Assessment of Flammability and Explosion Potential of Waste from Industries

by

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Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in 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 by unspecified sources or persons.

NIK NUR INTAN IZURA BT. NIK ZUNOH

ABSTRACT

This project presents the work on assessment of flammability and explosion potential of waste from industries. Nowadays, revolution in lifestyle leads to the industrial revolution that at last gives some problems of industrial waste which may be toxic, ignitable, corrosive or reactive. If improperly managed, this waste can pose dangerous health and environmental consequences. The objective of this work is to investigate the flammability and explosion potential from a waste generated from industries by understanding the problem, selecting some mitigation methodology and preparing the safety analysis. This report will give some information regarding the hazards of the waste from industries focusing more on fire and explosion hazards. Two different liquid waste samples are collected from Kualiti Alam Waste Management Centre, Seremban, Negeri Sembilan. The samples have been analyzed using gas chromatography (GC) to measure the compositions of all combustible species contain in them. The compositions have been identified for both samples. Gas Chromatography analysis also shows that both of the liquid waste samples majority are alkane group. It has been found from the GC results, that the both samples contain water. Therefore, the water extracted from the sample 1 and sample 2 using distillation experiments. Some properties related to flammability study have been measured. The density and heat of combustion of the waste samples have been calculated also using pyconometer and bomb calorimeter respectively. The results show that the density of sample 1 is 0.8023 g/ml and sample 2 is 0.77 g/ml while the heat of combustion for sample 1 is 26320 J/g and sample 2 is 38354 J/g. The results of the experimental work were used for consequences analysis to calculate equivalent of TNT mass, overpressure, impact of overpressure, pool fire and boiling expanding vapor cloud explosion (BLEVE).

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Industrial waste is a type of waste produced by industrial activity, such as that of factories, mills and mines. It has existed since the outset of the industrial revolution. In the United States, the amount of hazardous waste generated by manufacturing industries in the country has increased from an estimated 4.5 millions tons annually after World War II to some 57 millions tons by 1975. By 1990, this total had shot up to approximately 265 million tons (World Resources Institute, 1994).

According to U.S. Environmental Protection Agency (EPA, 1970), manufacturing, mining and agriculture industries along with commercial and domestic sources in the U.S., generate about 8 billion tons of waste each year, about 265 million tons of which were hazardous in 1990 under Resource Conservation and Recovery Ac (1976). The presence of hydrocarbons in the waste from industries exposes the system to the possibility of fire and explosion event. Any fire or explosion requires three basic ingredients such as fuel, an oxidant and an ignition source. Hydrocarbons fall in the fuel category. The most likely oxidant would be oxygen. Examples of credible ignition sources, based on DOE's operational history, include electrical discharge due to the buildup of static electricity and spontaneous reaction of chemicals such as nitric acid with organic compounds (Silva, 1991).

An explosion is the result of rapid expansion of gases. A deflagration is a reaction which propagates to the unreacted material at a speed that is less than the speed of sound in the unreacted substance. An explosion is assumed to be a deflagration unless defined otherwise (Bodurtha, 1980). A detonation is an exothermic reaction that proceeds in the unreacted substance at a speed greater than the speed of sound. It is accompanied by a shock wave in the material and inordinately high pressure (Silva, 1991). A deflagration can produce pressure rises in excess of 8:1. Pressure rises exceeding 40:1 can accompany a detonation (Hord, 1976; Zabetakis, 1965). A detonation can be produced either by direct ignition using a strong source such as an explosive charge or, given a suitable geometric situation, by transition from a deflagration (Silva, 1991).

In this study, investigation of fire and explosion will be studied on the waste sample taken from industries. This research will be conducted to study the consequences of fire and explosion resulting from any possible flammable waste accident.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

On January 13, 2003, a vapor cloud ignited, leading to a fire at an oilfield waste disposal facility near Rosharon, Texas, south of Houston. The fire occurred because of the problems come from the producer/shipper of the waste failed to identify the flammability and explosive hazard generated and also failed to communicate the hazard to employees and contractors who were required to handle the flammable and explosive liquid of the waste from industries. Some problems comes from management at the disposal facility whom did not have effective hazard communication practices in place to recognize the potential flammability and explosive hazard of each shipment of the waste from industries, nor did it implement safe handling practices for off-loading flammable liquid into the mud disposal and washout pad area (CSB, 2003).

The solutions that lead to some recommendations are for T&L Environmental Services. The CSB (2003) declared that the company had complied with five recommendations designed to ensure that customers know what is being delivered, that vacuum trucks are operated in a safe manner, that emergency procedures address abnormal diesel engine operation, and that adequate training be provided for all personnel. The Board noted that T&L will no longer handle flammable products. The Board found that T&L not only met recommendation requirements on procedures and good practices for safe operation but had "exceeded" the recommended action by installing automatic safety measures, notably the "Diesel Protection System Air Intake Shut down Valve." Also, the company issued flammable-atmosphere test meters to all drivers and requires the unloading area to be tested before transfer operations begin.

The waste sample from industries is mainly in the liquid form. However at certain conditions, some of the components from the liquid sample can vaporizes and turns into vapor form. Fire event can occur in the waste from industries if all three essential elements for combustion which are fuel, an oxidizer and an ignition source present in the system. The main purpose of this study is to study the consequences of fire and explosion resulting from any possible flammable waste accident.

1.2.2 Significant of Project

The prediction on flash points and flammability limits are important factors in development of safe practices for handling and storage of pure substances and mixture (Hristova and Tchaoushev, 2006).

For the flammable gas waste, the specific quantities calculated along the way to determining the dose are chosen to be the most 'diagnostic' of the process they represent. A quantity is diagnostic to a process if the output is directly dependent on that quantity likes a large value of the input indicates a large output. For example, gas release volume is diagnostic to the peak dome pressure resulting from a burn, but the composition of the gas is not. This is not to say the peak is independent of the gas composition, but the relationship between pressure and volume is most direct value (Stewart *et al.*, 1997).

The general properties the characterizations of flammable and explosive waste from industries will be studied for the purpose of studying the consequences of fire and explosion resulting from any possible flammable waste accident.

1.3 OBJECTIVES OF STUDY

The objectives of this study are:

1. To apply appropriate extraction method to extract the flammable liquid from the waste sample.
2. To study the properties and characteristics of the waste samples taken from industries that possibly contributes to fire and explosion.
3. To investigate the flammability and explosion potential of the waste generated from industries by understanding the problem, selecting a mitigation methodology and preparing the safety analysis.
4. To study the consequences of fire and explosion resulting from any possible flammable industrial waste accident.

1.4 SCOPE OF STUDY

The scope of study, as outlined by the objectives above, involving some study on the potential of waste samples to cause fire and explosion.

All calculations based on the measurable data gathered by analyze the liquid samples using gas chromatography for combustible liquid. The risk assessment for each model will be conducted according to the tests results.

1. After using the application of the flammability diagram for evaluating of fire and explosion hazard of flammable vapors, the achievement of this research is to study the consequences of fire and explosion resulting from any possible flammable industrial waste accident.

1.5 THE RELEVANCY OF PROJECT

Toxic Substances Control Act (1976) regulating the use and management was passed. Also Resource Conservation and Recovery Act (1976) were passed, regulating the generation, transportation, and management of hazardous wastes. In the 1984 reauthorization of RCRA, Congress added the Hazardous and Solid Waste Amendments (HSWA).

The flammability hazard posed by a material is really a quantification of the conditions under which copious amounts of fuel vapors capable of supporting uninhibited chemical chain reactions will be generated in typical occupied environments. Quantification of flammability hazard is usually expressed in terms of ease of flaming ignition, damaging heat and product output from flames, and spread of flame to involve new material surfaces or new locations in damaging flame behavior. In addition, the difficulty of extinguishment of the burning material should be included as part of flammability hazard (Emmons, 1972).

Next to natural disasters fires cause some of the greatest losses to property and human life around the world. The deliberate setting of a fire to destroy property or to take a human life is one of the most difficult crimes to investigate because much of the evidence at the scene is destroyed by the fire. Fortunately, the science of fire investigation is not static and more information to help investigators determine the origin and cause of a fire through careful examination of the scene and laboratory analysis of fire debris is published every year (Mark and Sandercock, 2007). Flammability limits data are essential for a quantitative risk assessment of explosion hazard associated with the use of combustible gas. The present work is to obtain the fundamental flammability data for prevention of the hazards in the practical applications (Liao *et al.*, 2004).

EPA, (1986) has listed the waste that hazardous in one of three categories:

i. Source-Specific Waste. This list includes waste from specific industries such as petroleum refining, wood preserving and secondary lead smelting, as well as sludge and production processes from these industries.
ii. Generic Waste. This list identifies waste from common manufacturing and industrial processes including spent solvents, degreasing operations.
iii. Commercial Chemical Products. This list includes some pesticides, creosote and other commercial chemicals.

Or it exhibits one or more of the following characteristics, subject to certain tests:

i. Ignitability;
ii. Corrosively;
iii. Reactivity;
iv. Toxicity.

Therefore, flammable waste of industries is one of the hazardous waste. As a conclusion, this research is important in order to study the consequences of fire and explosion resulting from any possible flammable industrial waste accident. Of course economic aspects must to take into account but the important thing is the safety of life.

CHAPTER 2

LITERATURE REVIEW

For the literature review, it will be focused on identifying past incidents of fire and explosion occurred due to waste from industries. In addition, it also including some properties of liquid and gas those are significant in the ignition of fire that may also result in explosion. Models for assessing the flammability mixture have been identified through literature searches and some empirical models.

2.1 PAST FIRE AND EXPLOSION INCIDENTS IN REFINERIES

2.1.1. Vapor cloud ignited, leading to a fire at an oilfield waste disposal facility

On January 13, 2003, a vapor cloud ignited, leading to a fire at an oilfield waste disposal facility (hereafter, disposal facility) near Rosharon, Texas, south of Houston. The fire occurred as two vacuum trucks were off-loading liquid wastes from oil and gas production wells (SHIB, 2008).

The trucks arrived at the disposal facility within a few minutes of each other and were parked approximately 16 feet apart. The two drivers got out of their trucks, left the engines running, and told the disposal facility employees that the trucks were to be drained and rinsed out. Both drivers then went to the drivers' shed to complete paperwork and to wait for the washout to be completed (CSB, 2003).

The fire was caused by the ignition of hydrocarbon vapor released during the off-loading of basic sediment and water (BS&W) from the two vacuum trucks into an open area collection pit. BS&W is an oil/gas exploration and production (E&P) waste liquid. The BS&W was contaminated with highly flammable condensate. During the off-loading, vapor off-gassed from the BS&W and was drawn into the air intakes of the vacuum trucks' running diesel engines. As a result, the engines began to race and backfire. The flammable vapor cloud ignited (CSB, 2003).

The post-incident investigation documented five possible vapor cloud ignition sources – the vacuum trucks' diesel engines, vacuum truck electrical systems, static electricity discharge from the off-loading liquid, (although equipped with a grounding cable, the trucks were not grounded during the off-loading), personnel smoking, and facility electrical wiring. The investigation determined that the diesel truck engines were most likely the ignition source based on physical evidence and the supporting eyewitness testimony (CSB, 2003). In some cases, the flammability hazard is not identified or recognized, and work practices are inadequate for safe handling of the potentially flammable liquid (CSB, 2003).

2.1.2 Arc welder dies in explosion while using an old barrel as a worktable.

A 38-year-old male arc welder died as a result of an explosion at a construction company. The victim was working near a farm building, a 2-story large wood frame structure, which was used as a workshop and for storage of material used in connection with the construction business (FACE, 1999). Figure 2.1 shows the barrel explosion.

Figure 2.1: Barrel explosion.

The victim was arc welding some brackets on the back of the truck. He was apparently welding with a wire welder and used a metal 55-gal barrel as a worktable while welding. Apparently the heat or sparks from the welding ignited residual vapors and/or material in the barrel, causing it to explode. The explosion knocked the victim down, and started a fire in the immediate area. An employee heard the first explosion and saw the building on fire near the back of the garbage truck. The employee ran to the area and found the victim, a large/obese man, lying on the ground, with exploded portions of the drum falling about him. The victim was unconscious, and not breathing. When the employee attempted to move the victim, there were secondary multiple explosions and fires, which forced him to stop. The fire increased rapidly and involved propane and acetylene tanks in the establishment (FACE, 1999).

Recommendations based on investigation are as follows:

i. Ensure that welders are suitably trained in the safe operation of their equipment and process.
ii. Ensure that welding should not be performed on or near used drums, until they have been thoroughly cleaned.
iii. Develop, implement, and enforce a written safety program. The safety program should include task specific safety procedures and employee training in hazard identification, avoidance, and control.
iv. Designate a competent person to conduct frequent and regular site safety inspections.

2.2 PROPERTIES OF COMBUSTIBLE GASES AND LIQUIDS

It is important to remember that there are a number of factors that predict the potential fire or explosion hazard of the waste from industries. A single fire hazard property such as lower flammability limit, lower detonation limit, minimum oxygen concentration, or flash point should not be used as the only criteria to quantify the possible danger (Silva, 1991). The flash point of a liquid is the minimum temperature at which it gives off sufficient vapor to form an ignitable mixture with air near the surface of the liquid or within the vessel used. An ignitable mixture is a mixture within the range of flammability that is capable of the propagation of flame away from the source of ignition when ignited. The flash point is often confused with the ignition temperature.

The ignition temperature of a substance whether solid, liquid, or gaseous, is the minimum temperature required to initiate or cause the self-sustained combustion independently of the heating or heated element. Ignition temperatures observed under one set of conditions may be changed substantially by a change of conditions. For this reason, ignition temperatures should be treated as only approximations (Silva, 1991). The lower flammable (or explosive) limit is defined by the minimum concentration of vapor in air or oxygen below which propagation of flame does not occur on contact with a source of ignition. The upper flammable (or explosive) limit is the maximum proportion of vapor or gas in air above which propagation of flame does not occur. These boundaries are usually expressed in terms of percentage by volume of gas or vapor in air (Silva, 1991). In popular terms, a mixture below the lower flammable limit is too "lean" to burn or explode and a mixture above the upper flammable limit too "rich" to burn or explode. There is no difference between the terms "flammable" and "explosive" as applied to the lower and upper limits of flammability (NFPA, 1986). In other words, the lower flammability limit (LFL) of a substance is equal to the lower explosibility limit (LEL). The limits of flammability are determined experimentally and are affected by temperature, pressure, direction of flame propagation, gravitational field strength, and surroundings (Silva, 1991).

A flame will not propagate if the oxygen concentration is decreased below the minimum oxygen for combustion. For flammability methane requires a minimum oxygen concentration of 12%. Hydrogen requires a minimum oxygen concentration of 5% (Bodurtha, 1980).

2.3 MODELS FOR ASSESSING MIXTURE FLAMMABILITY

Four models for assessing mixture flammability have been identified through literature searches and discussions with flammability experts. The four models being considered are an empirical model, the Le Chatelier rule, the group contribution method, and the adiabatic flame temperature method.

i. Empirical Model

The data obtained from the flammability testing will be used to develop an empirical model for predicting lower flammable limits for mixtures. The empirical model is an equation that expresses the flammable gas mixture lower explosive limits (MLEL) as a function of the concentrations of each compound tested (Connolly *et al.*, 1995). The coefficients in the equation are obtained through standard least squares statistical techniques and can be tested for their significant contribution towards predicting the MLEL. Experimental errors can be used to determine confidence limits for the predictions (Connolly *et al.*, 1995).

ii. Le Chatelier's Rule

The Le Chatelier rule is an empirical equation developed by Le Chatelier in the late 19th century that enables the flammability limits of a mixture to be calculated if the flammability limits of individual components of a mixture are known (Connolly *et al.*, 1995). The effects of a few inert or nonflammable compounds (i.e., carbon dioxide and nitrogen) on the MLEL can be evaluated using a graphical method. The Le Chatelier rule has been tested for many mixtures that are important in transportation, industrial applications, and mining (Connolly *et al.*, 1995).

iii. Group Contribution Method

The group contribution method provides an estimate of the flammability limits of a mixture based on knowledge of the chemical structure of each flammable compound in the mixture (Connolly *et al.*, 1995). The method does not account for the presence of inert (nonflammable) compounds that may be present in the mixture. Several group contribution methods have been proposed by various researchers (Shebeko et al., 1983; Season, 1991; ASTM, 1994; AIChE, 1994) for estimating the LEL of individual compounds.

