## Production of Biogas using Palm Oil Mill Effluent (POME) in Anaerobic Digester

by

Ahmad Budiman Bin Yaacob

Dissertation submitted in partial fulfillment
of the requirements for the
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Jan 2010

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# **CERTIFICATION OF APPROVAL**

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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Approved by,	
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UNIVERSITI TEKNOLOGI PETRONAS
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January 2010

# **CERTIFICATION OF ORIGINALITY**

This is to certify that I am responsible for the work submitted is this project, that the original work is my own except as specified in the references and acknowledgements and that the original work contained herein have not been undertaken or done by unspecified sources or persons.
(Ahmad Budiman Yaacob)

## **ABSTRACT**

The palm oil industry is one of the leading industries in Malaysia with a yearly production of more than 13 million tons of crude palm oil and plantations covering 11% of the Malaysian land area. However, the production of such amounts of crude palm oil result in even larger amounts of palm oil mill effluent (POME), estimated at nearly three times the quantity of crude palm oil. Palm oil mill effluent (POME) is a highly polluting wastewater that pollutes the environment if discharged directly due to its high chemical oxygen demand (COD) and biochemical oxygen demand (BOD) concentration. Anaerobic digestion has been widely used for POME treatment with large emphasis placed on capturing the methane gas released as a product of this biodegradation treatment method. The anaerobic digestion method is recognized as a clean development mechanism (CDM) under the Kyoto protocol. Certified emission reduction (CER) can be obtained by using methane gas as a renewable energy. This project aim is to do a research on the factors that contribute to the optimization of biogas production. Potential factors to the anaerobic digestion process of POME were indentified and tested in laboratory by using Anaerobic Respirometer. These factors such as addition of cosubstrate, volume of inoculums, volume of POME and PH of samples were analyzed and monitored to see its relation to the production of biogas. The total gas production volume and gas production rate in the experiment were gathered and their composition were tested in Gas Chromatography to analyze the percentage of Methane present. From this project those four (4) factors were identified to have significant effects to the biogas production volume, rate as well as the percentage of Methane present in the biogas composition. These factors are applicable to prove in this research by conducting experiment in the laboratory with existing equipments.

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## **CHAPTER 1**

## PROJECT BACKGROUND

#### 1.1 BACKGROUND OF STUDY

The palm oil industry in Malaysia has been expanding rapidly over the last four year decades with a yearly production of more than 13 million tons of crude palm oil and plantations covering 11% of the Malaysian land area. However, the production of such amounts of crude palm oil result in even larger amounts of palm oil mill effluent (POME), estimated at nearly three times the quantity of crude palm oil (Wu, 2009).

In the process of palm oil milling, POME is generated through sterilization of fresh oil palm fruit bunches, clarification of palm oil and effluent from hydrocyclone operations. POME is a viscous brown liquid with fine suspended solids at pH ranging between 4 and 5 (P.E. Poh, 2008).

POME is recognized not only because of large quantity generated but more significantly as a type of wastewater with the highest organic matters content where BOD and COD levels are at 25,000 mg/l and 50,000 mg/l respectively (Jaafar, 2004).

Various treatments have been used to treat POME in order to meet the Malaysian Department of Environment (DOE) discharge standard which is BOD of 100 mg/l. Anaerobic treatment of POME is widely used because of its low operational cost. During anaerobic treatment, a large amount of biogas is produced. Biogas is a mixture of colourless flammable gases obtained by anaerobic digestion of plant based (lignocelluloses) organic waste materials and also from other types of organic waste such as cow dung, pig slurry, effluent from slaughter houses and landfill (M. F. Basri, 2009)

The utilization of methane gas as a renewable energy from the anaerobic digestion can be used to obtain certified emission reduction (CER) credit by clean development mechanism (CDM) under the Kyoto protocol. Besides helping to reduce carbon emission to the environment, CDM has the advantage to offer developing countries such as Malaysia to attract foreign investments to sustain renewable energy projects (P.E. Poh, 2008)

Anaerobic Digestion technology has become a worldwide focus of research due to increasing demand for energy, cost saving and the protection of the environment. The most extensive study on the use of biomass through anaerobic digestion technology has been on palm oil wastes, which can be utilized to meet energy requirement of the palm oil mills and the electricity need of the workers (Lorestani, 2006)

#### 1.2 PROBLEM STATEMENT

Developing anaerobic digestion technology of POME can help to reduce carbon emission to the environment and in addition to that CDM also has the advantage to offer developing countries such as Malaysia to attract foreign investments to sustain renewable energy projects. Thus, palm oil mills could earn carbon credits as revenue by the utilization of methane gas as renewable energy from anaerobic digestion of POME. More emphasis has been given to develop anaerobic treatment for POME since the implementation of CDM (P.E. Poh, 2008).

Meanwhile, the palm oil mills in Malaysia face the challenge of balancing environment protection, their economic practicality and sustainable development after the Department of Environment (DOE) enforced the regulation for the discharge of effluent from the Crude Palm Oil (CPO) industry, under the Environmental Quality Order and Regulations 1997. Thus, there is an urgent need to find efficient and practical approach to preserve the environment while maintaining the sustainability of the economy (Lorestani, 2006)

The highly efficient anaerobic digestion design system allows maximum recovery of methane possible from the optimally controlled operation of anaerobic digestion of POME. The quantity of methane captured with acceptable percentage can be optimized by controlling the operating parameters as well as the conditions of the POME itself.

The aim of this study was to identify the factors that could contribute to the enhancing anaerobic digestion process and to improve biogas production from POME by simple laboratory scale of anaerobic system.

## 1.3 SCOPE OF STUDY

This research aims to scrutinize the performance of the biogas production volume and rate as well as its composition in anaerobic digester. There are factors have been identified that affects the production of biogas using POME such as inoculums composition, co-substrate addition, PH, temperature, organic loading rate (OLR), reactors type and design, retentation time and pretreatment process.. In this project the factors that appropriate with the existing anaerobic digestion systems are analyzed in order to study the performance of different parameters and conditions approaches.

The scope of research in this project is narrowed down so that the project is feasible and could be completed within the allocated time frame. The present research has the following objectives:

- i) To understand the anaerobic digestion process of palm oil mill effluent.
- ii) To identify the factors those affect the production of the biogas
- iii) To study the best experimental method in monitoring the biogas production volume and rate in anaerobic digestion process.
- iv) To determine the factors and conditions that lead to the optimization of biogas production volume, rate and composition.

## **CHAPTER 2**

## LITERATURE REVIEW

#### 2.1 OVERVIEW OF ANAEROBIC DIGESTION

Anaerobic digestion is one of the biological processes that have received a new fillip in recent years since the energy crisis of the early 1970s, especially following the Gulf war and energy price rises. The Anaerobic digestion process has captured many imaginations because it turns organic matter into a valuable source of renewable energy. During Anaerobic digestion organic matter is degraded in the absence of oxygen. The multi-step process results in a biogas (Mshandete, 2009).

It is appropriate that nations invest in new technologies and new sources of energy that will leave less of an environmental 'footprint' than coal or oil, and that will be more sustainable. Anaerobic digestion has successfully been used for many applications that have conclusively demonstrated its ability to recycle biological wastes (Abraham, 2005)

Anaerobic digestion is a biological process in which biodegradable organic matters are broken-down by bacteria into biogas, which consists of methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), and other trace amount of gases. The biogas can be used to generate heat and electricity. There is no Oxygen required in order for anaerobic digestion to be occurred (Koyama, 2008).

The process is naturally occurring by the decomposition and decay, by which organic matter is broken down to its simpler chemical components under anaerobic conditions. Anaerobic microorganisms digest the organic materials in the absence of oxygen, to produce methane and carbon dioxide as end products under ideal conditions. The biogas produce in anaerobic digestion plant usually contains small amount of hydrogen sulphide (H<sub>2</sub>S) and ammonia (NH<sub>3</sub>) as well as trace amount of other gases (Monnet, 2003).

In the process of degrading POME into methane, carbon dioxide and water, there is a sequence of reactions involved; hydrolysis, acidogenesis (including acetogenesis) and methanogenesis. Hydrolysis is where complex molecules (i.e., carbohydrates, lipids, proteins) are converted into sugar, amino acid and etc. In the step of acidogenesis, acidogenic bacteria will break down these sugar, fatty acids and amino acids into organic acids which mainly consist of acetic acid (from acetogenesis) together with hydrogen and carbon dioxide. Hydrogen and carbon dioxide will be utilized by hydrogenotropic methanogens while acetic acid and carbon dioxide will be utilized by acetoclastic methanogens to give methane as a final product (P.E. Poh, 2008).

Methanogenesis is the rate limiting step in anaerobic digestion of POME. As such, conventional anaerobic digesters require large reactors and long retention time to ensure complete digestion of treated influent. Nonetheless, high-rate anaerobic bioreactors have been proposed to reduce reactor volume, shorten retention time as well as capture methane gas for utilization (P.E. Poh, 2008).

## 2.2 ANAEROBIC DIGESTION PROCESS

In anaerobic digestion, organic matters are degraded to methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>) in discrete steps by the concerted action of several different metabolite groups of microorganism.

The digestion process follows four (4) major steps which are hydrolisis, acidogenesis, acetogenesis, and methanogenesis with hydrolisis as the rate limiting step of overall process. During hydrolisis, bacteria will break down insoluble organic polymers such a carbohydrate and to prepare them available for other bacteria. Then, acetogenesis will convert the sugars and amino acids into carbon dioxide, hydrogen, ammonia, and organic acids. Acetogenesis then convert these resulting organic acids into acetic acid along with additional ammonia, hydrogen, and carbon dioxide. Lastly, the methanogenesis process

takes place where the products are converted to methane and carbon dioxide (Wikimedia Foundation, 2009).

The main pathways of anaerobic digestion are shown in **Figure 2.1.** The salient features of those bacteria involved in the stabilization process are as follows:

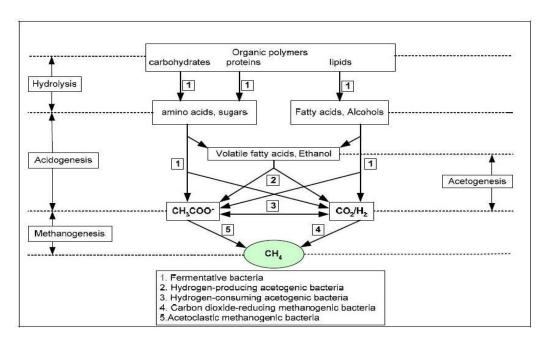
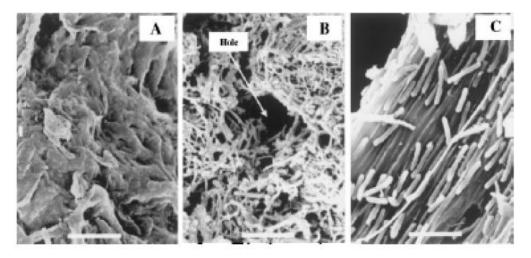


Figure 2.1: Anaerobic Conversion of Organic matter to methane (Lorestani, 2006)



**Figure 2.2**: (a) Microcrystalline cellulose particle before digestion, (b) Microcrystalline cellulose particle after anaerobic digestion for 9 days, (c) Microcrystalline cellulose particle after 9 days of anaerobic digestion (Lorestani, 2006)

## 2.2.1 Hydrolysis

The first step for most digestion process is hydrolysis during which particulate matters are converted to soluble compounds that can be hydrolyzed further to simple monomers to be subsequently utilized by fermentative bacteria. The group of non methanogenic responsible for the fermentation process consists of facultative and obligate bacteria (Lorestani, 2006).

In most cases biomass is made up of large organic polymers. In order for the bacteria in anaerobic digesters to access the energy potential of the material, these chains must first be broken down into their smaller constituent parts. These constituent parts or monomers such as sugars are readily available by other bacteria. The process of breaking these chains and dissolving the smaller molecules into solution is called hydrolysis. Therefore hydrolysis of these high molecular weight polymeric components is the necessary first step in anaerobic digestion (R.Mah, 2006).

Insoluble organic polymers such as carbohydrates, cellulose, proteins and fats are broken down and liquefied by enzymes produced by hydrolytic bacteria. Carbohydrates, proteins and lipids are hydrolysed to sugars which then decompose further to form carbon dioxide, hydrogen, ammonia and organic acids. Proteins decompose to form ammonia, carboxylic acids and carbon dioxide. During this phase gas concentrations may rise to levels of 80 per cent carbon dioxide and 20 per cent hydrogen (Residua, 2006).

