocolate	40	20 to 40	6.5	100		195*	6.7	-	-	480*	57	1.45	[24]
	30						5.3	-	-	9200*	42	0.78	
	20						4.8	-	-	-	-	-	
Olive mill wastewater	44.8	-	5.0	37.6	40	28	7.4	-	1.6	-	-	0.25	[25]
	22.4						7.3	-	2.4	-	-	0.47	
	11.2						7.4	-	3.5	-	-	0.87	
Olive mill wastewater	50	37	5.1	46	47.1	34.2	-	-	7.9	-	-	0.25	[26]
	12.5						-	-	15.8	-	-	0.80	
	5						-	-	39.3	-	-	0.50	

-The unit of TS, COD and VS is kg/m^3
*Volatile Fatty Acid (VFA mg/lt)
**Yield (m^3 methane/m^3 digester volume.day)

ammonium-nitrogen (NH_4-N) per liter substrate. Nonetheless, given enough time, the methanogens are capable of adapting to NH_4-N concentrations on the order of 5000-7000 mg/l substrate, the main prerequisite being that the ammonia (NH_3) level does not exceed 200-300 mg NH_3-N per liter substrate. The rate of ammonia dissociation in water depends on the process temperature and pH value of the substrate slurry.

C/N ratio: Microorganisms need both nitrogen and carbon for assimilation into their cell structures. Various experiments have shown that the metabolic activity of methanogenic bacteria can be optimized at a C/N ratio of approximately 8-20,

whereby the optimum point varies from case to case, depending on the nature of the substrate. [6,17,18]

2.2.2.6. Substrate solids content and agitation

Substrate solids content: The mobility of the methanogens within the substrate is gradually impaired by an increasing solids content, and the biogas yield may suffer as a result. However, reports of relatively high biogas yields from landfill material with a high solids content may be found in recent literature. No generally valid guidelines can be offered with regard to specific biogas production for any particular solids percentage.

Agitation: Many substrates and various modes of fermentation require some sort of substrate agitation or mixing in order to maintain process stability within the digester. The most important objectives of agitation are:

- removal of the metabolites produced by the methanogens (gas)
- mixing of fresh substrate and bacterial population (inoculation)
- preclusion of scum formation and sedimentation
- avoidance of pronounced temperature gradients within the digester
- provision of a uniform bacterial population density
- prevention of the formation of dead spaces that would reduce the effective fermentation volume.

In selecting or designing a suitable means of agitation, the following points should be considered:

1. The process involves a symbiotic relationship between various strains of bacteria, i.e. the metabolite from one species can serve as nutrition for the next species, etc. Whenever the bacterial community is disrupted, the process of fermentation will remain more or less unproductive until an equivalent new community is formed. Consequently, excessive or all-too-frequent mixing is usually detrimental to the process, and slow stirring is better than rapid agitation.
2. A thin layer of scum must not necessarily have an adverse effect on the process, as long as it does not grow thicker. For systems in which the digester is completely filled with substrate, so that any scum always remains sufficiently wet,

there is little or no danger that the extraction of gas could be impeded by the scum.

3. Some types of biogas systems can get along without any mechanical agitation at all. Such systems are usually operated either on substrates with such a high solid content, that no stratification occurs, or on substrates consisting primarily of solute substances.

Since the results of agitation and mixing are highly dependent on the substrate in use, it is not possible to arrive at a sufficiently uniform comparative evaluation of various mixing systems and/or intensity levels. Thus, each such system can only be designed on the basis of empirical data [17,21].

2.2.2.7. Inhibitory factors

The presence of heavy metals, antibiotics (Bacitracin, Flavomycin, Lasalocid, Monensin, Spiramycin, etc.) and detergents used in livestock husbandry can have an inhibitory effect on the process of biomethanation. The following table lists the limit concentrations (mg/l) for various inhibitors.

Table 4: Limiting concentrations for various inhibitors of biomethanation [17]

Substance	[mg/l]
Copper	10-250
Calcium	8000
Sodium	8000
Magnesium	3000
Nickel	100-1000
Zinc	350-1000
Chromium	200-2000
Sulfide (as Sulfur)	200
Cyanide	2

To maintain an anaerobic treatment system that will stabilize an organic waste efficiently, the nonmethanogenic and methanogenic bacteria must be in a state of dynamic equilibrium. To establish and maintain such a state, the reactor contents should be void of dissolved oxygen and free from inhibitory concentrations of free ammonia and such constituents as heavy metals and sulfides [17].

2.2.3. Raw Materials and Preparation

The Raw materials that can be considered as substrates for the methane-generating bioconversion process are naturally occuring organic materials, generally cellulosic in nature. The diverse nature of the potential row materials for methane generation is described in Table 5.

These fibrous materials may be residues that result from other uses or they may be harvested directly as substrates for the bioconversion process.

Table 5. Organic matter with potential for methane generation [17]

Crop Wastes	Sugar cane trash, weeds, corn and related crop stubble, straw, spoiled fodder
Wastes of animal origin	Cattle-shed wastes (dung, urine, litter), poultry litter, sheep and goat droppings, slaughterhouse wastes (blood, meet), fishery wastes, leather, wool wastes
Wastes of human origin	Feces, urine, refuse
By-products and wastes from agricultural-baseds industries	Oil cakes, bagasse, rice bran, tobacco wastes and seeds, wastes from fruit and vegetable processing, press-mud from sugar factories, tea waste, cotton dust from textile industries
Forest litter	Twings, bark, brances, leaves
Waste from aquatic growth	Marine algea, seaweeds, water hyacinths

Collection, Preparation and Storage: An important consideration in the generation of methane from agricultural and other wastes is the collection, preparation and storage of the raw materials to be used in the anaerobic digestion process. The collection and processing of raw materials depend on their nature. The quantities in which they are available may vary from country to country and from region to region within a country. Hence the method for collecting and handling the waste materials may vary.

Because of the diverses nature of the raw materials that can be used for methane generation, they can be solid, liquid, or semisolid in nature; thus, appropriate methods are needed for their processing and subsequent utilization for methane production.

Where the production of large quantities of methane is possible, due to the availability of large amounts of human, animal and agricultural wastes, the digester may be designed to receive wastes directly. In such situations it is common to use

equilibrating/mixing chambers ahead of the digester, to maintain control of the composition of feed stock. In situations where the raw material cannot be fed directly to the digester after collection, it may be stacked in a storage shed prepared for this purpose. It should be covered and not used for prolonged storage to avoid rotting and fly breeding in the manure pile. At the most, quantities that are sufficient for a 2-day loading of the digester should be stored in this way [6].

2.2.4. Characteristics of Biogas, Storage and Utilization

Pure methane is a colorless and odorless gas. It generally constitutes between 50 percent and 70 percent of the gas produced by anaerobic digestion. The other 30-50 percent is primarily carbon dioxide, with a small amount of hydrogen sulfide. Table 6 lists some of the important physical and chemical properties of methane.

Digester gas (biogas) burns with a blue flame and has a heat value ranging from about 22 000 to 26 000 kj/m^3 when its methane content ranges from 60 to 79 percent. It can be used directly in gas-burning appliances for heating, cooking, lighting, and refrigeration or as a fuel for internal-combustion engines having a compression ratio of 8:1 or greater.

Table 6. Selected Physical and Chemical Properties of Methane [6,30].

Chemical Formula	CH_4
Molecular Weight	16.042
Boiling Point at 760 mm	-161.49 °C
Freezing Point at 760 mm	-182.48 °C
Critical Pressure	673.1 psia
Critical Temperature	-82.5 °C
Specific gravity	
Liquid (-164 °C)	0.415
Gas (25 °C and 760 mm)	0.000658
Specific volume at 15.5 °C and 760 mm	1.47 l/g
Calorific value 15.5 °C and 760 mm	38 130.71 kJ/m^3
Flammability Limits	5 to 15 percent by volume
Ignition Temperature	650 °C
Combustion Equation	$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$

If the daily amount of available dung (fresh weight) is known, gas production will approximately correspond to the following values:

- 1 kg cattle dung 40 liters biogas

- 1 kg buffalo dung 30 liter biogas
- 1 kg pig dung 60 liter biogas
- 1 kg chicken droppings 70 liter biogas

If the live weight of all animals whose dung is put into the biogas plant is known, the daily gas production will correspond to the following values:

- cattle, buffalo and chickens: 1,5 liter biogas per day per 1 kg live weight
- pigs: 30 liters biogas per day per 1 kg weight

Table 7 lists the gas yields and methane contents for various substrates at the end of 10-20 day of hydraulic retention time (HRT) at a process temperature of roughly 30 °C [6,17].

Table 7. Gas yields and methane contents for various substrates.

Substrate	Gas yield (l/kg VS*)	Methane content (%)
Pig manure	340-550	65-70
Cow manure	90-310	65
Poultry droppings	310-620	60
Horse manure	200-300	
Sheep manure	90-310	
Barnyard dung	175-280	
Wheat straw	200-300	50-60
Rye straw	200-300	59
Barley straw	250-300	59
Oats straw	290-310	59
Corn straw	380-460	59
Rape straw	200	
Rice straw	170-280	
Rice seed coat	105	
Flax	360	59
Hemp	360	59
Grass	280-550	70
Elephant grass	430-560	60
Cane trash (bagasse)	165	
Broom	405	
Reed	170	
Clover	430-490	
Vegetables residue	330-360	
Potato tops/greens	280-490	
Field/sugar beet greens	400-500	
Sunflower leaves	300	59
Agricultural waste	310-430	60-70
Seeds	620	
Peanut shells	365	
Fallen leaves	210-290	58
Water hyacinth	375	
Algae	420-500	63
Sewage sludge	310-740	

VS = Total volatile solids, e.g. ca. 9% of total liquid manure mass for cows

2.2.4.1. Conditioning of Biogas

Sometimes the biogas must be treated/conditioned before utilization. The predominant forms of treatment aim at removing either water, hydrogen sulfide or carbon dioxide from the raw gas:

Reduction of the moisture content :The biogas is usually fully saturated with water vapor. This involves cooling the gas, e.g. by routing it through an underground pipe, so that the excess water vapor condenses out at the lower temperature. When the gas warms up again, its relative vapor content decreases. The "drying" of biogas is especially useful in connection with the use of dry gas meters, which otherwise would eventually fill up with condensed water.

Reduction of the hydrogen-sulfide content: The hydrogen sulfide in the biogas combines with condensate to form corrosive acids. Water-heating appliances and utensils and refrigerators are particularly at risk. The reduction of the hydrogen sulfide content may be necessary if the biogas is found to contain an excessive amount, i.e. more than 2% H_2S, and is to be used for fueling an engine. Since, however, most biogas contains less than 1% H_2S, desulfurization is normally not necessary, especially if it is to be used for operating a stationary engine.

For small-to-midsize systems, desulfurization can be affected by absorption onto ferric hydrate ($Fe(OH)_3$), also referred to as bog iron, a porous form of limonite. The porous, granular purifying mass can be regenerated by exposure to air.

The absorptive capacity of the purifying mass depends on its iron-hydrate content: bog iron containing 5-10% $Fe(OH)_3$ can absorb about 15 g sulfur per kg without being regenerated and approximately 150 g/kg through repetitive regeneration. It is a very noteworthy fact that many types of tropical soil (laterites) are naturally ferriferous and, hence, suitable for use as purifying mass.

Reduction of the carbon-dioxide content : The reduction of the carbon-dioxide content is very complicated and expensive. In principle, carbon-dioxide can be removed by absorption onto lime milk, but that practice produces "seas" of lime paste and must therefore be ruled out, particularly in connection with large-scale

plants, for which only high-tech processes like microscreening are worthy of consideration. CO_2 "scrubbing" is rarely advisable, except in order to increase the individual bottling capacity for high-pressure storage [6,17].

2.2.4.2. Biogas Appliances

Biogas is a clean gas that can, in principle, be used like other fuel gas for household and industrial purposes, especially for:

- Gas cookers/stoves
- Biogas lamps
- Radiant heaters
- Incubators
- Refrigerators
- Engines

Biogas Burners

The main prerequisite of biogas utilization is the availability of specially designed biogas burners or modified consumer appliances. The relatively large differences in gas quality from different plants, and even from one and the same plant (gas pressure, temperature, caloric value, etc.) must be given due consideration.

The heart of any gas appliance is the burner. In most cases, atmospheric-type burners operating on premixed air/gas fuel are considered preferable. Due to complex conditions of flow and reaction kinetics, gas burners defy precise calculation, so that the final design and adjustments must be arrived at experimentally. Compared to other gases, biogas needs less air per cubic meter for combustion. This means, with the same amount of air more gas is required. Therefore, gas jets are larger in diameter when using biogas. About 5.7 liter of air are required for total combustion of one liter biogas, while for butane it is 30.97 liters and for propane 23.82 liters.

Accordingly, the modification and adaptation of commercial-type burners is an experimental matter. With regard to butane and propane burners, i.e. the most readily available types, the following pointers are offered:

Butane/propane gas has up to three times the caloric value of biogas and almost twice its flame-propagation rate. Conversion to biogas always results in lower performance values.

Practical modification measures include:

- expanding the injector cross section by a factor of 2-4 in order to increase the flow of gas
- modifying the combustion-air supply, particularly if a combustion-air controller is provided
- increasing the size of the jet openings (avoid if possible)

The aim of all such measures is to obtain a stable, compact, slightly bluish flame.

Efficiency : The efficiency of using biogas is 55% in stoves, 24% in engines, but only 3% in lamps. A biogas lamp is only half that efficient than a kerosene lamp. The most efficient way of using biogas is in a heat-power combination where 88% efficiency can be reached. But this is only valid for larger installations and under the condition that the exhaust heat is used profitably. The use of biogas in stoves is the best way of exploiting the energy of farm household units.

Gas demand : The household demand for energy is greatly influenced by eating and cooking habits. Gas demand for cooking is lower in regions where e.g. preserved vegetables are eaten with white bread or millet soaked in milk than in areas where rice or beans are part of daily nourishment. For the utilization of biogas the following consumption rates in liter per hour (l/h) can be assumed:

- household burners: 200-450 l/h
- industrial burners: 1000-3000 l/h
- refrigerator 100 l (depending on outside temperature): 30-75 l/h
- gas lamp, equiv. to 60 W bulb: 120-150 l/h
- biogas / diesel engine per bhp: 420 l/h
- generation of 1 kWh of electricity with biogas/diesel mixture: 700 l/h
- plastics moulding press (15 g, 100 units) with biogas/diesel mixture: 140 l/h

The gas consumption for cooking per person and meal lies between 150 and 300 liter per day, the gas consumption per 5-member family for 2 cooked meals between 1500 and 2400 liter per day [6,17].

2.2.5. Residue: Importance and Utilization

Many reports has been written on methane production and the reduction and stabilization from various kinds of animal, crop-residue, and food-processing wastes by anaerobic digestion. However, characterization and utilization of residue after biogas production are very important. The sludge produced by anaerobic digestion may have a fertilizer value greater than that of the original raw waste [6,17].

2.2.5.1. Organic substances in fertilizers

While there are suitable inorganic substitutes for the nutrients nitrogen, potash and phosphorous from organic fertilizer, there is no substitute at all for other organic substances such as protein, cellulose, lignin, etc., which all contribute to increasing a soil's permeability and hygroscopicity while preventing erosion and improving agricultural conditions in general. Organic substances also constitute the basis for the development of the microorganisms responsible for converting soil nutrients into a form that can be readily incorporated by plants.

2.2.5.2. Nutrients and soil organisms

Due to the decomposition and breakdown of parts of its organic content, digested sludge provides fast-acting nutrients that quickly enter into the soil solution, thus becoming immediately available to the plants while simultaneously serving as primary nutrients for the development of soil organisms, e.g. the replenishment of microorganisms lost through exposure to air in the course of spreading the sludge over the fields, as well as for the actinomycetes (ray fungi) that act as organic digesting specialists in the digested sludge. (Preconditions: adequate aeration and moderate moisture.)

2.2.5.3. Reduction of soil erosion

The humic matter and humic acids present in the sludge contribute to a more rapid humification, which in turn helps reduce the rate of erosion (due to rain and

dry scatter) while increasing the nutrient supply, hygroscopicity, etc. The humic content is especially important in low-humus tropical soils. The relatively high proportion of stable organic building blocks such as lignin and certain cellulose compounds contributes to an unusually high formation rate of stable humus (particularly in the presence of argillaceous matter). The amount of stable humus formed with digested sludge amounts to twice the amount that can be achieved with decayed dung. It has also been shown that earthworm activity is stimulated more by fertilizing with sludge than with barnyard dung. Digested sludge decelerated the irreversible bonding of soil nutrients with the aid of its ion-exchanger contents in combination with the formation of organomineral compounds. At the same time, the buffering capacity of the soil increases, and temperature fluctuations are better compensated.

2.2.5.4. Reduction of nitrogen washout

The elevated ammonium content of digested sludge helps reduce the rate of nitrogen washout as compared to fertilizers containing substantial amounts of more water-soluble nitrates and nitrites (dung, compost). Soil nitrogen in nitrate or nitrite form is also subject to higher denitrification losses than is ammonium, which first requires nitrification in order to assume a denitrificable form. It takes longer for ammonium to seep into deeper soil strata, in part because it is more easily adsorbed by argillaceous bonds. However, some of the ammonium becomes fixed in a noninterchangeable form in the intermediate layers of clay minerals. All things considered, it may be regarded as a proven fact, that ammonium constitutes the more valuable form of nitrogen for plant nutrition. Comparative, nutritive-quality investigations between ammonium and nitrate yielded similar results. Certainly, the N-efficiency of digested sludge may be regarded as comparable to that of chemical fertilizers.

In addition to supplying nutrients, sludge also improves soil quality by providing organic mass. The porosity, pore-size distribution and stability of soil aggregates are becoming increasingly important as standards of evaluation in soil-quality analyses.

2.2.5.5. Effects on crops and fruits

Crop yields are generally acknowledged to be higher following fertilization with digested sludge. Most vegetable crops such as potatoes, radishes, carrots, cabbage, onions, garlic, etc., and many types of fruit (oranges, apples, guavas, mangos, etc.), sugar cane, rice and jute appear to react favorably to sludge fertilization.

By contrast, crops such as wheat, oilseed, cotton and baccra react less favorably. Sludge is a good fertilizer for pastures and meadows. The available data vary widely, because the fertilizing effect is not only plant-specific, but also dependent on the climate and type of soil. Information is still extensively lacking on the degree of reciprocity between soil fertility, type of soil and the effect of fertilizers (particularly N-fertilizers) in arid and semi-arid climates. Thus, once again, no definitive information can be offered to date. Nor, for the same reason, it is possible to offer an economic comparison of the cost of chemical fertilizers vs. biogas sludge. About the only undisputed fact that can be stated is that biogas sludge is better from an ecological standpoint. [6,17]

2.2.6. Economic Feasibility of Methane Production

The economic feasibility of methane production from wastes may vary widely. It is dependent on factors that include the availability of domestic sources of energy, the cost of imported fuel, the uses and actual benefits from methane production, public and private costs associated with the development and utilization of methane, and on the technology used to produce methane [31,32].

Categories of costs

As far as costs are concerned there are three major categories:

- manufacturing or acquisition costs (production costs)
- operation and maintenance costs (running costs)
- capital costs

2.2.6.1. Production costs

The manufacturing costs include everything which is necessary for the erection of the plant e.g.: the land, excavation-work, construction of the digestor, of the gasholder, of the lines, of the gas utilization system, of the dung storage system and out-buildings. The construction costs comprise wages and material.

The production costs of biogas plants are determined by the following factors:

- land needed
- model
- size
- amount of material and cost
- labor input and wages
- density of buildings
- the proportion of investor participation.

The production costs obviously vary according to local conditions.

2.2.6.2. Running costs

The operation and maintenance costs consist of wage and material cost for:

- acquisition (collection and transportation) of the substrate
- water supply
- feeding and operation of the plant
- supervision, maintenance and repair of the plant
- storage and disposal of biodung
- gas distribution and utilization
- administration

The running costs of a biogas plant with a professional management are just as important as the construction costs, for example for operation, maintenance, outlays for painting, service and repair.

2.2.6.3. Capital costs

Capital costs consist of redemption and interest for the capital taken up to finance the construction costs. For dynamic cost comparison the capital fixed in the plant is converted into equal annual amounts.

Interest rate

The capital cost, part from the depreciation rates or length of amortization, is dependent on the interest rate at which the capital is provided. In each case current interest rates are to be laid down for the cost calculation, which reflect the opportunity costs of the invested capital. To avoid distortions of the financing costs the comparisons should always be calculated with the same interest rate.

Lifetime of plants

In calculating the depreciation the economic lifetime of plants can be taken as 15 years. Providing maintenance and repair are duly carried out regularly. Certain parts of the plant have to be replaced after 8 - 10 years, e.g. the gas holder (steel). The steel parts need to be repainted every year, in exceptions every two years. As a rule real prices and interest rates should be used in the calculations. For cost calculation inflation rates are irrelevant as long as construction costs refer to one point of time. However, in calculating the reserves put by for constant servicing and repair the inflation rate should be considered.

Table 8. Major Cost Factors in Methane Production and Utilization Processes.

Cost associated with Processing	Public cost	Costs to user
1. Installation costs Capital Labor 2. Annual costs Maintenance Labor	1. Demonstration facilities 2. Sharing arrangements for installation costs 3. Technical assistance	1. Share of installation 2. Annual costs
Gas Utilization Costs	Collection and Transportation Costs	Residue Costs
1. Storage 2. Distribution system 3. Adaptation of existing equipment to use of methane as fuel 4. Purchase of additional equipment adapted to use methane as fuel	1. Labor 2. Equipment for transport 3. Raw material (if purchased)	1. Labor 2. Transportation to storage site 3. Storage 4. Transportation to utilization site

Methane production and utilization involves collection, transportation, processing, storage of product and residue, and utilization process. A feasibility study for methane production must include the entire production and utilization system, involving all these process; capital and labor requirements and annual costs must be determined for all processes and must be related to local material, labor, and price conditions. The major cost factors to be considered are summarized in Table 8 [6].

2.2.7. Biogas - Digester Types

The following, most important types of biogas plants are described here:

- Fixed-dome plants
- Floating-drum plants
- Balloon plants
- Horizontal plants
- Earth-pit plants
- Ferrocement plants

Of these, the two most familiar types are the fixed-dome plants and the floating-drum plants [17,33].

2.2.7.1. Fixed-dome plants

History: Fixed-dome plants are an appropriate technology for developing countries, specially for rural areas. They can, nevertheless, in certain dimensions also be used for agroindustrial and communal wastewater treatment. In the beginning, fixed-dome plants were mainly built in the People's Republic of China, but are now spread in several countries.

Function: A fixed-dome plant comprises a closed, dome-shaped digester with an immovable, rigid gas holder and a displacement pit. The gas is stored in the upper part of the digester. When gas production commences, the slurry is displaced into the compensating tank. Gas pressure increases with the volume of gas stored. If there is little gas in the holder, the gas pressure is low.

Digester: The digesters of fixed-dome plants are usually made of masonry. They produce just as much gas as floating-drum plants, but only if they are gas tight. However, utilization of the gas is less effective as the gas pressure fluctuates substantially. Burners cannot be set optimally. If the gas is required at constant pressure (e.g., for engines), a gas pressure regulator or a floating gasholder is necessary. Engines require a great deal of gas, and hence large gas holders. The gas pressure then becomes too high if there is no floating gasholder.

Gas tightness: The top part of a fixed-dome plant (the gas space) must be gas tight. Concrete, masonry and cement rendering are not gas tight. The gas space

must therefore be painted with a gas tight product (for example Latex or synthetic paints). Another possibility to reduce the risk of cracking consists in the construction of a weak-ring in the masonry of the digester. This "ring" is a flexible joint between one lower and one upper part of the hemispherical wall.

Substrate: Fixed-dome plants can handle fibrous substances in combination with animal excrements, since the motion of the substrate breaks up the scum each day.

Climate and size: Fixed-dome plants must be covered with earth up to the top of the gas-filled space as a precautionary measure (internal pressure up to 0,1-0,15 bar). The earth cover makes them suitable for colder climates, and they can be heated as necessary. Due to economic parameters, the recommended minimum size of a fixed-dome plant is 5 m^3. Digester volumes up to 200 m^3 are known and possible.

2.2.7.2. Floating-drum plants

The drum In the past, floating-drum plants were mainly built in India. A floating-drum plant consists of a cylindrical or dome-shaped digester and a moving, floating gasholder, or drum. The gasholder floats either directly on the fermentation slurry or in a water jacket of its own. The drum in which the biogas collects has an internal and external guide frame that provides stability and keeps the drum upright. The gas drum is prevented from tilting. If gas is drawn off, the gasholder falls again.

Size: Floating-drum plants are used chiefly for digesting animal and human excrements on a continuos-feed mode of operation, i.e. with daily input. They are used most frequently by small-to-midsize family farms (digester size: 5-15m^3) or institutions and large agroindustrial estates (digester size: 20-100m^3).

2.2.7.3. Balloon plants

A balloon plant consists of a heat sealed plastic or rubber digester bag (balloon), in the upper part of which the gas is stored. The inlet and outlet are attached direct to the skin of the balloon. The requisite gas pressure is achieved by weighting down the bag. When the gas space is full, the plant works like a fixed-dome plant- i.e., the balloon is not inflated; it is not very elastic. Since the material

has to be weather-resistant, specially stabilized, reinforced plastic or synthetic caoutchouc is given preference. The useful life amounts to 2-5 years.

The fermentation slurry is agitated slightly by the movement of the balloon skin. This is favorable to the digestion process. Even difficult feed materials, such as water hyacinths, can be used in balloon plant. The balloon material must be UV-resistant. Materials which have been used successfully include RMP (red mud plastic), Trevira and butyl.

2.2.7.4. Horizontal plants

Horizontal biogas plants are usually chosen when shallow installation is called for (groundwater, rock). They are made of masonry or concrete.

2.2.7.5. Earth-pit plants

Masonry digesters are not necessary in stable soil. It is sufficient to line the pit with a thin layer of cement (netting wire fixed to the pit wall and rendered) in order to prevent seepage. The edge of the pit is reinforced with a ring of masonry that also serves as anchorage for the gasholder. The gasholder can be made of metal or plastic sheeting. If plastic sheeting is used, it must be attached to a quadratic wooden frame that extends down into the slurry and is anchored in place to counter ist buoyancy. The requisite gas pressure is achieved by placing weights on the gasholder. An overflow point in the peripheral wall serves as the slurry outlet.

2.2.7.6. Ferrocement plants

The ferrocement type of construction can be executed as either a self-supporting shell or an earth-pit lining. The vessel is usually cylindrical. Very small plants (Volume under 6 m^3) can be prefabricated. As in the case of a fixed-dome plant, the ferrocement gasholder requires special sealing measures (provenly reliable: cemented-on aluminum foil).

2.2.8. Parts of Biogas Plants

The parts of biogas plants are:

- Influent collecting tank
- Inlet and outlet
- Digester
- Gas holders
- Gas pipe, valves and accessories
- Stirring facilities
- Heating systems
- Pumps

2.2.8.1.Influent collecting tank

Fresh substrate is usually gathered in an influent collecting tank prior to being fed into the digester. Depending on the type of system, the tank should hold one to two days worth of feed stock. An influent collecting tank can also be used to homogenize the various substrates and to set up the required consistency, e.g. by adding water to dilute the mixture of vegetable solids (straw, grass,etc.), or by adding more solids in order to increase the biomass. The fibrous material is raked off the surface, and any stones or sand settling to the bottom are cleaned out after the slurry is admitted to the digester. The desired degree of homogenization and reduction of the solids content can be achieved with the aid of an agitator or pump. A rock or wooden plug can be used to close off the inlet pipe during the mixing process.

2.2.8.2. Inlet and outlet

Size and material: The inlet (feed) and outlet (discharge) pipes lead straight into the digester at a steep angle. For liquid substrate, the pipe diameter should be 10-15 cm, while fibrous substrate requires a diameter of 20-30 cm. The inlet and the outlet pipe mostly consist of plastic or concrete.

Both the inlet and the outlet pipe must be freely accessible and straight, so that a rod can be pushed through to eliminate obstructions and agitate the digester contents. The pipes should penetrate the digester wall at a point below the slurry level. The points of penetration should be sealed off and reinforced with mortar.

Position of inlet and outlet: The inlet pipe end should be higher than the outlet pipe in the digester in order to promote more uniform through flow. In an fixed-dome plant, the inlet pipe defines the bottom limit of the gasholder, thus providing over pressure relief. In a floating-drum plant, the end of the outlet pipe determines the digester's slurry level.

Construction: Inlet and outlet pipe must be placed in connection with brick-laying. It is not possible to break holes later into the spherical shell; this would spoil the whole structure.

2.2.8.3. Digester

Requirements: No matter what mode of operation is used, the digester (fermentation tank) must meet the following requirements[33,34,35,36]:

- Water/gas tightness - water tightness in order to prevent seepage and the resultant jeopardization of soil and groundwater quality; gas tightness in order to ensure proper containment of the entire biogas yield and to prevent the ingress of air into the digester (which could lead to the formation of an explosive mixture).
- Insulation - if and to which extent depending on the process temperature and the local climate; heat loss should be minimized.
- Minimum surface area - keeps cost of construction to a minimum and reduce heat losses through the vessel walls.
- Structural stability - sufficient to withstand all static and dynamic loads, durable and resistant to corrosion.

Internal and external forces: There exist two forces which act on the digester. The external active earth pressure causes compressive forces within the masonry. The internal hydrostatic and gas pressures causes tensile stress in the masonry. Thus, the external pressure applied by the surrounding earth must be greater at all points than the internal forces. Round and spherical shapes are able to accept the highest forces - and do it uniformly. Edges and corners lead to peak stresses and, possibly, to tensile stresses and cracking.

Type of construction: From the standpoint of fluid dynamics and structural strength, an egg-shaped vessel is about the best possible solution. Both scum removal and sediment extraction are relatively uncomplicated. On the other hand, this type of construction is comparatively expensive, so that its use is usually restricted to large-scale sewage treatment plants. However, the Chinese fixed-dome version are of similar shape, but less expensive.

Simplified versions of such digester designs include simple cylinders with conical covers and bottoms. They are much easier to build and are sometimes available on the market as prefabricated units. Their disadvantage lies in their less favorable surface area, the cylinder should have a height equal to its diameter. Prone cylinders have become quite popular on farms, since they are frequently the more favorable solution for small-scale biomethanation. Cuboid digesters are often employed in batch-fed systems used primarily for fermenting solid material, so that fluid dynamics are of little interest.