However, no group contribution method has been proposed for mixtures of flammable gases (Connolly *et al.*, 1995). Based on an extension of the method for estimating the LEL of pure compounds of the American Institute of Chemical Engineers (AIChE) Data Prediction Manual (AIChE, 1994), the LEL was estimated for each of the gas mixtures and compared with the corresponding LEL estimated using the Le Chatelier rule. The absolute average error between the two methods was approximately 2 percent, with the group contribution method predicting a higher LEL in almost all cases (Connolly *et al.*, 1995).

iv. Adiabatic Flame Temperature Method

The adiabatic flame temperature method is based on calculating and comparing the adiabatic flame temperature of a potentially flammable gas mixture with the critical or limiting adiabatic flame temperature. In the event of an explosion, energy is released by the combustion of the flammable compounds. Initially, the energy is absorbed by unreacted reactants, the combustion products, and inert or nonflammable gases. Eventually, however, the energy will be dissipated from the system by various heat transfer processes. If a flammable gas mixture explodes in an adiabatic system (one in which there is no transfer of heat to or from the system), then it is possible to calculate an adiabatic flame temperature that corresponds to the temperature of the system after the explosion. The minimum temperature at which a flame can be sustained is referred to as the critical or limiting adiabatic flame temperature (Connolly *et al.*, 1995).

A number of computer codes are available to perform the complex thermodynamic chemical equilibrium calculations, including the American Society of Testing and Materials (ASTM) CHEETAH code (ASTM, 1994), the National Aeronautic and Space Administration (NASA) Lewis Research Center CET93/CETPC code (McBride et al., 1994), the Lawrence Livermore National Laboratory (LLNL) CHEETAH code (Fried, 1995), the University of Arizona CHEMEQ code (Wendt, 1993), and the NASA CET93/CETPC code (NFPA, 1988). If the adiabatic flame temperature of a potentially flammable gas mixture calculated by the code is above the critical or limiting flame temperature, then the mixture is flammable (Connolly *et al.*, 1995). Table 2.1 shows the Classifications of several Flammable Volatile organic compounds (VOCs) that are related with the fire and explosion of the waste from industries analysis.

Table 2.1: Classifications of Flammable VOCs (Coinnolly *et al.*, 1995).

Flammable VOC	Structural Type	Functional Group No.[a]	LEL (%)	LEL Group No.[b]
Acetone	ketone	2	2.6	2
Benzene	aromatic	1	1.3	1
Butanol	alcohol	3	1.7	2
Chlorobenzene	aromatic	1	1.3	1
Cyclohexane	cycloalkane	-	1.3	1
1,1-Dichloroethane	alkane	4	5.6	3
1,2-Dichloroethane	alkane	4	6.2	3
1,1-Dichloroethylene	alkene	4	6.5	3
cis-1,2-Dichloroethylene	alkene	4	5.6	3
Ethyl benzene	aromatic	1	1 .0	1
Ethyl ether	ether	-	1.9	2
Methanol	alcohol	3	6.7	3
Methyl ethyl ketone	ketone	2	1.9	2
Methyl isobutyl ketone	ketone	2	1.4	2
Toluene	aromatic	1	1.2	1
1,2,4-Trimethylbenzene	aromatic	1	0.9	1
1,3,5-Trimethylbenzene	aromatic	1	1 .0	1
o-Xylene	aromatic	1	1.1	1
p/m-Xylene	aromatic	1	1.1	1

[a] Functional group numbers are assigned as follows: (1) aromatics, (2) ketones, (3) alcohols, and (4) Alkanes / alkenes.

[b] LEL group numbers are assigned as follows: (1) 0.9%-1.3%, (2) 1.4%-2.6%, and (3) 5.6%-6.7%.

2.4 METHODS FOR ESTIMATING MIXTURE LFLs (MLFLs)

Given the flammability limits of each of the components in a mixture, the lower flammability limit (LFL) of the mixture may be calculated by LeChatelier's rule (Kuchta, 1985; LeChatelier, 1891) while MLFL is the mixture lower flammability limit (vol%) (Liekhus *et al.*, 2000).

$$LFLmix = \frac{1}{\sum_{i=1}^{n} \frac{yi}{LFLi}} \tag{1}$$

$$UFLmix = \frac{1}{\sum_{i=1}^{n} \frac{yi}{UFLi}} \tag{2}$$

where

LFL_i = the lower flammable limit for component i (in volume %) of component i in fuel and air

y_i = mole fraction of component i on a combustible basis

n = number of combustible species

$$MLFL = \frac{100}{\sum \frac{Ci}{LFLi}} \tag{3}$$

where

MLFL = the mixture lower flammability limit (vol%);

Ci = the concentration of component *i* in the gas mixture on an air-free basis (vol%);

LFL*i* = the lower flammability limit for compound *i* in the mixture (vol%)

If the volume percentage (vol %) for total combustible components is between the calculated LFL_{mix} and UFL_{mix}, then the mixture is combustible.

2.5 IGNITION SOURCES

Fires and explosions can be prevented by eliminating ignition sources. The sources are numerous and logically it is impossible to eliminate them all. The main reason for rendering a flammable liquid inert, for example, is to prevent a fire or explosion y ignition from an unidentified source. Although all resources of ignition are not likely to be identified, engineers must still continue to identify and eliminate the. Elimination of the ignition sources with the greatest probability of occurrence should be given the greatest attention (Crowl and Louvar, 2002). Table 2.2 shows the ignition sources over 25 000 major fire cases all over the world.

Table 2.2: Ignition Sources of Major Fires (Crowl and Louvar, 2002)

Electrical (wiring of motors)	23%
Smoking	18%
Friction (bearings or broken parts)	10%
Overheated materials (abnormally high temperatures)	8%
Hot surfaces (heat from boilers, lamps, etc.)	7%
Burner flames (improper use of torches, etc.)	7%
Combustion sparks (sparks and embers)	5%
Spontaneous ignition (rubbish, etc.)	4%
Cutting and welding (sparks, arcs, heat, etc.)	4%
Exposure (fires jumping into new areas)	3%
Incendiarism (fires maliciously set)	3%
Mechanical sparks (grinders, crushers, etc.)	2%
Molten substances (hot spills)	2%
Chemical action (processes not in control)	1%
Static sparks (release of accumulated energy)	1%
Lightning (where lightning rods are not used)	1%
Miscellaneous	1%

2.6 EXPLOSIONS

Explosion behavior is difficult to characterize. Many approaches to the problem have been undertaken, including theoretical, semiempirical, and empirical studies. Despite these efforts, explosion behavior is still not completely understood (Crowl and Louvar, 2002).

An explosion results from the rapid release of energy. The energy release must be sudden enough to cause a local accumulation of energy at the site of the explosion. This energy is then dissipated by a variety of mechanisms, including formation of a pressure wave, projectiles, thermal radiation, and acoustic energy. The damage from an explosion is caused by the dissipating energy. If the explosion occurs in a gas, the energy caused the gas to expand rapidly, forcing back the surrounding gas and initiating a pressure wave that moves rapidly outward from the blast source. The pressure wave contains energy, which results in damage to the surroundings. Thus, in order to understand explosion impacts, we must understand the dynamics of the pressure wave.

A pressure wave propagating in air is called a blast wave because the pressure wave is followed by a strong wind. A shock wave or shock front results if the pressure front has an abrupt pressure change. A shock wave is expected from highly explosive materials, but it can also occur from the sudden rupture of a pressure vessel. The maximum pressure over ambient pressure is called the peak overpressure. Explosion behavior depends on a large number of parameters (Crowl and Louvar, 2002). A summary of the more important parameters are:

i. Ambient temperature
ii. Ambient pressure
iii. Composition of explosive material
iv. Physical properties of explosive material
v. Nature of ignition source: type, energy, and duration
vi. Geometry of surroundings: confined or unconfined
vii. Amount of combustible material

viii. Turbulence of combustible material
ix. Time before ignition
x. Rate at which combustible material is released

2.7 FIRE

Fuel can be in solid, liquid, or vapour form, but vapour and liquid fuels are generally easier to ignition. The combustion always occurs in the vapour phase; liquids are volatised and solids are decomposed into vapour before combustion (Crowl and Louvar, 2002). The major distinction between fires and explosions is the energy release rate. Fires release energy slowly, whereas explosion release energy rapidly in the order of microseconds. Fires can also result from explosions, and explosions can result from fires (Crowl and Louvar, 2002).

2.8 FLASH POINT

Flash point is one of the major physical and chemical properties used to determine the fire and explosion hazards of liquids; therefore, the prediction of flash points is an important safety consideration. In this paper, flash point prediction methods based on vapor pressure, molecular structure, composition range, and boiling point of flammable liquids are reviewed, respectively. Le Chatelier's rule and Antoine equations are used in the correlation between vapor pressure and flash point. Research on the correlations between flash point and composition range of the mixture has focused on flash point predictions for binary and ternary solutions, and further investigation for multicomponent solutions is required in the future (Xinshuai and Zhenyi, 2010).

Flash point is one of the most important flammability characteristics of liquids and low-melting substances. The American Society for Testing and Materials (ASTM) defines flash point as the lowest temperature, corrected to a pressure of 101.3 kPa, at which the application of an ignition source causes the vapors of a sample specimen to ignite under specified testing conditions. Flash point is widely used to evaluate the fire and explosion hazards of liquids and has great practical significance in the handling and transporting of such compounds in bulk quantities. The Abel flash point tester was invented in the United Kingdom in the 19th century, and current measurement devices fall into two basic categories, the open cup or the closed cup design. There is often a significant demand for flash point data, and a reliable theoretical method for estimating flash points is desirable. In this paper, we present an overview of current flash point prediction methods, which are based on calculations from vapor pressure, composition range, molecular structure, and boiling point of flammable liquids, respectively (Xinshuai and Zhenyi, 2010).

In 1917, from the viewpoint of oxidation reaction in combustion chemistry, Thorton(1917), determined the amount of oxygen atoms needed at the upper and lower limit of inflammability. On the basis of this rule, Mack et al. (1923), evaluated the minimum volume fraction of the inflammable substance in air that gives an explosive mixture and acquired the partial pressure of the inflammable substance. The flash point temperature could then be read off directly from the vapor-pressure curve of pure substances. Additionally, the vapor pressure could be calculated by the method of Lewis and Weber (1922), if experimentally unavailable. The authors applied this to 2 compounds from aliphalic hydrocarbons, 6 from aromatic hydrocarbons, 11 from aliphatic esters, 7 from phenols, 2 from miscellaneous compounds, 8 from alcohols, and 1 from carbon disulfide and also tried to extend it to a mixture, provided the components of the mixture are all in the same series and the vapor pressure of the mixture in the region of flash point must be known. Apparently, the number of compounds considered is rather limited. Meanwhile, this mathematical model has unsatisfactory precision with the maximum deviation of isomeric compounds being 14 °C, so it may not be appropriate to predict flash points.

In 2000, according to the law that the net enthalpy of combustion at the flash point varies with the carbon number in compounds, Huang (2000), reported flash point prediction models for aliphatic alkanes, alcohols, aldehydes, and aliphatic alkenes, respectively. The calculated flash points are in good agreement with experimental data, with the average absolute relative deviation being only 0.72 %. However, this research did not include other chemical families and compounds with complicated structures.Generally; the evaporability of compounds is determined by boiling point: the lower the boiling point, the faster the evaporation. Flash point has a direct bearing on evaporability: the faster the evaporation rate, the lower the flash point. Therefore, there is a good relation between flash point and normal boiling point (Xinshuai and Zhenyi, 2010).

2.9 BOILING LIQUID EXPANDING VAPOUR EXPLOSION (BLEVE)

Among the most damaging of accidents that can occur in a chemical process plant is a boiling liquid expanding vapour explosion (BLEVE, pronounced “blev-ee”). A BLEVE is an explosion involving both the rapid vaporization of liquid and the rapid expansion of vapour in a vessel (Ibrahim, 2007). A BLEVE is the explosive release of expanding vapor and boiling liquid when a container holding a pressure liquefied gas fails catastrophically (Birk and Cunningham, 1994).

A BLEVE can occur on catastrophic failure of a vessel containing even high-pressure hot water in a steam boiler which is above its atmospheric boiling temperature. Such explosions can be very destructive of plant and equipment because they give rise to fragments from the exploding vessel. Any mechanism of catastrophic vessel failure (impact damage, exposure to fire, fatigue, corrosion, flawed construction, etc.) can give rise to a BLEVE. A BLEVE can give rise to a fireball. The hazards posed by the fireball will be principally due to thermal radiation (Ibrahim, 2007).

On 24 April 1957, a cast iron vessel used to produce a phenolic resin by the chemical reaction between formalin (a solution of formaldehyde gas in water) and phenol suddenly blew apart into several pieces. No fire ensued because the contents of the vessel were essentially non-flammable. However, the damage resulting from flying fragments and, to a lesser extent, from shock wave overpressure, was substantial (Ibrahim, 2007).

The term “boiling liquid expanding vapor explosion” (acronym “BLEVE”) was the brainchild of Smith, Marsh, and Walls (Walls, 1978). They were employed by Factory Mutual Engineering Division (now known as the Factory Mutual Research Corporation, or FMRC). Since that time the term BLEVE has been used routinely by Factory Mutual in its technical work and published materials. These engineers arrived at the conclusion that the understanding of this phenomenon could explain many other accidents and that the physical model conceived to study BLEVE could apply to any superheated liquid. So no chemical reaction or combustibility problems were necessary for a BLEVE to occur even in water heaters and steam boilers. In 1969, the USA experienced several railroad derailments in which tank cars of flammable liquefied gases came apart suddenly in two or more pieces. In some cases the cause of failure was impact; in others, it was exposure to fire. In all cases, casualities and damage from fire occurred as a result of the ignition of the products. These incidents were, in fact, BLEVEs. However, the term was not used by investigators and did not appear in reports published by the National Fire Protection Association (NFPA) or others. Until the spring of 1972, the use of the term BLEVE appears to have been restricted to Factory Mutual (Ibrahim, 2007).

BLEVE was first used by the NFPA in the article “Lessons from a PL-gas utility plant explosion and fire”, which appeared in the April 1972 issue of Fire Command (Walls, 1978). In January 1976, the 14th edition of the NFPA Fire Protection Handbook was published. The only discussion of BLEVEs in the handbook is contained in section 3, chapter 4, “Gases”. In the spring of 1977, the NFPA released written advisories and reports and then its film, “BLEVE”. The film explained the causes and consequences of BLEVEs and outlined the limited probability of firefighter action in mitigating a BLEVE under tank car derailment conditions (Walls, 1978; Wilbur and Walls, 1982). Birk et al. (1993) carried out tests on 11 automotive propane tanks using pool and torch fire exposure to study BLEVEs and their consequences. Birk et al. (1993) observed that there were two different kinds of BLEVE, and differentiated between the two by calling them strong or hot BLEVEs (when the liquid temperature was above the superheating limit for propane at atmospheric pressure) and weak or cold BLEVEs (accidents which occurred with a relatively low temperature).

There are several different approaches to describe BLEVEs. They include:

i. the superheat limit theory;
ii. the cloud formation theory; and
iii. the bursting vessel model (Lees, 1996).