The rate of hydrolisis is a function of factors such as PH, temperature and particle size of the substrate. Volatile fatty acids (VFA) production from the hydrolysis-acidification of the coffee pulp was investigated by Hourbroun and his coworkes and 23% (COD based) hydrolysis was achieved at an organic loading rate (OLR) of 5 g COD/Id (Lorestani, 2006)

## 2.2.2 Acidogenesis

In the acidogenesis step, the hydrolysis products are absorbed by the cells of fermentative bacteria to be fermented or anaerobically converted into compounds such as alcohols, short-chain fatty acids, formic acid, carbon dioxide, hydrogen, ammonia and sulfide. The organic substrates serve as both the electron donor and acceptors. The final products of the metabolic activities of these bacteria depend upon the initial substrate in figure 2.1 as well as the environmental conditions. As example consider the following reactions glucose;

$$C_6H_{12}O_6 + 2H_2O \longrightarrow 2CH_3COOH + 2CO_2 + 4H_2 \quad (2.1)$$
 $C_6H_{12}O_6 + 2H_2 \longrightarrow 2CH_3CH_2COOH + 2H_2O \quad (2.2)$ 
 $C_6H_{12}O_6 \longrightarrow CH_3CH_2COOH + 2CO_2 + 2H_2 \quad (2.3)$ 

The organic substrates serve as both the electron donors and acceptors. The final products of the metabolic activities of these bacteria depend upon the initial substrates as well as the environmental conditions (Lorestani, 2006).

Organic acids formed in the hydrolysis and fermentation stage are converted by acetogenic micro-organisms to acetic acid. At the end of this stage carbon dioxide and hydrogen concentrations begin to decrease (Residua, 2006).

#### 2.2.3 Acetogenesis

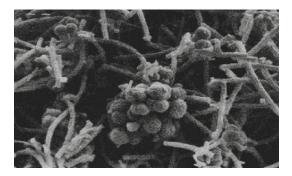
Acetogenesis is a process through which acetate is produced by anaerobic bacteria from a variety of energy (for example, hydrogen) and carbon (for example, carbon dioxide) sources. The different bacterial species that are capable of acetogenesis are collectively termed acetogens.

Acetogenesis is the third stage in anaerobic digestion process. Here simple molecules create through the acidogenesis phase are further digested by acetogens to produce largely acetic acid as well as carbon dioxide and hydrogen (A.D, 2007)

In the acetogenesis, about 68% of acetic acid and 32% of hydrogen are converted from Volatile Fatty Acids (VFAs). The process is very sensitive to the Hydrogen concentration and it was Syntrophic (mutually beneficial) relationship with the methanogens (Dr. Michael Robinson, 2005).

## 2.2.4 Methanogenesis

Methanogenesis refers to an anaerobic process in which the electron equivalents in organic matter ( $BOD_L$ ) are used to reduce carbon to its most reduced oxidation state in methane  $CH_4$ . Anaerobic treatment by methanogenesis is widely used for the stabilization of municipal wastewater sludge and municipal solid wastes (Bruce E.Rittmann, 2001)



**Figure 2.3**: Various types of methanogenic bacteria. The spherically shaped bacteria are of the methanosarcina genus; the long, tubular ones are methanothrix bacteria, and the short, curved rods are bacteria that catabolize furfural and sulfates. The total length of the broken bar at top left, which serves as a size reference, corresponds to 1 micron.

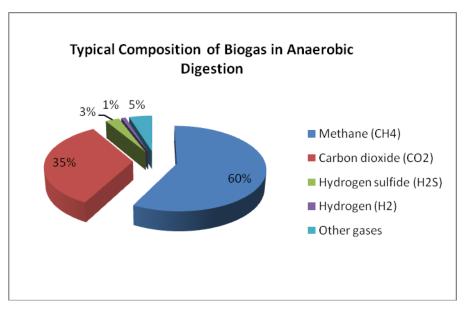
This is the terminal stage of anaerobic digestion where the methanogens utilize intermediate products of the preceding stages and convert them into methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>0). It is these components makes up the majority of the biogas emitted from the system. Methanogenesis is makes up the majority of the biogas emitted from the system. Methanogenesis is sensitive to both high and low pH and occurs between pH 6.5 and pH 8.

#### 2.3 BIOGAS PRODUCTION

## 2.3.1 Nature of Biogas

Biogas originates from bacteria in the process of bio-degradation of organic material under anaerobic conditions (without oxygen). The natural generation of biogas is an important part of the biogeochemical carbon cycle. Methanogens (methane producing bacteria) are the last link in a chain of micro-organisms which degrade organic material and return the decomposition products to the environment. In this process biogas is generated, a source of renewable energy.

Each year some 590-880 million tons of methane are released worldwide into the atmosphere through microbial activity. About 90% of the emitted methane derives from biogenic sources, i.e. from the decomposition of biomass. The remainder is of fossil origin (e.g. petrochemical processes). In the northern hemisphere, the present tropospheric methane concentration amounts to about 1.65 ppm (Kossmann, 2007).



**Figure 2.4**: Typical Composition of Biogas in Anaerobic Digestion (Wooster, 2009)

Like those of any pure gas, the characteristic properties of biogas are pressure and temperature dependent. They are also affected by the moisture content. The factors of main interest are (Kossmann):

- Change in volume as a function of temperature and pressure,
- Change in calorific value as a function of temperature, pressure and water vapor Content
- Change in water-vapor content as a function of temperature and pressure.

### 2.4 FEEDSTOCK

#### 2.4.1 Overview

The most important initial factors when considering the application of anaerobic digestion systems is the feedstock to the process. Digesters typically can accept any biodegradable material, however if biogas production is the aim, the level of putrescibility is the key factor in its successful application. The more putrescible the material the higher the gas yield possible from the system (Wikimedia Foundation, 2009)

Substrate composition is a major factor in determining the methane yield and methane production rates from the anaerobic digestion process. Techniques are available to determine the compositional characteristics of the feedstock, whilst parameters such as solids, elemental organic analyses are important for digester design and operation (Wikimedia Foundation, 2009).

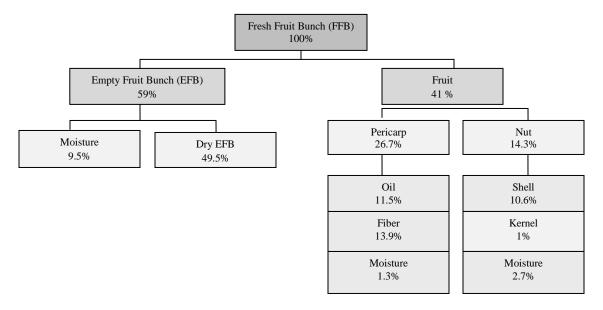
Various type of feedstock was suitable in having anaerobic digestion process. Examples of feedstock are sewage sludge, organic farm waste, municipal solid waste, green/botanical waste and organic commercial and industrial waste. In this project, the wastes from the palm oil mill industry are identified to be the most suitable substrates as a feedstock to be studied in anaerobic digestion experimental process.

## 2.4.2 Palm Oil Mill Wastes

The Malaysian palm oil industry has grown rapidly over the years and Malaysia has become the world's largest producer and exporter of palm oil and its products. In 2003, more than 3.79 million hectares of land were under oil palm cultivation, occupying more than one-third of the total cultivated area in Malaysia and 11% of the total land area (Ta Yeong Wu, 2008). The industry is growing rapidly and becomes a very important agriculture-based industry where the country today is the world's leading producer and exporter of palm oil, replacing Nigeria as the chief producer since 1971 (S.Yusoff, 2006).

The main product in the Palm Oil Mills industry is the Crude Palm Oil (CPO). Beside that the mills also generate many by-product and liquid or solids wastes which may a significant impact on the environment if they are not dealt with properly. These types of waste are give a significant impact in anaerobic digestion process in order to produce biogas. There are various forms of solid and liquid wastes from the mills. These include empty fruit bunches (EFB), Palm press fiber (PPF), palm kernel cake (PKC), palm kernel shell (PKS), sludge cake (SC) and

palm oil mill effluent (POME) appears in large quantities and are considered as wastes (P.Prasertsan, 1996)



**Figure 2.5**: Composition of fresh fruit bunch (P.Prasertsan, 1996)

## 2.4.3 Liquid Waste from Palm Oil Mill

The production of palm oil result in the generation of large quantities of polluted wastewater commonly referred to as palm oil mill effluent (POME). Typically, 1 tonne of crude palm oil production requires 5-7.5 tonnes of water; over 50% of which ends up as POME. The POME comprise a combination of wastewater from three main sources viz. clarification (60%), sterilization (36%) and hydrocyclone (4%) units (Lorestani, 2006)

Concurrent to the production of palm oil industry in Malaysia, a huge volume of Palm Oil Mill Effluent (POME) estimated at 35.7 million m<sup>3</sup> was generated in 2002 from a total about 350 or so palm oil mills distributed throughout Peninsular Malaysia, Sabah and Sarawak (Jaafar, 2004). POME is recognized not only because of the large quantity generated but more significantly as a type of wastewater with the highest organic matters content where BOD and COD levels are at 25,000 mg/l and 50,000 mg/l respectively (Ma A.N, 1993)

The raw POME feeding to the anaerobic digestion and aerobic/faculative treatment system is expected to have BOD and COD concentrations in a naroower range of 20000-25000 mg/l and 45000 – 50000 mg/l respectively.

**Table 2.1:** Typical characteristics of POME (Lorestani, 2006)

Parameter	Average	Metal	Average
PH	4.7	Phosphorus	180
Oil and Grease	4000	Potassium	2270
Biochemical Oxygen	25000	Magnesium	615
Chemical Oxygen Demand (COD)	50000	Calcium	439
Total Solids	40500	Boron	7.6
Suspended Solids	18000	Iron	46.5
Total Volatile Solids	34000	Manganese	2.0
Ammonical Nitrogen	35	Copper	0.89
Total Nitrogen	750	Zinc	2.3

#### 2.4.4 Solids Waste from Palm Oil Mill

The solid waste materials and by-products generated in the palm oil extraction process are presented as follows (Lorestani, 2006).

- 1) Empty fruit Bunches (EFB) -23 % of FFB,
- 2) Palm kernel 6% of FFB
- 3) Fibre 13.5 % of FFB
- 4) Shell -5.5% of FFB

Empty fruit bunches (EFB) is the major component of all solid wastes. Steam from the sterilization process results in a moisture content in the EFB as high as 60%, which make it unsuitable as fuel. It was reported that the EFB has 42% C, 0.8% N, 0.06% P, 2.4% K and 0.2% Mg (Sutanto, 1976). Palm press fiber (PPF) is a good combustible material as it has the oil retained in its cell wall. In factories which produce both steam and electrical power, all of the PPF is used. However

only 30% is consumed if power is not produced, therefore in some factories about 70% of PPF is considered as waste (P.Prasertsan, 1996).

The oil palm industry generates solid residues during the harvesting, replanting and milling processes. The residue that's comes from the milling processes are fruit fibres, shell and empty fruit bunches. Other residues include trunks and fronds are available at the plantation area. Currently shells and fibres are used as boiler fuel to generate steam and electricity for the mill's consumption. For old palm oil mills, the empty fruit bunch is burned in the incinerator to produce fertilizer. However, there are still a few companies disposed the empty fruit bunches using landfill method particularly mill without enough plantation or estates (Ludin, 2009)

**Table 2.2**: Potential Power Generation from Palm Oil Mill Solid Residues (Ludin, 2009)

Type of	Production	Residue	Residue	Residue	Potential	Potential
industry	(Thousand	Residue	product	Generated	Energy	Electricity
	Tonne)		Ratio	(Thousand	PJ	Generation
	59,800	EFB	21.14	12,641.7	57	521
Oil palm		Fiber	12.72	7,606.6	108	1032
		Shell	5.67	3,390.7	55	545
	Tota	ıl		16,670.6	220	2098



Figure 2.6: Palm Oil Mill Effluent (POME)





Figure 2.7: EFB

Figure 2.8: Shell

After considering the availability and economic point of view, the raw materials was used in this project would be from palm oil mill wastes. As state earlier, the palm oil industry in Malaysia is growing rapidly and becomes a very important agriculture-based industry, where the country today is the world's leading producer since and exporter of palm oil, replacing Nigeria as the chief producer since 1971 (T.Y.Wu, 2007). The wastes consist of the Palm Oil Mills Effluent (POME) Empty Fruit Brunches (EFF), Palm Kernel, Palm Shell, Palm fiber as well as waste from sterilizer. The figure below shows the conventional palm oil extraction process and source of waste generation.