Building material of digester: Digesters can be made from any of the following materials:

Steel vessels: Steel vessels are inherently gas tight, have good tensile strength, and are relatively easy to construct (by welding). In many cases, a discarded steel vessel of appropriate shape and size can be salvaged for use as a biogas digester. Susceptibility to corrosion both outside (atmospheric humidity) and inside (aggressive media) can be a real problem. As a rule, some type of anticorrosion coating must be applied and checked at regular intervals.

Concrete vessels: Concrete vessels have gained widespread acceptance in recent years. The requisite gas tightness necessitates careful construction and the use of gas tight coatings, linings and/or seal strips in order to prevent gas leakage due to the development of stress cracks at the points of transition between the top and sides. The prime advantage of concrete vessels is that they have a practically unlimited useful life, even though their construction is relatively inexpensive. This is especially true of large digesters in industrialized countries.

A digester of limited size can even be home-built using precast concrete blocks of the type customarily employed in agricultural building projects. A possible disadvantage in this connection is that the available statics usually only apply to circular vessels with a very high diameter/height ratio, so that the building of an appropriately shaped digester may be subject to the submittal of a separate static analysis.

Masonry: Masonry, usually comprising mud bricks (adobe) or rough-hewn stone blocks (rubble masonry), is used quite frequently and with much success in the construction of small-scale biogas systems. Cement-plastered/rendered masonry is a suitable - and inexpensive - approach for building an underground biogas system, whereby a dome-shaped digester is recommended. Masonry per se is well suited to do-it-yourself construction.

Plastics: Plastics have been in widespread use in the field of biogas engineering for a long time already. Basic differentiation is made here between flexible materials (sheeting) and rigid materials (PE, GRP, etc.). Diverse types of plastic sheeting can be used for constructing the entire digesting chamber (balloon gas holders) or as a vessel cover in the form of a gas tight

Sheeting made of caoutchouc (India rubber), PVC, and PE of various thickness and description have been tried out in numerous systems. The durability of plastic materials exposed to aggressive slurry, mechanical stress and UV radiation, as well as their gas permeability, vary from make to make and from material to material and are dependent on the production processes employed in their manufacture. Glass-reinforced-plastic digesters have long since proven quite suitable, as long as the in-service static stresses are accounted for in the manufacturing process. GRP vessels display good gas tightness and corrosion resistance. They are easy to repair and have a long useful life. The use of sandwich material (GRP - foam insulant - GRP) minimizes the on-site insulating effort and reduces the cost of transportation and erection.

Wood: A further suitable material for use in the construction of biogas systems is wood. It is often used for building liquid-manure hoppers and spreaders. Wooden

digesters require a vapor proof membrane to protect the insulation. Closed vessels of any appreciable size are very hard to render gas tight without the aid of plastic sheeting. Consequently, such digesters are very rare.

2.2.8.4. Gas holders

Basically, there are different designs of construction for gas holders used in simple biogas plants:

- floating-drum gas holders
- fixe-domes gas holders
- plastic gas holders
- separate gas holders
- Floating-drum gas holders

Most floating-drum gas holders are made of 2-4 mm thick sheet steel, with the sides made somewhat thicker than the top in order to counter the higher degree of corrosive attack. Structural stability is provided by L-bar bracing that simultaneously serves to break up surface scum when the drum is rotated.

2.2.8.5. Gas pipe, valves and accessories

The requirements for biogas pipe work, valves and accessories are essentially the same as for natural-gas installations. However, biogas is 100% saturated with water vapor and contains hydrogen-sulfide. Consequently, no piping, valves or accessories that contain any amounts of nonferrous metals may be used for biogas systems, because they would be destroyed by corrosion within a short time. Sewer-gas versions of most valves and accessories are available on the market. The gas lines may consist of standard steel pipes. Also suitable (and inexpensive) is plastic tubing made of rigid PVC or rigid PE. Flexible gas pipes laid in the open must be UV-resistant.

2.2.8.6. Types of stirring facilities

There exist different types of stirring facilities. The impeller stirrer has given good results especially in sewage treatment plants. The horizontal shaft stirs the

fermentation channel without mixing up the phases. Both schemes originate from large-scale plant practice. For simple household plants, poking with a stick is the simplest and safest stirring method.

2.2.8.7. Heating systems

Normally, small-scale biogas plants are built without heating systems because of the high costs.

As a rule of thumb, it is always of advantage for the quality of the biomethanation process to warm up the influent substrate to its proper process temperature before it is fed into the digester. At any rate, the occurrence of cold zones in the digester should be prevented .

In the following, a number of different ways to get the required amount of thermal energy into the substrate and/or digester are described. In principle, differentiation is made between:

* direct heating in the form of steam or hot water, and
* indirect heating via heat exchanger, whereby the heating medium, usually hot water, imparts heat to the substrate or slurry.

2.2.8.8. Pumps

Types of pump: There are two predominant types of pump for fresh substrate: centrifugal pumps and positive-displacement pumps (reciprocating pumps). Centrifugal pumps operate on the principle of a rapidly rotating impeller located in the liquid flow. They provide high delivery rates and are very robust, i.e. the internals are exposed to little mechanical stress. They do, however, require a free-flowing intake arrangement, because they are not self-priming (regenerative).

Types of impellers: Various types of impellers are used, whereby peripheral impellers are easier on the substrate than are ducted-wheel or spiral-type impellers.

2.3. Kinetics of Biological Growth

The need for a controlled environment and biological community in the design of biological waste treatment units can be described throughout the following

situations. Environmental conditions can be controlled by pH regulation, temperature regulation, nutrient or trace element addition, oxygen addition or exclusion, and proper mixing. Control of the environmental conditions will ensure that the microorganisms have a proper medium in which to grow. To ensure that the microorganisms must be allowed to remain in the system long enough to reproduce. This period depends on their growth rate, which is related directly to the rate at which they metabolize or utilize the waste. Assuming that the environmental conditions are controlled properly, effective waste stabilization can be ensured by controlling the growth of microorganisms [3,4,5].

Cell Growth: In batch culture system, the rate of growth of bacterial cells can be defined by the following relationships:

$$\frac{dX}{dt} = \mu . X \quad \text{or} \quad \frac{1}{X} . \frac{dX}{dt} = \mu \qquad (1)$$

Where μ : specific growth rate ($time^{-1}$)

X : biomass concentration (mass/unite volume)

Growth Cycle: In a typical batch process the number of living cells varies with time. After a lag phase, where no increase in cell numbers is evident, a period of rapid growth ensues, during which the cell numbers increase exponentially with time. Although this stage of batch culture is often called the logarithmic phase (exponential phase), naturally in a closed vessel the cells cannot multiply indefinitely, and a stationary phase follows the period of exponential growth. At this point the population achieves its maximum size. Eventually a decline in cell numbers occurs during the death phase (Figure 5.).

At the end of the lag phase the population of microorganisms is well adapted to its new environment. The cells can then multiply rapidly, and cell mass, or the number of living cells, doubles regularly with time [3,4,5].

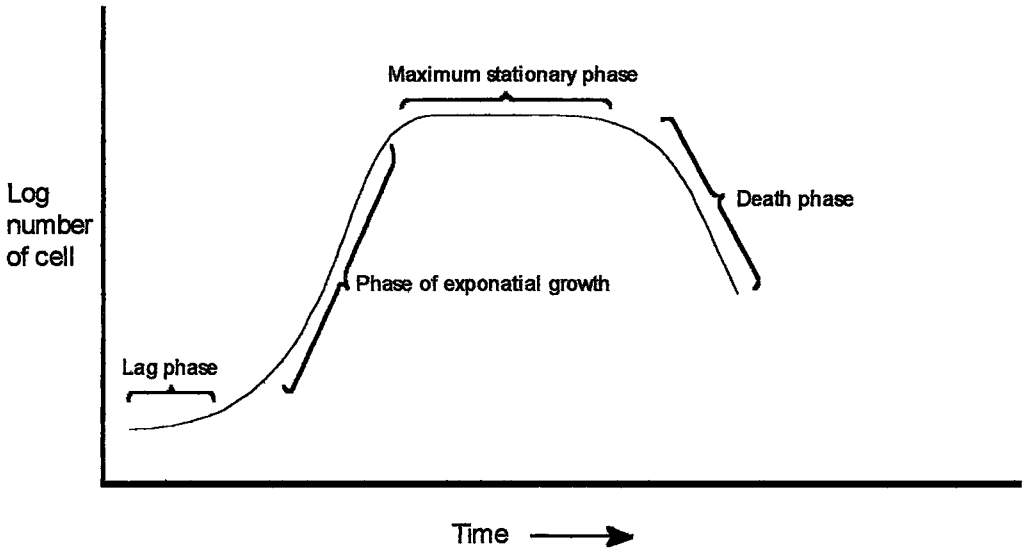

Figure 5. Typical growth curve for batch cultivation

Monod Growth Kinetics : If the concentration of one essential medium constituent is varied while the concentration of all other medium components are kept constant, the growth rate typically changes in a hyperbolic fashion. A functional relationship between the specific growth rate μ and an essential compound's concentration was proposed by Monod in 1942. The Monod equation states that

$$\mu = \frac{\mu_{max} s}{K_s + s} \tag{2}$$

Here $\mu_{max.}$ is the maximum growth rate achievable when $s >> K_s$ and the concentrations of all other essential nutrients are unchanged. s is the substrate concentration. K_s is that value of the limiting nutrient concentration at which the specific growth rate is half its maximum value; it is the division between the lower concentration range, where μ is strongly (linearly) dependent on s, and the higher range, where μ becomes independent of s [3,4,5].

Other Forms of Growth Kinetics : Other related forms of specific growth rate dependence have been proposed which in particular instances give better fits to experimental data:

Contois

$$\mu = \frac{\mu_m S}{BX + S} \quad (3)$$

Tessier

$$\mu = \mu_m (1 - e^{-s/K_s}) \quad (4)$$

Moser

$$\mu = \mu_m (1 + K_s S^{-\lambda})^{-1} \quad (5)$$

The last two examples render algebraic solution of the growth equations much more difficult than the Monod form. The equation of Contois contains an apparent Michaelis constant which is proportional to biomass concentration X. This last term will therefore diminish the maximum growth rate as population density increases, eventually leading to $\mu \propto x^{-1}$[5].

2.3.1. Ideal Reactors for Kinetics Measurements

It is difficult to obtain useful kinetic information on microbial populations from reactors that have spatially nonuniform conditions. Hence it is desirable to study kinetics in reactors that are well mixed.

2.3.1.1. Ideal Batch Reactor

Many biochemical processes involve batch growth of cell populations. After seeding a liquid medium with an inoculum of living cells, nothing (except possibly some gas) is added to the culture or removed from it as growth proceeds. Typically in such a reactor, the concentrations of nutrients cells, and products vary with time as growth proceeds.

A material balance on moles of component i;

$$\frac{d}{dt}(V_R . c_i) = V_R . r_{fi} \quad (6)$$

V_R : culture volume

c_i : moles i / unit culture volume

r_{fi} : moles i formed by reaction/unit culture volume . unit time

For biomass: $$r_G = (\frac{dX}{dt})_G \quad (7)$$

For substrate: $$r_S = (\frac{dS}{dt})_S \quad (8)$$

For product: $$r_P = (\frac{dP}{dt})_P \quad (9)$$

2.3.1.2. The Ideal Continuous Flow Stirred Tank Reactor (CSTR)

The diagram of this process is shown in Figure 6, which is a schematic diagram of a completely mixed stirred tank reactor. Such configurations for cultivation of cells are frequently called chemostats.

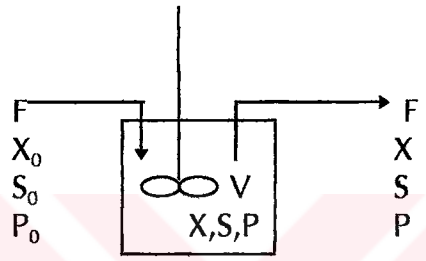

Figure 6. A schematic diagram of CSTR.

The material balances for various species are as follows:

For Biomass:

$$V.\frac{dX}{dt} = F.X_0 - F.X + (V.\frac{dX}{dt})_G \quad (10)$$

$$\frac{dX}{dt} = \frac{F}{V}.(X_0 - X) + \mu X \quad (11)$$

at steady state conditions

$$\frac{dX}{dt} = 0 \;, X_0 = 0 \text{ and } \frac{F}{V} = D \quad (12)$$

$$D = \mu$$

For Substrate:

$$V.\frac{dS}{dt} = F.S_0 - F.S + (V.\frac{dS}{dt})_{Cons.} \quad (13)$$

$$\frac{dX}{dt} = -Y_{X/S} \cdot \frac{dS}{dt} \quad \text{where} \quad Y_{X/S} = -\frac{\Delta X}{\Delta S} \tag{14}$$

$Y_{X/S}$: yield factor

$$\frac{dS}{dt} = \frac{F}{V}.(S_0 - S) - \frac{1}{Y_{X/S}} \frac{dX}{dt} \tag{15}$$

$$\frac{dS}{dt} = \frac{F}{V}.(S_0 - S) - \frac{\mu X}{Y_{X/S}} \tag{16}$$

at steady state conditions

$$\frac{F}{V}(S_0 - S) = \frac{\mu X}{Y_{X/S}} \; ; \; \frac{F}{V} = D \text{ and } D = \frac{1}{\theta}$$

Where θ is HRT. (hydraulic retention time)

$$\frac{(S_0 - S)}{\theta} = \frac{\mu X}{Y_{X/S}} = \dot{F} \tag{17}$$

$\dot{F}$: Substrate utilization rate

For Product:

$$V.\frac{dP}{dt} = F.P_0 - F.P + (V.\frac{dP}{dt})_{\text{Product.}} \tag{18}$$

$$\frac{dX}{dt} = -\frac{1.}{Y_{P/S}} \frac{dP}{dt} \quad \text{where} \quad Y_{P/X} = \frac{\Delta P}{\Delta X}$$

$Y_{P/X}$: product yield coefficient (19)

and

$$\frac{dP}{dt} = -Y_{P/S} \cdot \frac{dS}{dt} \quad \text{where} \quad \frac{dS}{dt} = \left(\frac{S_0 - S}{\theta}\right)$$

$$\frac{dP}{dt} = \frac{F}{V}.(P_0 - P) - Y_{P/X} \frac{dX}{dt} \tag{20}$$

$$\frac{dP}{dt} = \frac{F}{V}.(P_0 - P) - Y_{P/X} \mu X \tag{21}$$

at steady state conditions

$$.D(P_0 - P) = Y_{P/X} \mu X$$

2.3.2. Modeling of the Methane Production in Batch Digestion

The important rate quantities such as specific growth rate and the specific product formation rate are derivative quantities in batch culture. That is, it is necessary to differentiate the both biomass and product concentration data to estimate the specific growth rate and specific product formation rate. In steady state continuous culture, differentiation of data is not required to estimate these quantities.

The growth curve is defined as the logarithm of the number of organisms plotted against time, these growth rate changes result in a sigmoidal curve (Figure 5.) with a lag phase followed by an exponential phase and then by a stationary phase. Growth curve is similar to the product formation curve.

To describe such a curve and reduce measured data to a limited number of interesting parameters, investigators need adequate models. A number of models are found in the literature, such as the models of Gomperts, Logistic and Boltzman [38]. Most of the equations describing a sigmoidal growth curve contain mathematical parameters (i, b, c,....) rather than parameters with a biological meaning (A, μ_m and λ). It is difficult to estimate start values for the parameters if they have no biological meaning. Table 9 shows the models and biological meanings with their parameters.

2.3.3. Kinetic Models for Substrate Utilization and Methane Production

A number of kinetic models have been proposed for process of anaerobic digestion. Early models were based on a single-culture system and used the Monod equation or variations. More recently, several dynamic simulation models have been developed based on a continuous multiculture system; these correspond to the major bioconversion steps in anaerobic digestion but again make the assumption that culture growth obeys Monod-type kinetics. Investigators have a doubt on the validity of applying the Monod equation to waste treatment as the specific growth rate is expressed only as a function of the concentration of the limiting substrate in the reactor. The equation contains no term relating to input substrate concentration; this implies that the effluent substrate concentration is independent of the input concentration.

Table 9. Growth Models and derivation of biological parameters

Model	Gomperts	Logistic (3)	Boltzman	Logistic (4)
y	$i.e^{-e^{(b-cx)}}$	$\frac{i}{1+e^{(b-cx)}}$	$\frac{i-f}{1+e^{(x-c)/d}}+f$	$\frac{i-f}{1+(\frac{x}{x_0})^p}+f$
x_i	$\frac{b}{c}$	$\frac{b}{c}$	c	$X_0.\left(\frac{p-1}{p+1}\right)^{1/p}$
$(\frac{dy}{dx})_{x_{inf.}}$	$\frac{i.c}{e}$	$\frac{i.c}{4}$	$\frac{f-i}{4.d}$	$\frac{f-i}{4pX_0}.(p^2-).\left(\frac{p+1}{p-1}\right)^{1/p}$
λ	$\frac{b-1}{c}$	$\frac{b-2}{c}$	$\frac{2d(i+f)}{i-f}+c$	$\frac{X_0}{f-i}..\left(f.\left(\frac{p-1}{p+1}\right)^{\frac{p+1}{p}}-i\left(\frac{p+1}{p-1}\right)^{\frac{p-1}{p}}\right)$
$\lim_{x\to+\infty}$	i	i	f	f
$\lim_{x\to-\infty}$	0	0	i	f
$\lim_{x\to0}$	-	-	-	i

2.3.3.1. Kinetic Model on Basis of Monod-Type

For a continuous well-stirred fermenter working under steady state conditions

$$(-r_s)=\frac{(S_0-S)}{\theta} \qquad (22)$$

where $(-r_s)$ is the substrate uptake rate (g COD/liter.day), S_0 and S are the substrate concentrations (g COD/liter) at the fermenter inlet and outlet, and θ is the retention time (day).

If the volume of gas produced, $V_{G(lCH4STP)}$, is assumed to be proportional to the amount of substrate consumed, then

$$\frac{V_G}{\theta} = Y_{P/S}(S_0 - S)q \tag{23}$$

Where $Y_{P/S}$ is the yield coefficient (liters CH_4 STP /g COD), and q is the volumetric flow-rate of liquid feed(liters/day).

This equation allows one to relate the rate of substrate uptake to that of gas production, r_G, through the following expression:

$$r_G = Y_{P/S}(-r_S) \tag{24}$$

On the other hand, the rate of substrate consumption and the specific rate of microbial growth μ (day^{-1}), are related through

$$Y_{X/S}(-r_S) = \mu X \tag{25}$$

where $Y_{X/S}$ is the growth yield constant (g cell mass /g COD) and X is the cell mass concentration (g/liter).

For a system which specific growth rate conforms to the Monod equation:

$$r_G = [(Y_{P/S}X\mu_m / Y_{X/S}][S / (K_S + S)] \tag{26}$$

i. At low substrate concentrations, K_s >>S, so the equation simplifies to

$$r_G = (Y_{P/S}\mu_m / Y_{X/S}K_S)XS \tag{27}$$

For narrow time intervals, as anaerobic microorganisms grow very slowly ;

$$r_G \cong KS \tag{28}$$

where

$$K = (Y_{P/S}\mu_m / Y_{X/S}K_S)X \tag{29}$$

and

$$\ln r_G = \ln K + \ln S \tag{30}$$

The plot of $\ln r_G$ against lnS should be a straight line of unity slope and intercept equal to lnK.

ii. On the other hand, if X is assumed to remain constant throughout a series of experiments, then eqn. (26) can be written as

$$r_G = K_1[S / (K_S + S)] \quad (31)$$

where

$$K_1 = Y_{P/S} X \mu_m / Y_{X/S} \quad (32)$$

Linearization of eqn.31 yields:

$$1/r_G = (1/K_1) + (K_S / K_1)(1/S) \quad (33)$$

If the plot of $(1/r_G)$ against (1/S) has an intercept, K1 can be calculated, otherwise first assayed model can be confirmed [25,34].

2.3.3.2. Kinetic Model on Basis of Contois-Type

In the model proposed by Contois, specific growth rate is considered to be a function of the growth-limiting nutrient in both the input substrate and effluent by use of empirical constant (B) related to microbial concentration (X) (Eqn.3).

For a completely mixed system, the average solids retention time equals the hydraulic retention time and the rates of change of bacterial cell mass and substrate concentration are governed by eqn.12 and eqn.16.

Under steady state conditions eqn. 12 and 16 yield:

$$(S_0 - S)Y_{X/S} = X \quad (34)$$

and

$$\frac{(S_0 - S)}{\theta} = \dot{F} \quad (35)$$

Since the cell mass concentration is difficult to measure in anaerobic biological treatment systems, due to low yield, the relationship shown in Eqn. 34 is substituted for the cell mass in kinetic equations. Thus, the Contois' kinetic equation (Eqn.3) can be expressed as :

$$\frac{\mu}{\mu_m} = \frac{\frac{S}{S_0}}{K' + \frac{S}{S_0}(1 - K')} \quad (36)$$

where

$$K' = BY_{X/S} \quad (37)$$

This model shows that the μ_m occurs at wash out ($\mu \rightarrow \mu_m$ as $S \rightarrow S_0$). Thus the minimum retention time is numerically equal to the reciprocal of μ_m :

$$\theta_m = \frac{1}{\mu_m} \tag{38}$$

For a completely mixed continuous-flow system under steady-state

$$\frac{\mu}{\mu_m} = \frac{\theta_m}{\theta} = \frac{\frac{S}{S_0}}{K' + \frac{S}{S_0}(1-K')} \tag{39}$$

and

$$\frac{S}{S_0} = \frac{K'}{\frac{\theta}{\theta_m} - 1 + K'} \tag{40}$$

The overall process performance may be evaluated by using chemical oxygen demand (COD) or volatile solids concentration (VS) as a measure of the substrate concentration.

The biodegradable COD in fermenter is directly proportional to B_0-B and the biodegradable COD loading is directly proportional to B_0 , where B denotes the liters of CH_4 produced at STP/g COD added to digester and B_0 is the liters of CH_4 produced at infinite retention time at STP/g COD added. So;

$$\frac{S}{S_0} = \frac{B_0 - B}{B_0} = \frac{K'}{\frac{\theta}{\theta_m} - 1 + K'} \tag{41}$$

or

$$B = B_0 \left[1 - \frac{K'}{\frac{\theta}{\theta_m} - 1 + K'} \right] \tag{42}$$

Eqn. 42 shows that,

$$\text{if } \frac{\theta}{\theta_m} >> |K'-1|, \text{ then} \tag{43}$$

$$B = B_0 - K' B_0 \theta_m \frac{1}{\theta} \quad (44)$$

The plot of B vs. $1/\theta$ should be a straight line, intercept gives B_0. When K' is equal to unity, the inequality given above is always satisfied.

Eqn. 42 can be rearranged to give

$$\theta = \theta_m + \theta_m K' \left(\frac{B}{B_0 - B}\right) \quad (45)$$

From this equation, the plot of θ vs. $B/(B_0\text{-}B)$ yields a straight line with the intercept equal to θ_m and the slope equal to $\theta_m K$. Thus, this equation can be used to determine kinetic constants K' and θ_m and hence μ_m by using Eqn. 38.

Since B is the methane production/g COD added, the volumetric methane production rate (γ_v) equals B times the loading rate:

$$\gamma_v = \frac{B.S_{T0}}{\theta} = \frac{B_0 S_{T0}}{\theta}\left[1 - \frac{K'}{\frac{\theta}{\theta_m} - 1 + K'}\right] \quad (46)$$

Where S_{T0} is the total influent COD concentration [13,21].

2.3.3.3. Kinetic Model on the Basis of Monod and Contois Equations in Two Extreme Conditions.

Complex compounds cannot be taken up by the microorganisms without initial hydrolysis into assimilable compounds; substrate for growth and methane formation are the products of hydrolysis. Transport of hydrolyzed assimilable compounds is not rate limiting. The whole process of anaerobic digestion is carried out by a multicultural complex that utilizes the hydrolyzed assimilable compounds.

The digestion processes take place in three stages:

- Extracellular hydrolysis of complex compounds into soluble assimilable substrates,
- transport of soluble assimilable substrates into the microorganisms and
- utilization of assimilable substrates for growth and methane formation.

Stage I. Hydrolysis is assumed to be a first order reaction with respect to the concentration of hydrolysis of substrate S

$$-\frac{dS}{dt} = K_h(S - S_h) \tag{47}$$

Stage 2. Internalization/transport of hydrolyzed substrate into the microorganisms is considered to be directly related to the difference in concentrations of the hydrolyzed substrate outside and inside and to the concentration of the active biomass X (mass /volume). Hydrolyzed substrate entering the microorganisms is assumed to be metabolized very rapidly so that the intracellular concentration $S_u \approx 0$. Assuming that uptake of substrate is not rate limiting with respect to hydrolysis, then:

$$-\frac{dS}{dt} = k(S_h - S_u)X = k(S_h)X$$
$$K_h(S - S_h) = k(S_h)X \tag{48}$$
$$S_h = \frac{K_h S}{kX + K_h}$$

Stage III. Growth on hydrolyzed substrate is assumed to follow Monad kinetics and expressed as :

$$\mu = \frac{\mu_m s_h}{K_h + s_h} \tag{49}$$

Substituting the values of S_h from eqn. (48), eqn.(49) becomes:

$$\frac{\mu}{\mu_m} = \frac{S}{K_s kX / K_h + K_s + S} \tag{50}$$

Under steady-state conditions of continuous digestion in a completely mixed reactor, by use of eqn. (17) and eqn. (50) can be expressed as:

$$\frac{\mu_m}{\mu} = \frac{K_s k Y_{X/S}}{K_h} \frac{S_0 - S}{S} + \frac{K_s}{S} + 1 \tag{51}$$

which is the basic equation for substrate utilization in the anaerobic digestion of complex organic substances.

When $S >> K_s$, which may be the case in the practical anaerobic digestion of complex feeds, the second term of the right hand side of eqn. (51) becomes negligible and the equation degenerates to:

$$\frac{\mu_m}{\mu} = \frac{K_s k Y_{X/S}}{K_h} \frac{S_0 - S}{S} + 1 \tag{52}$$

which has the structure of Contois equation as described in eqn.(3), and is similar to the Chen-Hashimoto equation:

$$\frac{\mu_m}{\mu} = K \frac{S_0 - S}{S} + 1 \tag{53}$$

where $K=Y_{X/S}B$. From eqn. (52) and (53),

$$K = \frac{K_s k Y_{X/S}}{K_h} \tag{54}$$

and

$$B = \frac{K_s k}{K_h} \tag{55}$$

In the case of readily hydrolysable substrates, K_h may be very large in relation to other values and in the extreme case of soluble and assimilable substrates, such as glucose, will be infinity, When this is the case, the first term of the right-hand side of eqn.(61) becomes negligible and the equation is reduced to:

$$\frac{\mu_m}{\mu} = \frac{K_s}{S} + 1 \tag{56}$$

which is the Monod equation. Therefore eqn. (51) is a generalized equation relating the Monod and Contois equations, which holds in two extreme cases.

Effluent substrate concentration can also be related to input substrate concentration incorporating eqn. (17) into eqn. (51), hence:

$$S = \frac{AS_0}{\mu_m \Theta + A - 1} + \frac{K_S}{\mu_m \Theta + A - 1} \tag{57}$$

where

$$A = \frac{K_s k Y_{X/S}}{K_h} \tag{58}$$

At washout $S_0=S$, and eqn (51) is reduced to eqn. (56). This shows that if $S>>K_S$, $\mu \approx \mu_m$ at critical retention time.

Eqn. (51) can be rearranged as

$$\mu = \frac{S\mu_m}{A(S_0 - S) + K_s + S} \tag{59}$$

to show that as S approaches zero, μ approaches zero.

Incorporation of refractory coefficient: In the case of complex organic substrates, which are generally expressed as COD or VS, a part of substrate is usually refractory to biodegradation. The refractory coefficient, R, is expressed as S_r / S_{TO}, where S_r and S_{TO} are the refractory and total COD or VS concentration in the input feed, respectively . S_T denotes the effluent total COD or VS concentration. The following expression can written to describe the relationship of input biodegradable substrate concentration (S_0) to R:

$$S_0 = S_{TO}(1 - R) \tag{60}$$

and the biodegradable substrate concentration in the effluent (S) to R:

$$S = S_T(1 - R) \tag{61}$$

Considering the above relationships the basic eqn. (51) can be expressed as:

$$\mu_m \Theta = A\frac{S_{TO} - S_T}{S_T - RS_{TO}} + \frac{K_s}{S_T - RS_{TO}} + 1 \tag{62}$$

from which the relationship between total input and effluent concentrations as COD can be derived

$$\frac{S_T}{S_{TO}} = \frac{(1-R).A + \frac{K_S}{S_{TO}}}{(\mu_m \theta + A - 1)} + R \tag{63}$$

Kinetics of methane production: A reduction of 1 g COD is equivalent to the production of 0.35 dm^3 of CH_4 at STP. The biodegradable COD in fermenter is directly proportional to B_0-B and the biodegradable COD loading is directly proportional to B_0 , where B denotes the liters of CH_4 produced at STP/g COD added to digester and B_0 is the liters of CH_4 produced at infinite retention time at STP/g COD added. So;

$$\frac{S_0 - S}{S} = \frac{B}{B_0 - B} \tag{64}$$

By use eqn. (64) , eqn. (51)

$$\frac{B}{B_0} = 1 - \frac{A + K_s/S_0}{\mu_m \Theta + A - 1} \tag{65}$$

which represents the kinetic equation for methane fermentation. By use of eqn. (60), the above equation may be rearranged to give;

$$\frac{B}{B_0} = 1 - \frac{A + K_s/(S_{TO} - RS_{TO})}{\mu_m \Theta + A - 1} \tag{66}$$

Eqn. (65) and (66) show that, at constant input substrate concentration, as Θ approaches infinity, B/B_0 approaches unity.