In the superheat limit theory, a liquid (or liquefied gas) is "superheated" means that it is at a temperature sufficiently greater than that at which the same fluid would have quasi-equilibrium at normal atmospheric pressure. These conditions are present in the case of most liquefied gases.

One of the most commonly supported types of BLEVEs is that caused by superheated explosions. A liquid can be brought to the superheated state in two ways:

i. by rapid depressurization; or
ii. by rapid heating.

Here, rapid depressurization will be discussed. For a BLEVE to occur the release process must be much more violent. Consider a case where a puncture exists above the liquid level and the puncture is large enough to cause rapid depressurization of the vessel. If the depressurization is very rapid the liquid cannot boil fast enough to stay in thermodynamic equilibrium and this causes the liquid to enter the superheated state. All boiling requires some superheating in the liquid. However, as the superheating increases, the boiling becomes more violent. There is a limit to the degree of superheating that can be reached. At this limit boiling takes place homogeneously and the rate of boiling is explosive.

The essential features of a BLEVE are that:

i. the vessel fails;
ii. the failure results in flash-off of vapour from the superheated liquid; and
iii. if the liquid is flammable, the vapour ignites and forms a fireball.

The major consequences of a BLEVE, in order of decreasing importance are:

i. the thermal radiation from the resultant fireball;
ii. the fragments produced when the vessel fails; and
iii. the blast wave produced by the expanding vapour/liquid.

2.10 CHROMATOGRAPHIC ANALYSIS

The composition of a liquid sample can be determined by using the gas chromatography (GC). The field of gas chromatography (GC) is continually expanding. Emerging techniques such as gas chromatography– isotope ratio mass spectrometry (GC–IRMS) and multidimensional gas chromatography (two- and three-dimensional GC as well as GC-MS) are currently being explored in other scientific fields such as geochemistry and environmental chemistry; however, their potential to be used in the forensic examination of fire debris and ignitable liquids is clear (Mark and Sandercock, 2001-2007). GC–MS–MS was used to increase target compound selectivity and sensitivity which allowed the development of an ''expert system'' for pattern recognition of ignitable liquids in fire debris samples (Sittidech, 2002).

Comprehensive, two-dimensional gas chromatography (GC-GC) is a recent development that has received a lot of attention in the scientific literature over the past few years (Marriot and Ong, 2002). In GC-GC the entire sample undergoes a two dimensional separation with all of the components being separated first by boiling point and then by polarity. The sample is first separated conventionally on a non-polar column; the effluent from the first column is precisely modulated into sharp chemical pulses that then undergo a second, fast separation on a shorter, polar column. The effluent from the second column then goes to a detector. The resulting output consists of two orthogonal retention time axes, one for each column. The key element in GC-GC is the modulator and much work has focused on this aspect of the technique (Pursch *et al.*, 2002).

CHAPTER 3

METHODOLOGY

3.1 MATERIALS

Liquid waste samples as shown in Figure 3.1 and Figure 3.2 are collected from Kualiti Alam Waste Management Centre, Seremban, Negeri Sembilan. The sample is then stored under the low temperature to ensure that the sample will not vaporize out of the bottle. These liquid samples have been analyzed to measure the composition of all combustible species content using gas chromatography (GC). Once the composition being identified, the extraction process like distillation experiment need to be done to remove the water inside the waste samples before the flash point of the samples will be measured. Combustible gases are normally formed by several combustible elements that have the lower vapor pressure than the operating pressure. When all analyze of the waste samples are already performed, investigation will be done for the potential of fire and explosion regarding the characteristics and composition of the waste samples. Finally, the study the consequences of fire and explosion resulting from any possible flammable industrial waste accident will be studied.

Figure 3.1: Industrial waste (Sample 1).

Figure 3.2: Industrial waste (Sample 2).

3.2 METHODS AND TOOLS REQUIRED

There are different tools of equipment required for this project in order to achieve the final objectives of this study.

3.2.1 Chromatographic analysis for determining the composition if liquid sample

The compositions of a liquid sample can be determined using the gas chromatography (GC). The compositions of two waste liquid samples have been determined using the gas chromatography (GC) which is Shimadzu GCMS-QP5050 type. The GC is used to separate volatile components of a mixture. The column use is 30mx0.25mm ID x0.25 μm of BP1 type. First, a small amount of the waste samples to be analyzed are drawn up into a GC syringe. The syringe needle is placed into a hot injector port of the gas chromatograph, and the samples are injected. The injector is set to a temperature higher than the components' boiling points. So, components of the mixture evaporate into the gas phase inside the injector. A carrier gas is helium. It flows through the injector and pushes the gaseous components of the sample onto the GC column. It is within the column that separation of the components takes place. Molecules partition takes place between the carrier gas (the mobile phase) and the high boiling liquid (the stationary phase) within the GC column. After components of the mixture move through the GC column, they reach a detector. Ideally, components of the mixture will reach the detector at varying times due to differences in the partitioning between mobile and stationary phases. The detector sends a signal to the chart recorder which results in a peak on the chart paper. The area of the peak is proportional to the number of molecules generating the signal. To determine the percent composition, it is needed to find the area under each curve.

$$\text{Area} = (\text{height}) \times (\text{width at } \tfrac{1}{2} \text{ height})$$

GCMS used with injector temperature is 250 °C and the oven temperature is 40 °C for five minutes up to 150 °C at 3°C per minute. The interface temperature is 250 °C, with the column pressure of 65 kPa and flow of 1.2 ml/minute. In addition, the split ratio is 1:100 with injection volume of 0.5 microliter.

The full result of the GC analysis for the waste sample 1 is shown in Figure 3.3 while the full result of the GC analysis for the waste sample 2 is shown in Figure 3.4. All of the components presences for waste sample 1 are listed in Table 3.1 and Table 3.2, while all of the components presences for waste sample 2 are listed in Table 3.3 and Table 3.4. Gas Chromatography analysis shows that both of the liquid waste samples majority are alkane group.

All the values of summary for liquid waste sample 1 and 2 are getting from the calculation of percent total area multiply each of their chemical properties. The value for average molecular weight is getting from the sum of percent total area multiply the molecular weight of each component contains in the sample. The value for average flash point is getting from the sum of percent total area multiply the value of flash point of each component contains in the sample. The value for average vapor pressure, average enthalpy of vaporization and average boiling point are getting also from the sum of percent total area multiply the vapor pressure, enthalpy of vaporization and the value of boiling point of each component contains in the sample respectively.

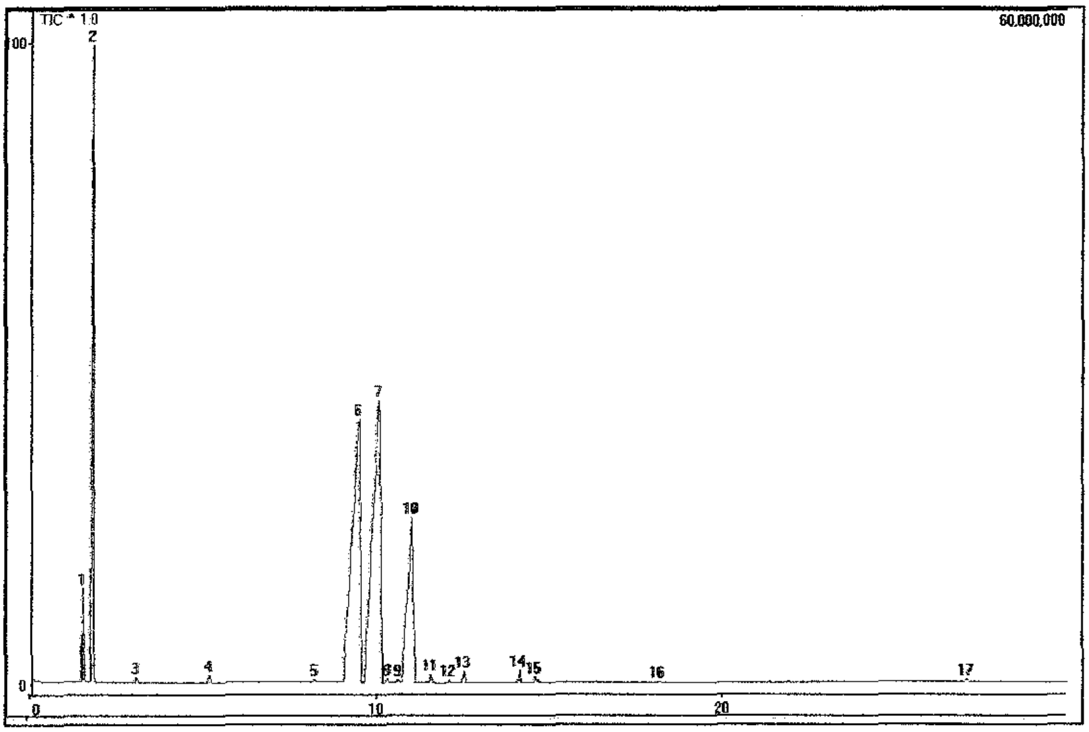

Figure 3.3: GC analysis for waste sample 1.

Summary of liquid waste sample 1 are:

1. Average Molecular Weight: 104.68 g/mol
2. Average Flash Point: 18.12°C
3. Average Vapor Pressure: 30.70 mmHg at 25°C
4. Average Enthalpy of Vaporization: 34.74 kJ/mol
5. Average Boiling Point: 127.21 °C

Table 3.1: Components presences in waste sample 1

									PHASE ,PRESSURE= 1 ATM			
PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	%Total Area	FORMULA	25 °C	35 °C	40 °C	GROUP
1	1.443	1.367	1.567	1.675	13540849	8083938	1.22	H_2O	Liquid	Liquid	Liquid	
2	1.735	1.667	1.867	3.057	170582857	55808625	15.37	$C_6H_{14}O$	Liquid	Liquid	Liquid	Alcohol
3	3.017	2.983	3.1	2.76	857940	310855	0.08	$C_4H_{10}O_2$	Liquid	Liquid	Liquid	Alcohol
4	5.11	5.067	5.233	2.739	1662168	606842	0.15	C_7H_8	Liquid	Liquid	Liquid	Arene
5	8.155	8.1	8.267	4.821	1144916	237495	0.1	C_8H_{16}	Liquid	Liquid	Liquid	Alkene
6	9.468	8.967	9.533	16.697	384232374	23012180	34.61	C_8H_{10}	Liquid	Liquid	Liquid	Arene
7	10.034	9.567	10.1	15.329	378445611	24687518	34.09	C_8H_{10}	Liquid	Liquid	Liquid	Arene
8	10.271	10.2	10.35	4.663	1326642	284504	0.12	C_9H_{20}	Liquid	Liquid	Liquid	Alkane
9	10.574	10.533	10.683	3.347	568961	169977	0.05	C_9H_{20}	Liquid	Liquid	Liquid	Alkane
10	10.985	10.683	11.05	10.067	144507416	14354925	13.02	C_8H_{10}	Liquid	Liquid	Liquid	Arene
11	11.526	11.483	11.667	2.907	1910311	657057	0.17	$C_6H_{14}O_2$	Liquid	Liquid	Liquid	Alcohol
12	12.05	11.983	12.15	3.556	857529	241173	0.08	C_9H_{20}	Liquid	Liquid	Liquid	Alkane
13	12.485	12.4	12.6	3.676	3620961	985000	0.33	C_9H_{12}	Liquid	Liquid	Liquid	Arene
14	14.09	14.017	14.167	3.645	3828200	1050353	0.34	C_9H_{12}	Liquid	Liquid	Liquid	Arene
15	14.547	14.467	14.617	3.337	1612644	483302	0.15	C_9H_{12}	Liquid	Liquid	Liquid	Arene
16	18.13	18.083	18.233	3.975	455777	114650	0.04	C_7H_8O	Liquid	Liquid	Liquid	Alcohol
17	27.07	27	27.167	3.956	875696	221376	0.08	$C_{10}H_{18}O$	Liquid	Liquid	Liquid	Alcohol
				TOTAL	1110030852	TOTAL	100					

Table 3.2: Chemical properties for the components presences in waste sample 1

	NAME	Molecular Weight, M	Flash Point (°C)	Vapor pressure @ 25°C (mmHg)	Enthalpy of Vaporization (kJ/mol)	Boiling Point at 760 mmHg (°C)	Temperature become liquid phase at P=1 atm	Molecular Weight, M	Flash Point (°C)	Vapor pressure @ 25°C (mmHg)	Enthalpy of Vaporization (kJ/mol)	Boiling Point at 760 mmHg (°C)
1	water	18.0153		24.5	40.65	100	100	0.219787		0.2989	0.49593	1.22
2	Diisopropyl ether	102.1748	-28	152	29.1	68.3	68.3	15.70427	-4.3036	23.3624	4.47267	10.49771
3	2-Propanol, 1-methoxy-	90.121	33.9	8.15	41.8	118.5	118.5	0.072097	0.02712	0.00652	0.03344	0.0948
4	Toluene	92.1384	10	27.7	33.48	110.6	110.6	0.138208	0.015	0.04155	0.05022	0.1659
5	Cyclohexane, ethyl-(CAS) Ethylcyclohexane	112.2126	18.9	12.4	34.04	129.4	129.4	0.112213	0.0189	0.0124	0.03404	0.1294
6	Ethylbenzene	106.165	25.9	9.21	35.57	136.2	136.2	36.74371	8.96399	3.187581	12.31078	47.13882
7	Benzene, 1,4-dimethyl-(CAS) p-Xylene	106.165	27.2	7.94	35.67	139.6	139.6	36.19165	9.27248	2.706746	12.1599	47.58964
8	Octane, 2-methyl-	128.2551	25.2	6.73	36.48	143.3	143.3	0.153906	0.03024	0.008076	0.043776	0.17196
9	Octane, 3-methyl-	128.2551	25.3	6.69	36.49	143.5	143.5	0.064128	0.01265	0.003345	0.018245	0.07175
10	p-Xylene	106.165	27.2	7.94	35.67	139.6	139.6	13.82268	3.54144	1.033788	4.644234	18.17592
11	Ethanol, 2-butoxy-	118.1742	60	0.552	47.06	167.7	167.7	0.200896	0.102	0.000938	0.080002	0.28509
12	Nonane	128.2551	31.1	4.63	36.91	151.7	151.7	0.102604	0.02488	0.003704	0.029528	0.12136
13	Benzene, (1-methylethyl)-	120.1916	31.1	4.48	37.32	152.4	152.4	0.396632	0.10263	0.014784	0.123156	0.50292
14	Benzene, propyl-	120.1916	42.1	3.09	38.08	160.5	160.5	0.408651	0.14314	0.010506	0.129472	0.5457
15	Benzene, 1-ethyl-3-methyl-	120.1916	38.3	3.01	38.13	161.1	161.1	0.180287	0.05745	0.004515	0.057195	0.24165
16	Benzenemethanol (CAS) Benzyl alcohol	108.1378	97.5	0.158	46.61	204.7	204.7	0.043255	0.039	6.32E-05	0.018644	0.08188
17	1-.alpha.-Terpineol	154.2493	89.4	0.0283	52.78	217.5	217.5	0.123399	0.07152	2.26E-05	0.042224	0.174
						TOTAL		104.6784	18.11884	30.69584	34.74346	127.2085

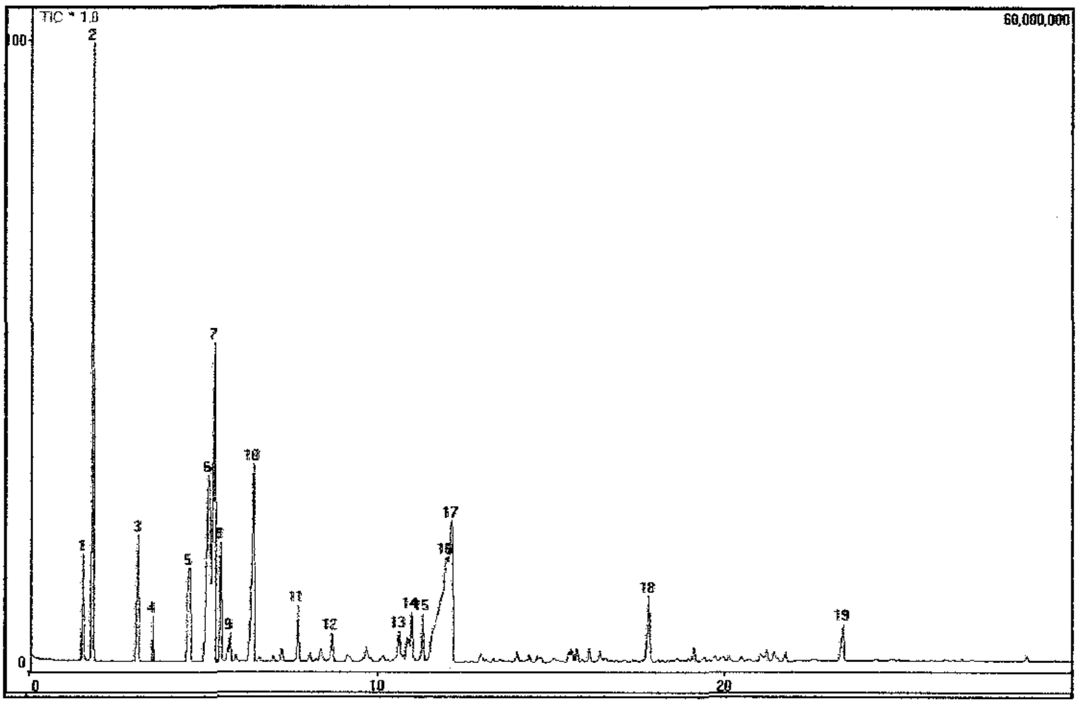

Figure 3.4: GC analysis for waste sample 2.