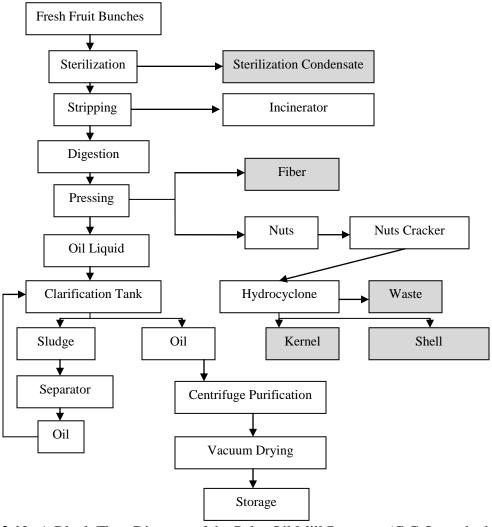


Figure 2.10: A Block Flow Diagram of the Palm Oil Mill Process (C.C.Onyegbado, 2007)

## 2.5 FACTORS OF BIOGAS PRODUCTION

## 2.5.1 Temperature

Anaerobic digestion will operate over a wide range of temperature. Almost researchers report that there are two distinct temperature ranges most suitable for gas production, and different bacteria that operate in each of these ranges. Typical operating temperatures of mesophilic digestion are 95°F to 98°F (35°C to 37°C). An advantage of mesophilic digestion is its prevalence. The energy demands associated with heating to mesophilic temperatures are modest and the stress on

concrete tanks is reasonable. Mesophilic digestion reaction rates are slower than more advanced process and therefore more tank volume would be required for the same amount of solids (Dave Parry 2004)

High temperature anaerobic digestion is occurs at thermophilic temperatures about 122°F to 135°F (50°C and 57°C). Thermophilic temperature is considerable based on the principle that higher temperature reduce pathogens and thermophilic bacteria result in more rapid reaction rates (Dave Parry 2004)

#### 2.5.2 Retention Time

A critical factor in methane production is the amount of time substrates spend in the digesters called retention time. Retention time is the time needed to achieve complete degradation of the organic matter. The retention time varies with the process parameters, such as process temperature and waste composition.

Too short retention time means an inefficient extraction of methane, so full revenue is not realized. Too long retention time means too much was spent on surplus capacity or not enough substrates are being added to maximize revenue.

The experiment was carried out to see the effect of Hydraulic Retention Time (HRT) with the feedstock of palm oil mill effluent. Palm oil mil effluent (POME) contains high amount of organic matter, oil & grease, total solids and suspended solids. Anaerobic treatment of POME was conducted at room temperature (30±2°C) and high temperature (50±0.5°C). The effects of hydraulic retention time (HRT), organic loading rate (OLR), COD: N ratio and temperature on the anaerobic digestion of POME were investigated. The Table 2.4 shows the characteristics of the decanter effluent before and after treatment (Pechsuth.M, 2001)

Table 2.3: Characteristic of the decanter effluent before and after treatment

		Dianustreatment	Anaerobic Digestion		
Parameter	POME	Biopretreatment Stage	POME	Biotreated POME	
Color	Brown	dark brown	blackish brown	blackish brown	
PH	4.5	4.48	5.53	5.65	
COD (mg/l)	90,700	34,800	39,800	24,900	
COD removal (%)	ND	61.6	56.1	72.6	
Oil & grease (mg/l)	21,000	2,600	ND	ND	
Oil & grease removal (%)	ND	87.5%	ND	ND	
Suspended solid (mg/l)	35,300	5,000	ND	ND	
Suspended solid removal (%)	ND	85.7%	ND	ND	

Effect of HRT on anaerobic digestion of POME was investigated at room temperature (30°C±1.0°C) and high temperature (50°C±0.5°C). The POME was treated at HRT of 12, 10, 7 and 5days with OLR of 7.92, 9.50, 13.57 and 19.00 kg/m3/d, respectively, and COD: N ratio of 85 (without any chemical added)

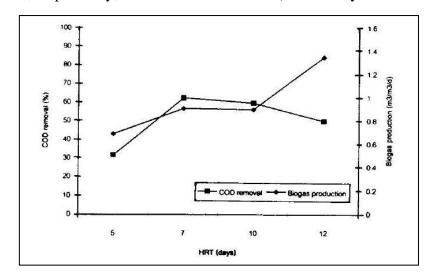


Figure 2.11: Effects of hydraulic retention time (HRT) on COD removal and biogas production from anaerobic digestion of palm oil mill effluent at room temperature  $(30\pm2^{\circ}C)$ 

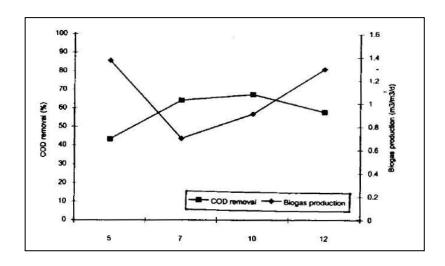


Figure 2.12: Effects of hydraulic retention time (HRT) on COD removal and biogas production from anaerobic digestion of palm oil mill effluent at high temperature ( $50\pm0.5^{\circ}$ C)

An increased in HRT resulted in an improvement of COD removal in turn produced increase in biogas production, methane concentration and methane yield. Increase of HRT resulted in increase of effluent PH and alkalinity and the portion of organic matter converted to methane. For that reason methane yield increased with the HRT.

#### 2.5.3 Pre-Treatment

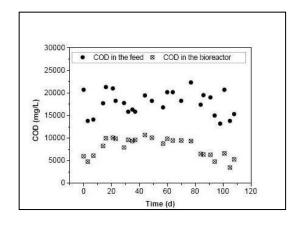
The physical, chemical and biological pre-treatment is the enhancement method for the first step of breaking complex molecules into simple monomers, to increase solubilization of organic material and improve the efficiency of the anaerobic treatment for the second step. The pre-treatment was required such as thermal, alkaline, ultrasonic or mechanical disintegration. The treatment can accelerated the solubilization (hydrolisis) and reduce the particle size, which subsequently improves the anaerobic digestion (Jeongsik Kim, 2002)

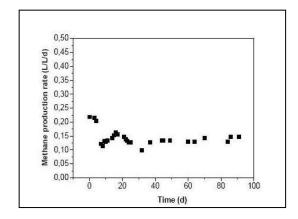
As example is in the effect of alkaline pre-treatment on anaerobic digestion of solid waste, the chemical treatment was based on lime, Ca(OH)<sub>2</sub> addition in order to enhance chemical oxygen demand (COD) solubilization, followed by anaerobic digestion of the organic fraction of municipal solid waste, OFMSW (Llorens, 2007)

The experiment was carried out in complexly mixed reactor, 1 L capacity. Optimal conditions for COD solubilization in the first step of pre-treatment were 62.0 mEq Ca(OH)<sub>2</sub>/L for 6.0 h. Under these conditions, 11.5% of the COD was solubilized. The anaerobic digestion efficiency of the OFMSW, with and without pre-treatment, was evaluated.

The highest methane yield under anaerobic digestion of the pre-treated waste was 0.15 m<sup>3</sup> CH<sub>4</sub>/kg volatile solids (VS), 172.0% of the control. Under that condition the soluble COD and VS removal were 93.0% and 94.0%, respectively. The results have shown that chemical pre-treatment with lime, followed by anaerobic digestion, provides the best results for stabilizing the OFMSW (Llorens, 2007).

Another example to show the effect of pre-treatment is in the experiment of Olive Mill Wastewater (OMW). The OMW was The OMW used for this experiment was pre-treated with *Pleurotus ostreatus* using the bioreactor. The anaerobic bioreactor operated at an HRT of 30 d. The feed of the anaerobic bioreactor was the pre-treated OMW, diluted at a ratio 1:2 and the nutrients were added in the feed (Blika, 2007). The results of the experiment are shown in the following graphs:





**Figure 2.13:** Influent and effluent COD values in anaerobic digestion of fungal-pretreated OMW

**Figure 2.14:** Methane production rate in anaerobic digestion of fungal-pretreated OMW

In fact, wastewater pre-treated with *Pleurotus ostreatus* had enhanced methane production. This shows that treatment by *Pleurotus ostreatus* decreases the toxicity of OMW to methanogenic bacteria.

## 2.5.4 Organic Loading Rate

Organic loading rate (OLR) is a measured of the biological conversion capacity of the anaerobic digestion. Feeding the system above its sustainable OLR, results in low biogas yield due to accumulation of inhibiting substances in the digester slurry (i.e. fatty acids).

Under such circumstances, the feeding rate of the system must be reduced. OLR is particularly important control parameter in continuous system. Many plants have been reported system failure due to overloading. OLR is expressed in kg Chemical Oxygen Demand (COD) or Volatile solids (VS) per cubic meter of reactor (Monnet, 2003).

#### 2.5.5 Other Factors

Another factors could be consider in optimization of biogas production in anaerobic digestion. For example are reactor types and designs to be as digester in the process system. CSTR is one of the reactor types which the effluent is added to the reactor and mixing is accomplished with gas mixers, mechanical mixers and recirculation pump. It has been proved as a technology that can achieve reasonable conversion from solids to gas (Bertoldo, 2008). High installation and operating costs, high hydraulic retention times are required to achieve an acceptable level of degradation, signifying large reactor sizes.

Other types of reactor are Upflow Anaerobic Sludge Blanket (UASB) reactor and Contact Digester. In UASB reactor, the biomass forms sludge granules, producing a sludge bed which is completely retained in the reactor where formation of the granular sludge bed requires a significant amount of time, causing longer start-up times when compared to other reactors. In Contact Digester, biomass is retained by separating and concentrating the solids in a separate reactor, returning these solids to the influent. The Solids separation can be achieved with gravity separators, solids thickeners, centrifuges, gravity belts, and membranes.

## **CHAPTER 3**

## **METHODOLOGY**

#### 3.1 INTRODUCTION

Throughout this project, there were three (3) main phase of research methodology which is Phase (I) was about literature review, Phase (II) based on the experimental works and Phase (III) was related to the result analysis where the problem statements of the project will be concluded.

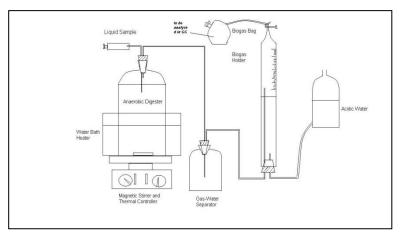
#### 3.1.1 Literature Review

A part of the literature reviews the problem statements of the project were identified according to the project's research title. The problem statements were intended to be clarified to ensure the works were in line with the objective of the research project. There were several sources which were used such as journal, website, books and paperwork. In the earlier of the project started the main focus was studying about the anaerobic digestion process. The information about this process was gathered in terms of their mechanism, stage of process involved, factors influencing anaerobic digester performance and the availability and suitability of the feedstock. The suitable experimental work methods were identified to be implemented in this project. Almost the information are getting from previous work relating to research problem and previous works relating to methodology and results.

#### 3.1.2 Experimental Works

In the phase (II), the project was focused on the experimental works. Due to the limitation of knowledge and facilities in the lab the experimental works and procedures were varied from time to time. At the first, the apparatus of

experiment was constructed to predict whether the process using the POME sample was produced a gas or not. It was based on reference from a project which titled on Mathematical Model for the Estimation of Anaerobic Sludge Activity by B.M.P Barampouti from National Technical University of Athens. The assembling of the apparatus is shown in *figure 3.1*.



**Figure 3.1**: Apparatus for anaerobic sludge activity measurement (E.M.P Barampouti, 2003)

The anaerobic activity analysis is run in apparatus as described in *Figure 3.1* above and the standard procedure is described as follow; 1.0 L of POME with the sludge is put in the digester of *Figure 3.1* and stored for 24 hours at 35 °C. The PH was corrected to 7.0 by using NaOH powder. The digester was connected with the apparatus of *Figure 3.1* after flushing with nitrogen gas and it placed in a water bath at 35 °C on magnetic stirrer and thermal controller. The rising biogas is collected in a graduated measuring cylinder of 2.0 l or more passing through an alkaline scrubber in order to absorb CO<sub>2</sub>. The data of methane production is collected by measuring the water displacement and in order to know the composition of biogas, the sample is collected and tested in GC (E.M.P Baramapouti, 2003)

As time goes by, this method was indentified not to be a practical enough to collect the biogas and tested it in Gas Chromatograph. There was a problem when the composition of the gas needs to be tested because the gas sample could not

hold for a long time and in the inappropriate tool. Then the new method was found where the digester itself is placed in the water bath shaker and the biogas was collected by having the biogas bag as shown in Figure 3.2;



Figure 3.2: Samples in water bath shaker

It was consisted of volumetric flask, water bath shaker and biogas collection bags. This method whereby was unable to measure the gas production rate as well as the gas production volume. So the last method was used by using the equipment named Anaerobic/Anaerobic Respirometer as shown in Figure 3.3. This method was chosen because the equipment used can measured the production rate and total gas volume of the biogas.

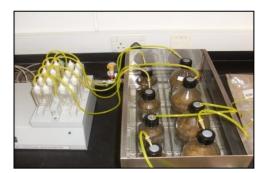


Figure 3.3: Anaerobic Respirometer

## 3.1.3 Results Analysis

In this section, the result obtained from the experiment was analyzed by constructing the graph to see the performance of the each process runs.