The volumetric methane production rate M_v, in terms of volume of CH_4 produced Per digestion volume Per unit time, may expressed by use of eqn. (66) [26]

$$M_V = \frac{BS_{TO}}{\Theta} = \frac{B_0 S_{TO}}{\Theta}\left[1 - \frac{A + K_s/(S_{TO} - RS_{TO})}{\mu_m \Theta + A - 1}\right] \tag{67}$$

2.4. The Characteristics of Olive

The oval olive fruit is a drupe with a large, hard shelled pit. Its size and composition differ widely according to variety, climatic conditions, water supply and size of the yield. The olive fruit reaches its maximum weight 6-8 months after blossoming late in spring and darkens progressively during ripening to a purplish black color at fully maturity. The ripe fruit will weigh from 1.5 to 13 gm. The pit, with its hard shell (endocarp), takes up between 15-30 % of the weight of the fruit. At full maturity the fruit meat (mescarp) contains 6-10 % soluble solids (with mannite as major sugar) and anywhere between 15-35 % oil. The seed kernel contain only about 5 % oil. The characteristics bitter glycoside, oleuropein, is more concentrated close to the peel (exocarp) [37].

Olive residue: Residue is the solid obtained from pressing olives and is formed of fragments of skin, pulp, stone and seed. It retains the olives' natural fat and moisture. Dried press covers residue from which the main particles of stone have been removed.

The quantity of residue from mechanical processing varies according to the type of olives and the method of pressing and ranges from 25 percent to 50 percent

of the weight of olive pressed. The commercial value of the residue depends on its water and fat content. Moisture usually accounts for between 20 percent 30 percent of the weight, while the fat content varies from a minimum of about 3.5 percent to 10-12 percent of the weight and in some cases even more, depending on the extraction process used.

It is used as stock feed, not all animals, however, take to it and, as it is full of large fragments of stone, only full-grown pigs with strong teeth can eat it and then only in limited quantities.

The residue can also be used as a fertilizer, after it has been properly steeped in order to avoid fermentation which would harm the plants [42].

CHAPTER III

EXPERIMENTAL

3.1. Experimental Set-up

Experimental studies consist of characterization and digestion of the substrate (olive residue) and biogas production under anaerobic conditions.

The set-ups used for digestions are illustrated in Figures 7 and 8. The one in Figure 7 consists of two main units, the first being 1.5 liter of bench scale jacketed jar fermenter (EYELA Jar Fermentor MBF) equipped with an automated pH controller (EYELA,pH controller, FC 10 Tokyo, Rikakika, Co.Ltd.), perilstaltic pump (EYELA Micro Tube Pump MP-3) and the second is a gas collection column working with gas-liquid displacement principle. Additional digesters for both batch and semi-continuous anaerobic digestion were constructed within an incubator (Figure 8) to control the temperature.

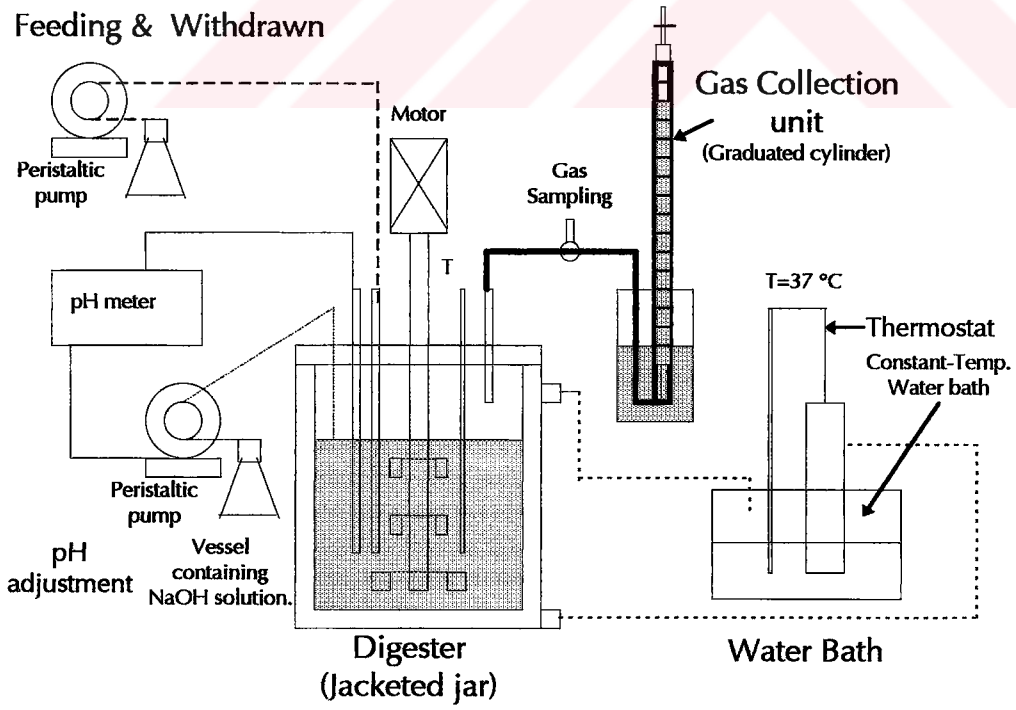

Figure 7.Diagram showing the experimental set-up (jacketed jar fermentor)

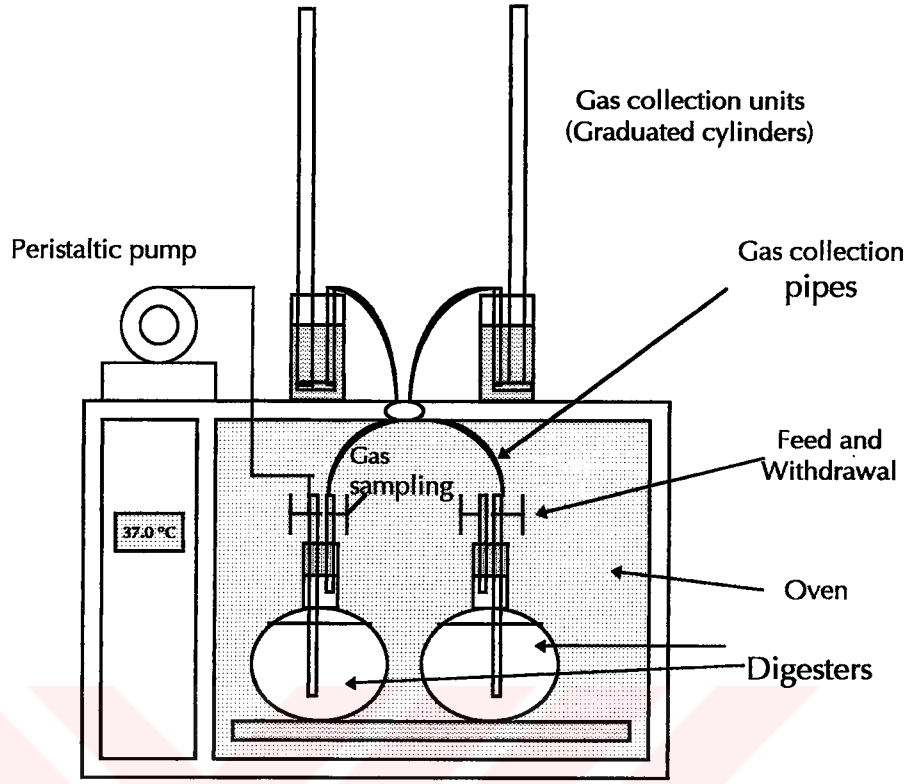

Figure 8. Diagram showing the experimental set-up (oven digester)

3.2. Experimental Procedure

3.2.1. Preparation of Culture Medium

To determine a suitable culture source, different cultures were obtained and inoculated to the olive residue water mixture. Several culture sources including cow dung, sewage, culture medium from Pakmaya A.Ş (A Turkish yeast production plant); and waste water from Gaziantep landfill area were used to obtain biogas. The results are given in the next chapter. In accordance with the results obtained, the best source was chosen as the culture source for the anaerobic digestion.

3.2.2. Slurry Preparation and Inoculation

The olive residue was first ground to pass 425 μm mesh size sieve and was mixed with tap water for the preparation of a slightly basic slurry containing 10 % total solids.

It was necessary to have a suitable culture of bacteria as inoculum, in order to initiate a rapid digestion of olive residue. During primary anaerobic digestion, pH, volume and composition of biogas were recorded at 37°C. After maximum biogas production, this slurry was used as inoculum in the digestion tests.

3.2.3. Anaerobic Digestion

Batchwise and semi-continuous digestions were carried out under anaerobic conditions at 37°C. Anaerobic conditions were provided by displacement of air with carbon dioxide. The temperature was maintained at 37°C by a jacketed water bath.

3.2.3.1. Primary Anaerobic Digestion to Determine Culture Source

Different culture sources (cow manure, sewage, culture from PAKMAYA and waste water from Gaziantep landfill) were tested to obtain the best biogas production.

750 ml of the culture (as obtained) was diluted by a factor of 2 and was

3.2.3.3. Semi-Continuous Anaerobic Digestion in Fermenter

Constant volume semi-continuous digestions were performed by feeding and withdrawing the same amounts of slurry so that the HRT (hydraulic retention time) was 30 days. Since the biogas production was expected to reach steady state conditions after at least 25 days, the feeding and withdrawing processes were initiated after this time. Meanwhile the broth was stirred twice a day for one minute and total gas production, gas compositions, and pH values were recorded daily. Sampling and analysis were carried out as before with pH adjustment.

The gas production and composition were recorded daily until the steady state was achieved for each run. Once this condition was satisfied, an effluent sample was taken from each digester and analyzed.

3.2.3.4. Batchwise Anaerobic Digestion in Oven Digester

Some of the experiments were carried out in a constant temperature oven. The sets of experiments were carried by varying dry solid content (5, 10, 15 %). Batchwise anaerobic digestion continued until steady state biogas production. The produced biogas was collected outside the oven as shown in Figure 8. Total gas production and gas compositions were recorded daily.

3.2.3.5. Semi-Continuous Anaerobic Digestion in Oven Digester

Two sets of experiments were carried out in the semi-continuous mode. The first set of experiments was carried out with 10 % dry solid content of feed stream while varying hydraulic retention times (10, 20, 30, and 40 days). The second set of experiments was conducted by varying the dry solid content (5, 10, 15 %) a constant HRT of 30 days.

3.2.4. Methods of Analysis

3.2.4.1. Determination of Biogas Volume and Composition

The biogas (saturated with water vapor) produced in each run was collected by displacement of water in a calibrated column, and it was analyzed in a gas chromatograph equipped with a thermal conductivity detector (HP 5830A) for

oxygen, methane and carbondioxide. Routine analyzes were made with the following operating parameters:

Column	: 6' 1/8'', Supelco INC.
Column packing	: Poropak Q
Carrier gas	: Hydrogen
Carrier flow rate	: 0.4 ml/s
Injection temperature	: 40 °C
Column temperature	: 35 °C
TCD temperature	: 50 °C

The chromatograph was calibrated with the standard gas mixtures of carbon dioxide, methane and oxygen. The output peaks were recorded on HP 18850A GC terminal.

3.2.4.2. Determination of Total Solids Concentration

The total solids concentration within the slurry was determined by drying it in an oven and infrared dryer at 105 °C. Weight of total solids after drying was taken as the amount of total solids in the slurry.

3.2.4.3. Determination of Volatile Solids Concentration

The dried solid samples from the total solids determination were ignited at 950 °C in a furnace for 7 min. The loss in weight was taken as the volatile solids fraction of the total solids.

3.2.4.4. Determination of Fixed Carbon

The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash, and volatile solid subtracted from 10.

% Fixed Carbon = 100-(% moisture + % ash +% volatile solid)

3.2.4.5. Chemical Oxygen Demand (COD)

Fed and withdrawn slurries were first diluted 200 times and then the COD of the samples were determined by the method of dichromate oxidizable matter in water: (ASTM-D-1252) [43].

50 ml of the diluted sample was placed in a refluxing flask and 1 g of $HgSO_4$,and 5.0 ml conc. H_2SO_4 were added. The refluxing flask was cooled and its content were stirred to avoid loss of materials. Meanwhile 1 g of Ag_2SO_4 and 25 ml of 0.25 N $K_2Cr_2O_7$ were added. The condenser was attached to the flask, 70 ml of H_2SO_4 was added through the open end of the condenser. After 2 hr refluxing, the flask was cooled and the condenser washed with 25 ml of water. The acid solution was diluted to about 300 ml by water addition and 8 to 10 drops of phenothroline ferrous sulfate were added as indicator. The solution was titrated with 0.25 N ferrous ammonium sulfate solution to the end point. The end point of the sample was deduced from a color change (from blue green to a reddish hue).

The COD in the sample was calculated in milligrams per liter (ppm), as follows:

$$\text{COD, mg/liter (ppm)} = \frac{[(A-B)*N*8000]*F}{S}$$

Where;

A : milliliters of $FeSO_4(NH_4)_2SO_4$ solution required for the titration of the blank

B : milliliters of $FeSO_4(NH_4)_2SO_4$ solution required for the titration of the sample

N : normality of the $FeSO_4(NH_4)_2SO_4$ solution

S : milliliters of sample used for the test

F : dilution factor

3.2.4.6. Determination of Nitrogen

Nitrogen content of the raw olive residue, influent slurry and effluent slurry were determined by Kjeldahl method according to AOAC [44].

0.2-0.5 g of sample was placed into the digestion flask. 0.7 g HgO, 15 g K_2SO_4 and 25 ml of H_2SO_4 were added to the sample flask, and it was heated at the inclined position. Digestion continued until a clear solution was obtained.

The digested sample was cooled and 200 ml of H_2O, 25 ml of sulfide solution were added and mixed to precipitate the Hg followed by addition of some Zn granules to prevent bumping. For each 10 ml of H_2SO_4 used, 15 g of NaOH was added. The digestion flask was then immediately connected to a condenser, and with tip of condenser was immersed in standard acid solution and 5-7 drops of methyl red as indicator. Heating continued until all NH_3 has distillated. Condenser was removed and washed after distillation. Distillated sample was titrated with standard NaOH solution.

The % N in the sample was calculated as follows:

$$\%\,N = \frac{((\text{ml std. acid} * \text{Normality of acid}) - (\text{ml std. NaOH} * \text{normality of NaOH})) * 1.4007}{\text{g sample}}$$

3.2.4.7. Determination of Sulfur

Sulfur content of olive residue was determined by Eschka method according to ASTM-D-3177[45].

1 g of olive residue and 3 g of Eschka mixture containing 2 parts of MgO with 1 part of Na_2CO_3 were mixed in a porcelain crucible and mixture was covered 1 g of Eschka mixture.

Crucible was placed in a cold muffle and its temperature was raised to 800 °C in about 1 h and it was maintained about 1 ½ h. Sample was heated with 100 ml of water for 30 min into a 200 ml beaker. After heating, sample was filtered and washed five times. 250 ml of filtrate saturated with 10 ml of bromine water. HCl was used to make the slightly acidic with methyl orange as indicator. And then 1 ml of HCl was added and sample was boiled. 10 ml of $BaCl_2$ was added. After addition, sample was boiled for 15 min. Boiled sample was filtered and washed with hot water. Finally, filter was burn and heated at 925 °C . Precipitate was taken as grams of $BaSO_4$. The % sulfur in the sample was calculated as follows:

$$\%\,S=((A-B)*13.738/C)$$

A = g of $BaSO_4$ precipitated,

B = g of $BaSO_4$ in the blank, and

C = g of sample used.

CHAPTER IV.

RESULTS AND DISCUSSION

In this study, the anaerobic digestion experiments were performed as batchwise and semi-continuous. In the first case, the substrate (slurry consisting of powdered olive residue and water) was fed into the different culture sources. After selection of culture medium (culture with highest biogas yield), slurry of olive residue have been digested. Table 10 illustrates the characteristics of slurry fed to the digesters and the number of experiments performed.

Table 10. Experiments performed in the anaerobic digestion of olive residue.

Exp. Sets.	Working Volume (ml)	Digestion Type	Runs	
			Dry Solid (%)	HRT (day)
A	1500 f	Batch	20	-
1	1500 f	Batch	10	-
2	1000 o	Batch	5	-
3	1000 o	Batch	10	-
4	1000 o	Batch	15	-
5	1500 f	Semi-cont.	10	30
6	1000 o	Semi-cont.	10	10
7	1000 o	Semi-cont.	10	20
8	1000 o	Semi-cont.	10	30
9	1000 o	Semi-cont.	10	40
10	1000 o	Semi-cont.	5	30
11	1000 o	Semi-cont.	15	30

f : fermenter (working volume=1500 ml) o: Oven digester (working volume=1000 ml)
A: Adaptation set

4.1. The Characteristics of Feed Slurry

The results of proximate and ultimate analysis of olive residue are given in Table 11. Given in experimental section, fixed carbon was calculated by the subtraction of sum of moisture, ash and volatile solid from 100. Calorific value of the olive residue was determined by bomb calorimeter.

Table 11. Chemical composition and calorific value of olive residue

	Constituents	%
Proximate Analysis	Moisture	30.4±0.1
	Ash	8.8±1.8
	Volatile solids	58.2±0.2
	Fixed carbon	2.7±1.5
Ultimate Analysis	Moisture	30.4±0.1
	Ash	8.8±1.8
	Sulfur	0.3±0.1
	Nitrogen	0.7±0.2
	Crude fat	8.2±1.5
	Calorific value (kcal/kg)	5221±36

The basic slurry of olive residue was utilized as the substrate in all experiments. The characteristics of olive residue-water mixture (slurry) are given in Table 12.

Table 12. Properties of a typical slurry (10 % olive residue-water mixture)

Volatile solids	8.3±0.1 %
COD	182.5±15 g/L
N	0.1±0.03 %
pH	6.0

4.2. Selection of Culture Source

Different culture media were tried with olive residue to produce biogas. The culture samples and biogas production results are shown in Table 13. Biogas could not be produced with cow dung, sewage and culture sample obtained from biogas plant of PAKMAYA A.Ş. Only waste water sample produced biogas. The percent of methane and carbondioxide in the gas were measured and recorded everyday during digestion. These are shown in Figure 9.

The culture medium in the digester is termed as the adapted culture medium, after production of biogas with waste water. This medium was used in all sets of experiments.

Table 13. Biogas production with different cultures

Culture	Biogas production
Cow Dung	-
Sewage	-
PAKMAYA	-
Waste Water	+

Methane production during digestion was observed to follow all the characteristics of growth curve. After ten days of digestion, methane production increased exponentially. At the end of 25 days, digestion reached the stationary phase. The methane produced in the stationary phase was observed to be 80 % by volume of the total biogas, the remaining being principally CO_2

The length of lag phase was measured to be about 10 days (Figure 9).

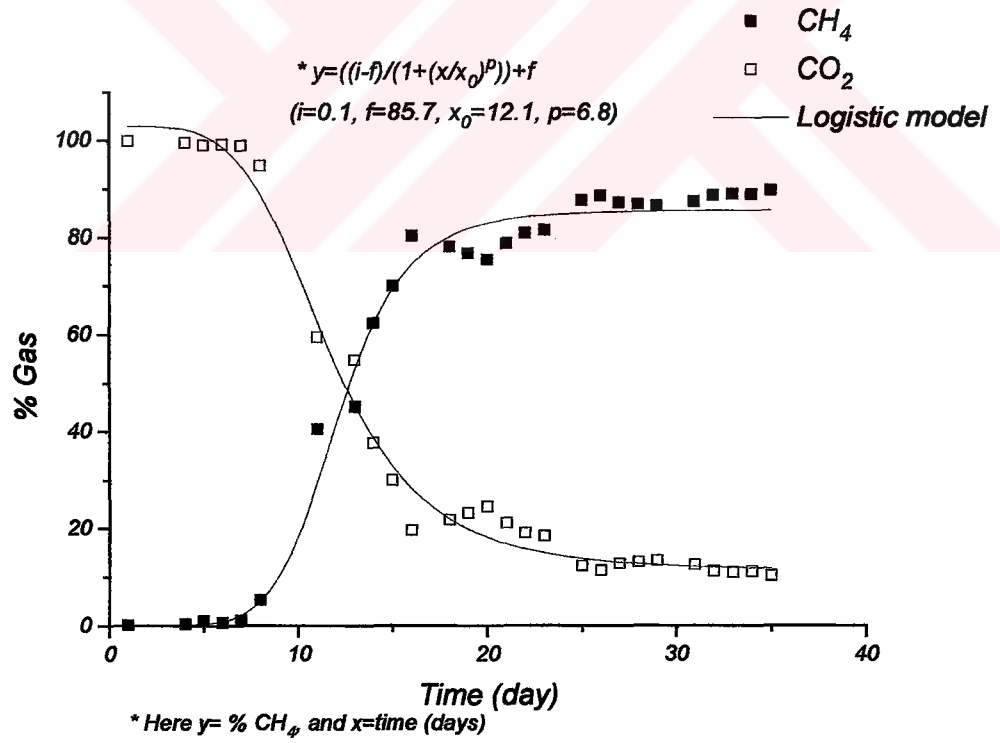

Figure 9. Percent (by volume) methane and carbondioxide in biogas measured during digestion of olive residue with waste water in the adaptation process

As can be seen in Figure 9, CO_2 consists of all the biogas at the end of the first day of digestion. The reason is the displacement air in the head space of the digester by flashing CO_2 externally. After ten days, the CO_2 production decreased sharply. At the end of 25^{th} day, it reached the stationary phase. In the stationary phase, CO_2 constitutes 30 % of the total biogas produced. The initial pH value of the slurry was 6.0. This value increased with increasing methane production. The pH of slurry reached its stationary value (7.0-7.5) at the maximum methane production rate.

Fitting Data to Various Equations: The results of the compositions and volumetric production rates of biogas and methane were fitted to some well-known curves defined in section 2.3.2. The best curve was chosen to be the Logistic Model in accordance with χ^2 criterion. The parameters of the model for each related figure are given in Appendix B.

4.3. Batchwise Anaerobic Digestion

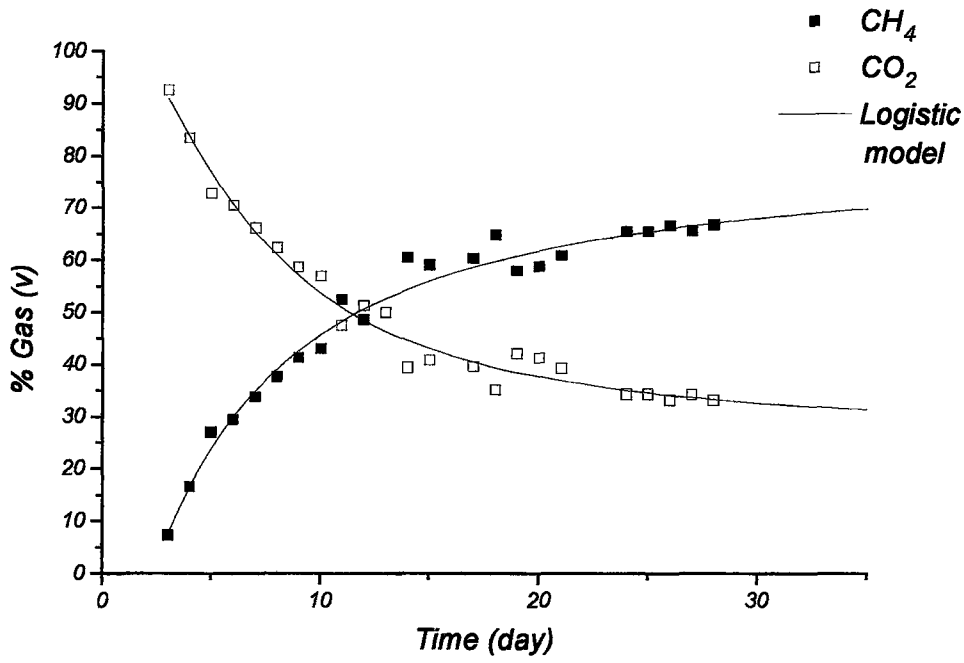

Figure 10. Biogas composition measured during batchwise anaerobic digestion of olive residue with 10 % DS (in fermentor)

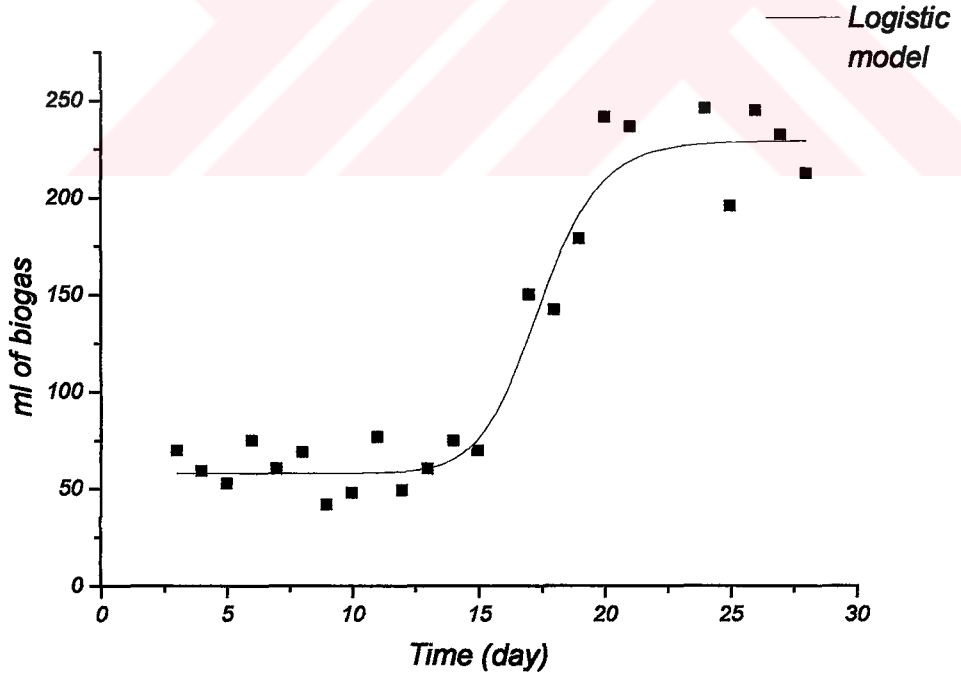

Figure 11. Volumetric biogas production during batchwise anaerobic digestion of olive residue at 10 % DS (in fermentor)

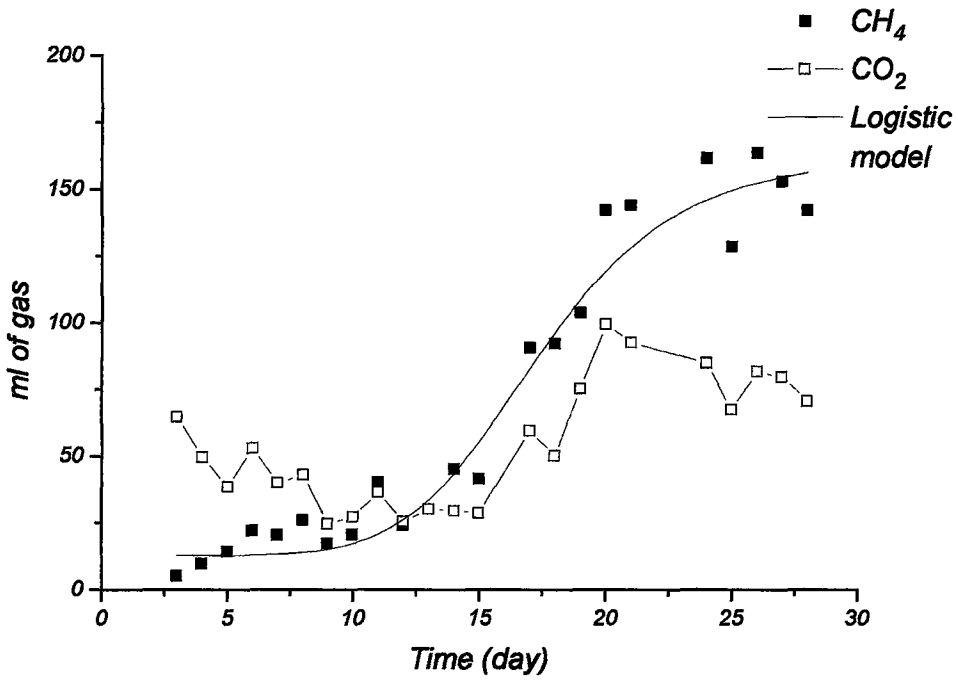

Figure 12. Volumetric methane and carbondioxide production during batchwise anaerobic digestion of olive residue at 10 % DS (in fermentor)

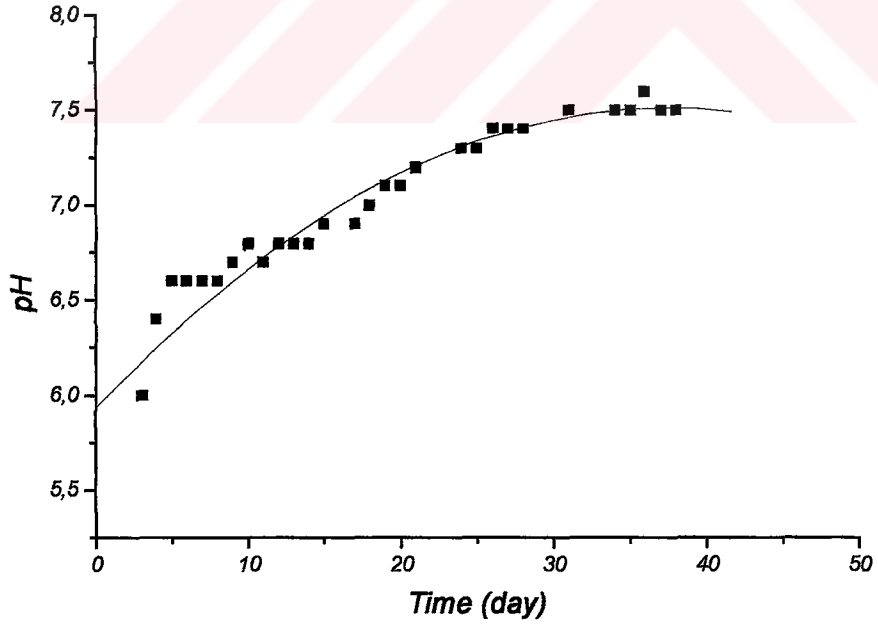

Figure 13. pH of the slurry during batchwise digestion of olive residue at 10 % DS (in fermentor)

4.3.2. Digestion in Oven Digester

Experiments were carried out in oven digester at 37°C (Figure 8) by varying initial substrate concentration (5, 10 and 15 % DS). In the oven, volumetric biogas production and compositions of gas were recorded daily. pH and other parameters could not be observed. Because it had no pH probe input. Biogas was collected outside the oven again by water-gas displacement method. The reactor working volume was 1000 ml. The compositions and volumetric biogas production trends were similar to those of the fermenter. But lag times and the amounts of biogas were different.