Summary of liquid waste sample 2 are:

i. Average Molecular Weight: 119.14 g/mol
ii. Average Flash Point: 29.92°C
iii. Average Vapor Pressure: 36.71 mmHg at 25°C
iv. Average Enthalpy of Vaporization: 37.96 kJ/mol
v. Average Boiling Point: 140.25 °C

Table 3.3: Components presences in waste sample 2

PKNO	R.TIME	I.TIME	F.TIME	A/H(sec)	AREA	HEIGHT	%Total	FORMULA	PHASE ,PRESSURE= 1 ATM			GROUP
									25 ^{0}C	35 ^{0}C	40 ^{0}C	
1	1.443	1.417	1.6	1.449	13747345	9488499	1.374934	H_2O	Liquid	Liquid	Liquid	
2	1.735	1.667	1.867	3.055	170464809	55792710	17.04895	$C_6H_{14}O$	Liquid	Liquid	Liquid	Alcohol
3	3.037	2.983	3.2	2.652	30045647	11328594	3.005	$C_4H_{10}O_2$	Liquid	Liquid	Liquid	Alcohol
4	3.46	3.417	3.533	1.871	7542635	4031379	0.754373	C_8H_{18}	Liquid	Liquid	Liquid	Alkane
5	4.534	4.383	4.617	5.829	48959183	8398809	4.896627	C_8H_{18}	Liquid	Liquid	Liquid	Alkane
6	5.075	4.917	5.117	6.235	104445739	16752200	10.44609	C_8H_{18}	Liquid	Liquid	Liquid	Alkane
7	5.235	5.117	5.317	4.568	131994154	28894158	13.20133	C_8H_{18}	Liquid	Liquid	Liquid	Alkane
8	5.421	5.317	5.5	2.847	30634396	10761424	3.063883	C_8H_{18}	Liquid	Liquid	Liquid	Alkane
9	5.693	5.55	5.783	3.914	9939970	2539816	0.994141	C_8H_{18}	Liquid	Liquid	Liquid	Alkane
10	6.368	6.2	6.417	4.742	83981983	17709986	8.399415	C_9H_{20}	Liquid	Liquid	Liquid	Alkane
11	7.656	7.55	7.733	3.229	16243479	5029925	1.624583	C_9H_{20}	Liquid	Liquid	Liquid	Alkane
12	8.63	8.55	8.733	3.537	8638861	2442459	0.864011	C_9H_{20}	Liquid	Liquid	Liquid	Alkane
13	10.576	10.517	10.633	3.205	7755124	2419390	0.775625	$C_{10}H_{22}$	Liquid	Liquid	Liquid	Alkane
14	10.927	10.867	10.983	3.208	12262029	3822453	1.22638	$C_{10}H_{22}$	Liquid	Liquid	Liquid	Alkane
15	11.259	11.167	11.333	3.749	15787650	4211469	1.578994	$C_{10}H_{22}$	Liquid	Liquid	Liquid	Alkane
16	11.929	11.4	11.967	16.328	153362964	9392831	15.33852	$C_7H_{12}O_3$	Liquid	Liquid	Liquid	Carbonyl
17	12.078	11.967	12.267	8.64	109925700	12722985	10.99416	$C_6H_{14}O_2$	Liquid	Liquid	Liquid	Alcohol
18	17.786	17.633	17.917	4.905	28522546	5815326	2.852668	$C_{10}H_{22}$	Liquid	Liquid	Liquid	Alkane
19	23.383	23.15	23.5	4.705	15600971	3315530	1.560323	$C_{11}H_{24}$	Liquid	Liquid	Liquid	Alkane
				TOTAL	999855185	TOTAL	100					

Table 3.4: Chemical properties for the components presences in waste sample 2

PK NO	NAME	Molecular Weight, M	Flash Point (°C)	Vapor pressure @ 25°C (mmHg)	Enthalpy of Vaporization (kJ/mol)	Boiling Point at 760 mmHg (°C)	Temp. at liquid Phase (P=1 atm)	Molecular Weight, M	Flash Point (°C)	Vapor pressure @ 25°C (mmHg)	Enthalpy of Vaporization (kJ/mol)	Boiling Point at 760 mmHg (°C)
1	Water	18.0153		24.5	40.65	100	100	0.247698		0.336859	0.558911	1.374934
2	Diisopropyl ether	102.1748	-28	152	29.1	68.3	68.3	17.41973	-4.77371	25.9144	4.961244	11.64443
3	2-Propanol, 1-methoxy-	90.121	33.9	8.15	41.58	118.5	118.5	2.708136	1.018695	0.244907	1.249479	3.560925
4	Pentane, 2,2,4-trimethyl-	114.2285		45.2	30.79	98.8	98.8	0.861709	0	0.340976	0.232271	0.74532
5	Hexane, 2,4-dimethyl-	114.2285	22.9	29.4	32.51	109.2	109.2	5.593344	1.121328	1.439608	1.591894	5.347117
6	Pentane, 2,3,4-trimethyl-	114.2285	5	24.5	32.36	113.5	113.5	11.93241	0.522304	2.559291	3.380354	11.85631
7	Pentane, 2,3,3-trimethyl-	114.2285	11.4	23.1	32.12	114.9	114.9	15.07968	1.504951	3.049507	4.240266	15.16832
8	Hexane, 2,3-dimethyl-	114.2285	29.7	23.1	33.17	115	115	3.499828	0.909973	0.707757	1.01629	3.523466
9	Hexane, 3,4-dimethyl-	114.2285	31.6	21.5	33.24	116.6	116.6	1.135592	0.314149	0.21374	0.330452	1.159168
10	Hexane, 2,2,5-trimethyl-	128.2551	19.8	16	33.65	123.6	123.6	10.77268	1.663084	1.343906	2.826403	10.38168
11	Hexane, 2,3,5-trimethyl-	128.2551	24.4	11.2	34.43	131.8	131.8	2.083611	0.396398	0.181953	0.559344	2.141201
12	Heptane, 2,5-dimethyl-	128.2551	54.2	9.42	35.78	135.8	135.8	1.108138	0.468294	0.08139	0.309143	1.173327
13	Heptane, 2,2,4-trimethyl- (CAS) 2,2,4-Trimethylheptane	142.2817	37.2	5.17	37.02	149.2	149.2	1.103572	0.288532	0.0401	0.287136	1.157232
14	Heptane, 2,2,4-trimethyl- (CAS) 2,2,4-Trimethylheptane	142.2817	37.2	5.17	37.02	149.2	149.2	1.744915	0.456214	0.063404	0.454006	1.82976
15	Heptane, 2,2,4-trimethyl-	142.2817	37.2	5.17	37.02	149.2	149.2	2.246619	0.587386	0.081634	0.584543	2.355859
16	Tetrahydrofurfurylacetate	144.1684	108.2	0.0031	55.13	263	263	22.1133	16.59628	0.000475	8.456125	40.3403
17	Ethanol, 2-butoxy-	118.1742	60	0.552	47.06	167.7	167.7	12.99226	6.596497	0.060688	5.173853	18.43721
18	Decane (CAS) n-Decane	142.2817	46.1	1.58	38.75	174.9	174.9	4.058824	1.31508	0.045072	1.105409	4.989316
19	Undecane	156.3083	60	0.564	41.48	196.3	196.3	2.438914	0.936194	0.0088	0.647222	3.062914
						TOTAL		119.141	29.92165	36.71447	37.96435	140.2488

3.2.2 Distillation

The distillation process has been done based on the uncertainty about the real liquid mixture composition, where there are probabilities that the water is soluble or miscible with other component and if that happen, they did not show different layers.

To set up the simple distillation apparatus, firstly round bottom flask is held in place in the set-up with a small three-pronged clamp with holder . A ring clamp and three-pronged clamp are placed on the ring stand. The ring clamp goes on the bottom and will hold the heat source, a heating mantle. Secure the round bottom flask to the ring stand using the three pronged clamp. The Y-adaptor is then placed on top of the round bottom flask. Next, a condenser is added to the Y-adaptor and the connection is secured with clip. The vacuum adaptor is connected to the condenser by using a clip. After that, a stemmed funnel is placed on top of the Y-adaptor and the liquid waste sample is poured so that it goes into the round bottom flask. The liquid volume needed is 200 ml. In a vacuum distillation, a round bottom flask is used as the receiving flask, and it is securely attached with either a clamp or a yellow clip. The next items to be added are the thermometer adaptor and thermometer. The thermometer and thermometer adaptor are connected on top of the Y-adaptor. Two pieces of Tygon tubing are connected to the condenser: one to each connection of the water-jacket of the condenser. The tubing to the lower connection goes to the water source; the upper connection goes to the drain. Connect two pieces of Tygon tubing to the condenser: one to each connection of the water-jacket of the condenser. The tubing to the lower connection goes to the water source; the upper connection goes to the drain. Cooling water is then turned on and the distillation can be started. Figure 3.5 shows the simple distillation set up.

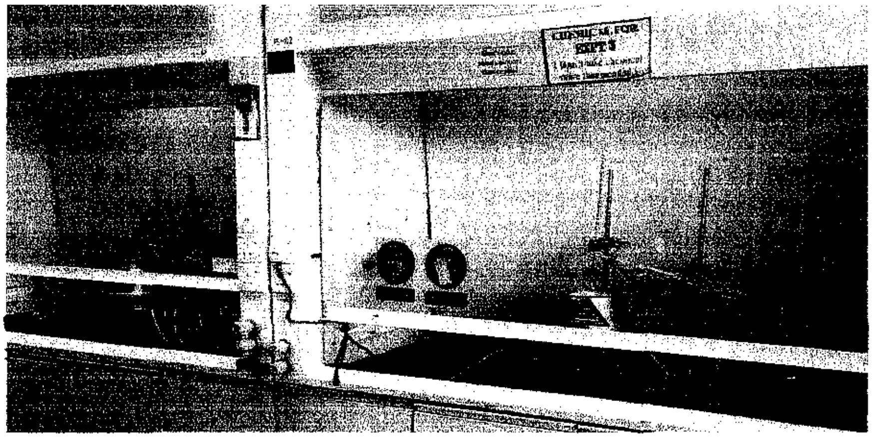

Figure 3.5: Full simple distillation set up.

From the observation made, the product (clear in colour) for both waste sample 1 and sample 2 start to be produced at the temperature of 68.3°C. After that, the distillate flasks for both samples have been changed to unused flasks. Then the waste samples continuously being distillate for the temperature of 100°C to remove only the water. The liquid sample's temperature changes between these two temperatures are fluctuating and they did not happen in uniform pattern. The distillation was done after four days. Figure 3.6 shows liquid waste sample 1 and Figure 3.7 shows liquid waste sample 2 before on going distillation process while Table 3.6 shows the results of the distillation process.

Figure 3.6: Liquid waste sample 1 before on going distillation process.

Figure 3.7: Liquid waste sample 2 before on going distillation process.

Table 3.5: Results of the distillation process

Waste Sample	Volume before distillation process	Volume after distillation process	Volume of water content in the samples	Color after distillation process
Sample 1 (green in colour)	200 ml	95 ml	105 ml	Orange
Sample 2 (solid white in colour)	200 ml	187 ml	13 ml	Solid white

3.2.3 Determining the Density

To determine the density for both of the liquid waste samples, firstly the volume of the pycnometer,V is first recorded. Then, determine the weight of empty, dry pycnometer, m_{empty}. The pycnometer is then filled with the liquid sample from the industrial waste until it is almost full. The pycnometer is then closed by using a capillary hole until the entire excess liquid waste samples spill out of the pycnometer. The weight of pycnometer from step 4, m_{filled} is then measured. Density is then calculated using the mass/volume relation. Figure 3.8 shows density determination by using pycnometer.

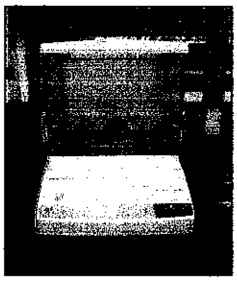

Figure 3.8: Density determination using pycnometer.

By using ρ=m/v where ρ = density, m = mass and v = volume, the density of the liquid can be determined. The density of the liquid waste sample 1 is determined as 0.802 g/mL or 802 kg/m^3. The density of the liquid waste sample 2 is determined as 0.770 g/mL or 770 kg/m^3.

Table 3.6: Density of the liquid waste Sample 1

	Volume (mL)	m_{empty} (g)	m_{filled} (g)	m_{liquid} (g)	Density (g/mL)
Sample 1 (orange in colour)	26.682	19.5267	40.9326	21.4059	0.8023

Table 3.7: Density of the liquid waste Sample 2

	Volume (mL)	m_{empty} (g)	m_{filled} (g)	m_{liquid} (g)	Density (g/mL)
Sample 2 (solid white in colour)	26.9180	19.8944	40.6237	20.7293	0.7700

3.2.4 Determining the Heat of Combustion

The heat of combustion of the liquid sample was measured using bomb calorimeter. The heat of combustion indicates the amount of heat released per unit mass or unit volume of a substance when the substance is completely burned. Figure 3.9 shows the picture of the bomb calorimeter.

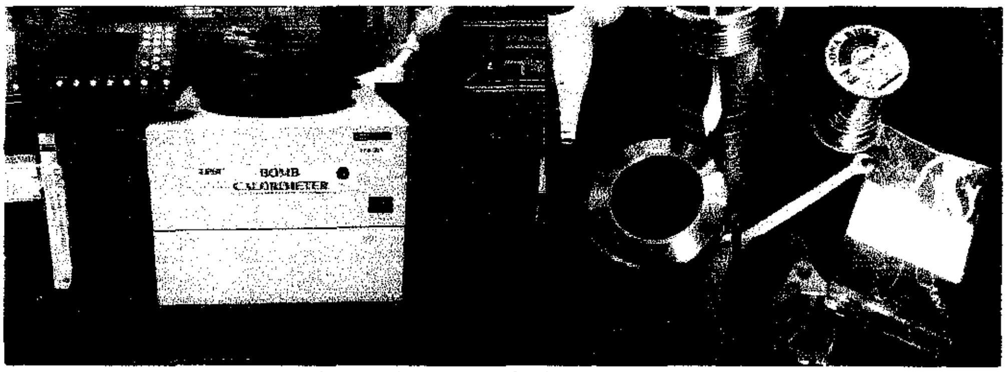

Figure 3.9: Bomb Calorimeter.