## 3.2 FLOW CHART

The overall research project was shown in the *Figure 3.4* below where it comprise of three (3) phase as stated earlier.

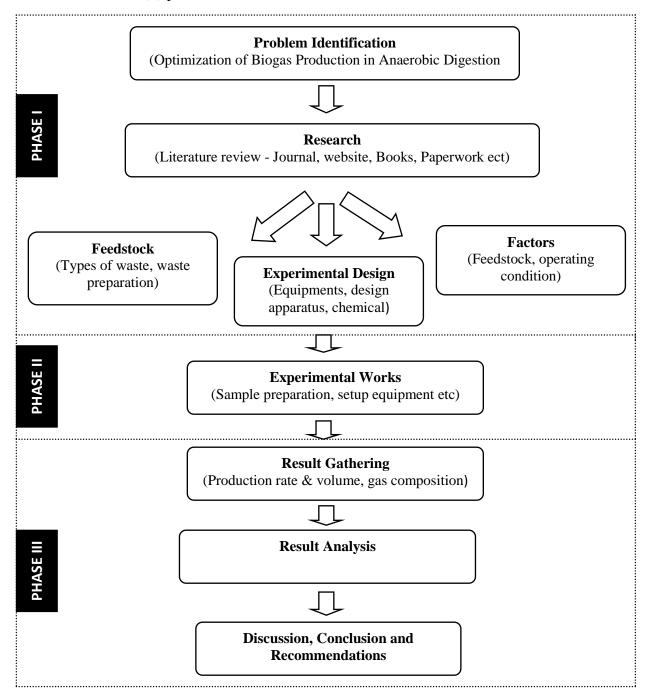


Figure 3.4: Flow chart of overall project

#### 3.3 PROJECT ACTIVITIES

The main project activities were based on the lab experiment works. As mentioned earlier few methods of experiments were conducted in order to get the correct result to be analyzed. The final method used was Anaerobic Respirometer. There were few steps to conduct the experiment by using the Anaerobic Respirometer.

# **Topic Selection**

- Project topic selection and submission
- Approval of Project Proposal by Coordinator



## **Preliminary Study**

- Study on dissertation journals, books, website and paperwork.
- Data and information gathering
- Literature review and submission of preliminary report, progress report, interim report and presentation for part I.



# **Screening Process**

- Study on anaerobic digestion system
- Study on factors influencing the anaerobic process
- Study on the experimental methods
- Data gathering for statistical facts and figures
- Submission of progress report I for part 2.



# **Experimental Work**

- Preparing the samples and conducts experiment
- Data collection on production rate, volume and composition of biogas



# **Data Analysis**

- Analyzing data
- Submission of progress report II for part 2



## **Documentation and Presentation**

Final report and presentation

# 3.3.1 Preparing Sample

The sample used as a feedstock in this project was from palm oil wastes comprise of two (2) types which were solids and liquid waste. Solids waste were come from fiber, shell and nuts where the liquid waste was palm oil mill effluent and sludge. The wastes were collected from Felcra Nasaruddin (a palm oil mill factory) in Bota Perak. The liquid and solid wastes were stored in the cold room at temperature 3 °C.

POME and sludge were stored in the cold room and will remove when to use it in the experiment. Whereas the solids waste need to be prepared in very small pieces. The samples first were heated up in the oven at 110 °C for about 3 hours to make them crunchier. Then the samples were mashed using mortar and blended into a small piece.

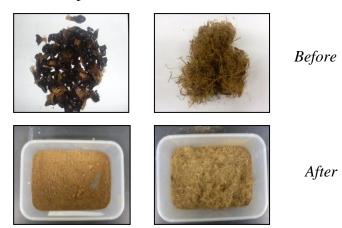


Figure 3.5: Before and after samples are blended



**Figure 3.6:** Liquid Samples

# 3.3.2 Experimental Setup

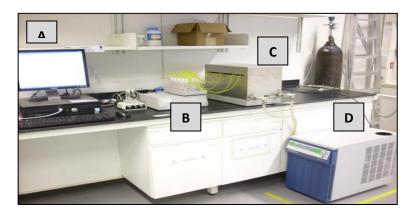
The CHALLENGE AER-200 Respirometer System was used in this project where it consists of biological reaction vessels, a stirring base for mixing the samples, a cell base containing eight flow measuring cells, an interface module, and a computer.

The system can be operated in the aerobic mode or in anaerobic mode. When operating in the anaerobic mode, gases produced by biological reactions flow through each cell under the influence of a slight pressure buildup caused by gas production in the reaction vessel and bubbles of a fixed volume are formed in the lower section of the cell. These bubbles in turn pass through a detection section thereby activating a counter in the interface module. Finally, the number of bubbles is registered by the computer to produce a measure of cumulative volume and rate of flow (Challenge AER-200 Series Aerobic/Anaerobic Respirometer Systems, 2004)

This data is stored by the computer for later processing. The lowest volume of measurement using the standard anaerobic cell is one bubble or about 0.15 mL; the upper range is two to three bubbles per second or about 20 to 25 mL/min. (High-sensitivity cells having about 0.05 mL per bubble or 8 to 10 mL/min are available from CHALLENGE) (Challenge AER-200 Series Aerobic/Anaerobic Respirometer Systems, 2004)

In order to setup the experiment, the test bottles and related parts were cleaned using water tab and rinsed thoroughly. The Teflon™-coated magnetic stirring bar was inserted in each bottle (reaction vessel). The samples that prepared were transferred into the bottles and each of it was flushed using nitrogen gas. The screw cap was placed the p with inserted butyl rubber septum on each test bottle. The sample of each bottle was then placed on the MS8-300 magnetic stirring base in a constant temperature 35 °C.

The test bottles were vented by briefly inserting a clean 20-gage needle through the septum. This venting prevents blowing cell fluid from the cell due to a gas buildup in the bottle during set up. The cell counters and timers from the Control Screen were reset and data acquisition was initiated by clicking on the **Start** button. The experiment was leaved for about 4 days and the composition of the gas produced was then tested in Gas Chromatograph to determine the present of Methane.



**Figure 3.7** A) Monitoring Computer, B) Cell Base, C) Magnetic Stirrer Base and D) Rotator



Figure 3.8: Gas Chromatograph (GC)

# 3.4 GANTT CHART

Table 3.1: Gantt chart

No.	Detail/ Week							FY	ΥP	<b>(I)</b>	)											FY	P	(II	)				
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Phase I																												
1	Selection of Topic																												
2	Preliminary Research Work																												
3	Submission of Preliminary Report				•																								
4	Seminar																												
5	Project Work																												
6	Submission of Progress Report																												
7	Project Work																												
8	Submission of Interim Report													•															
9	Oral Presentation														•														
	Phase II																												
10	Experimental Works																		•										
11	Submission of Progress Report I																												
	Experimental Works																						lacktriangle						
13	Submission of Progress Report 2																												
14	Poster Presentation (Pre-EDX)																												
15	Experimental Works and Analysis																												
16	EDX																									•			
17	Submission of Dissertation (soft bound)																												
18	Oral Presentation																												
19	Submission of Project Dissertation																												

**Project Milestone ●** Process

# 3.5 TOOLS AND EQUIPMENTS

In this project, there were several types of tools and equipments that were used in conducting the experiment. The tools and equipments were important in order to ensure the project run smoothly. Inappropriate tools or equipments used will lead to unsatisfactory result. The availability of tools or equipments play very important to ensure the project completed in set time. These are the list of tools and equipments that were used during the project.

**Table 3.2**: Tools and equipments

No	Name of equipments/tools	Purpose of equipments/tools
1	Oven	To heat up the solids waste
2	Mortar/ blender	To prepare the solids waste into small pieces
3	Anaerobic Respirometer	To measure the gas production rate and volume
4	Gas Chromatograph	To determine the percentage composition of biogas
5	PH meter	To check the PH of the samples before run the experiment
6	Cylinder, biker	To measure the quantity of the samples needed

# CHAPTER 4 RESULT AND DISCUSSION

#### 4.1 OVERALL RESULT

**Table 4.1:** Result of Overall Experiment

EXP	Cell	Sample		Compo	osition			Result	
			POME (ml)	Inoculums (ml)	Co- substrate (g)	РН	Average Production Rate (ml/hour)	Total Gas Volume (ml)	% Methane
	A-1	Sample 1	100	50	15	≈ 6.5	16.62	417	11.4620
1	A-2	Sample 2	100	50	20	≈ 6.5	12.57	306	4.7750
1	A-3	Sample 3	100	50	30	≈ 6.5	7.6	186	5.638
	A-4	Sample 4	100	50	10	≈ 6.5	8.35	203	4.9780
	A-1	Sample 5	100	100	-	≈ 6.5	4.76	462	5.0940
2	A-2	Sample 6	100	75	-	≈ 6.5	4.74	459	4.7980
2	A-3	Sample 7	100	50	-	≈ 6.5	4.80	465	6.1560
	A-4	Sample 8	100	25	-	≈ 6.5	4.18	405	4.9560
	A-1	Sample 9	400	50	-	≈ 6.5	18.70	1813	4.1770
3	A-2	Sample 10	300	50	-	≈ 6.5	17.26	1674	4.4050
3	A-3	Sample 11	200	50	-	≈ 6.5	9.93	973	4.6780
	A-4	Sample 12	100	50	-	≈ 6.5	5.50	533	3.9240
	A-5	Sample 13	100	50	-	4.6	0.26	25	0.0000
4	A-6	Sample 14	100	50	-	6.6	5.97	578	9.3930
	A-7	Sample 15	100	50	-	7.8	1.08	104	0.0000

= Variable changes

There were fifteen (15) samples in this experiment where the compositions of the samples were varied. The samples were placed in the cells named Cell A-1, Cell A-2, Cell A-3 and Cell A-4, Cell A-5, Cell A-6 and Cell A-7. For each experiment, only four (4) samples could perform the experiments.

The experiments were conducted in 24 hours for each factor studied at 35.5 °C and the where the production volume and production rate of biogas was measured through the sensor of Respirometer. The accumulated gas in the bottle samples were sent to the GC for analyzing the composition of biogas.

#### **4.2 DISCUSSIONS**

#### **EXPERIMENT 1:**

**Table 4.2: Result of Experiment 1** 

				Compo	osition		Result					
EXP	Cell	Sample	POME (ml)	Inoculums (ml)	Co- substrate (g)	РН	Average Production Rate (ml/hour)	Total Gas Volume (ml)	% Methane			
	A-1	Sample 1	100	50	15	≈ 6.5	16.62	417	11.4620			
1	A-2	Sample 2	100	50	20	≈ 6.5	12.57	306	4.7750			
1	A-3	Sample 3	100	50	30	≈ 6.5	7.6	186	5.638			
	A-4	Sample 4	100	50	10	≈ 6.5	8.35	203	4.9780			

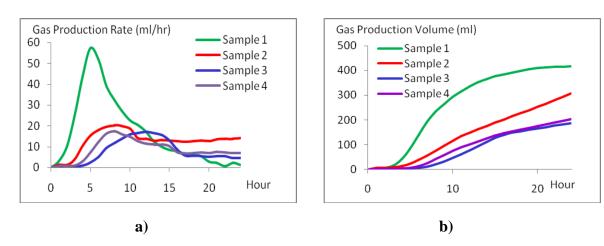


Figure 4.1: a) Gas Production rate for Experiment 1, b) Gas Production Volume for Experiment 1

Sample 1 = POME: 100 ml, Inoculums: 50 ml, Co-substrate: 15g Sample 2 = POME: 100 ml, Inoculums: 50 ml, Co-substrate: 20g Sample 3 = POME: 100 ml, Inoculums: 50 ml, Co-substrate: 30g Sample 4 = POME: 100 ml, Inoculums: 50 ml, Co-substrate: 10g

The variable changes in Experiment 1 were the quantity of co-substrate to the samples. Figure 4.5 a) and b) show the overall gas production volume and overall gas production rate in 24 hours time. Each sample contains the same amount of POME and Inoculums volume but the quantity of co-substrates were varied. Co-substrates were the solids waste from palm oil mills comprised of fiber, kernel

shell and EFB. At the beginning the gas production rate of sample 1 was very high and the highest among others sample. After an about 6 hours, the production rate was obviously decreasing until to the end of experiment.

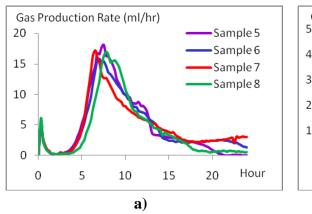
For the sample 2, the gas production rate was also high at the beginning and not constant until it apparently was dropped when approaching to the end. At that time only small amount of gas was produced. For the sample 3 and sample 4, the trend was slightly same where at the beginning both of them were increasing and start to drop from hour 10 to 15.