The data obtained for the production rates of CH_4 and CO_2 in the oven digester parallels those of the fermenter , and consequently the figures obtained by plotting those data showed similar trends. Gas compositions corresponding to 5, 10 and 15 % solids in the initial substrates are shown in Figures 14, 17 and 20 respectively. The corresponding volumetric methane production and total volumetric biogas production rates are plotted in Figures 15, 18, 21 and 16, 19, 21 respectively.

The biological parameters (specific volumetric methane production rate, lag time and stationary phase methane production rate) of methane production were determined by fitting the related data to some well-known curves defined in section 2.3.2. The parameters of the models and related biological meanings are tabulated in Table 14 and 15 respectively.

As described in section 3.2, the best models were selected by the χ^2 criteria and it was found to be the Logistic Model. Table 15 was prepared in accordance with this model. The derivation of these biological parameters were given in Table 9.

Asymptotic maxima, which increase with increasing initial substrate concentrations gives the stationary phase methane production rate. Specific volumetric methane production rates were calculated at the point of inflection. The values of specific volumetric methane production rates decrease with increasing the substrate concentration (Table 15.).

Table 14. Parameters of the models for methane production rate.

Models	Parameters*	Initial Substrate Concentration		
		5 %	10 %	15 %
Boltzman (4)	i	10.63	7.54	5.027
	f	518.98	556.29	531.422
	c	9.4	14.46	15.32
	d	0.99	2.25	3.168
	χ^2	18.03	15.85	2.87
Logistic (4)	i	11.467	11.43	2.86
	f	520.79	556.02	888
	c	9.33	14.22	20.65
	p	9.29	6.13	2.76
	χ^2	19.13	13.56	1.59
Gomperts (3)	i	522.044	902.2	757.44
	b	0.597	0.163	0.122
	c	8.53	15.487	15.475
	χ^2	23.89	16.84	1.9
Logistic (3)	i	521.49	767.36	548
	b	0.89	0.33	15.40
	c	9.35	16.46	0.2875
	χ^2	23.82	14.99	2.82

* Parameters obtained from models given in Table 9.

Table 15. Biological parameters of the Logistic model for methane production rate.

Biological Parameters		Initial Substrate Concentration		
		5 %	10 %	15 %
Lag Time	λ	7.25	9.5	7.26
Specific Volumetric Methane Production Rate	$(\frac{dy}{dx})_{x_i}$	128.26	60.28	33.83
Asymptotic Maximum	$\lim_{x \to +\infty}$	520.79	556.02	888.0

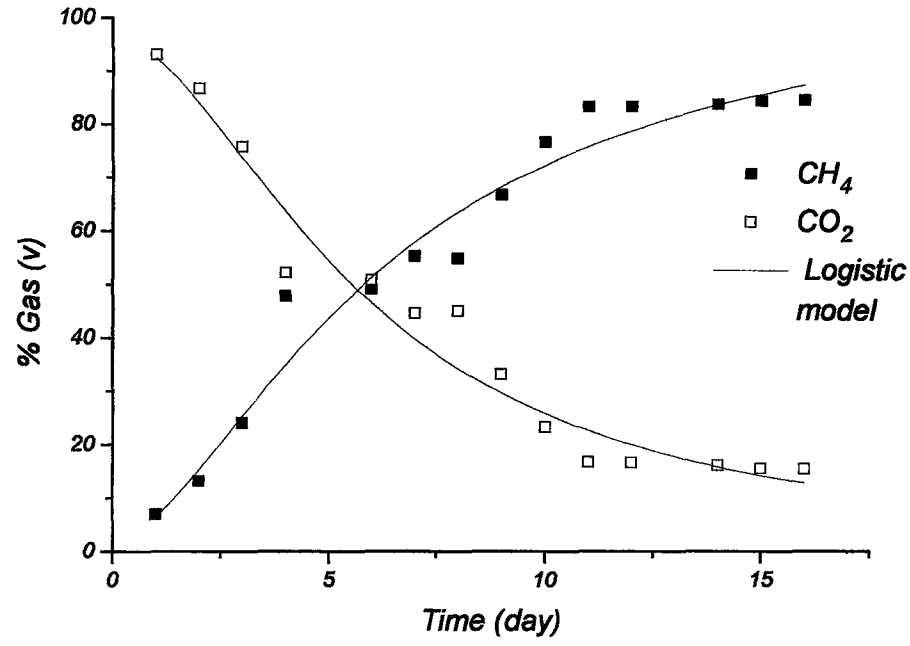

Figure 14. Biogas composition measured during digestion of olive residue with 5 % initial substrate concentration.

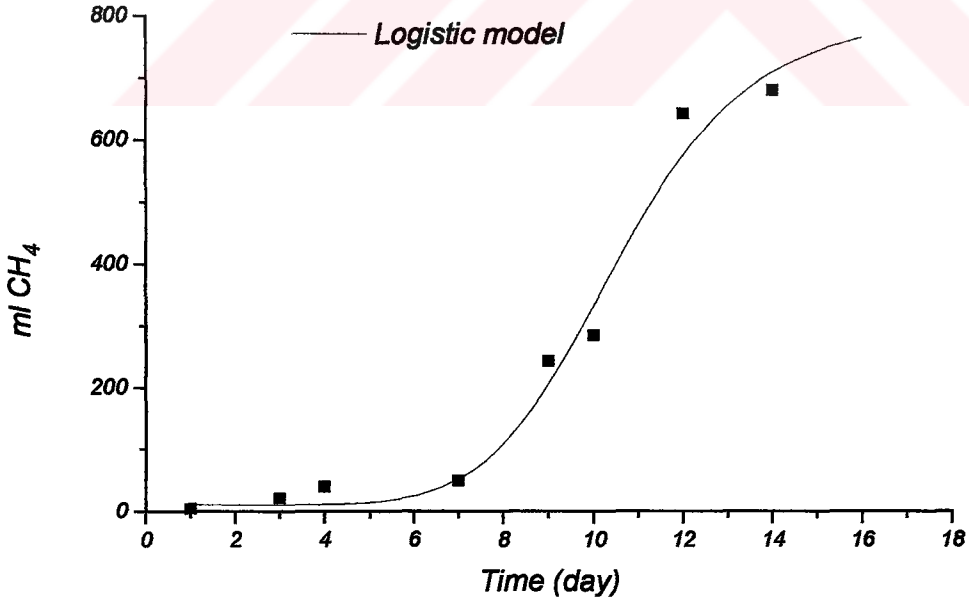

Figure 15. Volumetric methane production during batchwise anaerobic digestion of olive residue with 5 % initial substrate concentration.

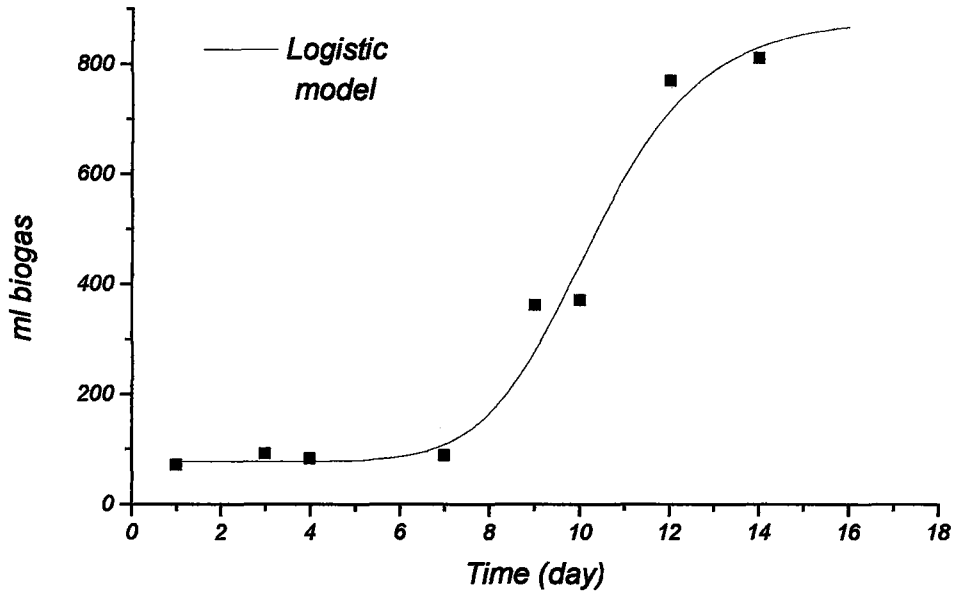

Figure 16. Volumetric biogas production during batchwise anaerobic digestion of olive residue with 5 % initial substrate concentration.

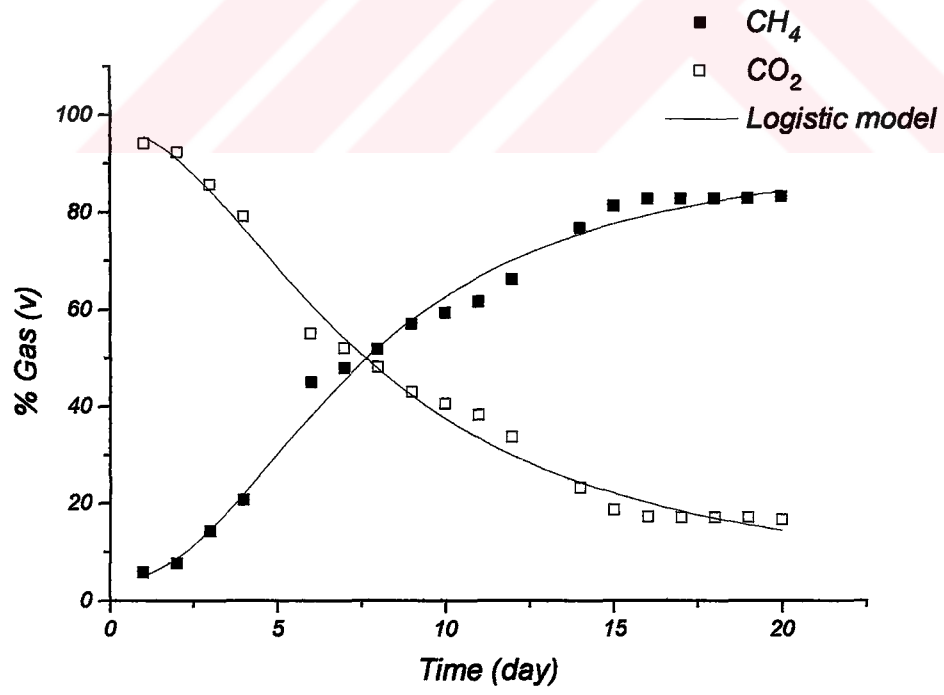

Figure 17. Biogas composition measured during batchwise digestion of olive residue with 10 % initial substrate concentration.

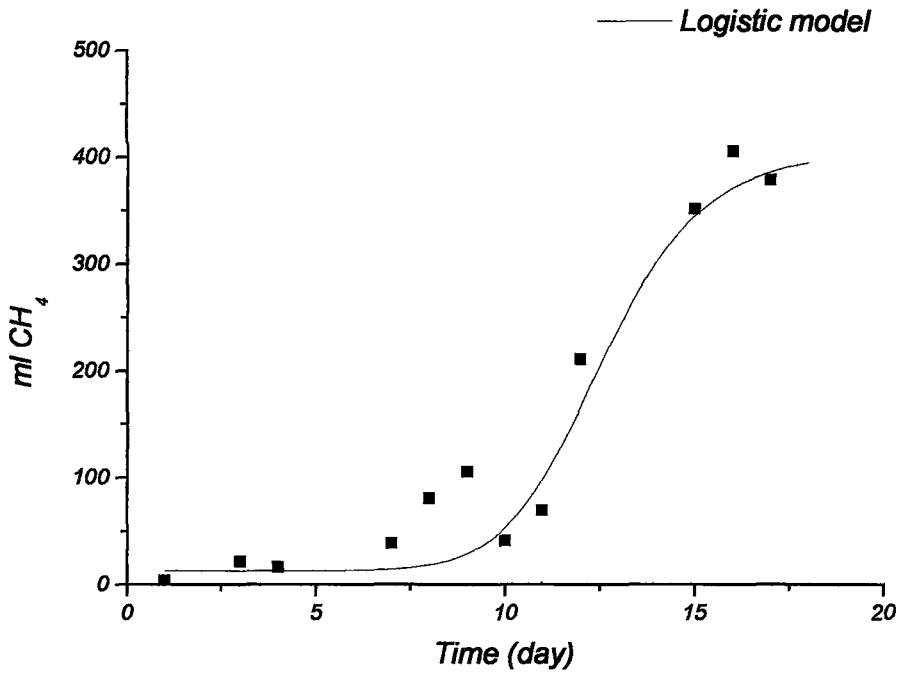

Figure 18. Volumetric methane production during batchwise anaerobic digestion of olive residue with 10 % initial substrate concentration.

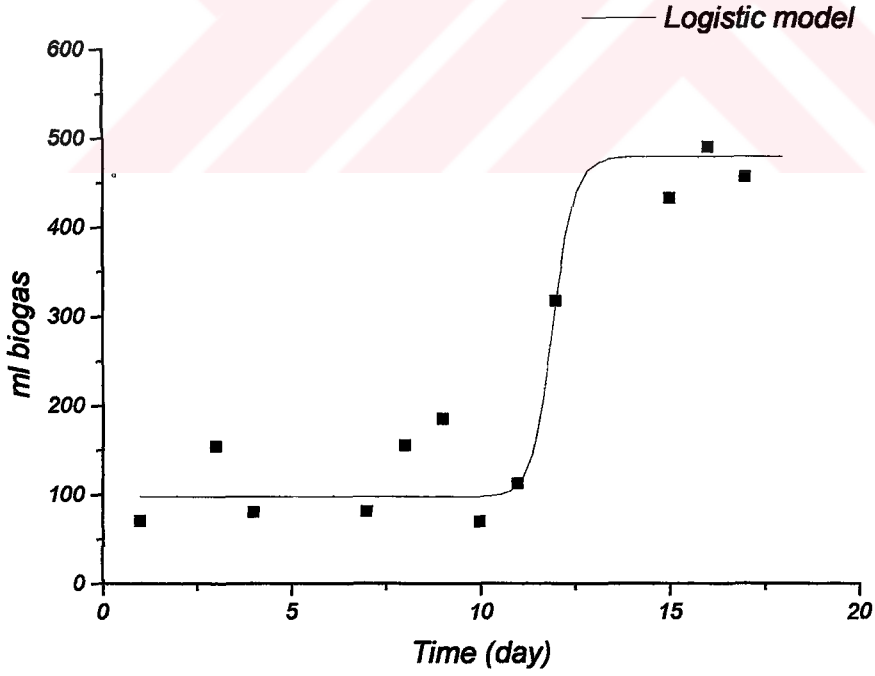

Figure 19. Volumetric biogas production during batchwise anaerobic digestion of olive residue with 10 % initial substrate concentration.

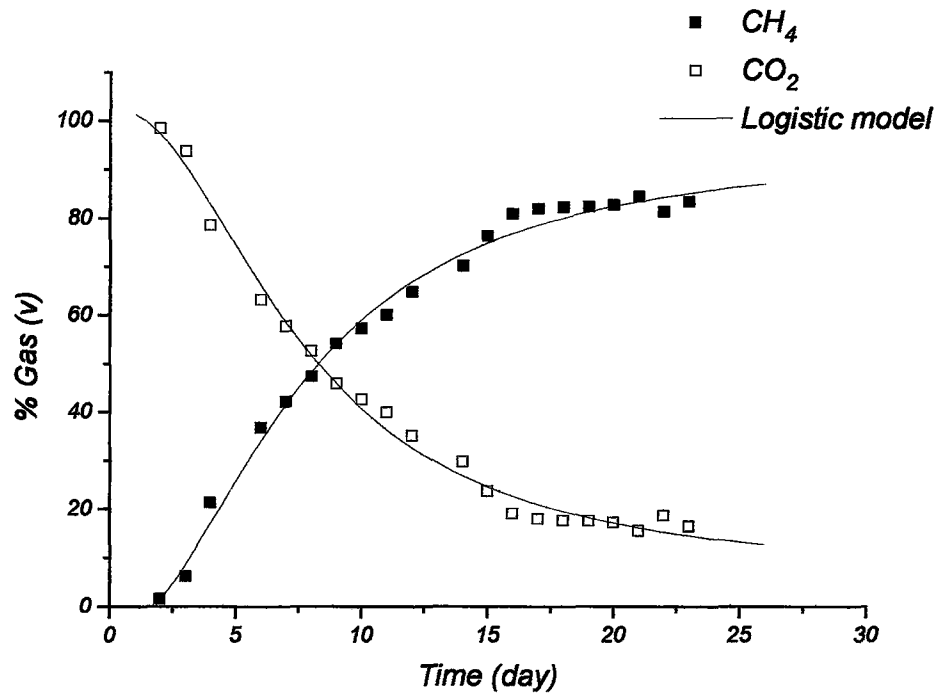

Figure 20. Biogas composition measured during digestion of olive residue with 15 % initial substrate concentration.

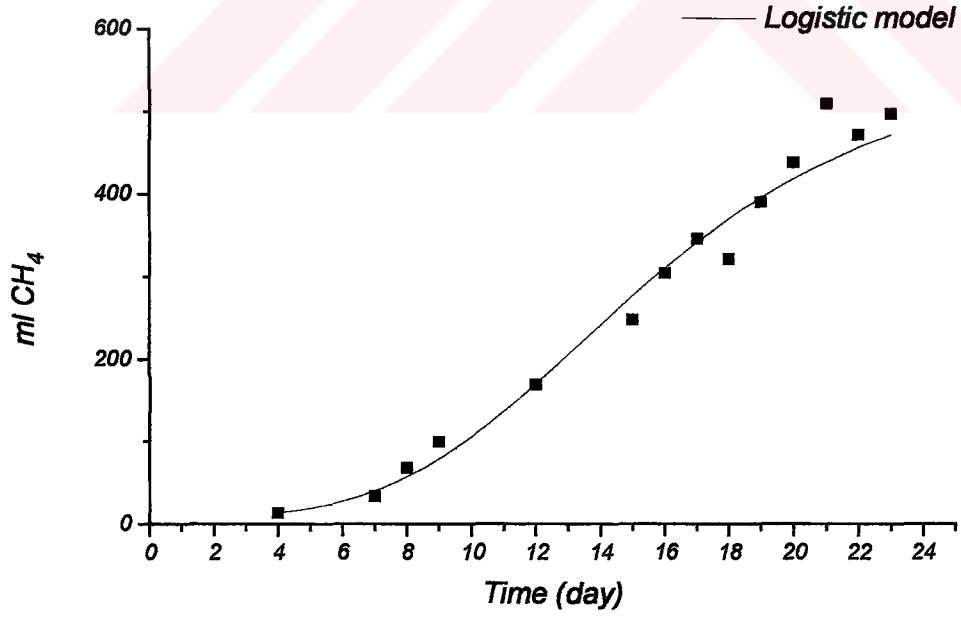

Figure 21. Volumetric methane production during batchwise anaerobic digestion of olive residue with 15 % initial substrate concentration.

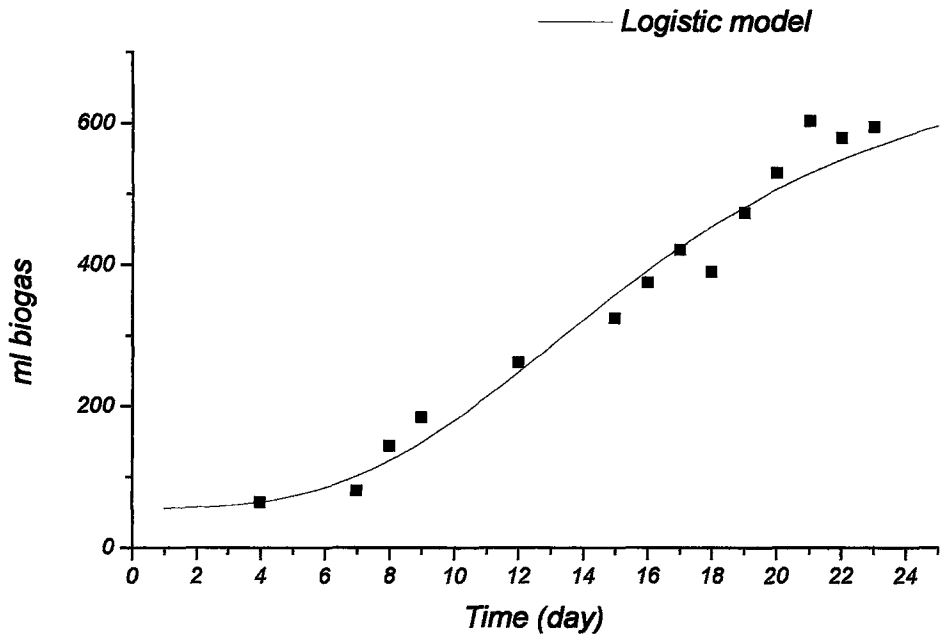

Figure 22. Volumetric biogas production during batchwise anaerobic digestion of olive residue with 15 % initial substrate concentration.

The methane composition in biogas during digestion of olive residue with 5, 10, and 15 % initial substrate concentration is shown in Figure 23 in which curves show same trend. The lag times in the methane production increases with increase in substrate concentration. Finally all curves reach the maximum value which is approximately 80 % by volume.

The same manner for lag time is observed in methane and biogas production rate as shown in Figure 24, and Figure 25 But their asymptotic values are not equal. The asymptotic values of methane production rates which are related to their initial substrate concentrations can be seen in Table 15. The asymptotic values . As shown in Figure 24 and 25, the smaller the substrate concentration the smaller the asymptotic value.

Specific methane production rates depend similarly on the initial substrate concentrations. Smaller substrate concentrations correspondence to low specific production rates.

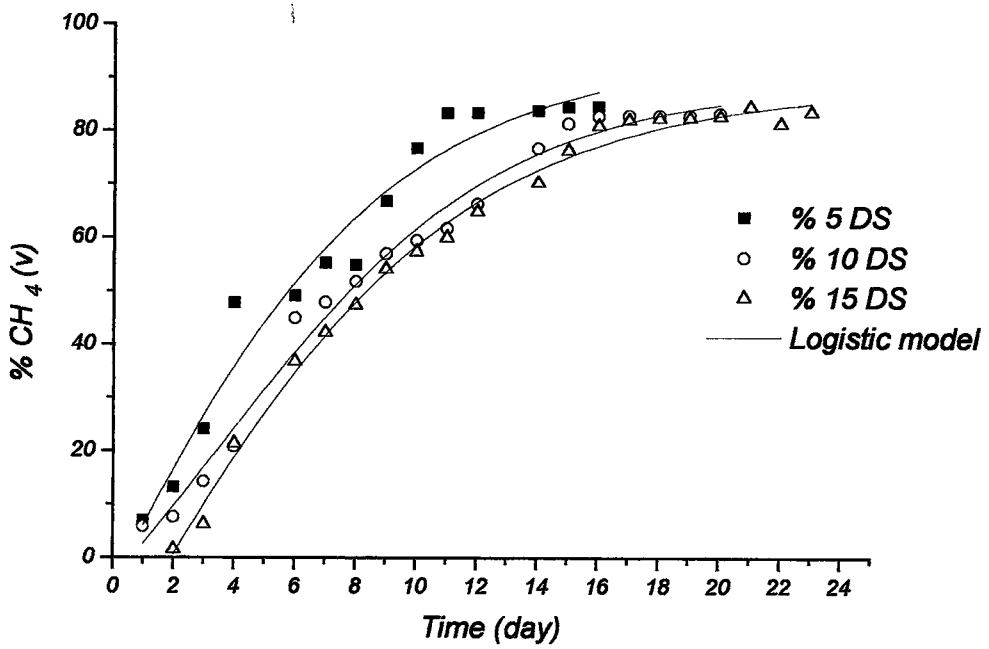

Figure 23. Percent methane in biogas measured during digestion of olive residue with 5, 10, and 15 % initial substrate concentrations.

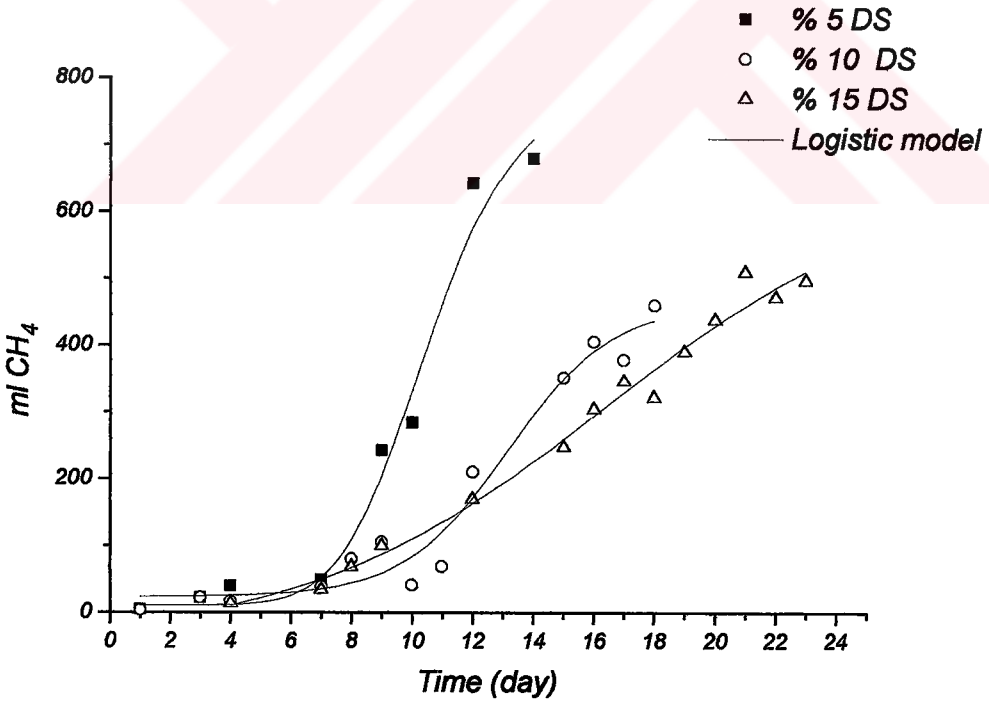

Figure 24. Volumetric methane production during batchwise anaerobic digestion of olive residue with 5, 10, 15 % initial substrate concentrations.

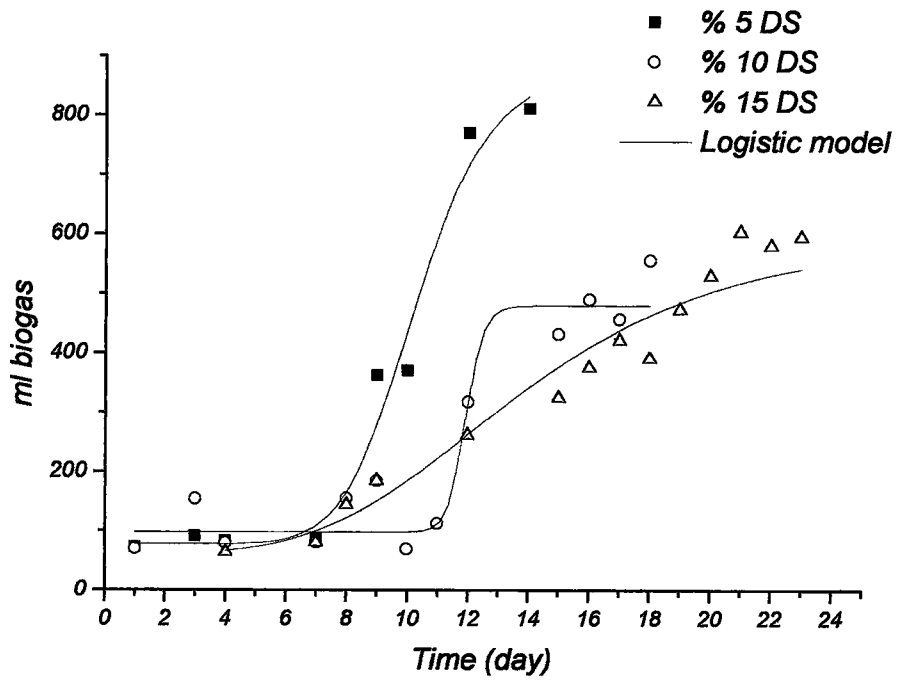

Figure 25. Volumetric biogas production during batchwise anaerobic digestion of olive residue with 5, 10, and 15 % initial substrate concentration.

4.4. Semi-continuous Anaerobic Digestion

4.4.1. Digestion in Fermenter

As it was pointed out in section 3.2.3.1, total gas production and biogas compositions have been measured and recorded everyday during digestion for different HRT and substrate concentrations. Figures 26 illustrates the composition of the biogas produced with time. It can be seen from this figure that % CH_4 in biogas increases continuously to a maximum level. It has no lag time. The reason is the use of the adapted culture medium. The amount of culture also affects the lag period. After the introduction of the feed into the digester, CH_4 production decreased continuously to a steady state value. At the same time, the percentage of the CO_2 fell to a minimum during the first 25 days, and then it increased to a steady state value. The steady state composition of CH_4 and CO_2 were deduced to be 48 % and 52 % respectively. In the semi-

continuous mode of anaerobic digestion a decrease in CH_4 and increase in CO_2 production may be attributed to the following:

a) Insufficient microorganism concentration to consume the substrate
b) Lower specific growth rate of the methanogenic microorganisms than the dilution rate
c) Higher specific growth rate of acedogenic microorganisms than specific growth rate of methanogenic microorganisms.
d) Adaptation phase of the microorganisms to the new substrate

Figure 27 gives the volumetric production rates of CH_4 and CO_2 . The steady state values of these as obtained by asymptotic maximum, are 115 and 125 ml/day respectively for CH_4 and CO_2 . The production trends followed in Figure 12 is similarly observed in Figures 27. The pH of the slurry was observed to reach a maximum value of 7.6 within 25 days (Figure 28.). It then decreased to 7.2. The pH of the feed was 6.0. The decrease in the pH of slurry is thus be explained by the introduction feed into the digester.