The mechanism of Bomb Calorimeter works is the ignition will go to the both of the verticals rods and with the reaction of the water, at first the heat will burn synthetic enamelleo copper wire. From there, cotton twist will be burn with heat combustion of 50 Joule/cotton twist. Lastly, this will lead to the burning of the samples after eight minutes of the burning process. Bomb Calorimeter is in adiabatic mode. The experiment has been done for two waste samples and the results are shown in Table 3.8, Table 3.9, Figure 3.10, Figure 3.11 and Figure 3.12.

Table 3.8: Mass and Heat of combustion for two waste samples

	Mass (g)	Heat of Combustion (J g^{-1})
Sample 1 (orange in colour)	0.4044	26,320
Sample 2 (solid white in colour)	0.3750	38,354

For sample 1, the main experiment starts at minute 7 with temperature of 22.6984 °C and having the venting process at temperature of 23.7001 °C at the minute of 17.

For sample 2, the main experiment starts at minute 8 with temperature of 22.7544 °C and having the venting process at temperature of 24.1031 °C at the minute of 17.

Table 3.9: Results of temperature versus time for two waste samples

Time (Minute)	Temperature (^oC)	
	Sample 1	Sample 2
0	0	0
1	22.6594	22.7449
2	22.6836	22.7487
3	22.6938	22.7545
4	22.6979	22.7564
5	22.6983	22.7558
6	22.699	22.7548
7	22.6984	22.7544
8	23.2468	23.5258
9	23.5454	23.8955
10	23.6392	24.0237
11	23.6742	24.0706
12	23.6907	24.0912
13	23.6968	24.1004
14	23.7002	24.103
15	23.7003	24.1039
16	23.7003	24.1034
17	23.7001	24.1031

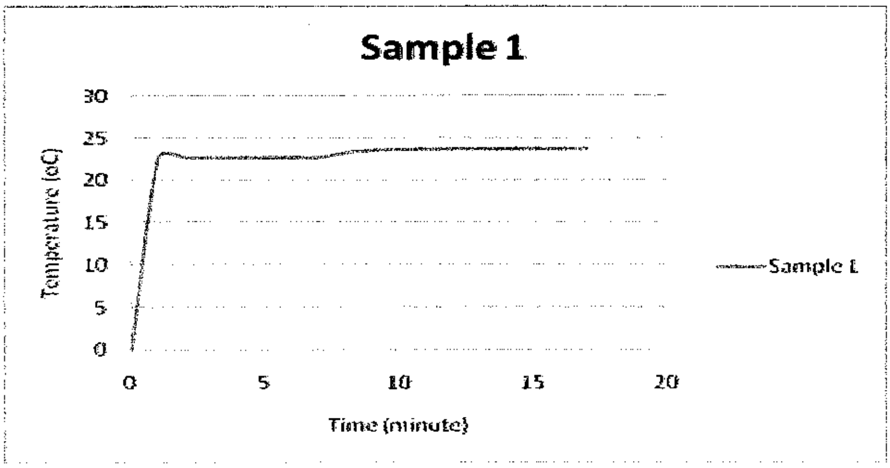

Figure 3.10: Reaction graph to get heat of combustion for sample 1.

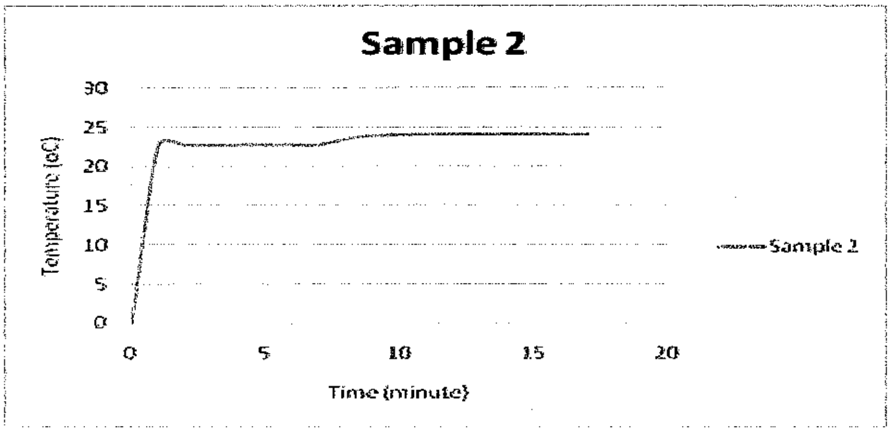

Figure 3.11: Reaction graph to get heat of combustion for sample 2.

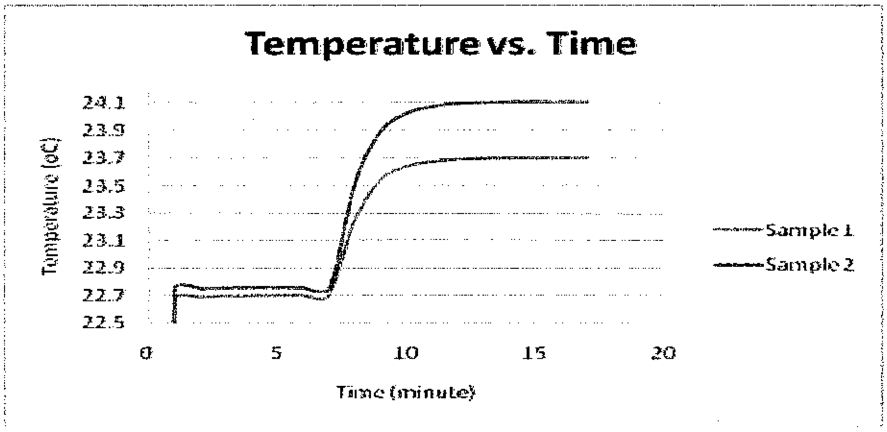

Figure 3.12: Graph focus on comparison for sample 1 and sample 2 graphs.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 GAS CHROMATOGRAPHIC ANALYSIS

The two samples were analyzed using GC. The GC analysis shows waste sample 1 having 17 components while waste sample 2 having 19 components which are already shown in Table 3.1 and Table 3.3. Both of the liquid waste samples contain high concentration of Diisopropyl ether which is the flammable material. These two samples are also containing majority of alkane group.

4.2 DISTILLATION PROCESS

The function of distillation process is to remove the water contain in both of the waste samples. The volume before distillation of waste sample 1 and waste sample 2 are 200 ml each. For waste sample 1, the volume left after distillation process is 95 ml which mean that the volume of water contains in the sample is 105 ml. The volume left after distillation process for waste sample 2 is 187 ml. This result gives that the volume of water contains in the sample is 13 ml. For the standard volume of 55 US gallons barrel which is 208 liters. After converting to the standard volume of 55 US gallons barrel, sample 1 contain 98.8 liter volume of flammable material and sample 2 contain 194.48 liter of flammable material.

4.3 DENSITY OF LIQUID SAMPLES

After subtracting the mass value of filling liquid contain in the flask with the mass of empty flask, this give the mass of the liquid. Density's result obtains after dividing the mass of the liquid waste sample with the volume of the flask used. Waste sample 1 is 0.80 g/ml and waste sample 2's density is 0.77 g/ml. After doing some conversion unit, the density of waste sample 1 is 802 kg/m^3 and waste sample 2's density is 770 kg/m^3.

4.4 HEAT OF COMBUSTION

The heat of combustion has been measured using Bomb Calorimeter. The results obtain show that heat of combustion for waste sample 1 is 26320 J/g and heat of combustion for waste sample 2 is 38354 J/g. After multiple the values obtain with their molecular weight value of each of the samples and also after doing some conversion unit, heat of combustion for waste sample 1 is 2755.18 MJ/m^3 and heat of combustion for waste sample 2 is 4569.49 MJ/m^3. These results are important in order to calculate the value of TNT mass and also to know the explosion efficiency.

4.5 EQUIVALENT MASS OF TNT

TNT equivalency is a simple method for equating a known energy of a combustible fuel to an equivalent mass of TNT. The approach is based on the assumption that an exploding fuel mass behaves like exploding TNT on an equivalent energy basis. The equivalent mass of TNT is estimated using equation (4).

$$m_{TNT} = \frac{\eta m \Delta H_c}{E_{TNT}} \qquad (4)$$

where

m_{TNT} is the equivalent mass of TNT (mass),

η is the empirical explosion efficiency (unitless),

m is the mass of hydrocarbon (mass),

ΔH_c is the energy of explosion of the flammable gas (energy/mass), and

E_{TNT} is the energy of explosion of TNT.

The typical value for the energy of explosion of TNT is 1120 cal/g = 4686 kJ/kg = 2016 Btu/lb. The heat of combustion for the flammable gas can be used in place of the energy of explosion for the combustible gas (Crowl and Louvar, 2002). From this equation, the TNT mass for waste sample 1 is 24.61 kg TNT and the value for TNT mass of waste sample 2 is 35.86 kg TNT. The mass of hydrocarbon, m is 219.09 kg which is the standard weight of 55 US gallons barrel.

4.6 IMPACT OF EXPLOSION

Results show that as distances increase, overpressures decrease. Overpressures give impact to death from lung hemorrhage, eardrum ruptures, structural damage and glass breakage. Using the probit equation where y is the probit variable from Crowl and Louvar (2002), death from lung hemorrhage is $y = -77.1 + 6.91\ln P$, eardrum ruptures is $y = -15.6 + 1.93\ln P$, structural damage is $y = -23.8 + 2.97\ln P$ and glass breakage is $y = -18.1 + 2.7\ln P$. After transformation the probit value to the percentage as show in Table 4.1, the conclusion can be made that for specific waste sample 1, there are no deaths at distance more than 10 meter from the source, zero percent of the exposed people suffer eardrum ruptures for the distance more than 35 meter, there will be no structural damages for the distances more than 50 meter and overpressure give high impact to glass breakage from 0 meter distance to 100 meter from the source but there is less than 100% percent of the impact on glass breakage for the distance more than 35 meter.

Table 4.1: Transformation of Probits to Percentages

%	0	1	2	3	4	5	6	7	8	9
0		2.67	2.95	3.12	3.25	3.36	3.45	3.52	3.59	3.66
10	3.72	3.77	3.82	3.87	3.92	3.96	4.01	4.05	4.08	4.12
20	4.16	4.19	4.23	4.26	4.29	4.33	4.36	4.39	4.42	4.45
30	4.48	4.5	4.53	4.56	4.59	4.61	4.64	4.67	4.69	4.72
40	4.75	4.77	4.8	4.82	4.85	4.87	4.9	4.92	4.95	4.97
50	5	5.03	5.05	5.08	5.1	5.13	5.15	5.18	5.2	5.23
60	5.25	5.28	5.31	5.33	5.36	5.39	5.41	5.44	5.47	5.5
70	5.52	5.55	5.58	5.61	5.64	5.67	5.71	5.74	5.77	5.81
80	5.84	5.88	5.92	5.95	5.99	6.04	6.08	6.13	6.18	6.23
90	6.28	6.34	6.41	6.48	6.55	6.64	6.75	6.88	7.05	7.33
%	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
99	7.33	7.37	7.41	7.46	7.51	7.58	7.65	7.75	7.88	8.09

The distance to a given overpressure is calculated from the equation (Ozog, 1996):

$$r = 0.3967 \times m_{TNT}^{1/3} \exp\left[3.5031 - 0.7241 \ln(p_o) + 0.0398(\ln p_o)^2\right] \quad (5)$$

where:

r is the distance (m) and

p_o is the peak overpressure (Psi).

z is the scaled distance (m/kg) given as (Baker *et. al.*, 1983):

$$z = \frac{r}{(m_{TNT})^{1/3}} \quad (6)$$

$$\frac{p_o}{p_a} = \frac{1616\left[1 + \left(\frac{z_e}{4.5}\right)^2\right]}{\sqrt{1 + \left(\frac{z_e}{0.048}\right)^2}\sqrt{1 + \left(\frac{z_e}{0.32}\right)^2}\sqrt{1 + \left(\frac{z_e}{1.35}\right)^2}} \quad (7)$$

p_s is the scaled overpressure (unitless)

p_o is the peak side-on overpressure, and

p_a is the ambient pressure

Table 4.2: Impact of overpressure of sample 1

Distance, (m)	Overpressure, (kPa)	Percentage of Deaths from lung hemorrhage, %	Percentage of Eardrum ruptures, %	Percentage of Structural damage, %	Percentage of Glass breakage, %
0.5	20905.85	100	100	100	100
1.0	8464.08	100	100	100	100
1.5	4641.18	100	100	100	100
2.0	2840.06	100	100	100	100
2.5	1853.40	100	100	100	100
3.0	1270.57	100	100	100	100
3.5	907.74	100	100	100	100
4.0	671.97	100	100	100	100
4.5	512.99	100	100	100	100
5.0	402.23	100	100	100	100
5.5	322.82	100	100	100	100
6.0	264.40	100	100	100	100
6.5	220.43	99.82	100	100	100
7.0	186.65	96.15	99.75	100	100
7.5	160.23	76.00	99.43	100	100
8.0	139.23	39.67	98.75	100	100
8.5	122.28	12.40	97.77	100	100
9.0	108.42	2.35	96.23	100	100
9.5	96.94	0	94.10	100	100
10.0	87.35	0	91.29	100	100
10.5	79.24	0	87.80	100	100
11.0	73.32	0	84.00	100	100
11.5	66.37	0	79.75	100	100
12.0	61.22	0	75.00	100	100
12.5	56.72	0	70.75	100	100
13.0	52.77	0	65.00	100	100
13.5	49.28	0	60.00	100	100
14.0	46.18	0	55.00	100	100
14.5	43.41	0	50.50	99.82	100
15.0	40.93	0	46.00	99.69	100
15.5	38.69	0	41.75	99.49	100
16.0	36.66	0	37.50	99.20	100
16.5	34.82	0	33.75	98.75	100
17.0	33.14	0	30.50	98.21	100
17.5	31.61	0	27.50	97.59	100
18.0	30.20	0	24.50	96.70	100
18.5	28.90	0	21.75	95.55	100
19.0	27.71	0	19.50	94.40	100

Distance, (m)	Overpressure, (kPa)	Percentage of Deaths from lung hemorrhage, %	Percentage of Eardrum ruptures, %	Percentage of Structural damage, %	Percentage of Glass breakage, %
19.5	26.60	0	17.50	92.71	100
20.0	25.57	0	15.80	91.00	100
25.0	18.33	0	0.51	64.00	100
30.0	14.19	0	0.16	34.50	100
35.0	11.55	0	0	15.60	99.86
40.0	9.71	0	0	0.62	99.41
45.0	8.36	0	0	0.24	98.14
50.0	7.33	0	0	0	95.73
55.0	6.51	0	0	0	91.71
60.0	5.84	0	0	0	86.60
65.0	5.27	0	0	0	79.67
70.0	4.79	0	0	0	71.33
75.0	4.38	0	0	0	62.00
80.0	4.01	0	0	0	51.50
85.0	3.69	0	0	0	43.67
90.0	3.41	0	0	0	33.33
95.0	3.16	0	0	0	27.00
100.0	2.93	0	0	0	21.25

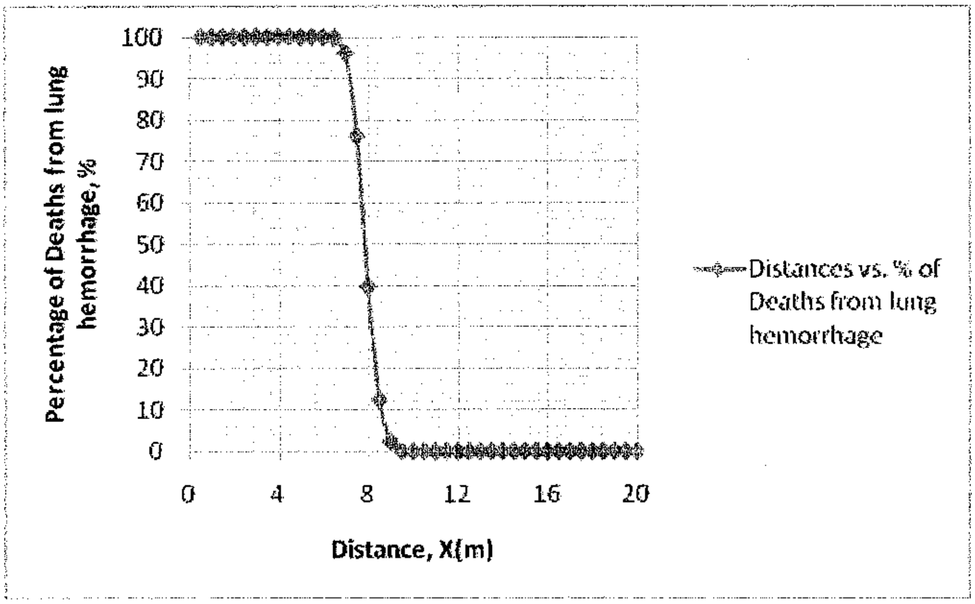

Figure 4.1: Distances vs. the percentages of death from lung hemorrhage for sample 1.