The composition of substrate had a significant influence on the overall production of biogas. The fermentation was done at 35.5 °C and initial PH 6.5 in the earlier of experiment for all the samples. Figure 4.1 b shows the accumulated biogas profile for different compositions of co-substrate and the result shows that the ratio of co-substrate to the Inoculums volume, 10:3 as suitable ratio for optimal biogas production which gave 417 ml day<sup>-1</sup> of accumulated biogas. In this study, the lowest biogas production obtained was 186 ml day<sup>-1</sup> for sample 3 which contains 30 g of co-substrate. This might be due to the too high composition of solid wastes causing the inhibition of bacteria in the sample.

#### **EXPERIMENT 2:**

**Table 4.3: Result of Experiment 2** 

		_		Compo	osition		Result					
EXP	Cell	Sample	POME (ml)	Inoculums (ml)	Co- substrate (g)	РН	Average Production Rate (ml/hour)	Total Gas Volume (ml)	% Methane			
	A-1	Sample 5	100	100	-	≈ 6.5	4.76	462	5.0940			
2	A-2	Sample 6	100	75	-	≈ 6.5	4.74	459	4.7980			
2	A-3	Sample 7	100	50	-	≈ 6.5	4.80	465	6.1560			
	A-4	Sample 8	100	25	-	≈ 6.5	4.18	405	4.9560			



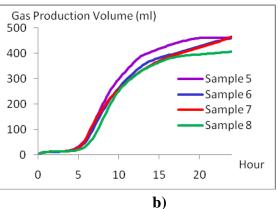


Figure 4.2: a) Gas Production rate for Experiment 2, b) Gas Production Volume for Experiment 2

Sample 5 = POME: 100 ml, Inoculums: 100 ml

Sample 6 = POME: 100 ml, Inoculums: 75 ml

Sample 7 = POME: 100 ml, Inoculums: 50 ml

Sample 8 = POME: 100 ml, Inoculums: 25 ml

The variable changes in Experiment 2 were the volume of Inoculums added into the samples. The changes of Inoculums volumes were 100 ml, 75 ml, 50 ml and 25 ml with the constant volume of POME which was 100 ml each. The graph 4.2 a shows that the rates of biogas production for each sample were slightly same until to the end of experiment. All the samples were increased at the beginning of experiment and started to decreased when reached at hour 8. In this run, Sample 7 with ratio of inoculums to POME, 1:2 gave high total biogas production volume,

biogas production rate and the percentage of methane (CH<sub>4</sub>). It composition was (Composition: POME = 100 ml and Inoculums = 50 ml). The lowest biogas production obtained was 405 ml day<sup>-1</sup> for sample 8 which contains 25 ml of inoculums. This might due to insufficient quantity of bacteria that could digest the POME itself through the anaerobic digestion process. Too high composition of inoculums also not necessarily gave the high production of biogas.

#### **EXPERIMENT 3:**

**Table 4.4: Result of Experiment 3** 

				Compo	osition		Result					
EXP	Cell	Sample	POME (ml)	Inoculums (ml)	Co- substrate (g)	РН	Average Production Rate (ml/hour)	Total Gas Volume (ml)	% Methane			
	A-1	Sample 9	400	50	-	≈ 6.5	18.70	1813	4.1770			
3	A-2	Sample 10	300	50	-	≈ 6.5	17.26	1674	4.4050			
3	A-3	Sample 11	200	50	-	≈ 6.5	9.93	973	4.6780			
	A-4	Sample 12	100	50	-	≈ 6.5	5.50	533	3.9240			

Sample 9

Sample 10

Sample 11

Sample 12

Hour

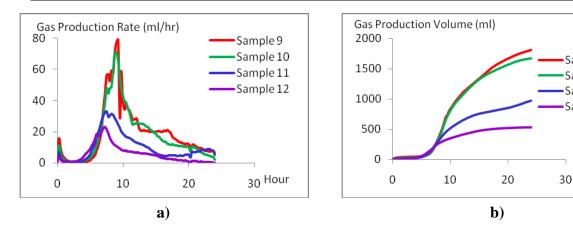


Figure 4.3: a) Gas Production rate for Experiment 3, b) Gas Production Volume for Experiment 3

Sample 9 = POME: 400 ml, Inoculums: 50 ml

Sample 10 = POME: 300 ml, Inoculums: 50 ml

Sample 11 = POME: 200 ml, Inoculums: 50 ml

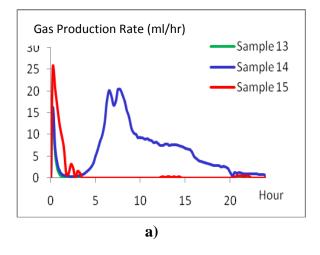
Sample 12 = POME: 100 ml, Inoculums: 50 ml

In Experiment 3, the volume of POME was different but the volume of Inoculums of each samples were same. The highest volume of POME used was 400 ml for sample 9 and the lowest was 100 ml for sample 12. From this experiment, the volume of POME gave significant effect to the biogas production volume and biogas production rate. Sample 9 gave the highest value in term of highest total biogas production rate and biogas production volume. The composition was (Composition: POME = 400 ml and Inoculums = 50 ml). This showed that the volume of POME itself in the batch fermentation of anaerobic digestion process enhanced the performance of biogas production.

#### **EXPERIMENT 4:**

**Table 4.5: Result of Experiment 4** 

				Compo	osition		Result					
EXP	Cell	Sample	POME (ml)	Inoculums (ml)	Co- substrate (g)	РН	Average Production Rate (ml/hour)	Total Gas Volume (ml)	% Methane			
	A-5	Sample 13	100	50	-	4.6	0.26	25	0.0000			
4	A-6	Sample 14	100	50	-	6.6	5.97	578	9.3930			
	A-7	Sample 15	100	50	-	7.8	1.08	104	0.0000			



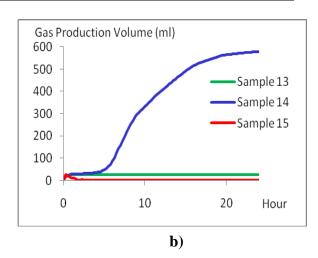


Figure 4.4: a) Gas Production rate for Experiment 4, b) Gas Production Volume for Experiment 4

Sample 13 = POME: 100 ml, Inoculums: 50 ml, PH: 4.6

Sample 14 = POME: 100 ml, Inoculums: 50 ml, PH: 6.6

Sample 15 = POME: 100 ml, Inoculums: 50 ml, PH: 7.8

It is known that the pH value plays a crucial role in influencing the biogas production efficiency for anaerobic degradation of POME. In this study, different initial pH values (4.8, 6.6 and 7.8) were tested for biogas production. Figure 4.4 b shows the accumulated biogas profile for different initial pH values in 24 h of anaerobic fermentation. The result of the biogas profile for sample 13 with initial pH 4.6 and sample 15 with initial pH 7.8 cannot be plotted and showed in the graph because the production of the accumulated biogas was very low and zero production after certain hours. One of the possible reasons for the lower biogas yield at initial pH 4.6 and PH 7.8 was due to acids and alkaline production in the system.

Generally, acid accumulation in the system causes a sharp drop of the pH, thus inhibiting biogas production. The bacteria involved could not sustain its metabolic activity at pH values less than 6.0 and complete inhibition was reported in the pH range of 4.0-6.0 (Nazlina, 2009).

The optimal initial pH for biogas production from POME in this study was pH 6.6 which near to PH 7.0. The control of pH could significantly affect biogas production and stimulate microorganisms to produce biogas. When the initial pH was higher than 7.5 the culture required more adaptation time for biogas production.

# **CHAPTER 5**

## CONCLUSION AND RECOMMENDATIONS

## 5.1 CONCLUSION

In this study, enhancing biogas production could be achieved under proper controlled conditions with enrichment of biogas producing bacteria from POME sludge in mesophilic conditions. The experimental results showed that biogas production from POME was optimal based on the initial pH 6.6, ratio between cosubstrate to the inoculums volume of 10:3, Volume of POME which is 400 ml and the ratio of inoculums to POME volume of 1:2. From the experiment it showed that the Palm Oil Mills Effluent (POME) can be considered as a good substrate for biogas production under suitable operating conditions.

Co-substrate addition with acceptable ratio to the POME and Inoculums volume could increase the rate and volume production of biogas as well as percentage of methane yield. Different volume of POME and Inoculums also will result different rate and volume production of biogas and the percentage of methane. And last but not least the best pH condition is neutral within the range of 6-7 for the optimum process of the anaerobic digestion.

# 5.2 **RECOMMENDATIONS**

In order to ensure the continuation of the project to become successful, there are several recommendations are suggested:

- i) The range for the operating conditions (PH, POME and Inoculums volume and the quantity of co-substrate) needed to enlarge for the better result obtained.
- ii) The used of commercial type of microorganisms that available in market to enhance the biogas production as well as the methane percentage.
- iii) The experiment should be carried on in the continuous reactor instead of batch fermentation system with larger scale of experiment to get more accurate and reliable result.
- iv) Enhancing the equipments required to perform the experiments to ensure the project is run better and smoothly with the specific task and planning.

#### REFERENCES

- Abraham, E. R. (2005). Biogas: Can It Be an Important Source of Energy? *Env Sci Pollut Res*, 67-71
- Bertoldo, D. (2008). Anaerobic Digestion of Biomass for Biogas Production. Department of Chemical Engineering Lakehead University
- Blika, P. (2007). Anaerobic digestion of olive mill wastewater. 2Institute of Chemical Engineering and High Temperature Chemical Processes (ICEHT), 1-8.
- Challenge AER-200 Series Aerobic/Anaerobic Respirometer Systems. CES, Inc.
- C.C.Onyegbado, J. a. (2007). A Review of Palm Oil Mill Effluent (POME) Water Treatment. *Global Journal of Environment Research*, 54-62
- Dave Parry, C. C. (January 2004). High Performance Anaerobic Digestion. *Bioenergy Subcommittee*, 2-17
- Dr. Michael Robinson, P. (2005). Anaerobic Digestion Process Theory. Department of Civil
- E.M.P Barampouti, S. a. (2003). A Mathematical Model for the Estimation of Anaerobic Sludge Activity. 8th International Conference on Environment Science and Technology, 72-78
- Jaafar, S. T. (2004, February). Waste to Energy: Methane Recovery from Anaerobic Digestion of Palm Oil Mill Effluent. *Energy Smart*, p. 4.
- Jeongsik Kim, C. P.-H.-W. (November 2002). Effects of various Pretreatments for Enhanced Anaerobic Digestion with Waste Activated Sludge. *Journal of Bioscience and Bioengineering*, 271-275
- Kossmann, W. (n.d.). Volume 1: Biogas Basics. *Biogas Digest*, 1-45.
- Koyama, K. (2008, August 14). *Renewable Energy Research Biomass (Anaerobic Digestion)*. Retrieved October 2009, 2009, from The California Energy Commission: http://www.energy.ca.gov/research/renewable/biomass/anaerobic\_digestion/
- Llorens, M. T. (2007). Effect of Alkaline Pretreatment on Anaerobic Digestion of Solid Wastes. *National Center for Scientific Researcher (CNIC)*

- Lorestani, A. A. (2006). Biological Treatment of Palm Oil Mill Effluent (POME) Using An Up-Flow Anaerobic Sludge Fixed Film (UASFF) Bioreactor. Universiti Sains Malaysia
- Ludin, N. (2009). *Palm Oil Biomass for Electricity Generation in Malaysia*. Retrieved 9 16, 2009, from Pusat Tenaga Malaysia: http://www.ptm.org.my/biogen
- Ma A.N, S. a. (1993). Current Status of Palm Oil Processing Wastes Management in Waste Management in Malaysia. *Current Status and Prospects for Bioremendiation, B.G Yeoh et al.* (Eds), 111-136
- M. F. Basri, S. Y. (2009). Improved biogas production from palm oil mill effluent. *World J Microbiol Biotechnol*, 505
- Mshandete, A. M. (2009). The Anaerobic Digestion of Cattail Weeds to Produce Methane Using American Cockroach Gut Microorganisms. *ARPN Journal of Agricultural and Biological Science*, 45
- Monnet, F. (November 2003). *An Introduction to Anaerobic Digestion of Organic Wastes*. Scotland: Remade Scotland
- Nazlina, H.M.Y., A.R. Nor Aini, F. Ismail, M.Z.M. Yusof and M.A. Hassan, 2009. Effect of different temperature, initial ph and substrate composition on biohydrogen production from food waste in batch fermentation. Asian J. Biotechnol., 1: 42-50.
- Pechsuth.M. (2001). High-rate anaerobic treatment of palm oil mill effeluent. Songklanakarin J. Sci. Technol, 780-787.
- P.E. Poh, M. C. (2008). Development of anaerobic digestion methods for palm oil. *Elsivier-Bioresource Technology*, 1
- P.Prasertsan, S. a. (1996). Biomass Residues From Palm Oil Mills in Thailand:An Overview on Quantity and Potential Usgae. *Pergamon*, 388.
- R.Mah, R. a. (2006). Hydrolytic Bacteria in Anaerobic digestion of biomass, 15
- Residua. (2006). Anaerobic Digestion. Warmer Bulletin
- S.Yusoff. (2006). Renewable Energy From Palm Oil-Innovation on Effective Utilization of Waste. *J.Cleaner Prodcut*, 87-93
- T.Y.Wu, A. J. (2007). Palm Oil Mill Effeluent (POME) Treatment and Bioresources Recovery Using Ultrafiltration Membrane:Effect of Pressure on Membrane Fouling. *Biochemical Engineering Journal*, 309-317.