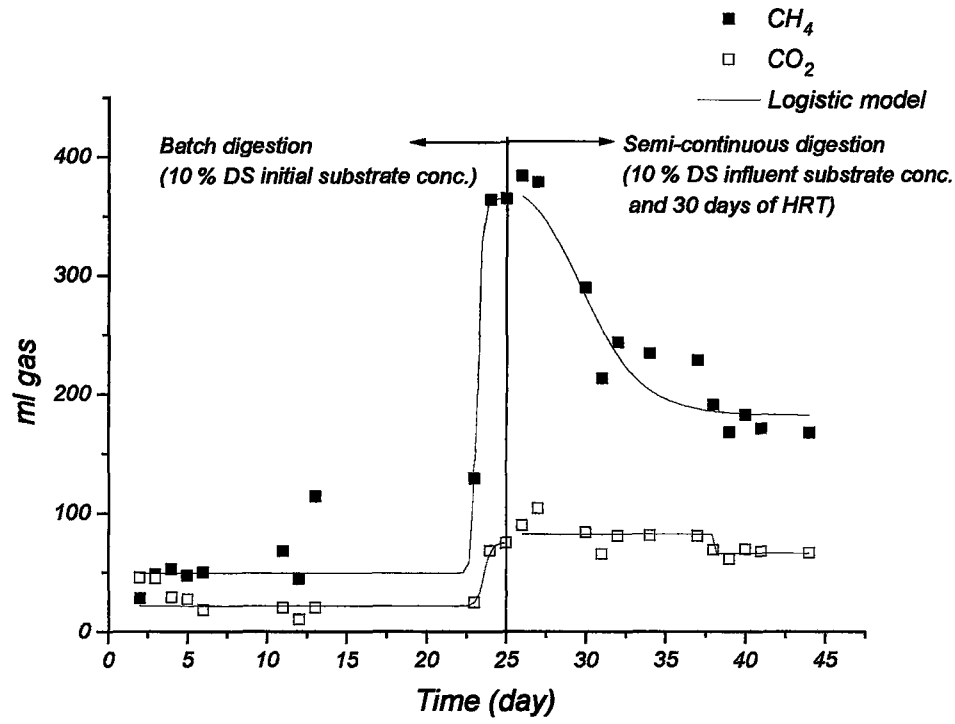

Figure 27. Volumetric methane and carbondioxide production during batch and semi-continuous digestion of olive residue

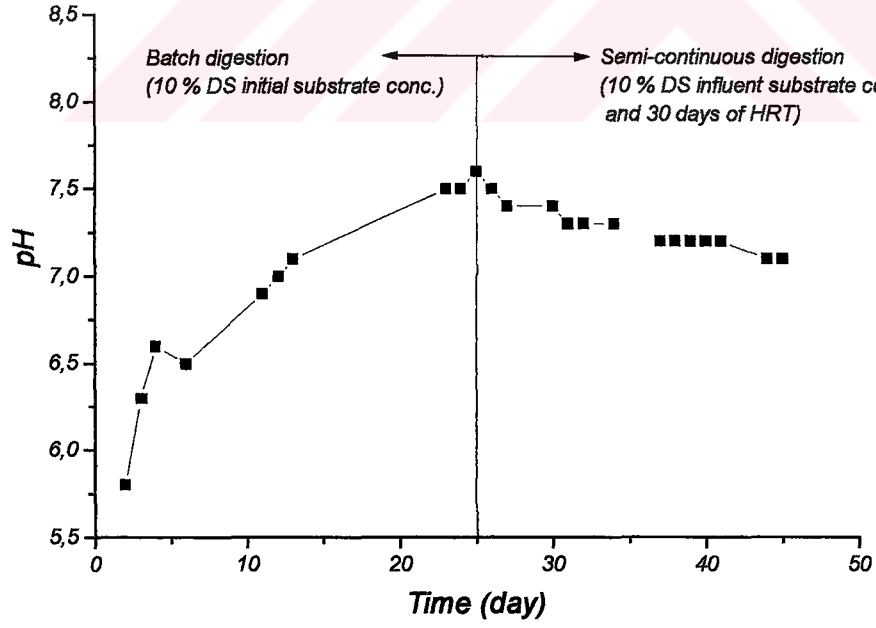

Figure 28. PH of the effluent slurry during batch and semi-continuous digestion of olive residue

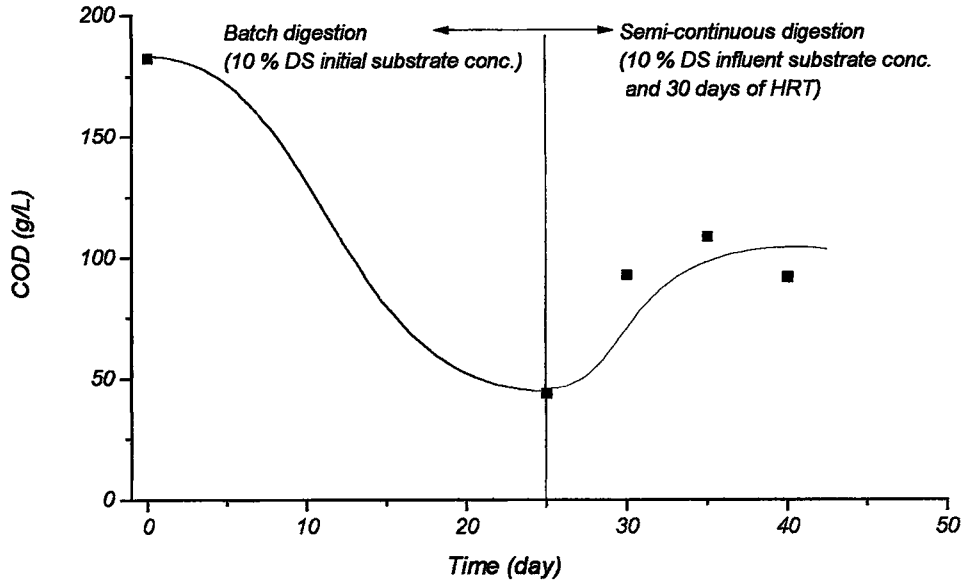

Figure 29. COD of the effluent slurry during batch and semi-continuous digestion of olive residue.

Some of the feed was discharged without being consumed. This was confirmed by the reduction of the oxidizable matter in the digester which can be considered as COD. As it is seen in Figure 29, the COD of the slurry decreased from its initial value of 182.5 g/L to the final 436.7 g/L within 25 days. And then it increased to the equilibrium value (≈97.6 g/L). The equilibrium value is higher than the value at 25^{th} days. Theoretically, it must have been the same, in the absence of problems such as washing out of the substrate.

Figure 26 shows the production trends of CH_4 and CO_2 in the semi-continuous mode of digestion. The respective percentages of each gas reached their steady-state values shortly after 40 days. The volumetric production of CH_4 and CO_2 are illustrated in Figure 27 in a similar manner. An increase of this rate is observed for both CH_4 and CO_2 during batch stages. After feeding, biogas production decreased sharply and then the gas composition reached its steady state values.

4.4.2. Digestion in Oven Digester

Two sets of experiments were carried out to optimize the operational parameters. Digesters were operated at hydraulic retention times of 10, 20, 30, and 40 days at a constant initial substrate concentrations (10 % DS). The results are presented in Tables 16 and 17. During digestion, pH of the broth remained essentially constant at 7.0 for all set of experiments.

Total biogas production, methane production rate and percent methane in the biogas have been measured and recorded everyday during each digestion run. Experiments carried out in the oven digester were rather illustrative in depicting the effect of HRT and initial substrate concentration on production rates and biogas compositions.

Daily gas productions and methane percent in the each set were taken as the steady-state values. The gas yields in each set of experiments were calculated as L of biogas generated per g of COD added to the digester Per L of digester volume. The maximum biogas production rate and yield were calculated to be 0.69 L/day.L of digester volume and 0.076 L/g COD added.L of digester volume (HRT=20 days, DS %=10).

Figure 30, 33, 36, and 39 show percent methane in biogas for HRT's corresponding to 10, 20, 30, and 40 days respectively. In all cases, % methane in the biogas was observed to attain its maximum value after 15th day of digestion. Each graph with 10 % DS exhibits essentially the same asymptotic composition around 80 % methane by volume. Percent methane corresponding to 5 and 15 % DS showed a similar trend but the maximum methane composition reached after 10 and 18 days respectively (Figures 42 and 45).

Figures 31, 34, 37, 40 and 32, 35, 38, 41 show methane and biogas production rates for HRT's corresponding to 10, 20, 30, and 40 days respectively. The asymptotic values of methane productions are given in Table 17. Figures 42, 43, 44, 45, 46, 47 illustrate the effect of initial substrate concentration on the biogas composition,methane and biogas production rates.

In Table 16, the observed biogas production rates and compositions are summarized together with the corresponding initial substrate concentrations (% DS) and HRT's.

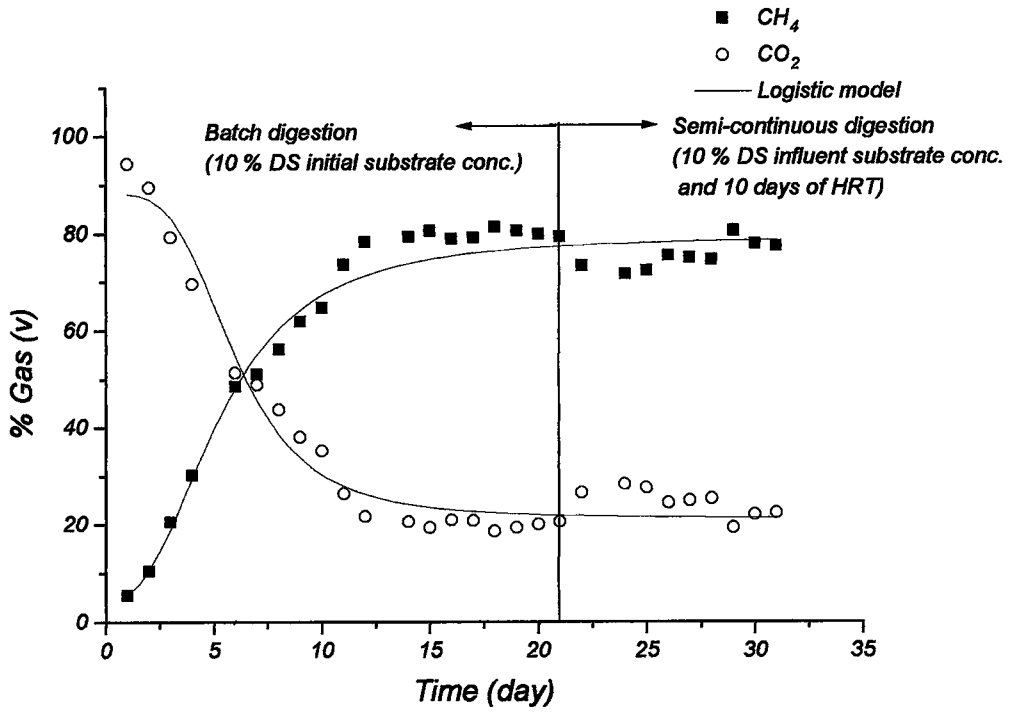

Figure 30. Biogas composition during batch and semi-continuous digestion of olive residue (HRT=10 days).

Table 16. Effect of HRT on gas production and effluent characteristics during semi-continuous digestion of olive residue

Operational Parameters				
HRT (days)	10	20	30	40
DS in feed slurry (%)	10	10	10	10
COD in feed slurry (g/L)	182.53±14.9	182.53±14.9	182.53±14.9	182.53±14.9
COD loading (g/day)	18.25±1.5	9.13±0.75	6.08±0.5	4.56±0.37
Gas Production (Per L digester volume)				
% CH_4 (v)	79.5±1.4	81.9±1.4	84.0±1.7	82.6±1.9
Biogas (L/day)	0.525±0.16	0.692±0.07	0.472±0.03	0.393±0.04
CH_4 (L/day)	0.384±0.07	0.550±0.05	0.390±0.03	0.320±0.04
Gas yield (L/g COD added)	0.028±0.007	0.076±0.002	0.078±0.002	0.086±0.002
CH_4 yield (L/g COD added)	0.021±0.002	0.06±0.001	0.064±0.001	0.07±0.003
CH_4 yield (L/g COD used)	0.112±0.011	0.135±0.001	0.122±0.001	0.128±0.006
Effluent Characteristics				
COD in effluent (g/L)	148.53±12.1	101.30±8.3	86.45±7.1	82.96±6.8
COD removal (g/.day)	14.85±1.2	5.065±0.41	2.88±0.24	2.074±0.17
DS in effluent slurry (%)	4.84	4.082	6.49	6.78

Table 17. Effect of the initial substrate concentration on gas production and effluent characteristics during semi-continuous digestion of olive residue

Operational Parameters			
HRT (days)	30	30	30
DS in feed slurry (%)	5	10	15
COD in feed slurry (g/L)	91.27±7.5	182.53±14.9	273.8±22.4
COD loading (g/day)	3.04±0.25	6.08±0.5	9.13±0.75
Gas Production (Per L digester volume)			
% CH_4 (v)	81.4±1.8	84.0±1.7	90.7±2.4
Biogas (L/day)	0.215±0.033	0.473±0.027	0.768±0.081
CH_4 (L/day)	0.180±0.026	0.391±0.032	0.622±0.043
Gas yield (L/COD added)	0.070±0.005	0.078±0.002	0.084±0.002
CH_4 yield (L/g COD added)	0.059±0.004	0.064±0.001	0.068±0.001
CH_4 yield (L/g COD used)	0.118±0.023	0.122±0.001	0.105±0.001
Effluent Characteristics			
COD in effluent (g/L)	45.85±3.28	86.45±7.06	96.06±7.85
COD removal (g/day)	1.51±0.21	2.88±0.24	3.20±0.26
DS in effluent slurry (%)	3.36	6.49	6.91
pH	7.96	7.65	7.25
g COD used/day	1.53±0.04	3.20±0.26	5.93±0.48

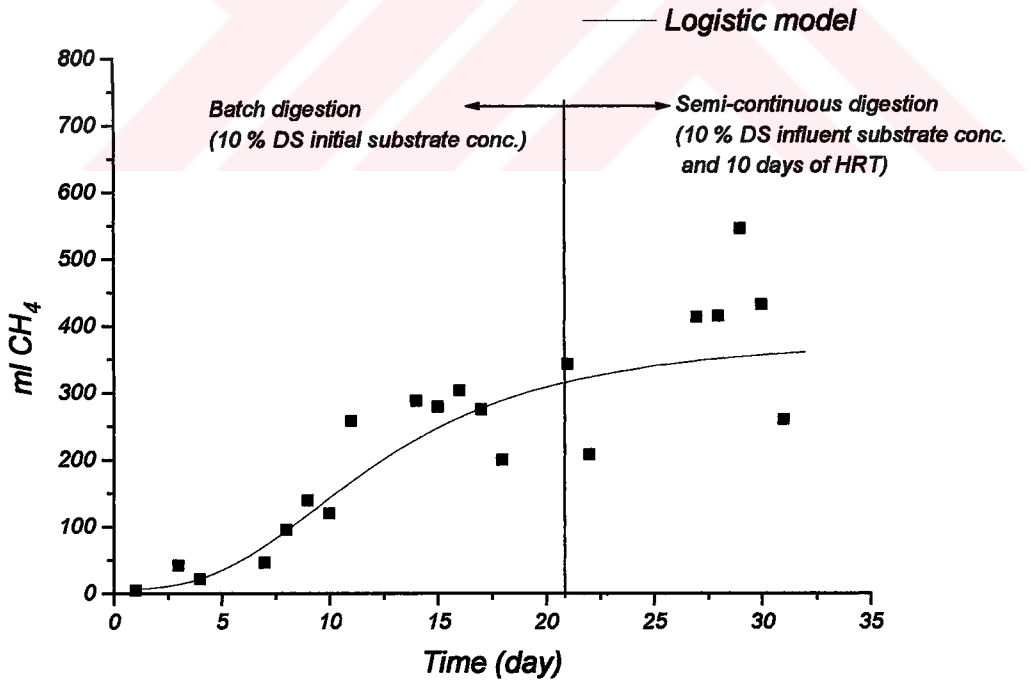

Figure 31. Volumetric methane production during batch and semi-continuous digestion of olive residue (HRT=10 days)

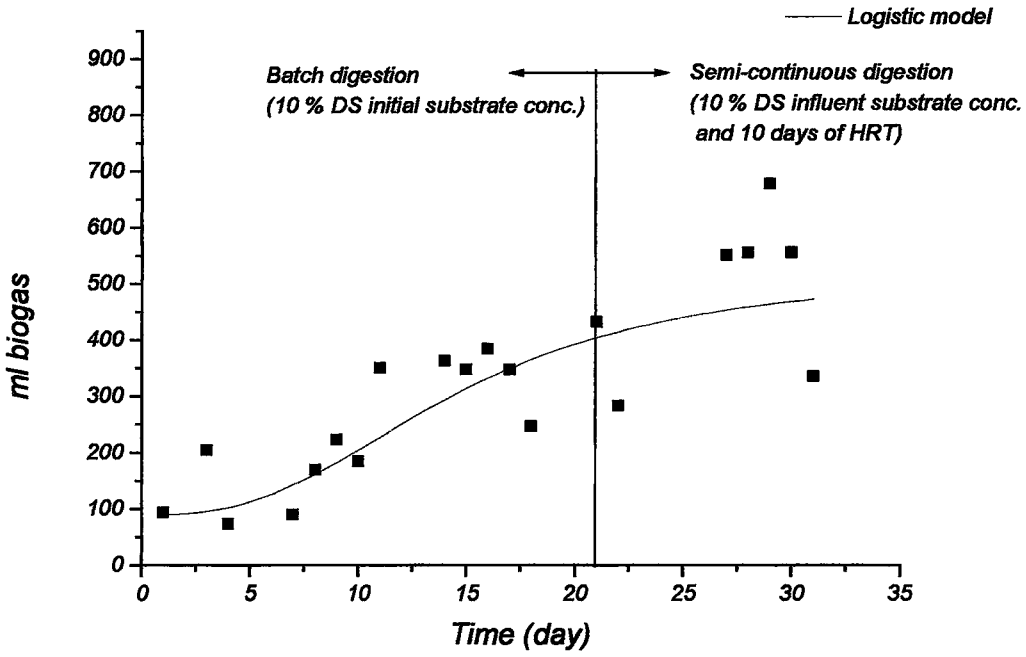

Figure 32. Biogas production during batch and semi-continuous digestion of olive residue (HRT=10 days)

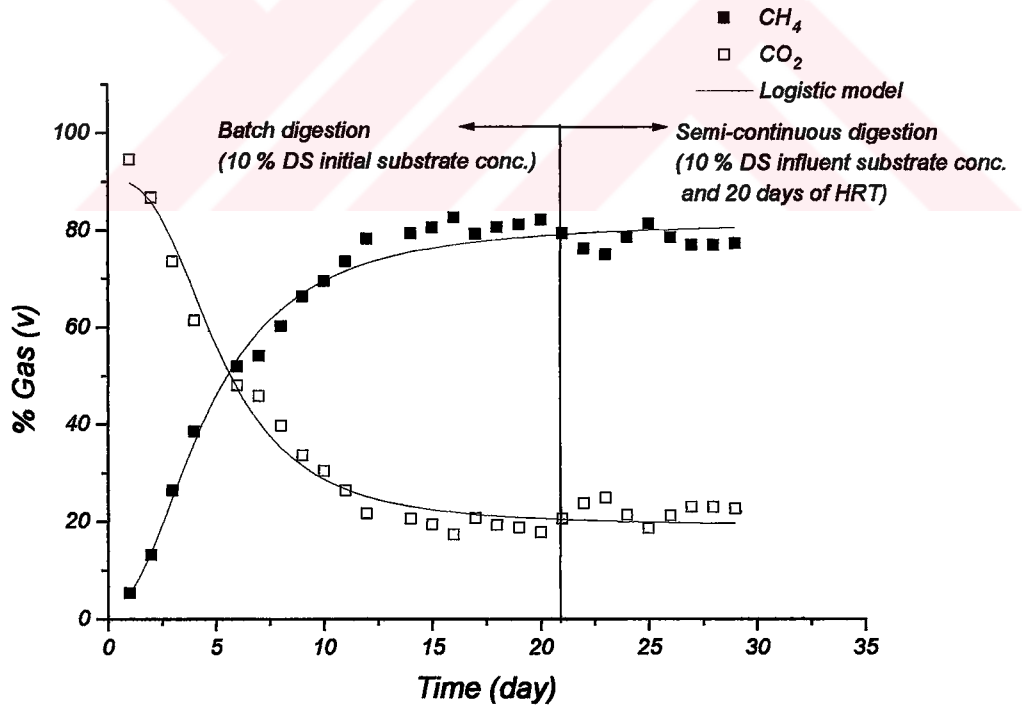

Figure 33. Biogas composition during batch and semi-continuous digestion of olive residue (HRT=20 days)

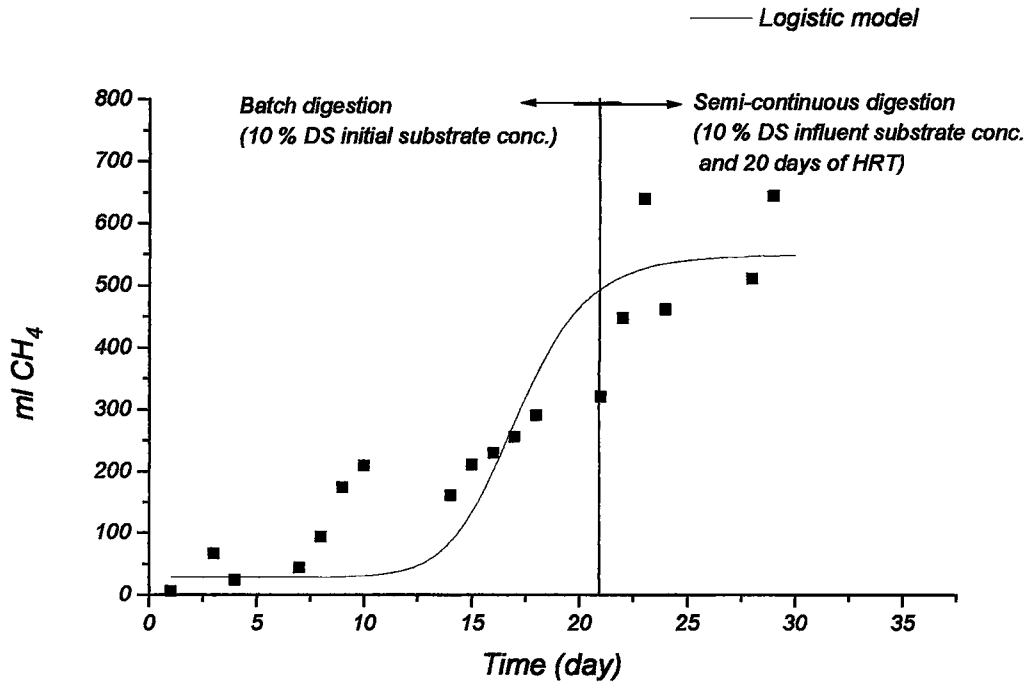

Figure 34. Volumetric methane production during batch and semi-continuous digestion of olive residue (HRT=20 days)

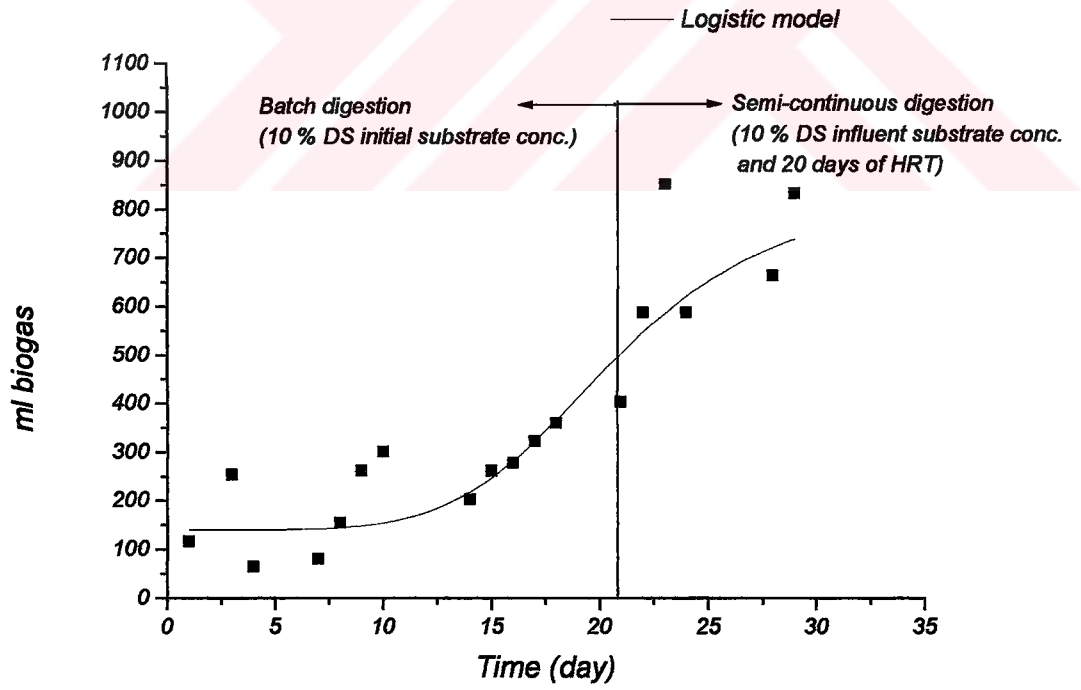

Figure 35. Biogas production during batch and semi-continuous digestion of olive residue (HRT=20 days)

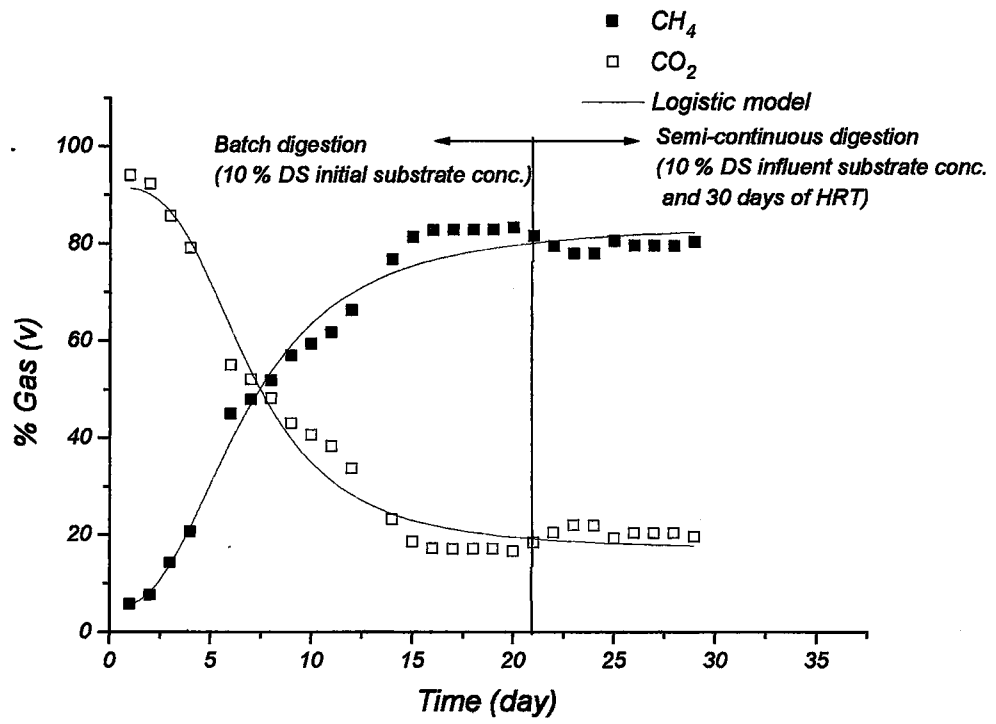

Figure 36. Biogas composition during batch and semi-continuous digestion of olive residue (HRT=30 days)

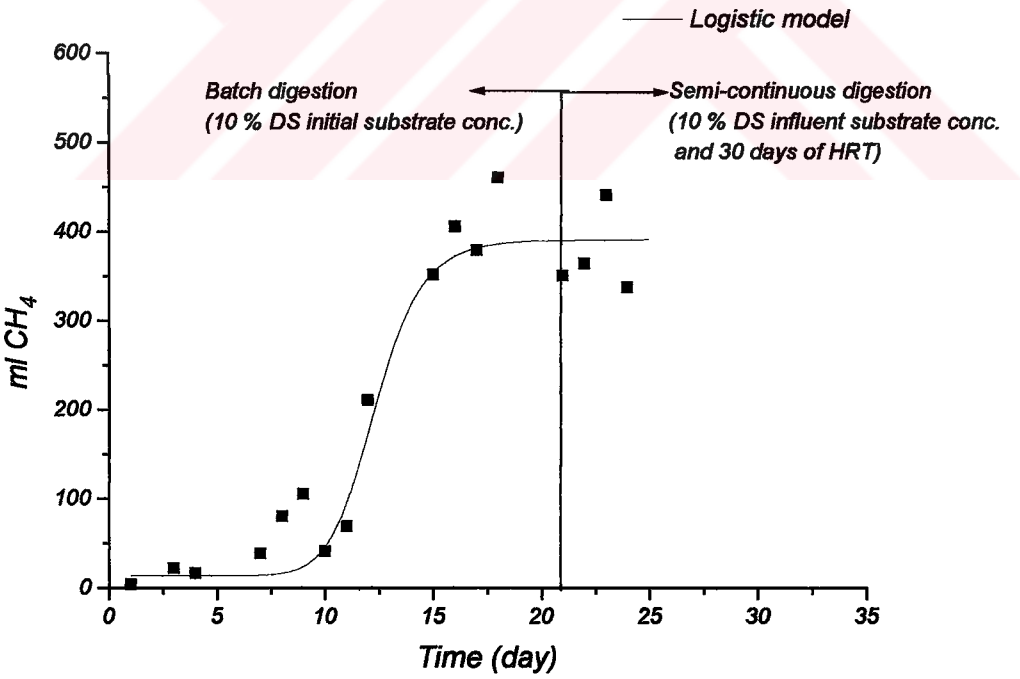

Figure 37. Volumetric methane production during batch and semi-continuous digestion of olive residue (HRT=30 days)