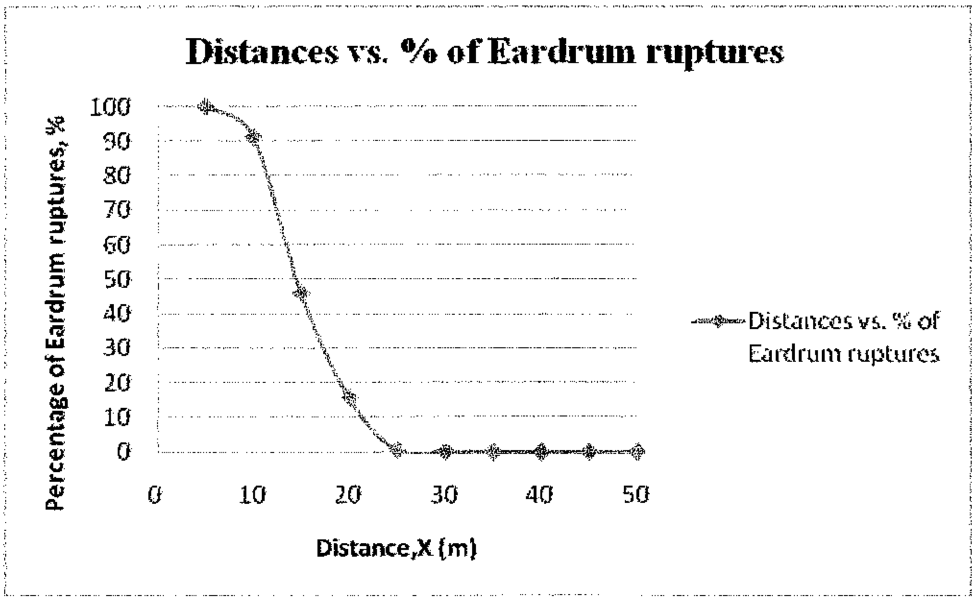

Figure 4.2: Distances vs. the percentages of eardrum ruptures for sample 1.

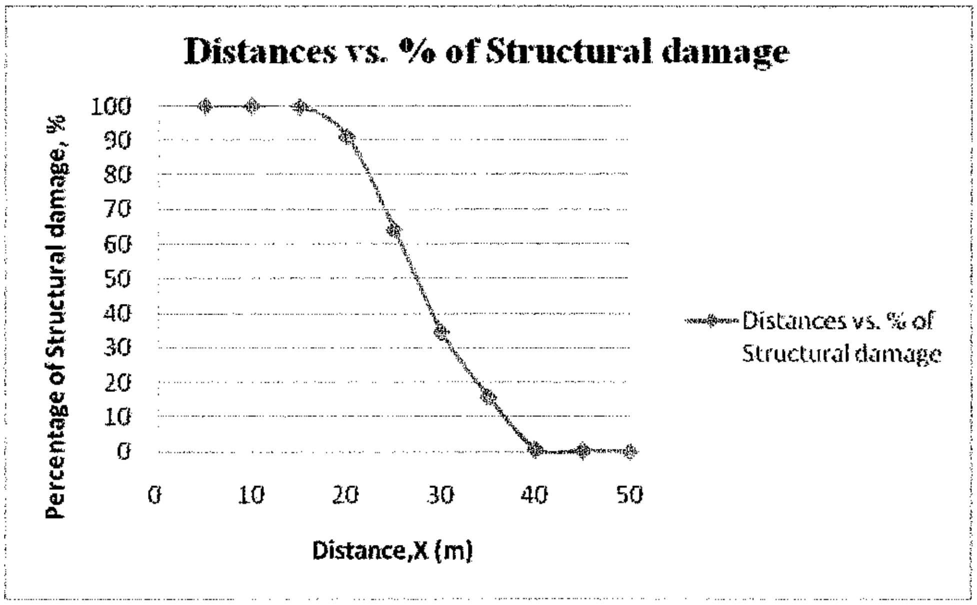

Figure 4.3: Distances vs. the percentages of structural damage for sample 1.

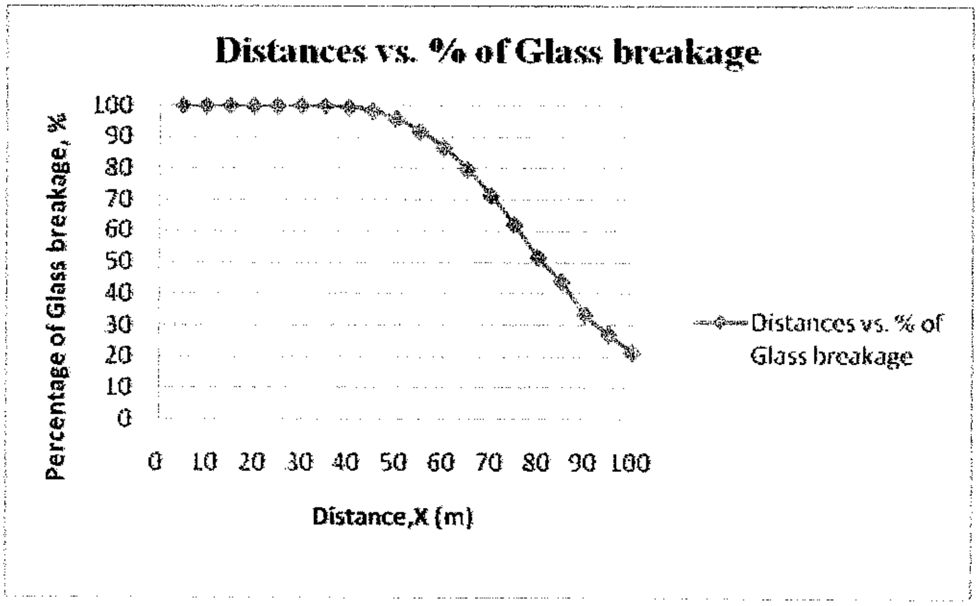

Figure 4.4: Distances vs. the percentages of glass breakage for sample 1.

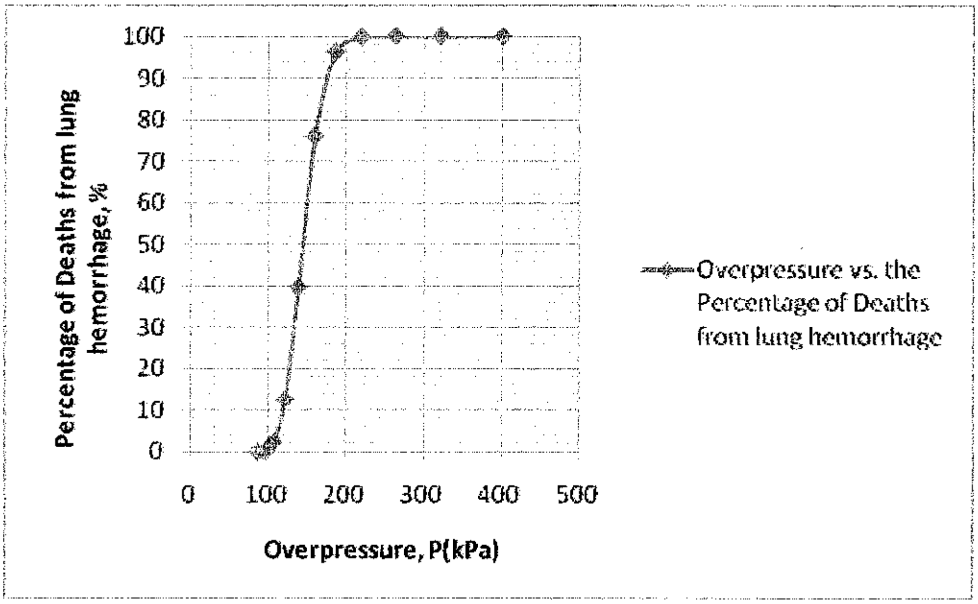

Figure 4.5: Overpressure vs. the percentage of deaths from lung hemorrhage for sample 1.

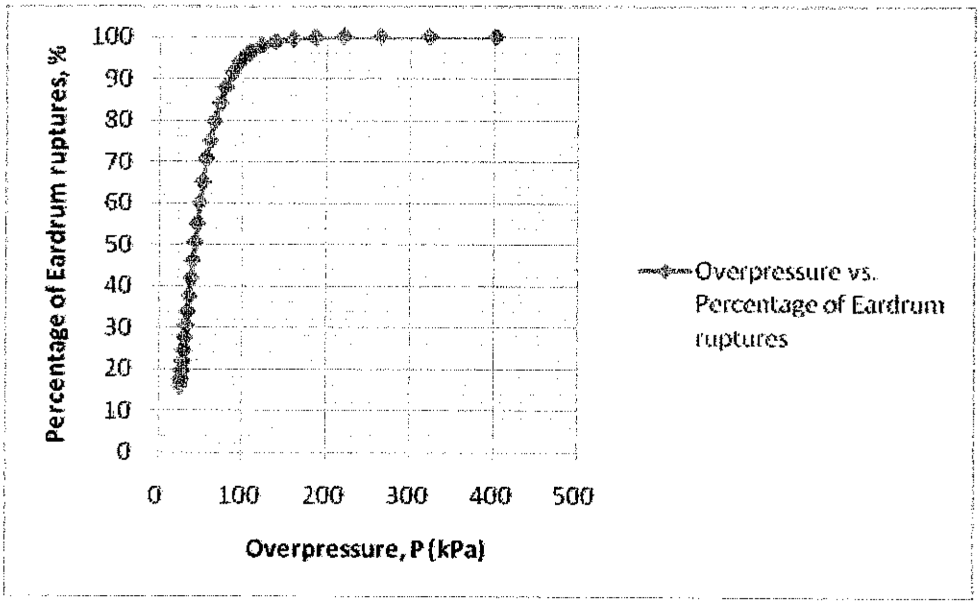

Figure 4.6: Overpressure vs. the percentage of eardrum ruptures for sample 1.

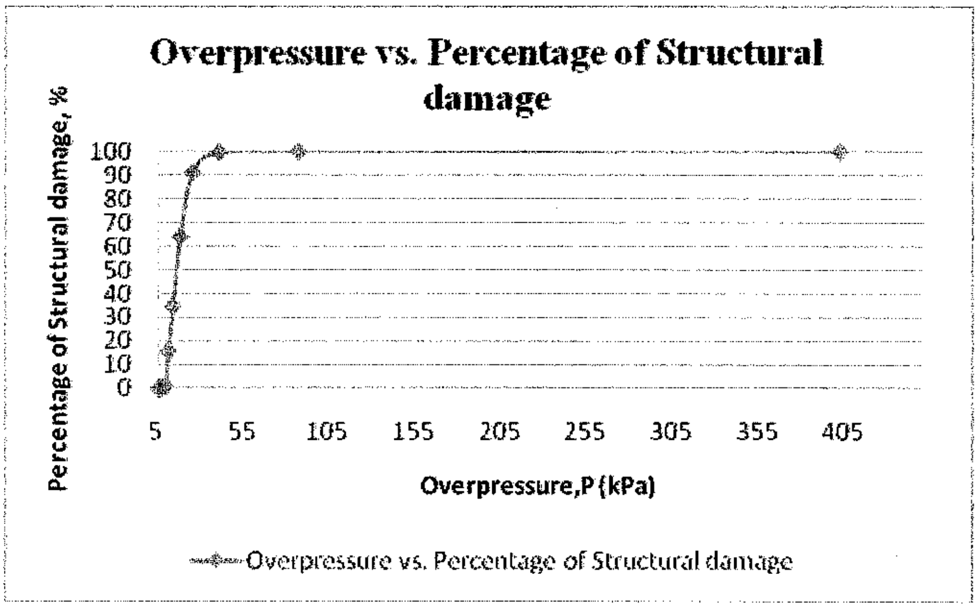

Figure 4.7: Overpressure vs. the percentage of structural damage for sample 1.

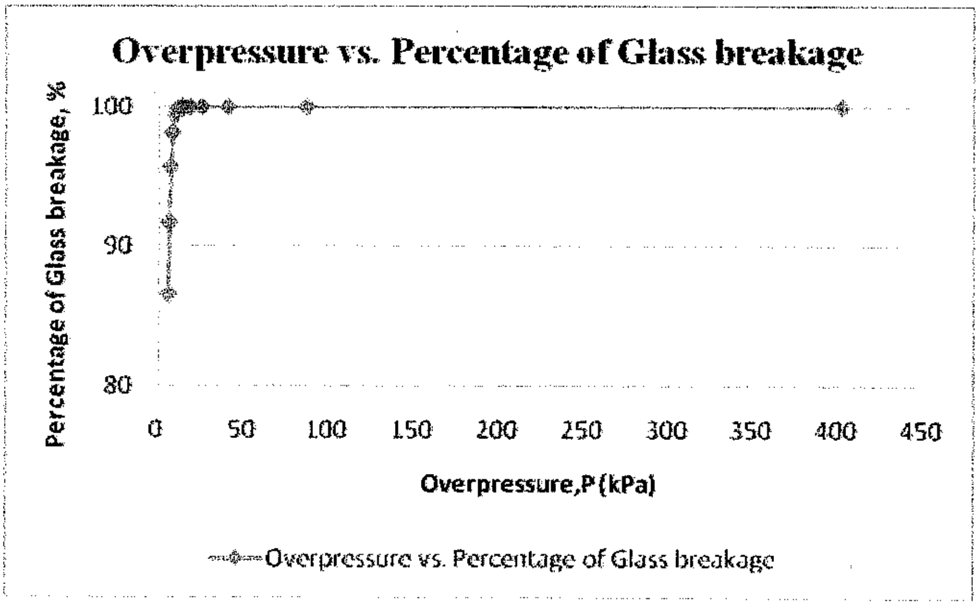

Figure 4.8: Overpressure vs. the percentage of glass breakage for sample 1.

After transformation the probit value to the percentage as show in Table 4.1, for specific waste sample 2, there are no deaths at distance more than 15 meter from the source, 0% of the exposed people suffer eardrum ruptures for the distance more than 40 meter, there will be no structural damages for the distances more than 60 meter and overpressure give a lot of impact to glass breakage from 0 meter distance to 100 meter but there is less than 100% of the impact on glass breakage for the distance more than 40 meter.