- Wooster, OARDC. (2009, April 7). Waste to Energy Workshop: Advances and Opportunities for Ohio's Livestock & Food Processing Industries. Ohio, USA
- Wikimedia Foundation. (2009). Retrieved 8 15, 2009, from Anaerobic Digestion: http://en.wikipedia.org/wiki/Anaerobic\_digestion
- Wu, T. Y. (2009). A holistic approach to managing palm oil mill effluent (POME): Biotechnological. *Elsivier Biotechnology Advances*, 40-52

# **APPENDIXES**

Experiment : Run 1

Elaspe	Sampl	e 1	Sampl	e 2	Sam	ple 3	Samp	ole 4
Т	Volume	Rate	Volume	Rate	Volume	Rate	Volume	Rate
0	0	0	0	0	0	0	0	0
1	3.39	2.99	6.45	1.35	0.96	0.51	1.17	0.72
2	6.38	10.21	7.8	1.25	1.47	0.36	1.89	0.64
3	16.59	24.89	9.05	3.85	1.83	0.41	2.53	0.9
4	41.48	44.02	12.9	10.53	2.24	0.97	3.43	3.02
5	85.5	57.31	23.43	15.41	3.21	2.38	6.45	7.31
6	142.81	51.6	38.84	18.1	5.59	5.26	13.76	12.22
7	194.41	39.34	56.94	19.62	10.85	9.3	25.98	16.14
8	233.75	32.42	76.56	20.25	20.15	11.86	42.12	17.32
9	266.17	27.16	96.81	19.98	32.01	13.88	59.44	15.79
10	293.33	22.44	116.79	18.55	45.89	15.89	75.23	14.68
11	315.77	20.29	135.34	14.16	61.78	16.45	89.91	12.74
12	336.06	17.26	149.5	13.8	78.23	17.22	102.65	11.54
13	353.32	12.49	163.3	12.81	95.45	16.67	114.19	11.05
14	365.81	9.9	176.11	13.13	112.12	15.48	125.24	11.05
15	375.71	8.43	189.24	13.03	127.6	13.01	136.29	10.19
16	384.14	7.85	202.27	12.77	140.61	8.33	146.48	7.13
17	391.99	6.47	215.04	12.36	148.94	5.64	153.61	6.77
18	398.46	5.88	227.4	12.64	154.58	5.58	160.38	6.9
19	404.34	5.36	240.04	12.95	160.16	5.54	167.28	7.12
20	409.7	2.63	252.99	12.72	165.7	5.23	174.4	6.99
21	412.33	2.23	265.71	13.62	170.93	5.45	181.39	7.49
22	414.56	0.6	279.33	13.75	176.38	5.31	188.88	7.26
23	415.16	2.16	293.08	13.71	181.69	4.67	196.14	6.86
24	417.32	1.3	306.79	14.02	186.36	4.58	203	6.99

Experiment: Run 2

Elaspe	Sampl	· · · · · · ·	Sampl		Sam	ple 7	Samp	ole 8
T	Volume	Rate	Volume	Rate	Volume	Rate	Volume	Rate
0	0	0	0	0	0	0	0	0
0.25	5.31	5.31	5.42	5.42	5.5	5.5	6.09	6.09
0.5	8.21	2.9	7.88	2.46	8.43	2.93	8.84	2.75
0.75	9.77	1.56	9.14	1.26	9.98	1.55	10.1	1.26
1	10.75	0.98	10.04	0.9	10.95	0.97	10.91	0.81
1.25	11.19	0.44	10.48	0.44	11.59	0.64	11.41	0.5
1.5	11.51	0.32	10.75	0.27	11.91	0.32	11.68	0.27
1.75	11.64	0.13	10.93	0.18	12.14	0.23	11.95	0.27
2	11.73	0.09	11.02	0.09	12.32	0.18	12.13	0.18
2.25	11.91	0.18	11.2	0.18	12.5	0.18	12.4	0.27
2.5	12.35	0.44	11.69	0.49	12.96	0.46	12.58	0.18
2.75	12.76	0.41	12.05	0.36	13.28	0.32	12.85	0.27
3	13.2	0.44	12.41	0.36	13.65	0.37	13.12	0.27
3.25	13.78	0.58	12.86	0.45	14.06	0.41	13.39	0.27
3.5	14.54	0.76	13.4	0.54	14.66	0.6	13.67	0.28
3.75	15.61	1.07	14.16	0.76	15.39	0.73	14.03	0.36
4	17.17	1.56	15.32	1.16	16.49	1.1	14.52	0.49
4.25	19.49	2.32	17.02	1.7	18.23	1.74	15.33	0.81
4.5	22.61	3.12	19.35	2.33	20.61	2.38	16.33	1
4.75	26.67	4.06	22.44	3.09	23.95	3.34	17.63	1.3
5	31.93	5.26	26.57	4.13	28.4	4.45	19.48	1.85
5.25	38.31	6.38	31.85	5.28	34.44	6.04	22.01	2.53
5.5	46.21	7.9	38.44	6.59	42.78	8.34	25.57	3.56
5.75	56.64	10.43	46.41	7.97	53.81	11.03	30.17	4.6
6	68.73	12.09	56.09	9.68	67.65	13.84	36.03	5.86
6.25	82.06	13.33	67.78	11.69	83.95	16.3	43.61	7.58
6.5	96.78	14.72	81.63	13.85	101.17	17.22	52.81	9.2
6.75	113.46	16.68	97.08	15.45	117.39	16.22	63.41	10.6
7	130.01	16.55	112.85	15.77	132.59	15.2	75.68	12.27
7.25	147.63	17.62	128.04	15.19	145.92	13.33	90.25	14.57
7.5	165.73	18.1	143.4	15.36	158.61	12.69	106.53	16.28
7.75	182.06	16.33	157.96	14.56	171.29	12.68	123.48	16.95
8	198.29	16.23	171.63	13.67	183.43	12.14	140.08	16.6
8.25	213.9	15.61	184.89	13.26	194.74	11.31	155.32	15.24
8.5	228.89	14.99	197.75	12.86	205.5	10.76	170.75	15.43
8.75	242.85	13.96	209.98	12.23	215.44	9.94	186.31	15.56
9	255.42	12.57	221.72	11.74	224.79	9.35	201.46	15.15
9.25	267.2	11.78	233	11.28	233.85	9.06	215.94	14.48