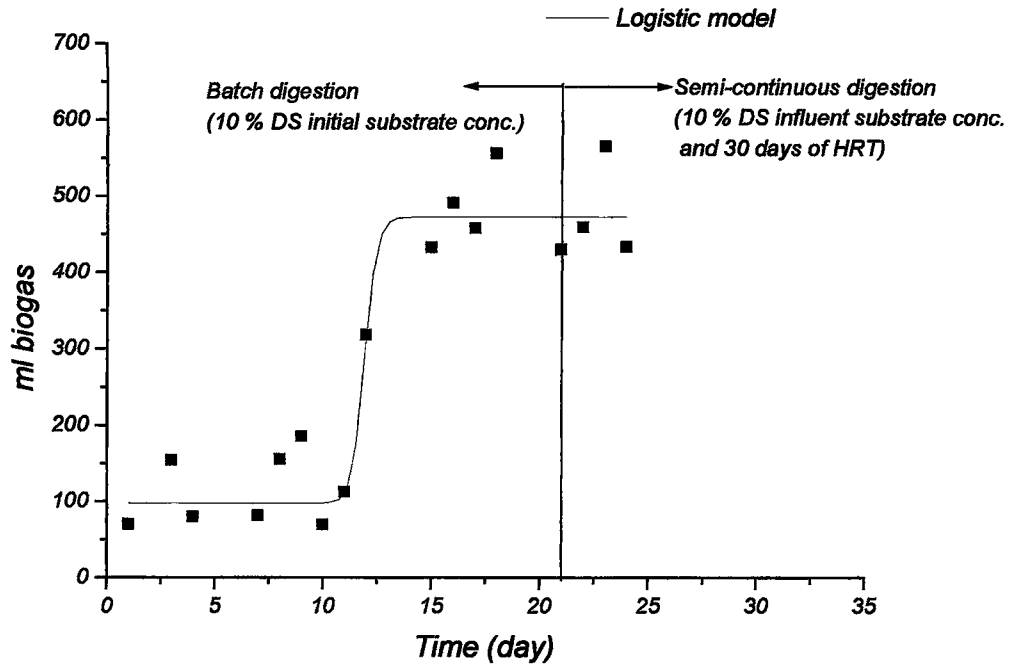

Figure 38. Biogas production during batch and semi-continuous digestion of olive residue (HRT=30 days)

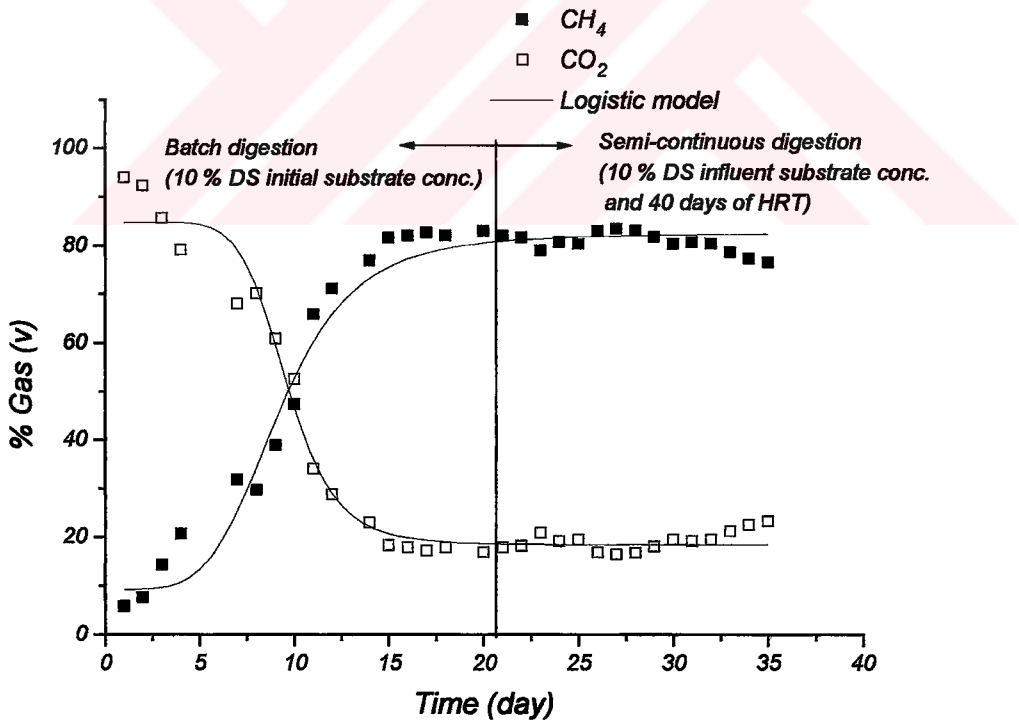

Figure 39. Biogas composition during batch and semi-continuous digestion of olive residue (HRT=40 days)

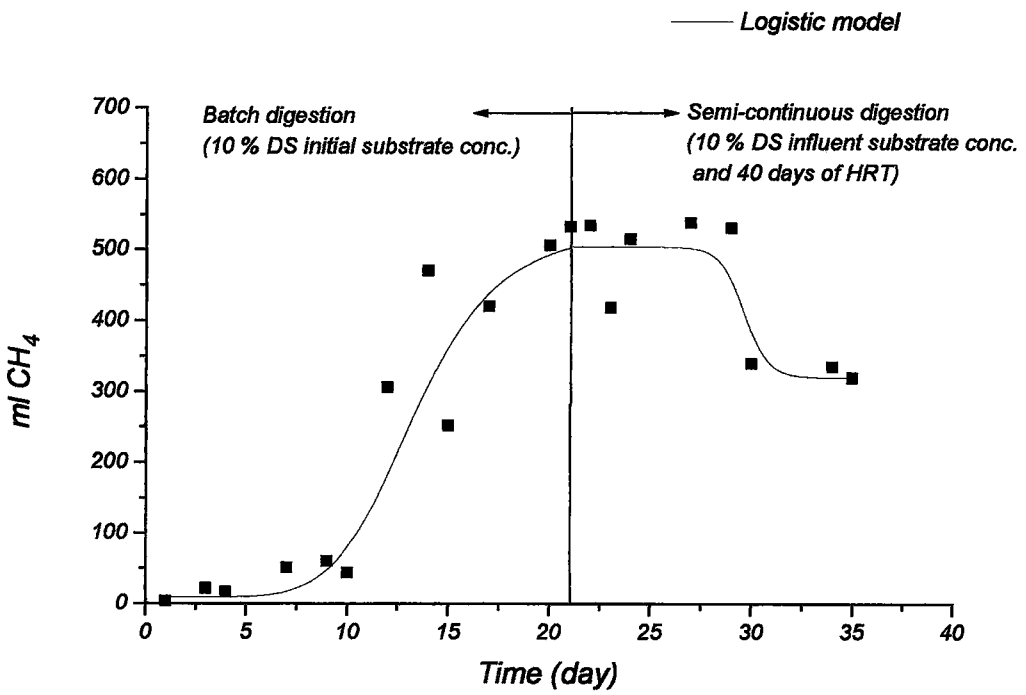

Figure 40. Volumetric methane production during batch and semi-continuous digestion of olive residue (HRT=40 days)

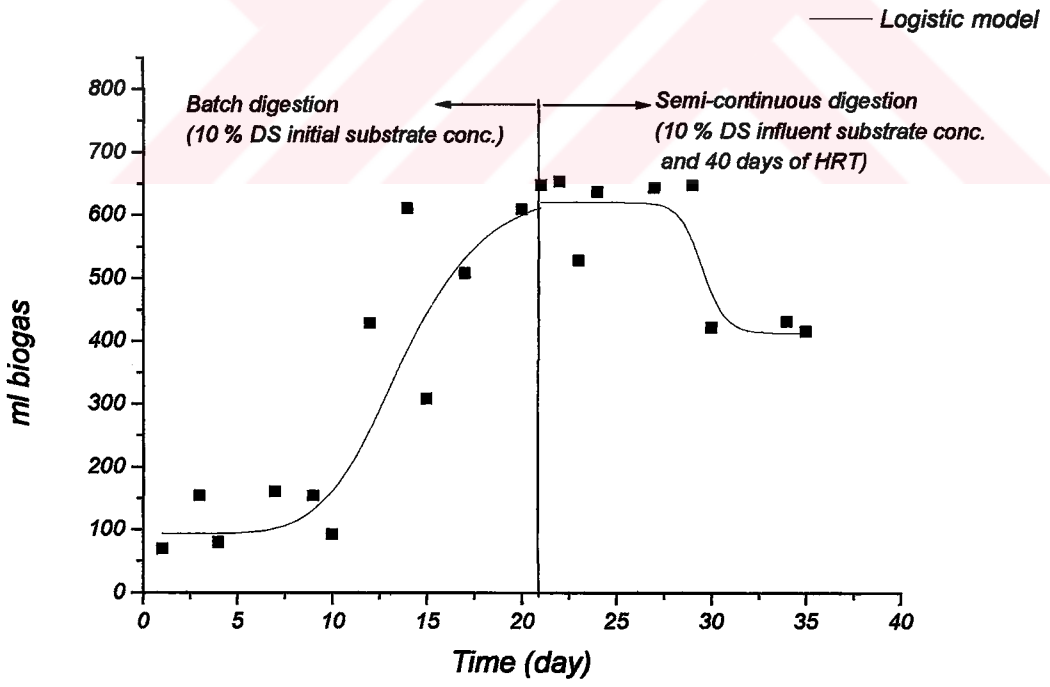

Figure 41. Biogas production during batch and semi-continuous digestion of olive residue (HRT=40 days)

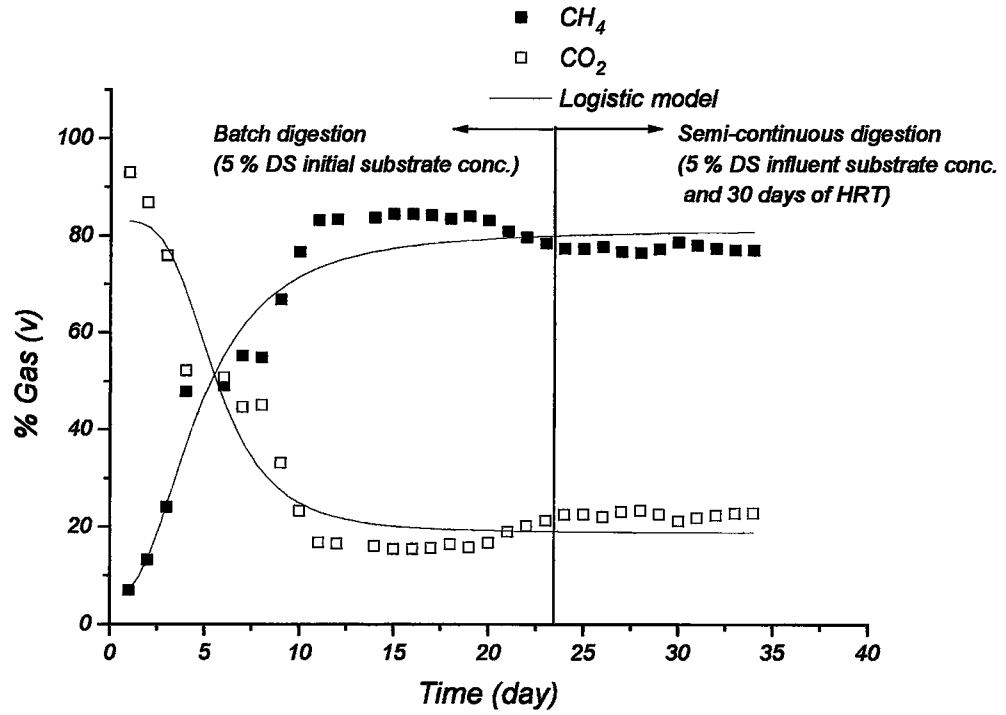

Figure 42. Biogas composition during batch and semi-continuous digestion of olive residue (5 % DS)

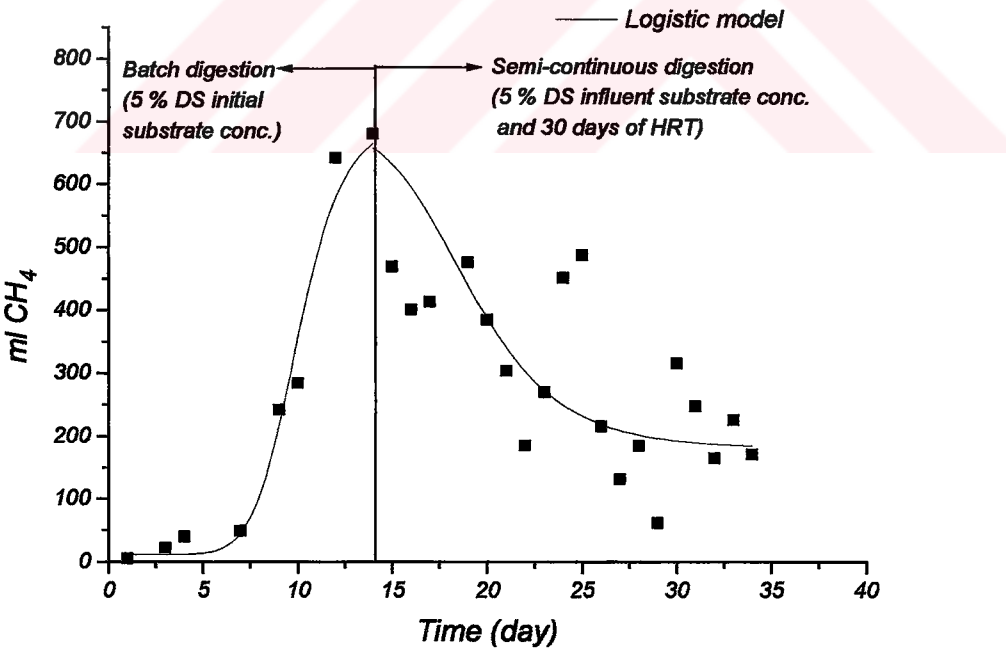

Figure 43. Volumetric methane production during batch and semi-continuous digestion of olive residue (5 % DS)

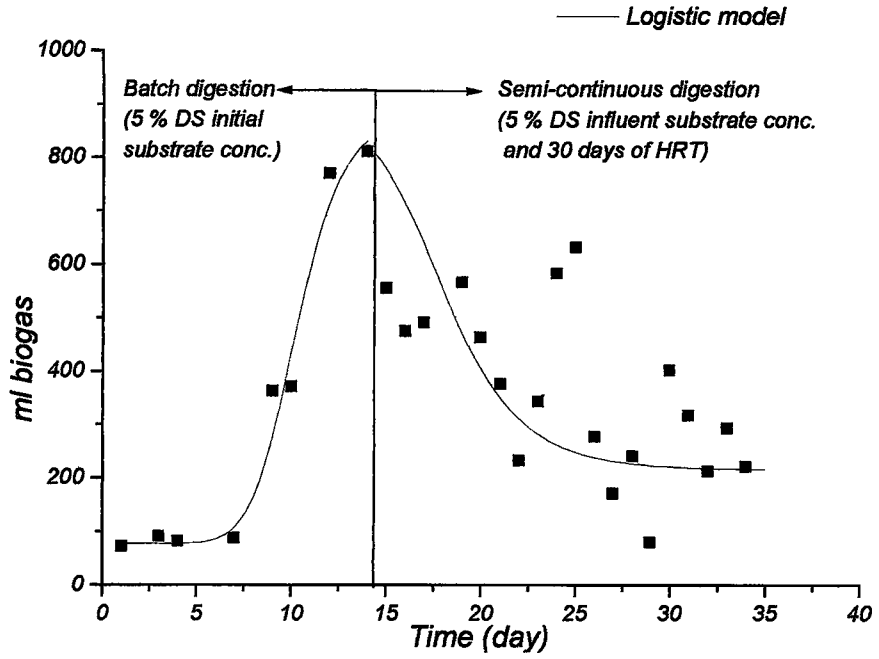

Figure 44. Biogas production during batch and semi-continuous digestion of olive residue (5 % DS)

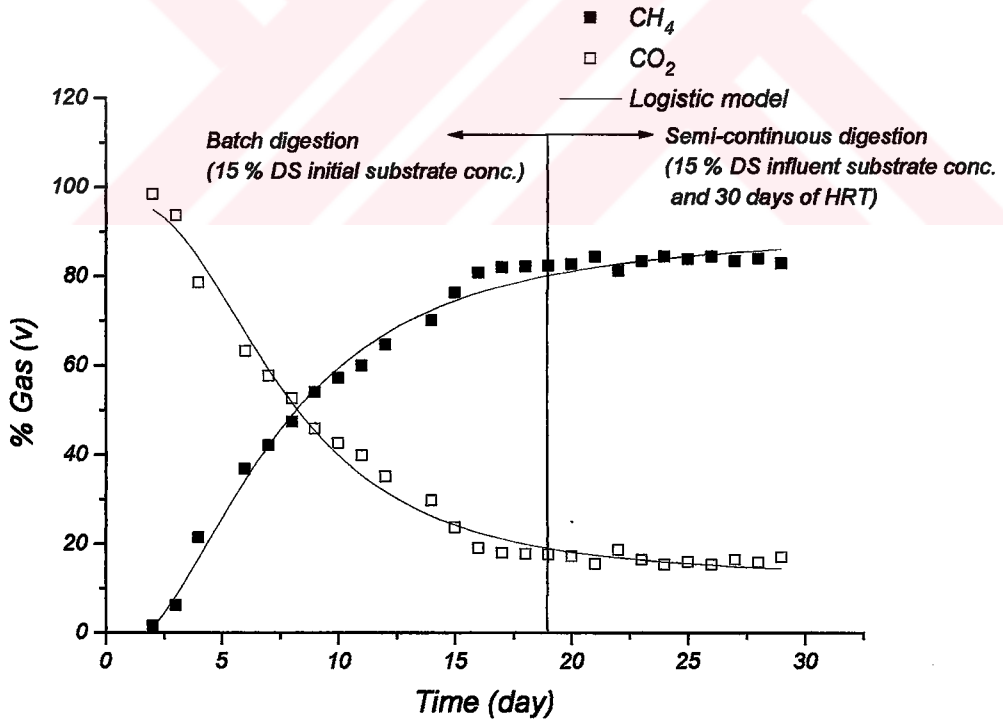

Figure 45. Biogas composition during batch and semi-continuous digestion of olive residue (15 % DS)

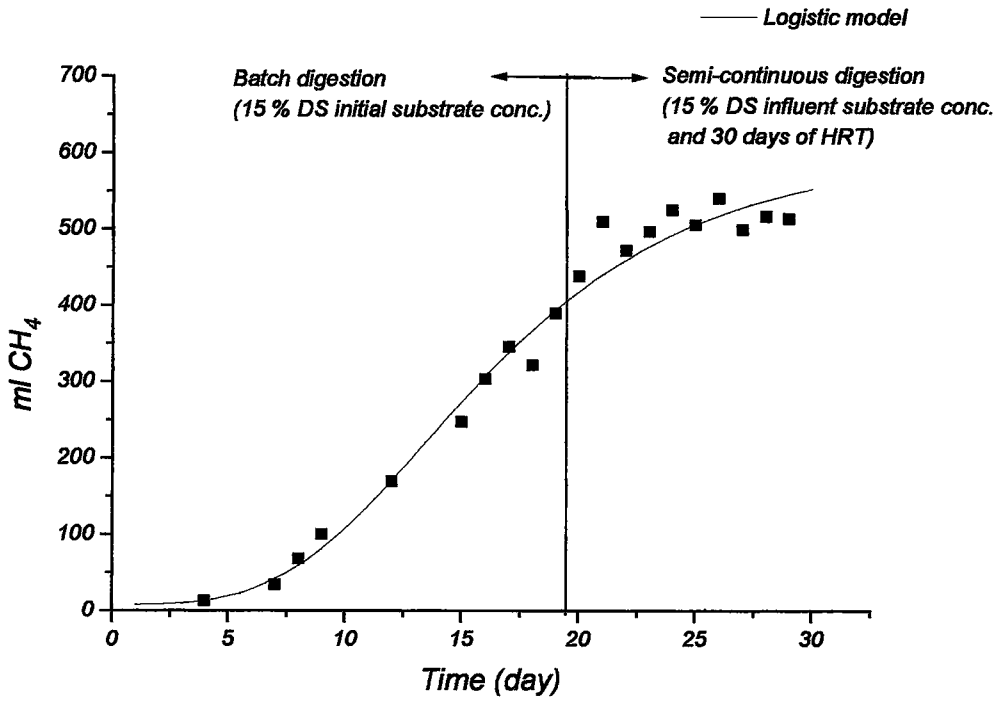

Figure 46. Volumetric methane production during batch and semi-continuous digestion of olive residue (15 % DS)

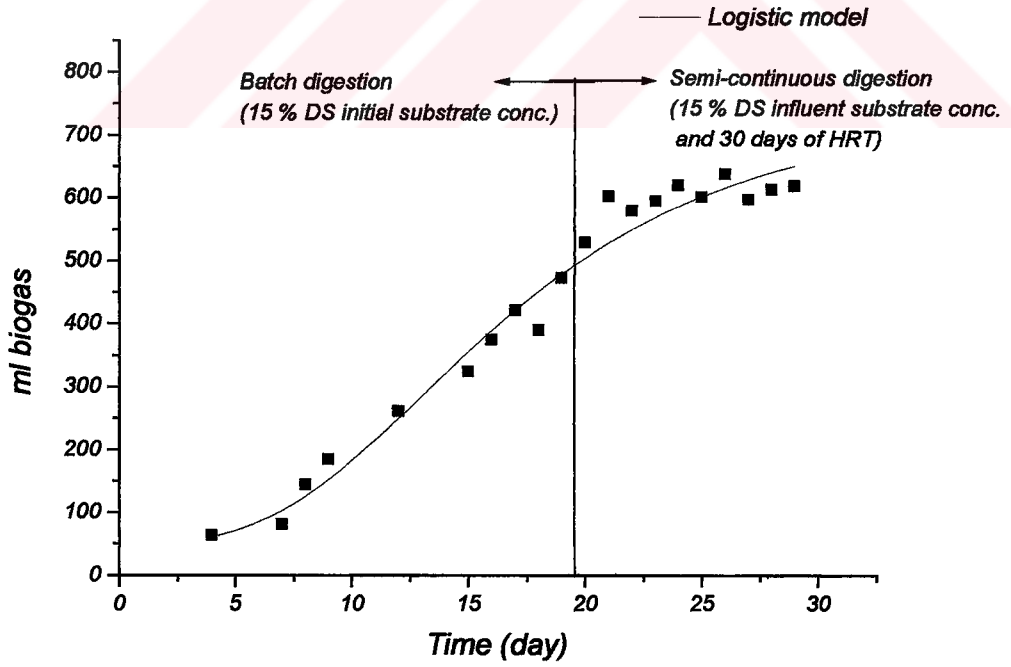

Figure 47. Biogas production during batch and semi-continuous digestion of olive residue (15 % DS)

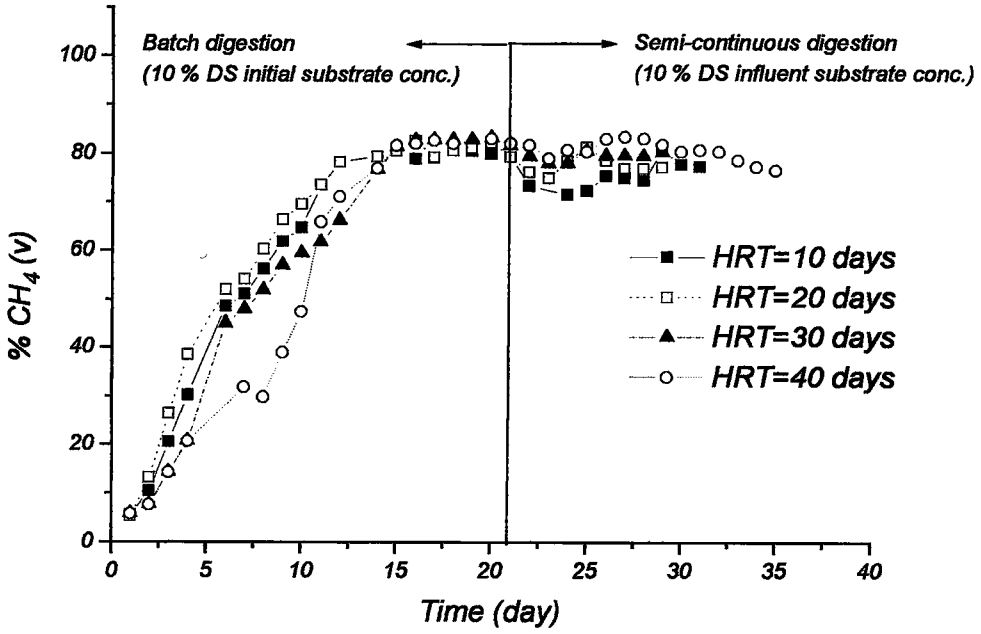

Figure 48. Effect of HRT on percent methane in biogas during batch and semi-continuous digestion of olive residue with 10 % DS.

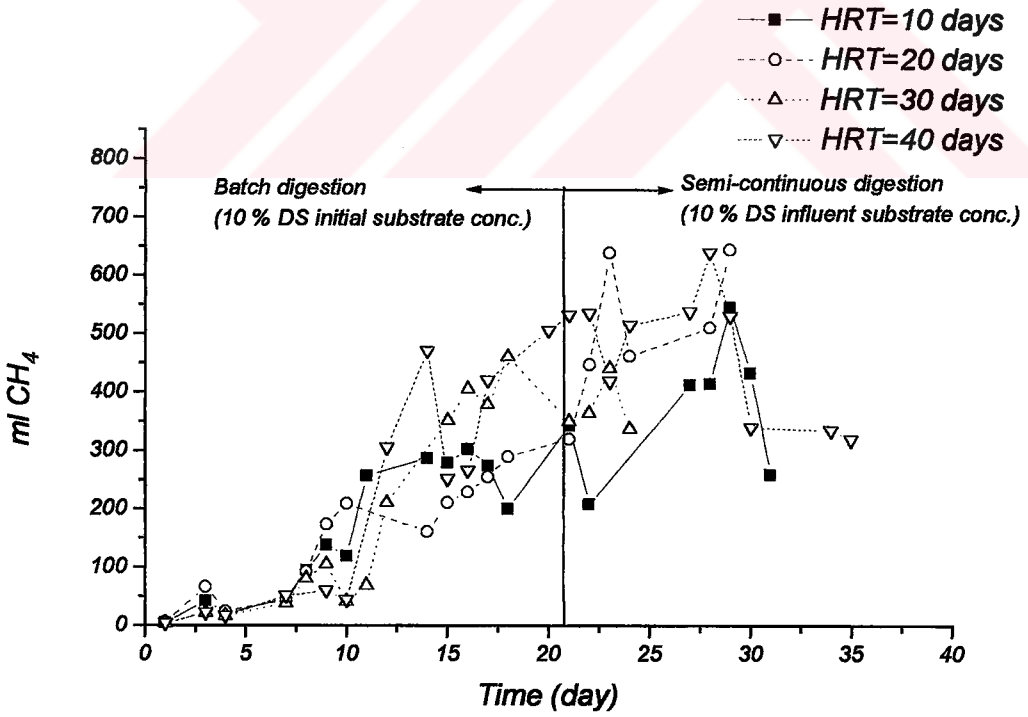

Figure 49. Effect of HRT on volumetric methane production during batch and semi-continuous digestion of olive residue with 10 % DS.

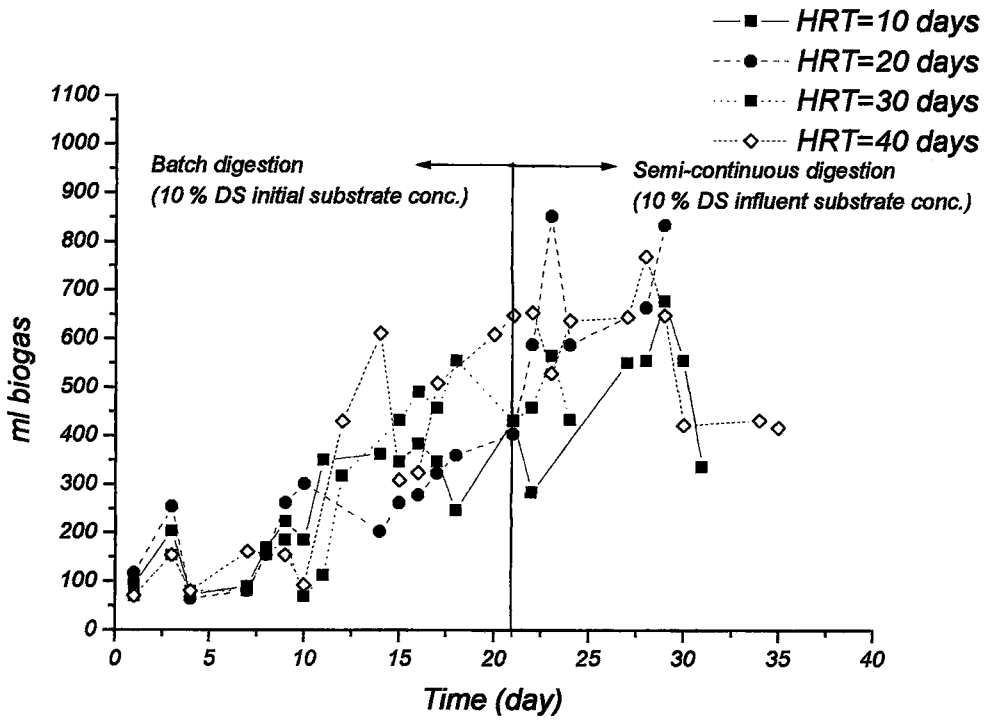

Figure 50. Effect of HRT on volumetric biogas production during batch and semi-continuous digestion of olive residue with 10 % DS.