Table 4.3: Impact of overpressure of sample 2

Distance, (m)	Overpressure, (kPa)	Percentage of Deaths from lung hemorrhage, %	Percentage of Eardrum ruptures, %	Percentage of Structural damage, %	Percentage of Glass breakage, %
0.5	24334.49	100	100	100	100
1.0	10049.4	100	100	100	100
1.5	5643.69	100	100	100	100
2.0	3546.67	100	100	100	100
2.5	2368.1	100	100	100	100
3.0	1652.01	100	100	100	100
3.5	1194.89	100	100	100	100
4.0	891.68	100	100	100	100
4.5	683.89	100	100	100	100
5.0	537.34	100	100	100	100
5.5	431.3	100	100	100	100
6.0	352.78	100	100	100	100
6.5	293.41	100	100	100	100
7.0	247.68	100	100	100	100
7.5	211.85	99.58	99.89	100	100
8.0	183.35	95	99.73	100	100
8.5	160.36	76.5	99.44	100	100
9.0	141.57	44.5	98.86	100	100
9.5	126.05	17.5	98.07	100	100
10.0	113.09	4.7	96.85	100	100
10.5	102.15	0	95.18	100	100
11.0	92.86	0	93	100	100
11.5	84.88	0	90.45	100	100
12.0	77.99	0	87.42	100	100
12.5	71.99	0	83.8	100	100
13.0	66.74	0	80	100	100
13.5	62.12	0	75.8	100	100
14.0	58.02	0	71.75	100	100

Distance, (m)	Overpressure, (kPa)	Percentage of Deaths from lung hemorrhage, %	Percentage of Eardrum ruptures, %	Percentage of Structural damage, %	Percentage of Glass breakage, %
14.5	54.37	0	67	100	100
15.0	51.11	0	62.5	100	100
15.5	48.18	0	58.5	100	100
16.0	45.53	0	54	99.89	100
16.5	43.13	0	50	99.81	100
17.0	40.95	0	46	99.69	100
17.5	38.96	0	42	99.52	100
18.0	37.14	0	38.75	99.28	100
18.5	35.47	0	35.4	98.96	100
19.0	33.93	0	32	98.46	100
19.5	32.51	0	29	98.04	100
20.0	31.2	0	26.33	97.35	100
25	22.03	0	9.67	81.50	100
30	16.90	0	3.54	54.33	100
35	13.65	0	1.36	30.00	100
40	11.42	0	0	14.43	99.84
45	9.81	0	0	6.57	99.44
50	8.58	0	0	2.82	98.39
55	7.61	0	0	1.21	96.54
60	6.83	0	0	0	93.71
65	6.18	0	0	0	89.60
70	5.63	0	0	0	84.40
75	5.16	0	0	0	77.67
80	4.74	0	0	0	70.00
85	4.38	0	0	0	62.00
90	4.06	0	0	0	53.50
95	3.77	0	0	0	45.67
100	3.51	0	0	0	37.50

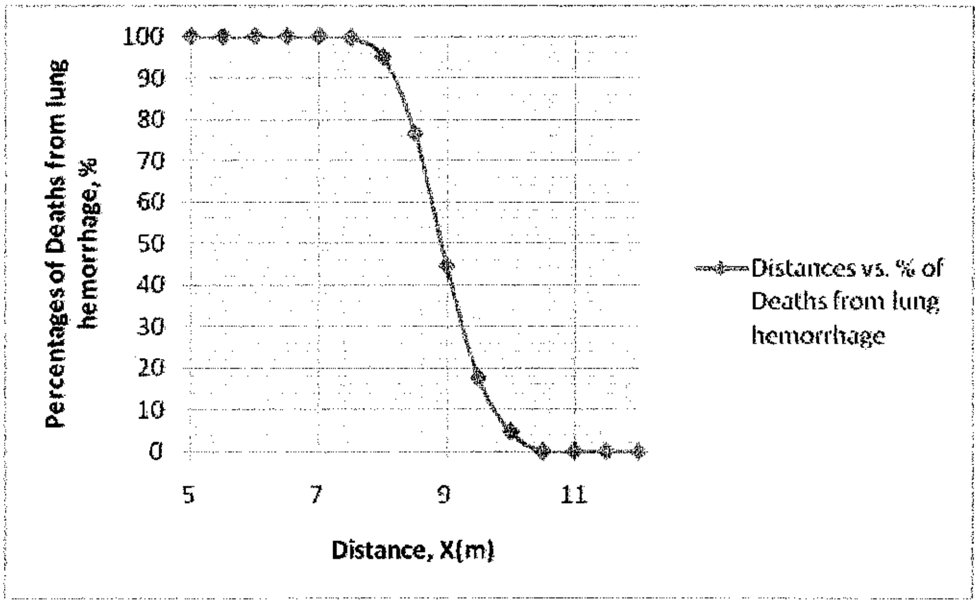

Figure 4.9: Distances vs. the percentages of death from lung hemorrhage for sample 2.

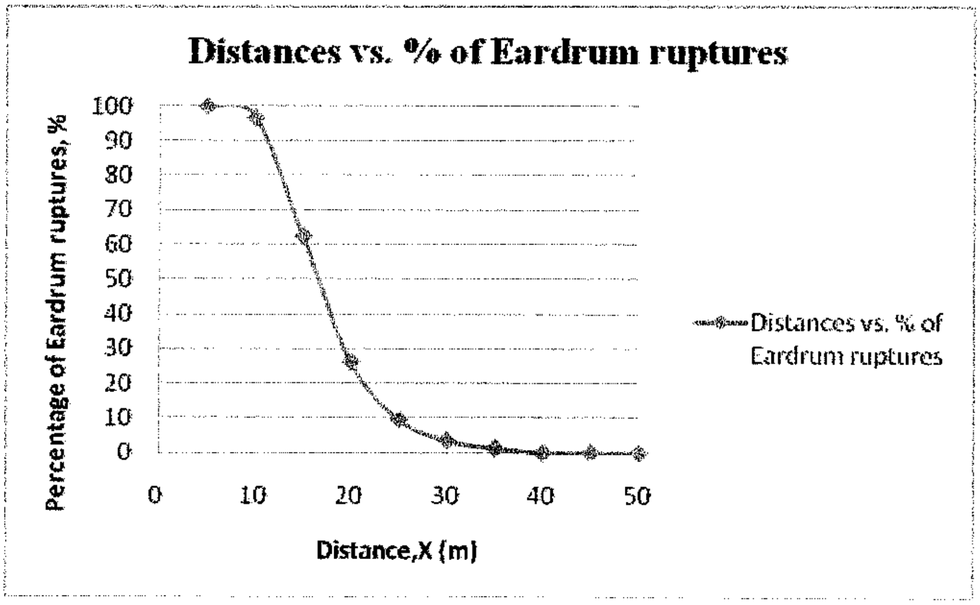

Figure 4.10: Distances vs. the percentages of eardrum ruptures for sample 2.

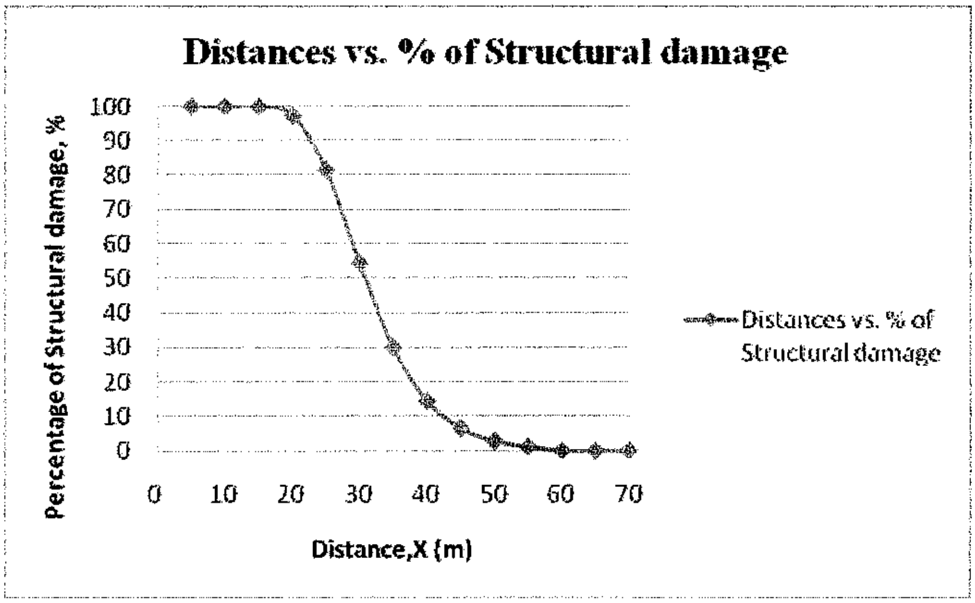

Figure 4.11: Distances vs. the percentages of structural damage for sample 2.

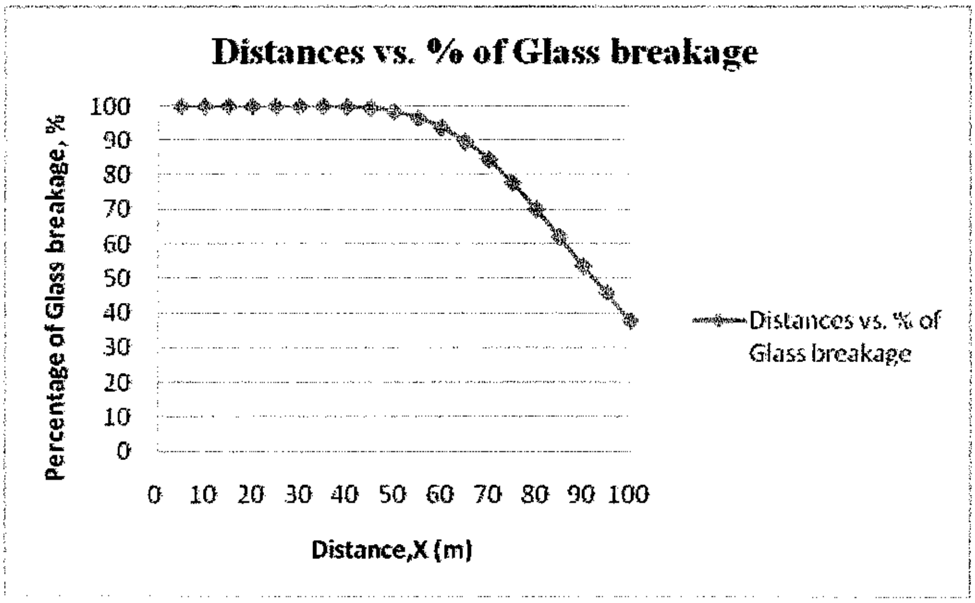

Figure 4.12: Distances vs. the percentages of glass breakage for sample 2.

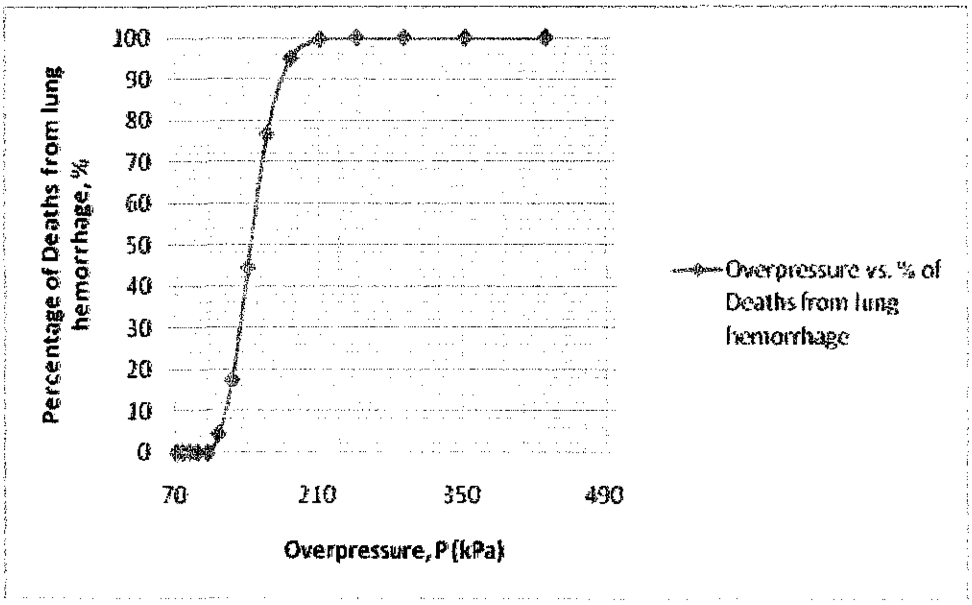

Figure 4.13: Overpressure vs. the percentage of deaths from lung hemorrhage for sample 2.

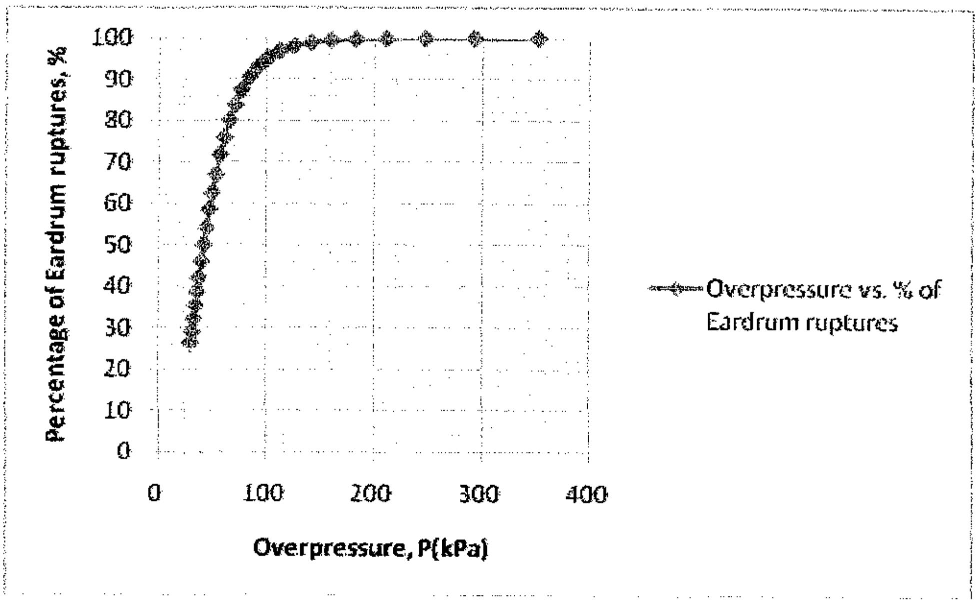

Figure 4.14: Overpressure vs. the percentage of eardrum ruptures for sample 2.

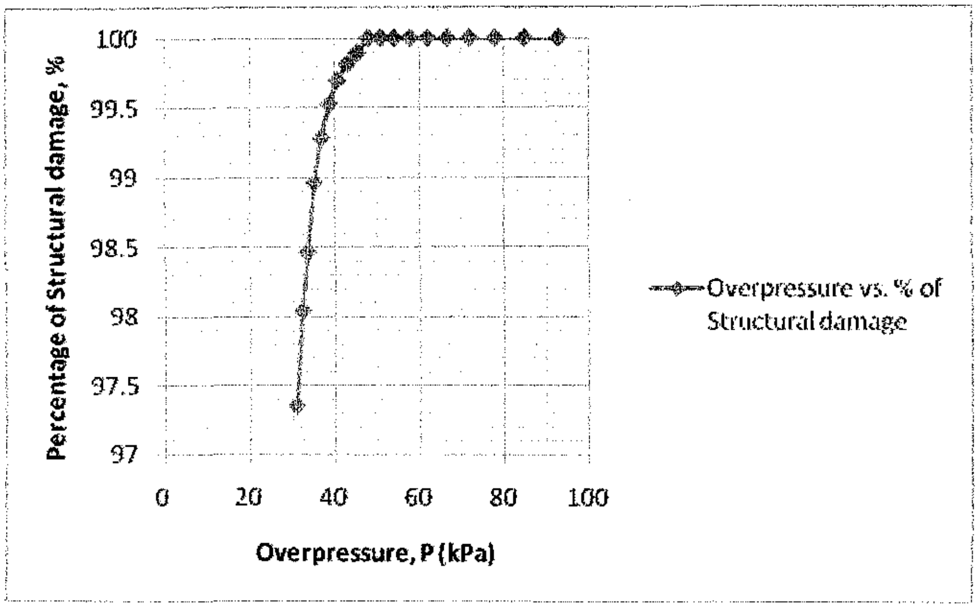

Figure 4.15: Overpressure vs. the percentage of structural damage for sample 2.