9.5         278.08         10.88         243.8         10.8         242.6         8.75         229.15         13.21           9.75         288.38         10.3         253.97         10.17         250.76         8.16         241.28         12.13           10         298.24         9.86         263.92         9.95         258.77         8.01         251.97         10.69           10.25         307.96         9.72         273.24         9.32         266.37         7.6         261.94         9.97           10.5         317.37         9.41         282.2         8.96         273.7         7.33         270.74         8.8           10.75         326.03         8.66         290.53         8.33         280.75         7.05         278.58         7.84           11         334.54         8.51         298.46         7.93         287.58         6.83         285.89         7.31           11.5         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         395.92         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.2									
10         298.24         9.86         263.92         9.95         258.77         8.01         251.97         10.69           10.25         307.96         9.72         273.24         9.32         266.37         7.6         261.94         9.97           10.5         317.37         9.41         282.2         8.96         273.7         7.33         270.74         8.8           10.75         326.03         8.66         290.53         8.33         280.75         7.05         278.58         7.84           11         334.54         8.51         298.46         7.93         287.58         6.83         285.89         7.31           11.5         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12.25         375.8         7.76         334.61         6.85         318.26         5.81         311.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.5 </td <td>9.5</td> <td>278.08</td> <td>10.88</td> <td>243.8</td> <td>10.8</td> <td>242.6</td> <td>8.75</td> <td>229.15</td> <td>13.21</td>	9.5	278.08	10.88	243.8	10.8	242.6	8.75	229.15	13.21
10.25         307.96         9.72         273.24         9.32         266.37         7.6         261.94         9.97           10.5         317.37         9.41         282.2         8.96         273.7         7.33         270.74         8.8           10.75         326.03         8.66         290.53         8.33         280.75         7.05         278.58         7.8           11         334.54         8.51         298.46         7.93         287.58         6.83         285.89         7.31           11.25         343.06         8.52         306.34         7.88         294.13         6.55         292.97         7.08           11.5         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75	9.75	288.38	10.3	253.97	10.17	250.76	8.16	241.28	12.13
10.5         317.37         9.41         282.2         8.96         273.7         7.33         270.74         8.8           10.75         326.03         8.66         290.53         8.33         280.75         7.05         278.58         7.84           11         334.54         8.51         298.46         7.93         287.58         6.83         285.89         7.31           11.25         343.06         8.52         306.34         7.88         294.13         6.55         292.97         7.08           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.45         5.06           12.7	10	298.24	9.86	263.92	9.95	258.77	8.01	251.97	10.69
10.75         326.03         8.66         290.53         8.33         280.75         7.05         278.58         7.84           11         334.54         8.51         298.46         7.93         287.58         6.83         285.89         7.31           11.25         343.06         8.52         306.34         7.88         294.13         6.55         292.97         7.08           11.75         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           1	10.25	307.96	9.72	273.24	9.32	266.37	7.6	261.94	9.97
11         334.54         8.51         298.46         7.93         287.58         6.83         285.89         7.31           11.25         343.06         8.52         306.34         7.88         294.13         6.55         292.97         7.08           11.5         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.39           12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.5         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.47         4.99         342.62         4.42           13.5 <td>10.5</td> <td>317.37</td> <td>9.41</td> <td>282.2</td> <td>8.96</td> <td>273.7</td> <td>7.33</td> <td>270.74</td> <td>8.8</td>	10.5	317.37	9.41	282.2	8.96	273.7	7.33	270.74	8.8
11.25         343.06         8.52         306.34         7.88         294.13         6.55         292.97         7.08           11.5         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.25         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.99         5.18         338.2         4.46           13.75 </td <td>10.75</td> <td>326.03</td> <td>8.66</td> <td>290.53</td> <td>8.33</td> <td>280.75</td> <td>7.05</td> <td>278.58</td> <td>7.84</td>	10.75	326.03	8.66	290.53	8.33	280.75	7.05	278.58	7.84
11.5         351.8         8.74         313.64         7.3         300.4         6.27         299.46         6.49           11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           14.25	11	334.54	8.51	298.46	7.93	287.58	6.83	285.89	7.31
11.75         359.92         8.12         320.77         7.13         306.49         6.09         305.78         6.32           12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         358.06         4.25         354.31         3.25           14.5 <td>11.25</td> <td>343.06</td> <td>8.52</td> <td>306.34</td> <td>7.88</td> <td>294.13</td> <td>6.55</td> <td>292.97</td> <td>7.08</td>	11.25	343.06	8.52	306.34	7.88	294.13	6.55	292.97	7.08
12         368.04         8.12         327.76         6.99         312.45         5.96         311.87         6.09           12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         358.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5	11.5	351.8	8.74	313.64	7.3	300.4	6.27	299.46	6.49
12.25         375.8         7.76         334.61         6.85         318.26         5.81         317.77         5.9           12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75 <td>11.75</td> <td>359.92</td> <td>8.12</td> <td>320.77</td> <td>7.13</td> <td>306.49</td> <td>6.09</td> <td>305.78</td> <td>6.32</td>	11.75	359.92	8.12	320.77	7.13	306.49	6.09	305.78	6.32
12.5         382.94         7.14         341.02         6.41         323.94         5.68         323.46         5.69           12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15	12	368.04	8.12	327.76	6.99	312.45	5.96	311.87	6.09
12.75         388.47         5.53         346.93         5.91         329.39         5.45         328.73         5.27           13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15	12.25	375.8	7.76	334.61	6.85	318.26	5.81	317.77	5.9
13         392.17         3.7         352.58         5.65         334.61         5.22         333.74         5.01           13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25	12.5	382.94	7.14	341.02	6.41	323.94	5.68	323.46	5.69
13.25         395.6         3.43         358         5.42         339.79         5.18         338.2         4.46           13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.75	12.75	388.47	5.53	346.93	5.91	329.39	5.45	328.73	5.27
13.5         398.9         3.3         363.06         5.06         344.78         4.99         342.62         4.42           13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75	13	392.17	3.7	352.58	5.65	334.61	5.22	333.74	5.01
13.75         402.16         3.26         367.4         4.34         349.41         4.63         346.91         4.29           14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16	13.25	395.6	3.43	358	5.42	339.79	5.18	338.2	4.46
14         405.32         3.16         370.94         3.54         353.81         4.4         351.06         4.15           14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25	13.5	398.9	3.3	363.06	5.06	344.78	4.99	342.62	4.42
14.25         408.4         3.08         373.86         2.92         358.06         4.25         354.31         3.25           14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5 </td <td>13.75</td> <td>402.16</td> <td>3.26</td> <td>367.4</td> <td>4.34</td> <td>349.41</td> <td>4.63</td> <td>346.91</td> <td>4.29</td>	13.75	402.16	3.26	367.4	4.34	349.41	4.63	346.91	4.29
14.5         411.52         3.12         376.54         2.68         362.19         4.13         358.05         3.74           14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75<	14	405.32	3.16	370.94	3.54	353.81	4.4	351.06	4.15
14.75         414.56         3.04         379.1         2.56         366.17         3.98         361.57         3.52           15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17.25 </td <td>14.25</td> <td>408.4</td> <td>3.08</td> <td>373.86</td> <td>2.92</td> <td>358.06</td> <td>4.25</td> <td>354.31</td> <td>3.25</td>	14.25	408.4	3.08	373.86	2.92	358.06	4.25	354.31	3.25
15         417.5         2.94         381.52         2.42         369.97         3.8         364.9         3.33           15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25 <td>14.5</td> <td>411.52</td> <td>3.12</td> <td>376.54</td> <td>2.68</td> <td>362.19</td> <td>4.13</td> <td>358.05</td> <td>3.74</td>	14.5	411.52	3.12	376.54	2.68	362.19	4.13	358.05	3.74
15.25         420.4         2.9         383.94         2.42         373.68         3.71         368.11         3.21           15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25         441.23         2.32         401.63         2.1         396.44         2.29         386.91         1.62           17.5	14.75	414.56	3.04	379.1	2.56	366.17	3.98	361.57	3.52
15.5         423.3         2.9         386.31         2.37         377.44         3.76         371.13         3.02           15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25         441.23         2.32         401.63         2.1         396.44         2.29         386.91         1.62           17.5         445.69         2.19         405.98         2.2         400.89         2.25         389.21         1.03           18 </td <td>15</td> <td>417.5</td> <td>2.94</td> <td>381.52</td> <td>2.42</td> <td>369.97</td> <td>3.8</td> <td>364.9</td> <td>3.33</td>	15	417.5	2.94	381.52	2.42	369.97	3.8	364.9	3.33
15.75         426.11         2.81         388.55         2.24         380.78         3.34         373.97         2.84           16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25         441.23         2.32         401.63         2.1         396.44         2.29         386.91         1.62           17.5         443.5         2.27         403.78         2.15         398.64         2.2         388.18         1.27           17.75         445.69         2.19         405.98         2.2         400.89         2.25         389.21         1.03           18<	15.25	420.4	2.9	383.94	2.42	373.68	3.71	368.11	3.21
16         428.83         2.72         390.84         2.29         383.85         3.07         376.58         2.61           16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25         441.23         2.32         401.63         2.1         396.44         2.29         386.91         1.62           17.5         443.5         2.27         403.78         2.15         398.64         2.2         388.18         1.27           17.75         445.69         2.19         405.98         2.2         400.89         2.25         389.21         1.03           18         447.83         2.14         408.17         2.19         403.09         2.2         390.07         0.86           18.25 </td <td>15.5</td> <td>423.3</td> <td>2.9</td> <td>386.31</td> <td>2.37</td> <td>377.44</td> <td>3.76</td> <td>371.13</td> <td>3.02</td>	15.5	423.3	2.9	386.31	2.37	377.44	3.76	371.13	3.02
16.25         431.51         2.68         393.12         2.28         386.74         2.89         379.07         2.49           16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25         441.23         2.32         401.63         2.1         396.44         2.29         386.91         1.62           17.5         443.5         2.27         403.78         2.15         398.64         2.2         388.18         1.27           17.75         445.69         2.19         405.98         2.2         400.89         2.25         389.21         1.03           18         447.83         2.14         408.17         2.19         403.09         2.2         390.07         0.86           18.25         449.79         1.96         410.32         2.15         405.33         2.24         390.88         0.81           18.7	15.75	426.11	2.81	388.55	2.24	380.78	3.34	373.97	2.84
16.5         433.96         2.45         395.23         2.11         389.35         2.61         381.32         2.25           16.75         436.5         2.54         397.38         2.15         391.82         2.47         383.4         2.08           17         438.91         2.41         399.53         2.15         394.15         2.33         385.29         1.89           17.25         441.23         2.32         401.63         2.1         396.44         2.29         386.91         1.62           17.5         443.5         2.27         403.78         2.15         398.64         2.2         388.18         1.27           17.75         445.69         2.19         405.98         2.2         400.89         2.25         389.21         1.03           18         447.83         2.14         408.17         2.19         403.09         2.2         390.07         0.86           18.25         449.79         1.96         410.32         2.15         405.33         2.24         390.88         0.81           18.75         453.45         1.79         414.8         2.28         409.86         2.33         392.42         0.82           19 <td>16</td> <td>428.83</td> <td>2.72</td> <td>390.84</td> <td>2.29</td> <td>383.85</td> <td>3.07</td> <td>376.58</td> <td>2.61</td>	16	428.83	2.72	390.84	2.29	383.85	3.07	376.58	2.61
16.75     436.5     2.54     397.38     2.15     391.82     2.47     383.4     2.08       17     438.91     2.41     399.53     2.15     394.15     2.33     385.29     1.89       17.25     441.23     2.32     401.63     2.1     396.44     2.29     386.91     1.62       17.5     443.5     2.27     403.78     2.15     398.64     2.2     388.18     1.27       17.75     445.69     2.19     405.98     2.2     400.89     2.25     389.21     1.03       18     447.83     2.14     408.17     2.19     403.09     2.2     390.07     0.86       18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	16.25	431.51	2.68	393.12	2.28	386.74	2.89	379.07	2.49
17     438.91     2.41     399.53     2.15     394.15     2.33     385.29     1.89       17.25     441.23     2.32     401.63     2.1     396.44     2.29     386.91     1.62       17.5     443.5     2.27     403.78     2.15     398.64     2.2     388.18     1.27       17.75     445.69     2.19     405.98     2.2     400.89     2.25     389.21     1.03       18     447.83     2.14     408.17     2.19     403.09     2.2     390.07     0.86       18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	16.5	433.96	2.45	395.23	2.11	389.35	2.61	381.32	2.25
17.25     441.23     2.32     401.63     2.1     396.44     2.29     386.91     1.62       17.5     443.5     2.27     403.78     2.15     398.64     2.2     388.18     1.27       17.75     445.69     2.19     405.98     2.2     400.89     2.25     389.21     1.03       18     447.83     2.14     408.17     2.19     403.09     2.2     390.07     0.86       18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	16.75	436.5	2.54	397.38	2.15	391.82	2.47	383.4	2.08
17.5     443.5     2.27     403.78     2.15     398.64     2.2     388.18     1.27       17.75     445.69     2.19     405.98     2.2     400.89     2.25     389.21     1.03       18     447.83     2.14     408.17     2.19     403.09     2.2     390.07     0.86       18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	17	438.91	2.41	399.53	2.15	394.15	2.33	385.29	1.89
17.75     445.69     2.19     405.98     2.2     400.89     2.25     389.21     1.03       18     447.83     2.14     408.17     2.19     403.09     2.2     390.07     0.86       18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	17.25	441.23	2.32	401.63	2.1	396.44	2.29	386.91	1.62
18     447.83     2.14     408.17     2.19     403.09     2.2     390.07     0.86       18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	17.5	443.5	2.27	403.78	2.15	398.64	2.2	388.18	1.27
18.25     449.79     1.96     410.32     2.15     405.33     2.24     390.88     0.81       18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	17.75	445.69	2.19	405.98	2.2	400.89	2.25	389.21	1.03
18.5     451.66     1.87     412.52     2.2     407.53     2.2     391.6     0.72       18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	18	447.83	2.14	408.17	2.19	403.09	2.2	390.07	0.86
18.75     453.45     1.79     414.8     2.28     409.86     2.33     392.42     0.82       19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	18.25	449.79	1.96	410.32	2.15	405.33	2.24	390.88	0.81
19     455.14     1.69     417     2.2     412.15     2.29     393.09     0.67       19.25     456.66     1.52     419.33     2.33     414.54     2.39     393.72     0.63	18.5	451.66	1.87	412.52	2.2	407.53	2.2	391.6	0.72
19.25 456.66 1.52 419.33 2.33 414.54 2.39 393.72 0.63	18.75	453.45	1.79	414.8	2.28	409.86	2.33	392.42	0.82
	19	455.14	1.69	417	2.2	412.15	2.29	393.09	0.67
19.5     458     1.34     421.66     2.33     416.87     2.33     394.26     0.54	19.25	456.66	1.52	419.33	2.33	414.54	2.39	393.72	0.63
	19.5	458	1.34	421.66	2.33	416.87	2.33	394.26	0.54

19.75	459.07	1.07	424.03	2.37	419.3	2.43	394.76	0.5
20	460	0.93	426.41	2.38	421.68	2.38	395.3	0.54
20.25	460.72	0.72	428.78	2.37	424.06	2.38	395.93	0.63
20.5	461.21	0.49	431.24	2.46	426.49	2.43	396.56	0.63
20.75	461.52	0.31	433.75	2.51	428.96	2.47	397.2	0.64
21	461.7	0.18	436.22	2.47	431.44	2.48	397.83	0.63
21.25	461.74	0.04	438.68	2.46	434	2.56	398.59	0.76
21.5	461.74	0	441.1	2.42	436.61	2.61	399.32	0.73
21.75	461.74	0	443.52	2.42	439.31	2.7	399.95	0.63
22	461.74	0	445.8	2.28	442.11	2.8	400.71	0.76
22.25	461.79	0.05	448.04	2.24	444.99	2.88	401.44	0.73
22.5	461.83	0.04	450.06	2.02	447.1	2.11	402.07	0.63
22.75	461.92	0.09	452.12	2.06	450.21	3.11	402.65	0.58
23	461.97	0.05	453.96	1.84	453.15	2.94	403.28	0.63
23.25	462.01	0.04	455.66	1.7	456.12	2.97	403.83	0.55
23.5	462.01	0	457.14	1.48	459.24	3.12	404.41	0.58
23.75	462.01	0	458.57	1.43	462.21	2.97	404.91	0.5
24	462.01	0	459.83	1.26	465.24	3.03	405.45	0.54

Experiment: Run 3

Elaspe	Sampl	e 9	Sample	10	Samp	le 11	Samp	le 12
Т	Volume	Rate	Volume	Rate	Volume	Rate	Volume	Rate
0	0	0	0	0	0	0	0	0
0.25	15.48	15.48	11.11	11.11	6.78	6.78	3.79	3.79
0.5	24.62	9.14	16.98	5.87	9.89	3.11	5.73	1.94
0.75	30.1	5.48	20.43	3.45	11.77	1.88	6.86	1.13
1	33.81	3.71	22.8	2.37	13.1	1.33	7.85	0.99
1.25	36.22	2.41	24.37	1.57	14.01	0.91	8.43	0.58
1.5	37.91	1.69	25.63	1.26	14.75	0.74	8.97	0.54
1.75	39.2	1.29	26.66	1.03	15.43	0.68	9.29	0.32
2	40.23	1.03	27.37	0.71	15.94	0.51	9.65	0.36
2.25	41.03	0.8	28	0.63	16.44	0.5	10.28	0.63
2.5	41.7	0.67	28.49	0.49	16.81	0.37	10.96	0.68
2.75	42.37	0.67	29.08	0.59	17.36	0.55	11.95	0.99
3	42.95	0.58	29.66	0.58	18	0.64	13.03	1.08
3.25	43.66	0.71	30.42	0.76	18.87	0.87	14.75	1.72
3.5	44.24	0.58	31.14	0.72	19.74	0.87	16.69	1.94
3.75	44.78	0.54	31.9	0.76	20.79	1.05	19.44	2.75
4	45.58	0.8	33.06	1.16	22.53	1.74	23.36	3.92
4.25	46.52	0.94	34.68	1.62	24.78	2.25	28.77	5.41
4.5	47.54	1.02	36.65	1.97	27.71	2.93	35.22	6.45