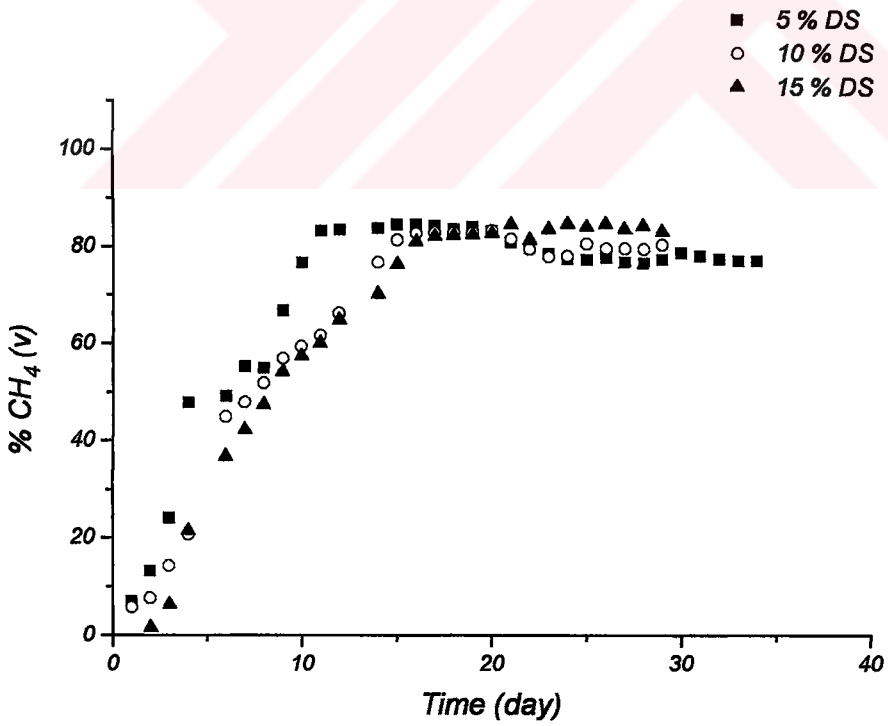

Figure 51. Effect of dry solid concentration on percent methane in biogas during batch and semi-continuous digestion of olive residue with 30 days HRT.

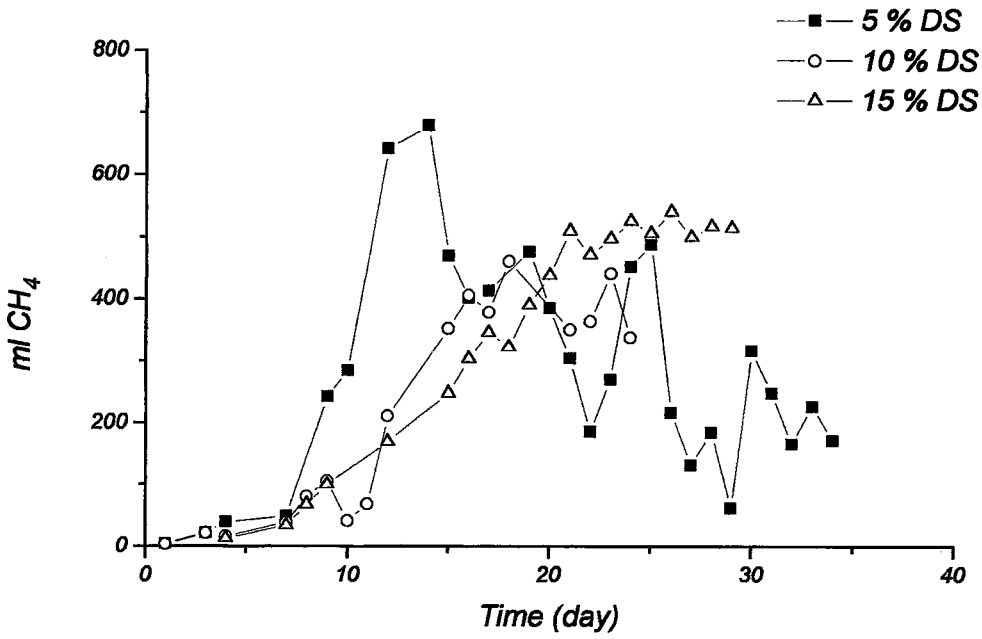

Figure 52. Effect of dry solid concentration on volumetric methane production during batch and semi-continuous digestion of olive residue with 30 days HRT.

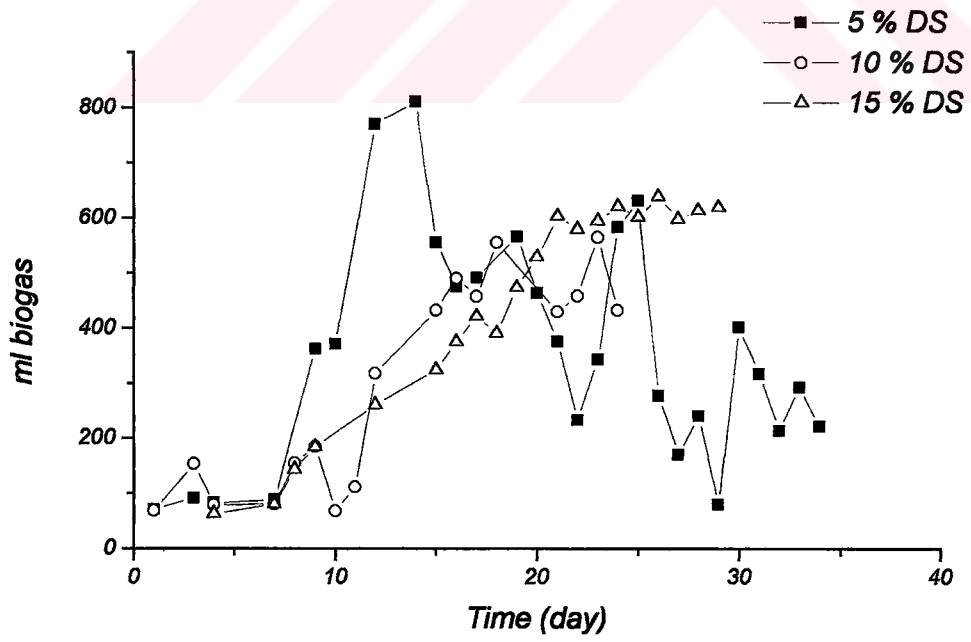

Figure 53. Effect of dry solid concentration on volumetric biogas production during semi-continuous digestion of olive residue with 30 days HRT.

Figure 48 illustrates the effect of influent substrate concentration on methane content in the biogas production. Figures 49 and 50 compare the effect of HRT on the volumetric methane and biogas production rates respectively. As seen, methane generation rate increases with HRT's. The effect of dry solid concentration, methane content in biogas, volumetric methane and biogas production are given in Figures 51, 52, and 54 respectively corresponding to HRT of 30 days.

4.5. Modeling of Substrate Utilization and Methane Production

Kinetic models to describe the anaerobic digestion of olive residue was studied. Two complementary kinetic descriptions, for substrate utilization and methane production, were derived. The model equations accounted for extracellular hydrolysis of complex substrates and considered the hydrolyzed products as the limiting substrate for cell growth and product formation according to Monod kinetics.

Due to the low methane yield obtained in this study, it was not possible to measure the bacterial cell mass concentration. Therefore, the substrate concentrations were measured in terms of COD. The effluent substrate concentration depends on influent substrate concentration if COD is used as an indicator of the substrate concentration.

4.5.1. Estimation of The Non-biodegradable Matter

The substrate concentrations measured at the digester outlet are given in Table 18. As a fraction of substrate was not biodegradable, it was estimated in order to perform the subsequent calculations; this was accomplished by a graphical procedure involving extrapolation to an infinite residence time. When logarithm of substrate concentration (in g COD/L) is plotted against reciprocal of HRT, the intercept gives the non-biodegradable matter in the processed olive residue [25]. The amount of non-biodegradable matter was calculated as 67.6 g COD/L. , corresponding to 37 % of total COD in the olive residue.

Table 18. Methane production rates and effluent COD values in the oven digester

HRT (day)	liter CH_4/day (at STP)	g COD/liter
10	0,38±0.07	148,53±12.1
20	0,55±0.05	101,30±8.3
30	0,39±0.03	86,45±7.1
40	0,32±0.04	82,96±6.8

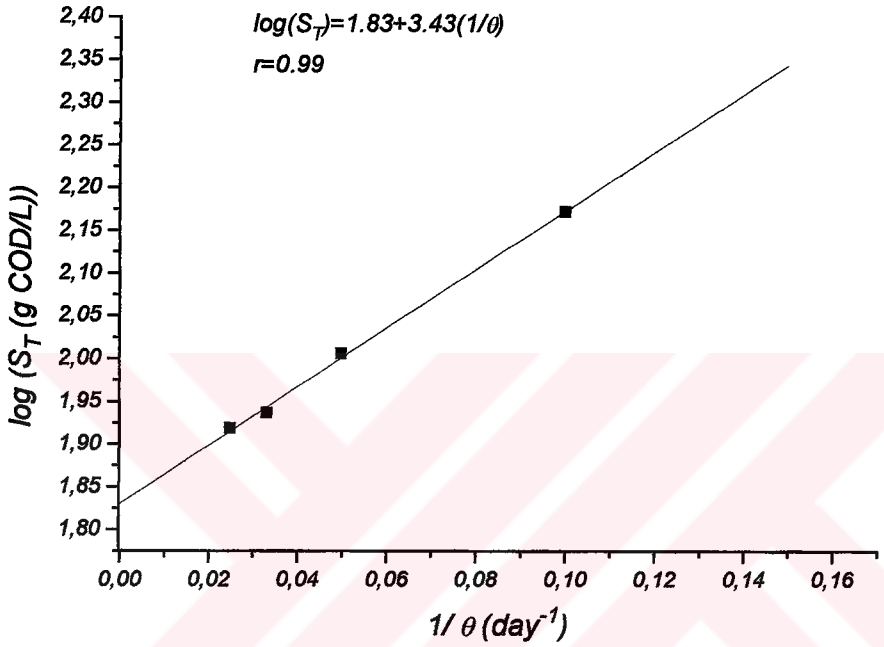

Figure 54. Estimation of the non-biodegradable matter contained in the processed olive residue.

4.5.2. Determination of the Yield Coefficient

Under steady state conditions, the relation between substrate uptake rate ($-r_s$) and gas production rate (r_G) was discussed in section 2.3.3.1. Eqn.(24) gives the relation between ($-r_s$) and (r_G). Thus, when r_G is plotted against ($-r_S$), the slope of the straight line passing through the origin should give the yield coefficient $Y_{P/S}$ which was determined to be 0.19 L CH_4 /g COD used (Figure 55).

4.5.3. Kinetic Model on Monod Basis

In Monod equation the specific growth rate is expressed only as a function of the limiting substrate concentration in the reactor [25]. The equation contains no term relating to input substrate concentration. The effluent concentration, expressed as chemical oxygen demand (COD), is not independent of the substrate concentration entering the reactor when pure or heterogeneous cultures are used. However when the substrate was measured as glucose, the Monod equation is predicted to be applicable to pure cultures but not to heterogeneous cultures [26] as it was the case in this study.

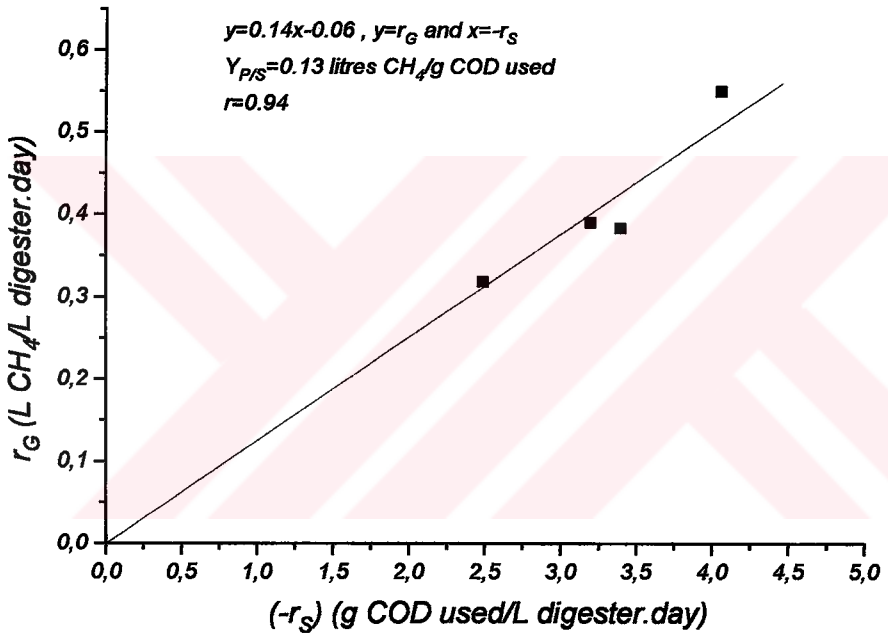

Figure 55. Determination of the yield coefficient ($Y_{P/S}$)

By fitting the (r_G, S) data pairs to a straight line, the constant defined in eqn. 29 was not obtained. Linear regression analysis was applied and the goodness of fit was observed by regression coefficient. The next limitation, defined in section 2.3.3.1, was used. In this way, ($1/r_G$, 1/S) data pairs were plotted, but the fit was not good. In this analysis, the curve must have no intercept, but some intercepts were observed. And (r) values obtained were less than 0.5.

Deviation from the Monod kinetic, is probably be due to characteristics of mixed culture system used in digestion as well as the nonhomogenous characteristics of the substrate. This complexity of the culture system has necessitated the use of generalized measures of feed and effluent strength, namely COD, which may not truly reflect the nature of the growth-limiting substrate. Utilizable carbon in the digester is derived from the hydrolysis of polymeric compounds, constituting the waste, by exoenzymes in the extracellular medium or on the surface of the microorganisms: only these hydrolyzed compounds can be considered as the growth-limiting substrate in terms of Monod relationship. Extracellular hydrolysis is often considered as the rate limiting step in the anaerobic digestion of agricultural wastes such as olive residue [26].

4.5.3. Kinetic Model on Contois Basis

To evaluate the attainable methane production B_0, the minimum retention time θ_m, the kinetic constant K and volumetric production rate γ_v , a Contois type kinetic model (discussed in section 2.3.3.2) was applied. For the evaluation of B_0 the recorded data (Table 19), plotted as B vs 1/HRT are shown in Figure 56. A linear regression analysis has been applied for the determination of B_0 which was calculated to be 0.088 L CH_4 /g COD added.

$B/(B_0-B)$ (Eqn 45) was plotted against θ (HRT) in attempt to find K and θ_m. Linear regression coefficient of the plot was 0.71. Therefore minimum retention time θ_m and the kinetic constant K could not be determined. Also the relation between volumetric methane production rate and θ (HRT) could not be calculated.

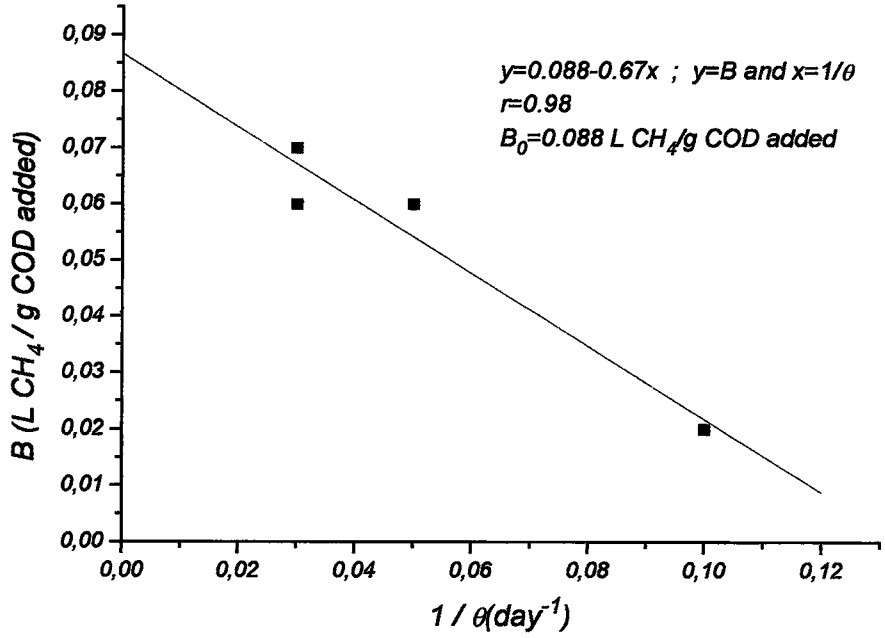

Figure 56. Variation of methane production with reciprocal retention time

The results obtained by the model on the basis of Contois were not satisfactory. The reason can be attributed to the ill-defined of Contois constants.

4.5.3. Kinetic Model on Basis of Monod and Contois Equation in Two Extreme Conditions.

The parameters μ_m, A, K_s, B_0 and the refractory coefficient, R, were determined in accordance with the model described in section 2.3.3.3, using a non-linear regression analysis. The values thus obtained are given in Table 19.

The refractory coefficient, R gives the percent non-biodegradable matter in the olive residue. This matter was estimated in section 4.5.1. as 67.61 g COD/L which is close enough to the value estimated by the present method (67.54 g COD/L.)

The Ks value for olive residue (0.3 g/l) is comparable to that reported for sugar (0.24 g/l) and acetate (0.21 g/l) in anaerobic fermentation [26].

Table 19. The kinetic constants and refractory coefficient (R) in the anaerobic digestion of olive residue.

A	μ_m (day^{-1})	K_s (g/L)	B_0 (L CH_4/g COD)	R
$0.56\pm4.4*10^{-3}$	$0.12\pm1.1*10^{-3}$	0.3 ± 1.0	$0.083\pm4.6*10^{-5}$	$0.37\pm1.4*10^{-1}$

The maximum specific methane yield, B_0, was found to be 0.083 LCH_4/g COD added. This value is close to the value reported by Tosun [21].

A correlation between the experimental data and those obtained from the model discussed was assessed with respect to the total substrate concentration S_T . As can be seen from Figure 57, the experimental data correlate well with predicted values with a regression coefficient of 0.998. Theoretical values were calculated with a 95 % confidence band. Figure 58, compares the predicted values with experimental values by plotting each against HRT.

Methane production rate (M_v) is an important factor in the design and operation of anaerobic treatment systems. Figure 59 shows the effect of HRT on M_v . Here M_v increases with increasing HRT until a critical retention time (≈15 days) at which point there is a rapid decline. This critical value should be considered as the optimum HRT for the methane production. The correlation coefficient for HRT and methane production rate was found to be 0.97 using the mentioned model (Fig.59).

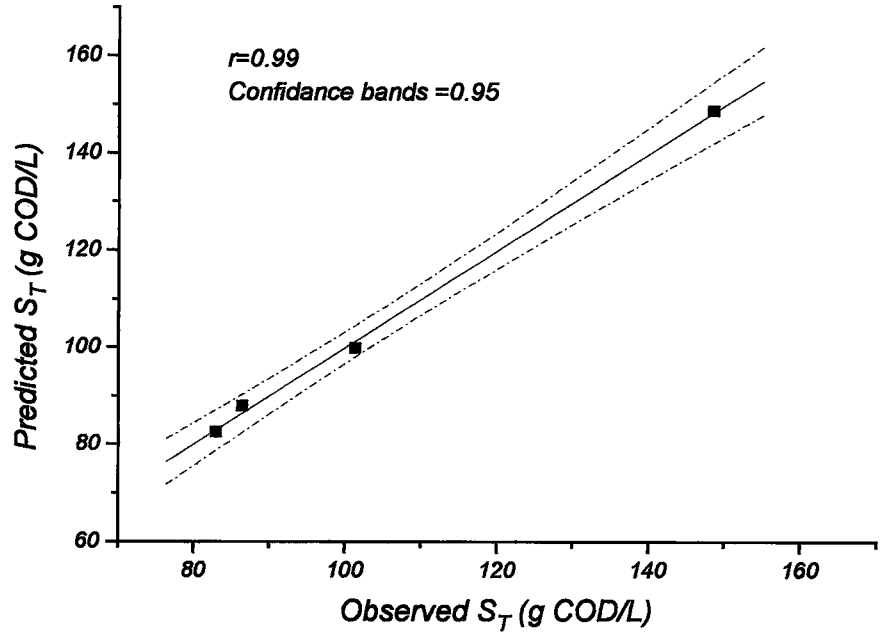

Figure 57. Comparison of observed and predicted effluent substrate concentrations for olive residue

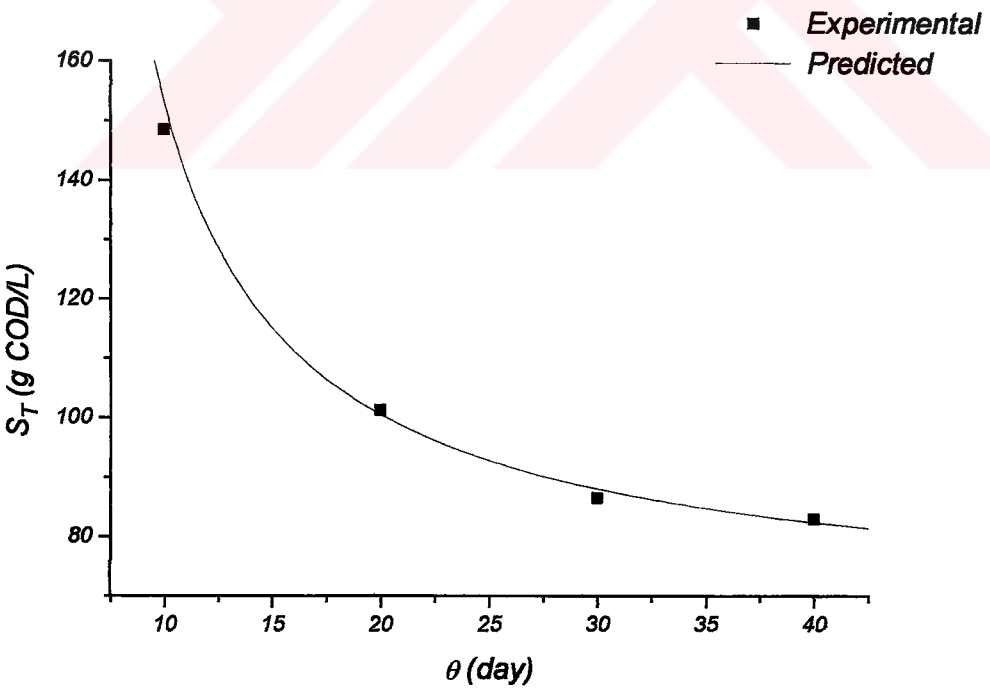

Figure 58. Effect of HRT on the effluent substrate concentration (S_T) values in the digestion of olive residue.

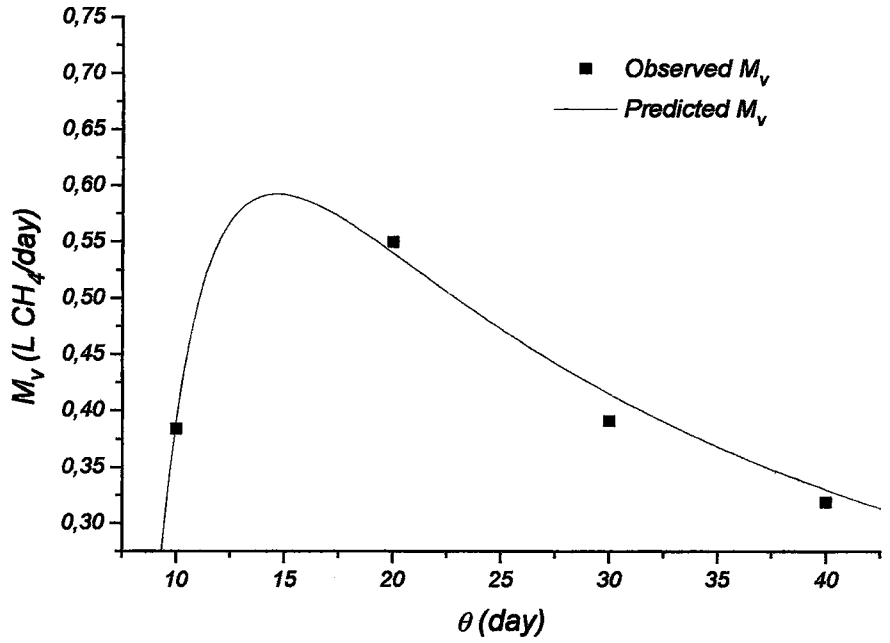

Figure 59. Effect of HRT on the volumetric methane production rate (M_v).

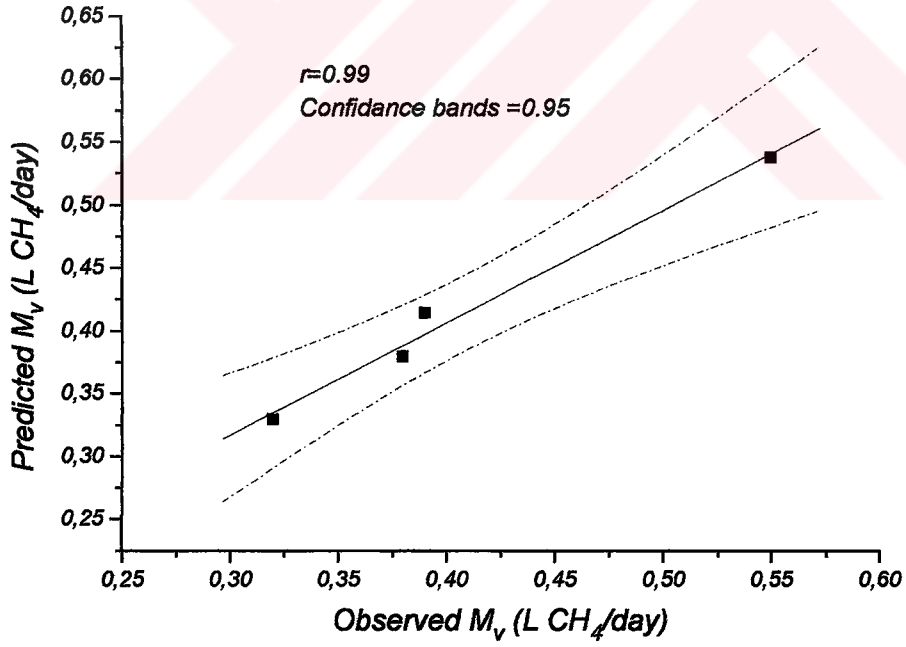

Figure 60. Comparison of observed and predicted methane production rates for olive residue.

CHAPTER V

CONCLUSION

Biological conversion of olive residue to biogas by anaerobic digestion was studied. Laboratory runs have been used to determine the rate parameters and quality of biogas produced at various substrate concentrations and hydraulic retention times. This study illustrates the effect of digester type, initial substrate concentrations and hydraulic retention times on the degree of digestion of olive residue and methane production yield at 37 °C.

The followings are concluded in the light of the observations made in this study:

- Olive residue was digested by a mixed culture supplied from Gaziantep landfill area.
- The maximum methane composition was observed to be around 80 % by volume in all sets. The maximum biogas production rate and yield were determined to be 0.692 (L/day) and 0.076 (L/g COD added) in the oven digester corresponding to 10 % DS substrate concentration and 20 days of HRT.
- The biogas production rate was lower in the fermenter compared to the oven digester.
- A model obtained from the combination of the Monod and Contois equations was observed to represent the kinetic data of the present study satisfactorily. The optimum HRT was calculated to be around 15 days.
- The refractory coefficient , R, defined as a fraction of non-biodegradable matter in the substrate was calculated to be 0.37.
- The digester constructed in the oven was observed to give very satisfactory results with respect to methane production rate and the quality of the gas compared to previous studies.

REFERENCES

1. Mohammed Nazir, 1991. "Biogas Plants Construction Technology for Rural Areas", Bioresource Technology 35, 283-289

2. Geoffrey W.Barnard, and David O.Hall, Energy from Renewable Resources, pp. 614.

3. George Tchobanoglous, Hilary Theisen, and Samuel Vigil, 1993. Integrated Solid Waste Management, McGraw-Hill, Inc.

4. George Tchobanoglous and Franklin L. Burton,1991 Waste Water Engineering, . McGraw-Hill, Inc.

5. James E. Bailey and David F.Ollis, 1986. Biochemical Engineering Fundamentals, McGraw-Hill, Inc.

6. Methane Generation from Human, Animal, and Agricultural Wastes, National Academy of Science, 1977.

7. Sedat Dönmez, 1981, "Biyogaz Reaktörlerinin Mikrobiyolojisi", Uluslararası Biyogaz Semineri, DPT, 191-200

8. Enver Tali Çetin, 1983. "Biyogaz Oluşumunun Biyokimyasal İlkleri ve Metan Bakterilerinin Beslenme İhtiyaçları" Endüstriyel Mikrobiyoloji, İTU, Bayda, 352-369.

9. M.P.Bryant, 1976. "The Microbiology of Anaerobic Degradation and Methanogenesis with Special Referencesto Sewage" Microbial Energy Conversion Seminar, Göttingen, Federal Republic of Germany 4-8 October

10. Ronald M. Atlas, 1988. Microbiology Fundamentals and Applications, Macmillan Publishing Company

11. Thomas D.Brock, Michael T.Madigan, 1991. Biology of Microorganisms, Prentice-Hall International Editions

12. Altan Erasalan, 1981, "Biyogaz Oluşumunun Biyokimyasal İlkleri ve Metan Bakterilerinin Beslenme İhtiyaçları", Uluslararası Biyogaz Semineri, DPT, 191-200

13. Andrew G.Hashimoto, 1983. "Conversion of Straw-Manure Mixtures to Methane at Mesophilic and Thermophilic Temperatures", Biotechnology and Bioengineering, vol.25, pp.185-200

14. V.H.Varel, H.R.Isaacson, and M.P.Bryant, 1977. "Thermophilic methane production from cattle waste", Applied and Environmental Microbiology, Feb., p.298-307

15. Mehmet Kobya, Orhan Özbay, and Erdem Kocadağıstan, 1994. "Sığır gübresinden değişik sıcaklıklarda biyogaz üretimi" Enerji ve Çevre Semozyumu, Mersin Üniversitesi, 237-241.