4.75	48.84	1.3	39.16	2.51	31.6	3.89	42.84	7.62
5	50.67	1.83	42.69	3.53	37.19	5.59	51.86	9.02
5.25	53.34	2.67	47.31	4.62	44.93	7.74	62.55	10.69
5.5	57.13	3.79	53.54	6.23	55.05	10.12	75.45	12.9
5.75	62.48	5.35	61.82	8.28	68.01	12.96	91.06	15.61
6	70.2	7.72	73.11	11.29	84.96	16.95	109.32	18.26
6.25	81.04	10.84	87.81	14.7	104.65	19.69	126.91	17.59
6.5	96.56	15.52	107.16	19.35	127.6	22.95	144.32	17.41
6.75	118.81	22.25	132.25	25.09	155.12	27.52	164.52	20.2
7	151.95	33.14	162.36	30.11	185.08	29.96	186.49	21.97
7.25	195.79	43.84	200.26	37.9	217.32	32.24	209.49	23
7.5	252.26	56.47	248.06	47.8	250.25	32.93	231.09	21.6
7.75	309.08	56.82	292.63	44.57	279.79	29.54	249.72	18.63
8	361.57	52.49	340.35	47.72	309.97	30.18	265.91	16.19
8.25	420.67	59.1	389.4	49.05	341.35	31.38	279.89	13.98
8.5	478.29	57.62	449.52	60.12	372.03	30.68	292.29	12.4
8.75	547.82	69.53	519.1	69.58	401.21	29.18	303.84	11.55
9	624.98	77.16	590.42	71.32	428.23	27.02	314.57	10.73
9.25	704.23	79.25	656.19	65.77	453.01	24.78	324.49	9.92
9.5	733.05	28.82	711.51	55.32	475.45	22.44	333.74	9.25
9.75	791.92	58.87	759.49	47.98	495.65	20.2	342.13	8.39
10	830.67	38.75	802.32	42.83	514.38	18.73	350.16	8.03
10.25	864.88	34.21	841.52	39.2	532.06	17.68	357.64	7.48
10.5	902.93	38.05	880.36	38.84	548.96	16.9	365.58	7.94
10.75	938.12	35.19	915.26	34.9	565.13	16.17	372.93	7.35
11	971.74	33.62	947.34	32.08	580.93	15.8	380.19	7.26
11.25	1001.89	30.15	974.53	27.19	596.22	15.29	387.45	7.26
11.5	1029.59	27.7	999.35	24.82	611.02	14.8	394.31	6.86
11.75	1057.42	27.83	1024.58	25.23	624.76	13.74	401.25	6.94
12	1085.97	28.55	1049.84	25.26	637.9	13.14	407.79	6.54
12.25	1112.81	26.84	1075.87	26.03	650.82	12.92	414.42	6.63
12.5	1134.76	21.95	1101	25.13	663.14	12.32	420.87	6.45
12.75	1155.36	20.6	1126.05	25.05	675	11.86	426.96	6.09
13	1176.28	20.92	1151.05	25	686.63	11.63	433.05	6.09
13.25	1197.42	21.14	1175.91	24.86	697.85	11.22	439.14	6.09
13.5	1217.71	20.29	1199.56	23.65	708.3	10.45	445	5.86
13.75	1238.59	20.88	1222.82	23.26	718.24	9.94	450.73	5.73
14	1258.7	20.11	1244.68	21.86	727.49	9.25	456.23	5.5
14.25	1278.64	19.94	1266	21.32	735.91	8.42	461.42	5.19
14.5	1298.75	20.11	1286.39	20.39	743.52	7.61	466.47	5.05
14.75	1318.82	20.07	1305.61	19.22	750.25	6.73	471.34	4.87

15	1338.94	20.12	1324.74	19.13	756.84	6.59	476.44	5.1
15.25	1359.1	20.16	1341.85	17.11	762.52	5.68	480.77	4.33
15.5	1379.25	20.15	1358.43	16.58	767.93	5.41	484.78	4.01
15.75	1399.32	20.07	1373.75	15.32	772.74	4.81	488.07	3.29
16	1419.22	19.9	1388.08	14.33	777.41	4.67	491.18	3.11
16.25	1440.04	20.82	1401.79	13.71	781.99	4.58	494.12	2.94
16.5	1460.29	20.25	1415.19	13.4	786.61	4.62	496.82	2.7
16.75	1481.26	20.97	1427.6	12.41	791.24	4.63	499.44	2.62
17	1501.59	20.33	1439.69	12.09	796.05	4.81	502.05	2.61
17.25	1520.9	19.31	1451.34	11.65	800.9	4.85	504.62	2.57
17.5	1537.5	16.6	1463.17	11.83	805.76	4.86	506.97	2.35
17.75	1553.46	15.96	1474.68	11.51	810.57	4.81	509.22	2.25
18	1568.63	15.17	1486.02	11.34	815.56	4.99	511.48	2.26
18.25	1583.03	14.4	1497.13	11.11	820.19	4.63	513.33	1.85
18.5	1596.55	13.52	1508.1	10.97	824.72	4.53	515	1.67
18.75	1609.57	13.02	1519.03	10.93	829.53	4.81	516.76	1.76
19	1622.24	12.67	1529.7	10.67	834.16	4.63	518.24	1.48
19.25	1634.68	12.44	1540.18	10.48	839.01	4.85	519.55	1.31
19.5	1646.77	12.09	1550.62	10.44	844.14	5.13	521.04	1.49
19.75	1659.12	12.35	1560.92	10.3	849.41	5.27	522.21	1.17
20	1671.16	12.04	1570.82	9.9	854.81	5.4	523.11	0.9
20.25	1680.93	9.77	1578.26	7.44	858.29	3.48	523.48	0.37
20.5	1692.26	11.33	1588.52	10.26	865.35	7.06	524.69	1.21
20.75	1704.03	11.77	1598.46	9.94	872.22	6.87	526.09	1.4
21	1714.87	10.84	1607.96	9.5	879.18	6.96	527.26	1.17
21.25	1725.26	10.39	1617.01	9.05	886.55	7.37	528.39	1.13
21.5	1734.81	9.55	1624.94	7.93	893.79	7.24	528.93	0.54
21.75	1744.35	9.54	1632.02	7.08	901.48	7.69	529.65	0.72
22	1753.45	9.1	1638.52	6.5	909.73	8.25	530.51	0.86
22.25	1762.01	8.56	1644.43	5.91	918.06	8.33	531.14	0.63
22.5	1769.73	7.72	1649.85	5.42	926.63	8.57	531.68	0.54
22.75	1777.4	7.67	1655	5.15	935.24	8.61	532.13	0.45
23	1784.85	7.45	1659.8	4.8	944.03	8.79	532.63	0.5
23.25	1792.21	7.36	1664.19	4.39	952.73	8.7	533.04	0.41
23.5	1799.65	7.44	1668.26	4.07	960.75	8.02	533.44	0.4
23.75	1807.37	7.72	1671.89	3.63	968.03	7.28	533.67	0.23
24	1813.84	6.47	1674	2.11	973.11	5.08	533.89	0.22

**Experiment: Run 4** 

Elaspe	Sample	ЕХ <u>Г</u> е 13	Sample 15			
T	Volume	Rate	Volume	Sample 14 olume Rate		Rate
0	0	0	0	0	Volume 0	0
0.25	16.29	16.29	16.13	16.13	25.39	25.39
0.5	22.03	5.74	23.33	7.2	46.09	20.7
0.75	24.01	1.98	26.5	3.17	62.09	16
1	24.74	0.73	28	1.5	74.07	11.98
1.25	24.97	0.23	28.81	0.81	83.28	9.21
1.5	25.06	0.09	29.35	0.54	89.98	6.7
1.75	25.11	0.05	29.85	0.5	90.79	0.81
2	25.11	0	30.22	0.37	91.9	1.11
2.25	25.11	0	30.53	0.31	94.99	3.09
2.5	25.11	0	30.8	0.27	97.04	2.05
2.75	25.11	0	31.17	0.37	97.04	0
3	25.11	0	31.57	0.4	98.56	1.52
3.25	25.11	0	32.12	0.55	99.68	1.12
3.5	25.11	0	32.8	0.68	99.68	0
3.75	25.11	0	33.7	0.9	99.68	0
4	25.11	0	35.02	1.32	99.68	0
4.25	25.11	0	36.96	1.94	99.68	0
4.5	25.11	0	39.5	2.54	99.68	0
4.75	25.11	0	42.99	3.49	99.68	0
5	25.11	0	47.93	4.94	99.68	0
5.25	25.11	0	54.45	6.52	99.68	0
5.5	25.11	0	62.83	8.38	99.68	0
5.75	25.11	0	72.8	9.97	99.68	0
6	25.11	0	85.75	12.95	99.68	0
6.25	25.11	0	102.92	17.17	99.68	0
6.5	25.11	0	122.99	20.07	99.68	0
6.75	25.11	0	141.88	18.89	99.68	0
7	25.11	0	158.64	16.76	99.68	0
7.25	25.11	0	176.53	17.89	99.68	0
7.5	25.11	0	196.87	20.34	99.68	0
7.75	25.11	0	217.26	20.39	99.68	0
8	25.11	0	236.33	19.07	99.68	0
8.25	25.11	0	253.86	17.53	99.68	0
8.5	25.11	0	269.53	15.67	99.68	0
8.75	25.11	0	283.58	14.05	99.68	0
9	25.11	0	295.04	11.46	99.68	0
9.25	25.11	0	305.41	10.37	99.68	0

9.5	25.11	0	315.47	10.06	99.68	0
9.75	25.11	0	324.76	9.29	99.68	0
10	25.11	0	334.04	9.28	99.68	0
10.25	25.11	0	343.24	9.2	99.68	0
10.5	25.11	0	352.21	8.97	99.68	0
10.75	25.11	0	361.22	9.01	99.68	0
11	25.11	0	370.01	8.79	99.68	0
11.25	25.11	0	378.62	8.61	99.68	0
11.5	25.11	0	386.73	8.11	99.68	0
11.75	25.11	0	395.02	8.29	99.68	0
12	25.11	0	402.85	7.83	99.68	0
12.25	25.11	0	410.33	7.48	99.82	0.14
12.5	25.11	0	417.8	7.47	100.08	0.26
12.75	25.11	0	425.5	7.7	100.22	0.14
13	25.11	0	433.2	7.7	100.44	0.22
13.25	25.11	0	440.72	7.52	100.66	0.22
13.5	25.11	0	448.29	7.57	100.84	0.18
13.75	25.11	0	455.85	7.56	101.07	0.23
14	25.11	0	463.42	7.57	101.25	0.18
14.25	25.11	0	470.8	7.38	101.47	0.22
14.5	25.11	0	478.05	7.25	101.65	0.18
14.75	25.11	0	485.21	7.16	101.65	0
15	25.11	0	492.09	6.88	101.65	0
15.25	25.11	0	498.75	6.66	101.65	0
15.5	25.11	0	505.32	6.57	101.65	0
15.75	25.11	0	511.35	6.03	101.65	0
16	25.11	0	516.33	4.98	101.65	0
16.25	25.11	0	520.81	4.48	101.65	0
16.5	25.11	0	524.71	3.9	101.65	0
16.75	25.11	0	528.42	3.71	101.65	0
17	25.11	0	532.05	3.63	101.65	0
17.25	25.11	0	535.49	3.44	101.65	0
17.5	25.11	0	538.8	3.31	101.65	0
17.75	25.11	0	541.92	3.12	101.65	0
18	25.11	0	544.96	3.04	101.65	0
18.25	25.11	0	547.81	2.85	101.65	0
18.5	25.11	0	550.58	2.77	101.65	0
18.75	25.11	0	553.34	2.76	101.65	0
19	25.11	0	555.83	2.49	101.65	0
19.25	25.11	0	558.5	2.67	101.65	0
19.5	25.11	0	561.09	2.59	101.65	0

19.75	25.11	0	563.31	2.22	101.65	0
20	25.11	0	564.57	1.26	101.65	0
20.25	25.11	0	564.98	0.41	101.65	0
20.5	25.11	0	566.2	1.22	101.78	0.13
20.75	25.11	0	567.34	1.14	102.27	0.49
21	25.11	0	568.51	1.17	102.72	0.45
21.25	25.11	0	569.65	1.14	103.17	0.45
21.5	25.11	0	570.64	0.99	103.48	0.31
21.75	25.11	0	571.55	0.91	103.93	0.45
22	25.11	0	572.5	0.95	104.42	0.49
22.25	25.11	0	573.41	0.91	104.51	0.09
22.5	25.11	0	574.31	0.9	104.51	0
22.75	25.11	0	575.17	0.86	104.51	0
23	25.11	0	576.03	0.86	104.51	0
23.25	25.11	0	576.85	0.82	104.51	0
23.5	25.11	0	577.67	0.82	104.51	0
23.75	25.11	0	578.44	0.77	104.51	0
24	25.11	0	578.89	0.45	104.51	0