16. J.T.Pfeffer, 1976. "Methane from Urban Waste- Process Requirements" Microbial Energy Conversion Seminar, Göttingen, Federal Republic of Germany 4-8 October

17. "Production and Utilization of Biogas in Rural Areas of Industrialized and Developing Countries", Schriftenreihe der gtz, No. 97, 1978

18. J.P. Blanchard and T.A. Gill, "Methane Production: Recent Advances Contributing to Greater Process Stability and Economy"

19. E.P.Sanches, P.Weiland and L.Travieso,1992. "Effect of hydrolic retention time on the anaerobic biofilm reactorEfficiency applied to screened cattle waste treatment", Biotecnology Letters, Vol.14, No.7 , pp.635-638

20. Joo-Hwa Tay, 1991. "Complete reclamation of oil palm wastes", Resource, Conservation and Recycling, 5, 383-392

21. Tosun Ayşe, 1987."Biogas Production from Agricultural Wastes-Semi-Continuous Digestion of Wheat Straw", A Master's Thesis in Chemical Engineering, Metu.

22. Hakan Polat, Nevin Selçuk, Selçuk Soyupak,1993. "Biogas Production from Agricultural Wastes: Semicontinuous Anaerobic Digestion of Sunflower Heads", Energy Sources, Volume 15, pp.67-75

23. Prema Viswanath, S.Sumithra Devi and Krishna Nand, 1992. "Anaerobic Digestion of Fruit and Vegetable Processing Wastes for Biogas Production", Bioresource Technology 40 43-48

24. D.R.Renade, T.Y.Yeole, K.K.Meher, R.V.Gadre, S.H.Godbole, 1989. "Biogas from Solid Waste Originated During Biscuit and Chocolate Production: A Preliminary Study", Biological Wastes, 28, 157-161

25. A. Martin, R. Borja I.Garcia and J.A.Fiestas, 1991. "Kinetics methane production from olive mill wastewater", Process Biochemistry 26 101-107.

26. Antonio Martin, Rafael Borja and Charles J.Banks, 1994. "Kinetic model for substrate utilization and methane production during anaerobic Digestion of olive mill wastewater and condensation water waste", J.Chem. Thec. Biotechnol. , 60, 7-16

27. Joan Mata-Alvarez, 1989, "A simulation study of a continuous two-phase dry digestion system", Biotechnology and Bioengineering, Vol. 34, pp.609-616

28. Joan Mata-Alvarez, 1987. "A dynamic simulation of a two-phase anaerobic digestion system for solid wastes", Biotechnology and Bioengineering, Vol. 30, pp.844-851

29. Ikbal,Kenji Kida, and Yorikazu Sonodo,1994. "Liquefaction and gasification during anaerobic digestion of coffee waste by two-phase methane fermentation with slurry-state liquefaction", Journal of Fermentation and Bioengineering Vol.77, No.1, 85-89

30. Robert H. Perry, Don W. Green, and James O. Maloney, 1984. Perry's Chemical Engineers' Handbook, Mc Graw Hill Book Company.

31. U. Loll,1976. "Engineering, operation and Economics of biodigestion" Microbial Energy Conversion Seminar, Göttingen, Federal Republic of Germany 4-8 October

32. F.G. Konstandt, 1976. "Engineering, Operation and Economics of Methane Gas Production" Microbial Energy Conversion Seminar, Göttingen, Federal Republic of Germany 4-8 October

33. L.Van Den Berg, 1986 "High Rate Reactors for Methane Production" Biotechnology and Renewable Energy Edited by Murray Moo-Young Sadıq Hasnain, Jonathan Lamptey, Elsevier Applied Science Publishers

34. W.L.Bolle, J.van Breugel, G.C.van Eybergen, N.W.F.Kossen, W.van Gils, 1986. "Kinetics of Anaerobic Purification of Industrial", Wastewater, Biotechnology and Bioengineering, Vol. 28, pp.542-548

35. J.K. Parickh and K.S. Parickh, 1976. "Potential of Biogas Plants and to Realize it" Microbial Energy Conversion Seminar, Göttingen, Federal Republic of Germany 4-8 October

36. Collin Parker and Tim Roberts, 1985. Energy from Waste, an evaluation of conversion technologies Elsevier Applied Science Publishers

37. Norman W. Desrosier, 1984. Elements of Food Technology, AVI Publishing Company, Inc.

38. M.H. Zwietering, I.Jongenburger, F.M. Rombouts and K.Van T Riet, 1990. "Modelling of Bacterial Growth Curve" Applied and Environmental Microbiology, June p.1875-1881.

39. Terry Sincich, 1990. Statistics by Example, fourth edition, Delen Publishing Company.

40. Osman Yıldız, 1994Sığır ve Tavuk Gübresinden Biyogaz Eldesi ve Küçük işletmeler Açısından İrdelenmesi" cia Terebinthus", Enerji ve Çevre Semozyumu, Mersin Üniversitesi, 421-429.

41.W.C.Boyle, 1976."Enercy Recovery from Sanitary Landfills-a Review" Microbial Energy Conversion Seminar, Göttingen, Federal Republic of Germany 4-8 October

42. G.Frezzotti, M.Manni, A.Aten, 1956. "Olive Oil Processing in Rural Mills" FAO Agricultural Development , Paper no:58, Rome.

43. "Chemical Oxygen Demand (Dichromate Oxygen Demand) of Waste Water", 1974, ASTM D 1252.7

44. AOAC. 1975."Official Methods of Analysis" Association of Official Analytical Chemists, Washington, DC.

45. "Total Sulfur in the Analysis of Coal and Coke", 1974, ASTM D 3177-73

APPENDICES

A. Compositions and Volumetric Production Rates of Biogas

Table A.1.Composition of biogas during digestion of olive residue in the adaptation process

Time (day)	% CH_4	% CO_2
1	0,1	99,9
4	0,4	99,6
5	1,0	98,9
6	0,7	99,3
7	1,1	98,9
8	5,2	94,8
11	40,5	59,5
13	45,2	54,8
14	62,3	37,7
15	69,9	30,0
16	80,3	19,7
18	78,2	21,8
19	76,7	23,3
20	75,4	24,6
21	78,8	21,2
22	80,9	19,1
23	81,6	18,5
25	87,7	12,3
26	88,6	11,4
27	87,2	12,8
28	86,8	13,2
29	86,6	13,4
31	87,4	12,6
32	88,7	11,3
33	89,0	10,9
34	88,8	11,2
35	89,7	10,3

Table A.2.Composition of biogas during batchwise digestion of olive residue

Time (day)	% CH_4	% CO_2
3	7,4	92,6
4	16,6	83,4
5	27,1	72,9
6	29,4	70,6
7	33,8	66,2
8	37,7	62,3
9	41,3	58,7
10	43,1	56,9
11	52,5	47,5
12	48,6	51,4
13	50,0	49,9
14	60,5	39,5
15	59,2	40,8
17	60,4	39,7
18	64,8	35,2
19	57,9	42,0
20	58,8	41,2
21	60,8	39,2
24	65,6	34,4
25	65,6	34,4
26	66,7	33,3
27	65,7	34,3
28	66,8	33,2
37	62,8	37,2

Table A.3.Volumetric production rates during batchwise digestion of olive residue

Time (day)	ml of biogas	ml CH_4	ml CO_2
3	5,2	64,8	70,0
4	9,9	49,6	59,5
5	14,4	38,6	53,0
6	22,1	52,9	75,0
7	20,4	40,1	60,5
8	25,9	43,0	69,0
9	17,4	24,6	42,0
10	20,7	27,3	48,0
11	40,4	36,6	77,0
12	24,1	25,4	49,5
13	30,3	30,3	60,5
14	45,4	29,6	75,0
15	41,4	28,6	70,0
17	90,7	59,6	150,3
18	92,4	50,2	142,5
19	103,8	75,3	179,1
20	142,2	99,5	241,7
21	144,1	92,8	236,8
24	161,7	84,9	246,6
25	128,5	67,5	196,0
26	163,7	81,7	245,5
27	153,0	79,7	232,7
28	142,3	70,6	212,9

Table A.4.Composition of biogas during batchwise digestion of olive residue with 5 % DS initial substrate concentration

Time (day)	% CH_4	% CO_2
1	7,0	93,0
2	13,2	86,8
3	24,2	75,8
4	47,8	52,2
6	49,2	50,8
7	55,3	44,7
8	54,9	45,1
9	66,7	33,2
10	76,7	23,3
11	83,2	16,8
12	83,4	16,7
14	83,8	16,2
15	84,4	15,6
16	84,5	15,5

Table A.5.Volumetric production rates during batchwise digestion of olive residue with 5 % DS initial substrate concentration

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	72,4	5,0	67,4
3	91,7	22,2	69,6
4	83,1	39,7	43,3
7	88,8	49,1	39,7
9	363,1	242,4	120,7
10	370,8	284,3	86,5
12	771,2	642,8	128,4
14	812,1	680,3	131,8
15	556,2	469,7	86,5
16	475,1	401,6	73,6

Table A.6.Composition of biogas during batchwise digestion of olive residue with 10 % DS initial substrate concentration

Time (day)	% CH_4	% CO_2
1	5,9	94,2
2	7,7	92,3
3	14,4	85,7
4	20,8	79,2
6	45,0	55,0
7	47,9	52,1
8	51,8	48,2
9	57,0	43,0
10	59,4	40,6
11	61,7	38,3
12	66,3	33,8
14	76,7	23,3
15	81,3	18,7
16	82,7	17,3
17	82,9	17,2
18	82,8	17,2
19	82,8	17,2
20	83,3	16,7

Table A.7.Volumetric production rates during batchwise digestion of olive residue with 10 % DS initial substrate concentration

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	70,5	4,1	66,4
3	154,5	22,2	132,3

Table A.8.Composition of biogas during batchwise digestion of olive residue with 15 % DS initial substrate concentration

Time (day)	% CH_4	% CO_2
2	1,5	98,5
3	6,3	93,7
4	21,4	78,6
6	36,8	63,2
7	42,2	57,8
8	47,4	52,6
9	54,1	45,9
10	57,4	42,7
11	60,0	40,0
12	64,8	35,2
14	70,2	29,8
15	76,3	23,7
16	80,9	19,1
17	82,0	18,0
18	82,3	17,7
19	82,4	17,6
20	82,7	17,3
21	84,5	15,6
22	81,3	18,7
23	83,5	16,5

Table A.9.Volumetric production rates during batchwise digestion of olive residue with 15 % DS initial substrate concentration

Time (day)	ml of biogas	ml CH_4	ml CO_2
4	64,0	13,7	50,3
7	81,0	34,2	46,8
8	144,0	68,2	75,8
9	185,0	100,1	84,9
12	261,5	169,5	92,0
15	324,5	247,6	76,9
16	375,5	303,8	71,7
17	421,5	345,7	75,8
18	390,8	321,6	69,2
19	473,4	389,9	83,5
20	529,6	438,0	91,6
21	603,4	509,6	93,8
22	580,2	471,6	108,6
23	595,2	497,0	98,2

Table A.10.Composition of biogas during semi-continuous digestion of olive residue with 10 % DS initial substrate concentration and 30 day HRT in fermenter

Time (day)	% CH_4	% CO_2
2	18,2	81,8
3	28,0	72,0
4	39,5	60,5
6	38,7	61,4
11	49,5	50,5
12	55,1	44,9
13	61,2	38,8
23	67,4	32,6
24	65,8	34,2
25	66,0	34,0
26	63,9	36,1
27	60,9	39,1
30	56,9	43,1
31	55,6	44,4
32	54,1	45,9
34	52,2	47,8
37	51,1	48,9
38	50,6	49,4
39	50,1	49,9
40	49,9	50,1
41	48,8	51,3
44	47,8	52,2
45	47,8	52,2

Table A.11.Volumetric production rates during batchwise digestion of olive residue with 5 % DS initial substrate concentration

Time (day)	ml of biogas	ml CH_4	ml CO_2
2	13,9	62,6	76,5
3	27,1	69,9	97,0
4	33,6	51,4	85,0
6	27,4	43,6	71,0
11	45,0	46,0	91,0
12	31,4	25,6	57,0
13	85,1	53,9	139,0
23	107,2	51,8	159,0
24	294,5	153,3	447,8
25	300,7	155,0	455,7
26	313,3	177,1	490,4
27	304,4	195,6	500,0
30	220,2	167,0	387,2
31	160,9	128,3	289,2
32	182,0	154,4	336,4
34	170,9	156,2	327,1
37	164,0	156,7	320,7
38	136,5	133,2	269,6
39	118,8	118,3	237,1
40	130,7	131,1	261,7
41	120,8	127,0	247,8
44	115,9	126,4	242,3
45	122,5	134,0	256,5

Table A.12. Composition of biogas during semi-continuous digestion of olive residue (HRT=10, DS= 10 %)

Time (day)	% CH_4	% CO_2
1	5,6	94,4
2	10,5	89,5
3	20,7	79,3
4	30,3	69,7
6	48,6	51,5
7	51,1	48,9
8	56,2	43,8
9	61,9	38,1
10	64,8	35,3
11	73,6	26,4
12	78,3	21,7
14	79,4	20,6
15	80,5	19,5
16	79,0	21,0
17	79,2	20,8
18	81,3	18,7
19	80,6	19,4
20	79,9	20,1
21	79,3	20,7
22	73,4	26,6
24	71,6	28,4
25	72,3	27,7
26	75,5	24,5
27	75,0	25,0
28	74,6	25,4
29	80,6	19,4
30	77,8	22,2
31	77,4	22,6

Table A.13. Volumetric production rates during semi-continuous digestion of olive residue (HRT=10, DS= 10 %)

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	93,7	5,2	88,4
3	204,7	42,3	162,4
4	72,4	22,0	50,5
7	89,8	45,9	43,9
8	169,8	95,5	74,3
9	224,0	138,7	85,3
10	185,4	120,1	65,4
11	350,6	258,0	92,6
14	363,1	288,2	74,9
15	347,7	280,0	67,7
16	384,4	303,5	80,8
17	347,7	275,2	72,4
18	246,7	200,5	46,2
21	432,6	343,1	89,5
22	284,0	208,4	75,6
27	551,4	413,7	137,7
28	556,2	414,9	141,4
29	677,5	546,0	131,4
30	556,2	433,0	123,3
31	335,9	260,1	75,8

Table A.14. Composition of biogas during semi-continuous digestion of olive residue (HRT=20, DS= 10 %)

Time (day)	% CH_4	% CO_2
1	5,3	94,7
2	13,3	86,8
3	26,5	73,5
4	38,6	61,4
6	51,9	48,1
7	54,1	45,9
8	60,3	39,7
9	66,4	33,6
10	69,5	30,5
11	73,6	26,4
12	78,3	21,7
14	79,4	20,6
15	80,5	19,5
16	82,6	17,4
17	79,3	20,7
18	80,7	19,4
19	81,2	18,8
20	82,2	17,8
21	79,3	20,7
22	76,2	23,8
23	75,0	25,0
24	78,5	21,5
25	81,3	18,7
26	78,6	21,4
27	76,9	23,1
28	77,0	23,0
29	77,3	22,7

Table A.15. Volumetric production rates during semi-continuous digestion of olive residue (HRT=20, DS= 10 %)

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	116,9	6,2	110,6
3	254,9	67,5	187,5
4	64,2	24,8	39,4
7	81,1	43,9	37,2
8	155,8	93,9	61,9
9	262,7	174,4	88,3
10	301,3	209,5	91,8
14	203,2	161,3	41,9
15	262,7	211,5	51,1
16	278,1	229,7	48,4
17	323,0	256,0	67,0
18	359,9	290,3	69,7
21	404,5	320,8	83,7
22	588,7	448,3	140,4
23	852,9	640,0	212,9
24	588,3	462,1	126,2
28	664,4	511,3	153,1
29	834,4	645,1	189,2

Table A.16. Composition of biogas during semi-continuous digestion of olive residue (HRT=30, DS= 10 %)

Time (day)	% CH_4	% CO_2
1	5,9	94,2
2	7,7	92,3
3	14,4	85,7
4	20,8	79,2
6	45,0	55,0
7	47,9	52,1
8	51,8	48,2
9	57,0	43,0
10	59,4	40,6
11	61,7	38,3
12	66,3	33,8
14	76,7	23,3
15	81,3	18,7
16	82,7	17,3
17	82,9	17,2
18	82,8	17,2
19	82,8	17,2
20	83,2	16,8
21	81,6	18,4
22	79,4	20,6
23	78,0	22,0
24	78,0	22,0
25	80,6	19,4
26	79,5	20,5
27	79,6	20,4
28	79,5	20,5
29	80,3	19,7

Table A.17. Volumetric production rates during semi-continuous digestion of olive residue (HRT=30, DS= 10 %)

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	70,5	4,1	66,4
3	154,5	22,2	132,3
4	80,2	16,7	63,5
7	81,1	38,9	42,3
8	155,8	80,7	75,0
9	185,4	105,7	79,8
10	69,5	41,3	28,2
11	112,4	69,4	43,1
12	318,3	210,9	107,4
15	432,6	351,9	80,8
16	490,8	406,1	84,7
17	457,6	379,1	78,5
18	556,2	460,7	95,5
21	429,8	350,6	79,2
22	458,9	364,5	94,4
23	565,5	441,0	124,5
24	433,2	337,9	95,3

Table A.18. Composition of biogas during semi-continuous digestion of olive residue (HRT=40, DS= 10 %)

Time (day)	% CH_4	% CO_2
1	5,9	94,2
2	7,7	92,3
3	14,4	85,7
4	20,8	79,2
7	31,9	68,1
8	29,8	70,2
9	39,0	61,0
10	47,4	52,6
11	66,0	34,0
12	71,1	28,9
14	77,0	23,0
15	81,6	18,4
16	82,1	17,9
17	82,7	17,3
18	82,1	17,9
20	83,1	16,9
21	82,1	17,9
22	81,8	18,2
23	79,1	20,9
24	80,8	19,2
25	80,4	19,6
26	83,1	16,9
27	83,5	16,5
28	83,2	16,9
29	81,8	18,2
30	80,4	19,6
31	80,8	19,2
32	80,4	19,6
33	78,7	21,3
34	77,4	22,6
35	76,6	23,4

Table A.19. Volumetric production rates during semi-continuous digestion of olive residue (HRT=40, DS= 10 %)

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	70,5	4,1	66,4
3	154,5	22,2	132,3
4	80,2	16,7	63,5
7	161,3	51,4	109,9
9	154,5	60,3	94,2
10	92,7	43,9	48,8
12	429,8	305,8	124,1
14	611,9	470,9	141,0
15	309,0	252,2	56,8
16	324,5	266,3	58,1
17	508,9	420,8	88,1
20	609,7	506,5	103,2
21	649,0	532,5	116,4
22	654,4	535,3	119,1
23	529,3	418,5	110,8
24	638,0	515,3	122,7
27	644,7	538,5	106,2
28	769,5	639,8	129,6
29	649,0	531,1	117,9
30	422,5	339,8	82,8
34	432,6	335,0	97,6
35	417,2	319,6	97,6

Table A.20. Composition of biogas during semi-continuous digestion of olive residue (HRT=30, DS= 5 %)

Time (day)	% CH_4	% CO_2
1	7,0	93,0
2	13,2	86,8
3	24,2	75,8
4	47,8	52,2
6	49,2	50,8
7	55,3	44,7
8	54,9	45,1
9	66,8	33,2
10	76,7	23,3
11	83,2	16,8
12	83,4	16,7
14	83,8	16,2
15	84,4	15,6
16	84,5	15,5
17	84,3	15,7
18	83,5	16,5
19	84,1	15,9
20	83,2	16,9
21	80,9	19,1
22	79,7	20,3
23	78,5	21,5
24	77,4	22,6
25	77,3	22,7
26	77,8	22,2
27	76,7	23,3
28	76,6	23,4
29	77,3	22,7
30	78,7	21,3
31	78,0	22,0
32	77,4	22,6
33	77,0	23,0
34	77,1	22,9

Table A.21. Volumetric production rates during semi-continuous digestion of olive residue (HRT=30, DS= 5 %)

Time (day)	ml of biogas	ml CH_4	ml CO_2
1	72,4	5,0	67,4
3	91,7	22,2	69,6
4	83,1	39,7	43,3
7	88,8	49,1	39,7
9	363,1	242,4	120,7
10	370,8	284,3	86,5
12	771,2	642,8	128,4
14	812,1	680,3	131,8
15	556,2	469,7	86,5
16	475,1	401,6	73,6
17	491,2	414,0	77,2
19	566,9	476,8	90,2
20	463,5	385,4	78,1
21	376,3	304,4	71,9
22	233,3	185,9	47,3
23	343,6	269,8	73,8
24	584,1	452,1	132,0
25	632,1	488,7	143,4
26	278,1	216,3	61,8
27	171,5	131,6	39,9
28	241,0	184,5	56,5
29	80,2	62,0	18,2
30	401,7	316,1	85,6
31	317,9	248,0	69,8
32	213,9	165,7	48,3
33	293,6	226,1	67,5
34	222,5	171,6	50,9

Table A.22. Composition of biogas during semi-continuous digestion of olive residue (HRT=30, DS= 15 %)

Time (day)	% CH_4	% CO_2
2	1,5	98,5
3	6,3	93,7
4	21,4	78,6
6	36,8	63,2
7	42,2	57,8
8	47,4	52,6
9	54,1	45,9
10	57,4	42,7
11	60,0	40,0
12	64,8	35,2
14	70,2	29,8
15	76,3	23,7
16	80,9	19,1
17	82,0	18,0
18	82,3	17,7
19	82,4	17,6
20	82,7	17,3
21	84,5	15,6
22	81,3	18,7
23	83,5	16,5
24	84,6	15,4
25	84,0	16,0
26	84,6	15,4
27	83,5	16,5
28	84,1	15,9
29	83,0	17,0

Table A.23. Volumetric production rates during semi-continuous digestion of olive residue (HRT=30, DS= 5 %)

Time (day)	ml of biogas	ml CH_4	ml CO_2
4	64,0	13,7	50,3
7	81,0	34,2	46,8
8	144,0	68,2	75,8
9	185,0	100,1	84,9
12	261,5	169,5	92,0
15	324,5	247,6	76,9
16	375,5	303,8	71,7
17	421,5	345,7	75,8
18	390,8	321,6	69,2
19	473,4	390,0	83,5
20	529,6	438,0	91,6
21	603,4	509,6	93,8
22	580,2	471,6	108,6
23	595,2	497,0	98,2
24	621,1	525,5	95,7
25	602,1	505,6	96,5
26	639,0	540,3	98,7
27	598,5	499,7	98,8
28	614,2	516,7	97,5
29	619,8	514,3	105,5

B. Logistic Model Parameters of the Performed Experiments

Table B.1. Logistic model parameters of the adaptation process curves

Figure no.	Curve	χ^2	l	f	c	d
9	% CH_4	0.39	0.1±0.2	85.7±1.5	12.1±0.2	6.8±0.4
9	% CO_2	0.52	108.9±3.9	11.2±1.1	11.6±0.5	4.6±0.6

Table B.2. Logistic model parameters of the batchwise digestion of olive residue in fermentor

Figure no.	Curve	χ^2	i	f	c	d
11	% CH_4	0.17	-33.2±32.5	80.4±10.3	4.9±1.9	1.2±0.5
11	% CO_2	0.17	107.9±17.4	26.9±5.2	6.6±1.5	1.7±0.5
12	ml CH_4	2.81	12.8±2.3	163.5±15.8	17.4±0.9	6.3±1.3
13	ml biogas	2.46	58.4±3.7	229.8±10.4	17.4±0.4	14.5±3.9

Table B.3. Logistic model parameters of the batchwise digestion of olive residue in oven digester (DS= 5 %)

Figure no	Curve	χ^2	i	f	c	d
15	% CH_4	0.67	1.4±5.5	107.1±21.2	6.4±1.6	1.6±0.5
15	% CO_2	1.01	96.3±13.8	-0.7±15.1	5.8±1.1	1.8±0.8
16	ml CH_4	13.62	10.9±7.1	808.3±190.4	10.6±1.0	7.0±2.2
17	ml biogas	10.87	77.9±16.8	887.0±146.8	10.3±0.7	8.4±3.0

Table B.4. Logistic model parameters of the batchwise digestion of olive residue in oven digester (DS= 10 %)

Figure no.	Curve	χ^2	i	f	c	d
18	% CH_4	0.19	4.1±1.3	93.5±4.8	7.5±0.5	2.2±0.2
18	% CO_2	0.27	97.3±5.2	1.9±7.0	7.7±0.6	2.0±0.4
19	ml CH_4	19.09	13.3±7.1	408.2±43.2	12.6±0.7	9.5±3.2
20	ml biogas	14.48	97.9±14.3	480.0±41.7	11.9±0.2	42.2±405

Table B.5. Logistic model parameters of the batchwise digestion of olive residue in oven digester (DS= 15 %)

Figure no.	Curve	χ^2	i	f	c	d
21	% CH_4	0.19	-5.6±2.3	94.7±4.8	7.4±0.4	2.0±0.2
21	% CO_2	0.23	102.7±6.8	6.1±4.5	7.6±0.5	2.1±0.4
22	ml CH_4	2.79	10.5±7.0	586.1±14.8	15.6±0.4	3.6±0.3
23	ml biogas	3.99	56.6±17.9	725.7±20.5	15.9±0.6	3.2±0.4

Table B.6. Logistic model parameters of the semi continuous digestion of olive residue in fermentor (HRT=30 days , DS=10 %)

Figure no.	Curve	χ^2	I	f	c	d
27	% CH_4-b	0.1	0.8±48.9	85.9±3.3	2.3±1.6	1.7±0.7
27	% CO_2-b	0.29	87.1±37.1	14.7±2.4	2.8±1.5	1.9±0.8
27	% CH_4-s	0.41	-	67.8±15.7	-	2.3±10.3
27	% CO_2-s	0.41	-	32.2±4.9	-	2.3±10.5
28	ml CH_4-b	8.40	49.3±7.2	365.0±55.5	23.2±2.0	-
28	ml CO_2-b	5.93	21.9±4.0	75.1±21.5	23.6±0.7	115.4±161.1
28	ml CH_4-s	2.95	383.5±19.8	182.3±10.9	29.9±0.7	16.9±6.5
28	ml CO_2-s	1.12	82.4±3.3	66.2±4.3	-	

b= Batchwise side of the curve s= semi-continuous side of the curve

Table B.7. Logistic model parameters of the semi continuous digestion of olive residue in oven digester (HRT=10 days , DS=10 %)

Figure no.	Curve	χ^2	i	f	c	d
31	% CH_4	0.22	4.7±1.3	79.5±1.4	5.3±0.2	2.5±0.2
31	% CO_2	0.55	88.3±4.9	21.3±1.2	6.0±0.5	3.6±0.7
32	ml CH_4	21.09	6.9±10.2	384.4±71.8	12.2±2.5	2.8±1.0
33	ml biogas	29.30	89.0±39.8	525.4±155.3	14.6±5.0	2.7±1.6

Table B.8. Logistic model parameters of the semi continuous digestion of olive residue in oven digester (HRT=20 days , DS=10 %)

Figure no.	Curve	χ^2	i	f	c	d
34	% CH_4	0.14	2.6±1.5	81.9±1.4	4.6±0.2	2.2±0.2
34	% CO_2	0.39	90.5±5.3	19.1±1.2	5.2±0.4	2.8±0.5
35	ml CH_4	37.26	28.1±12.1	550.1±49.4	17.1±0.7	10.5±0.7
36	ml biogas	26.24	140.5±20.4	836.2±71.5	20.6±2.0	5.3±1.2

Table B.9. Logistic model parameters of the semi continuous digestion of olive residue in oven digester (HRT=300 days , DS=10 %)

Figure no.	Curve	χ^2	i	f	c	d
37	% CH_4	0.19	4.9±1.1	84.0±1.7	6.7±0.2	2.6±0.2
37	% CO_2	0.52	91.6±4.7	16.9±1.6	6.9±1.0	3.1±0.5
38	ml CH_4	15.95	14.0±6.4	391.4±32.4	12.3±0.7	11.4±4.6
39	ml biogas	11.87	97.9±13.0	473.0±26.5	11.9±0.2	42.5±36.6

Table B.10. Logistic model parameters of the semi continuous digestion of olive residue in oven digester (HRT=40 days , DS=10 %)

Figure no.	Curve	χ^2	i	f	c	d
40	% CH_4	0.57	9.3±1.2	82.6±1.9	9.2±0.3	4.6±0.7
40	% CO_2	0.33	84.8±2.6	18.5±0.6	9.6±0.2	7.5±1.0
41	ml CH_4-b	25.18	9.7±8.4	529.9±49.6	13.3±0.7	6.4±1.6
41	ml CH_4-s	7.75	504.6±30.8	319.7±35.3	29.6±0.7	50.1±5.7
42	ml biogas-b	35.79	93.8±30.7	650.5±38.5	13.7±1.1	6.2±2.4
42	ml biogas-s	7.83	621.0±34.5	413.8±40.3	29.5±0.7	49.8±6.9

b= Batchwise side of the curve s= semi-continuous side of the curve

Table B.11. Logistic model parameters of the semi continuous digestion of olive residue in oven digester (HRT=30 days , DS=5 %)

Figure no.	Curve	χ^2	i	f	c	d
43	% CH_4	0.46	4.2±2.4	81.4±1.8	4.6±0.3	2.5±0.3
43	% CO_2	1.11	83.1±7.0	18.9±1.2	5.5±0.6	3.8±1.0
44	ml CH_4-b	12.31	11.4±6.7	697.5±49.4	10.1±0.3	8.1±1.8
44	ml CH_4-s	42.9	697.5±49.4	180.1±25.5	19.0±1.0	9.0±2.7
45	ml biogas-b	10.87	77.9±16.8	887.5±146.	10.3±0.7	8.4±3.0
45	ml biogas-s	63.4	887.5±146.	215.2±33.8	19.0±1.0	9.0±2.7

b= Batchwise side of the curve s= semi-continuous side of the curve

Table B.12. Logistic model parameters of the semi continuous digestion of olive residue in oven digester (HRT=30 days , DS=15 %)

Figure no.	Curve	χ^2	i	f	c	d
46	% CH_4	0.15	-4.6±1.7	90.7±2.4	7.1±0.2	2.1±0.2
46	% CO_2	0.24	97.6±4.7	12.0±1.6	7.6±0.4	2.6±0.3
47	ml CH_4	2.17	8.4±6.9	621.7±42.8	16.2±0.9	3.9±0.4
48	ml biogas	3.01	51.0±18.7	768.1±80.9	16.6±1.4	2.94±0.5

VITA

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