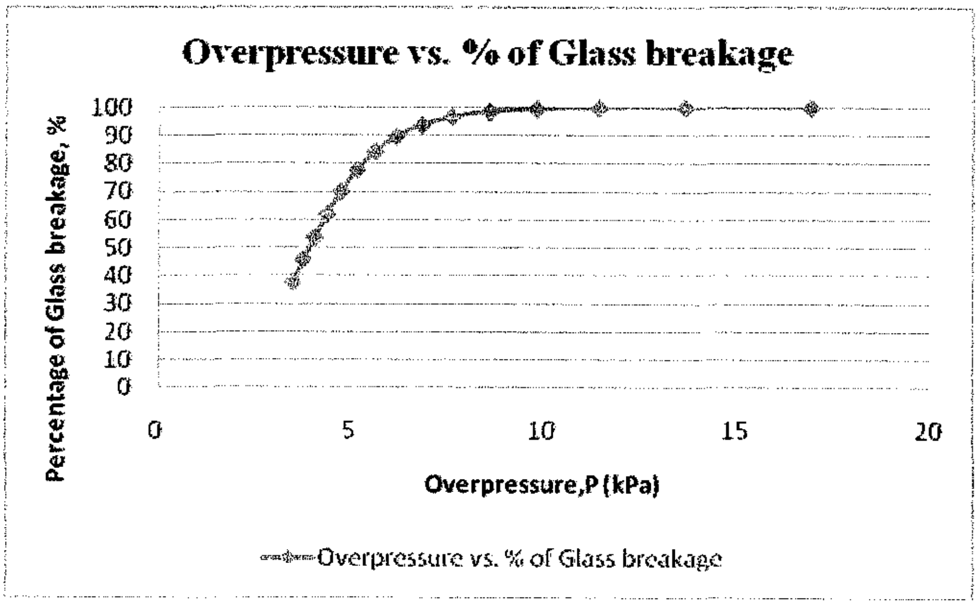

Figure 4.16: Overpressure vs. the percentage of glass breakage for sample 2.

4.7 IMPACT OF BLEVE

BLEVE can give a risk of heat radiation which is generated from the fireball. In order to characterize the radiation from fireballs, it is necessary to define the size and dynamics of fireball.

The radiation received by a target (for the duration of the BLEVE incident) is given by Roberts, (1982):

$$Q_R = \tau E F_{21} \qquad \textbf{(8)}$$

where:

Q_R is radiation received by a target (kW/m^2),

τ is the atmospheric transmissivity (dimensionless),

E is surface emitted flux (kW/m^2) and

F_{21} is view factor (dimensionless).

Recommend a correlation formula that accounted for humidity is given by Pietersen and Huerta, (1984) :

$$\tau = 2.02(P_w l)^{-0.09} \qquad (9)$$

where:

P_w is water partial pressure (N/m^2), and

l is bath length (m).

The path length and distance from the flam surface to the target is (CCPS, 1994):

$$l = \left[H_{BLEVE}^2 + r^2\right]^{0.5} - \left[0.5D_{\max}\right] \qquad (10)$$

Thermal radiation is usually calculated using surface emitted flux, E,(CCPS, 1994):

$$E = \frac{F_{rad} m \Delta H_c}{\pi (D_{\max})^2 t_{BELVE}} \qquad (11)$$

where F_{rad} is the radiation fraction (dimensionless).

The radiation fraction, F_{rad} as given by Roberts, (1982) is equal to (0.25-0.4)

For sample 1 that contains 26320 kJ/kg heat of combustion, the initial flammable mass taken is 35000 kg and water partial pressure in air is 2810 Pascal. It has radiation fraction of 0.3 and having a distance of 100m from fireball center on ground. From the BLEVE thermal flux calculation, the results show that the maximum fireball diameter is 189.7 meter. The fireball combustion duration is 14.9 seconds and the center height of fireball is 142.3 meter. The value for initial ground level hemisphere diameter is 246.6 meter with the surface emitted flux is 164.4 kW/m^2. With the maximum value of fireball diameter, it affects the 79.1 path length and having transmissivity of 0.667.The horizontal view factor is 0.24 while vertical view factor is 0.17. The value of received flux for horizontal is 26.70 kW/m^2 while vertical is 18.76 kW/m^2.

The mass of both samples are following to the standard volume of 55 US Gallons barrel which having weight of 219.09 kg.

Table 4.4: Mass of fuel, maximum fireball diameter and fireball duration for sample 1

Mass (kg)	Maximum fireball diameter(m)	Fireball combustion duration(s)
35000	189.7	14.9
40000	198.4	15.2
45000	206.3	15.5
50000	213.7	15.8
55000	220.6	16.0

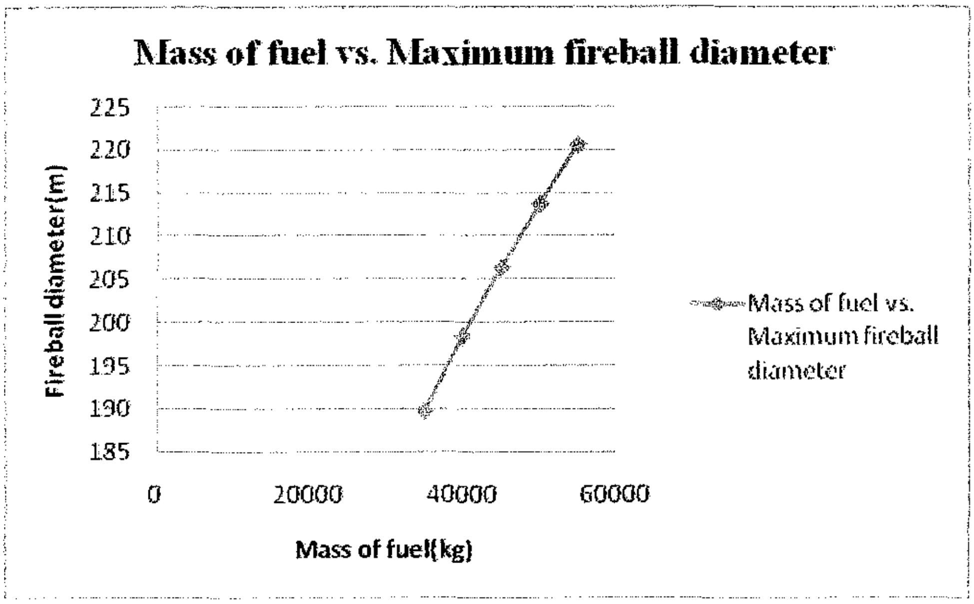

Figure 4.17: Mass of fuel vs. the maximum fireball diameter for sample 1.

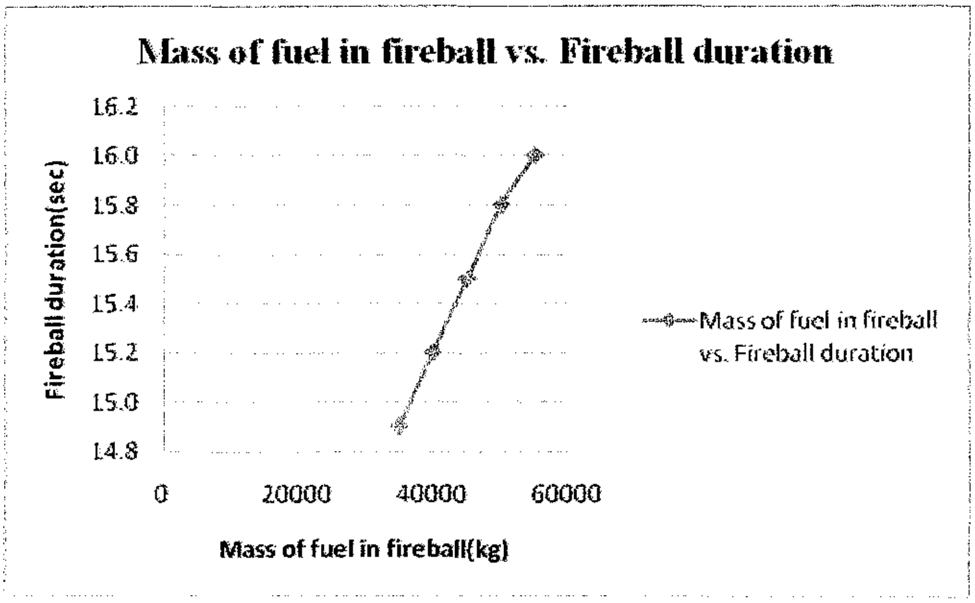

Figure 4.18: Mass of fuel in fireball vs. the fireball duration for sample 1.

For sample 2 that contain 38354 kJ/kg heat of combustion, with the same value of consideration for the initial flammable mass which is 30000 kg and water partial pressure in air which is 2810 pascals. It has radiation fraction of 0.3 and having a distance of 100m from fireball center on ground. From the BLEVE thermal flux calculation, it gives the same results for the maximum fireball diameter which is 189.7

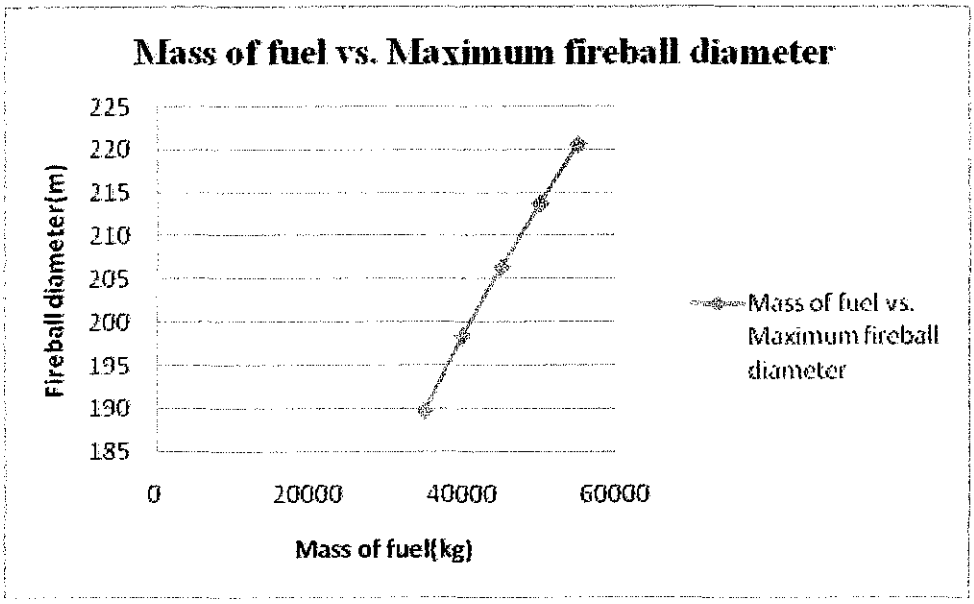

Figure 4.17: Mass of fuel vs. the maximum fireball diameter for sample 1.

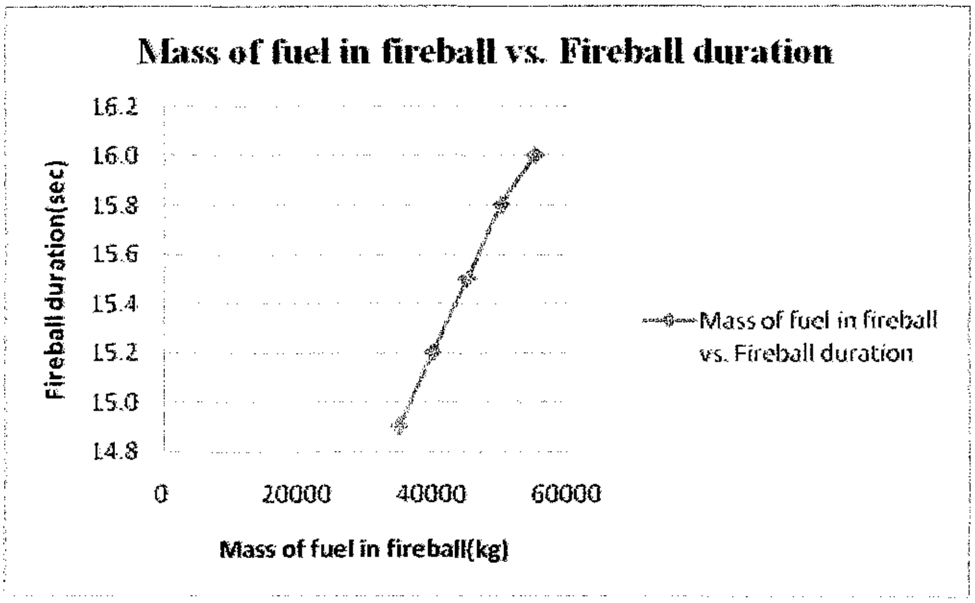

Figure 4.18: Mass of fuel in fireball vs. the fireball duration for sample 1.

For sample 2 that contain 38354 kJ/kg heat of combustion, with the same value of consideration for the initial flammable mass which is 30000 kg and water partial pressure in air which is 2810 pascals. It has radiation fraction of 0.3 and having a distance of 100m from fireball center on ground. From the BLEVE thermal flux calculation, it gives the same results for the maximum fireball diameter which is 189.7

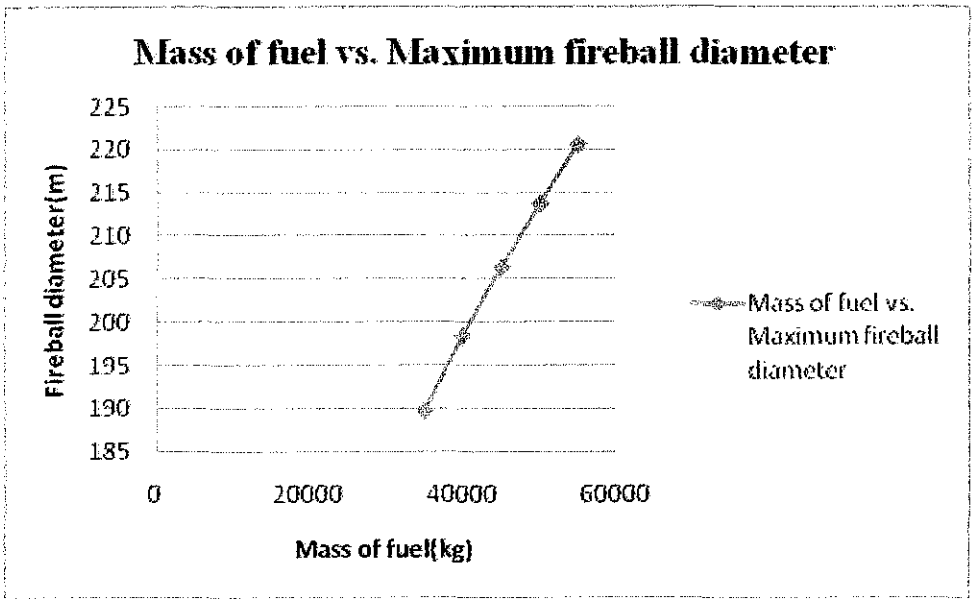

Figure 4.17: Mass of fuel vs. the maximum fireball diameter for sample 1.

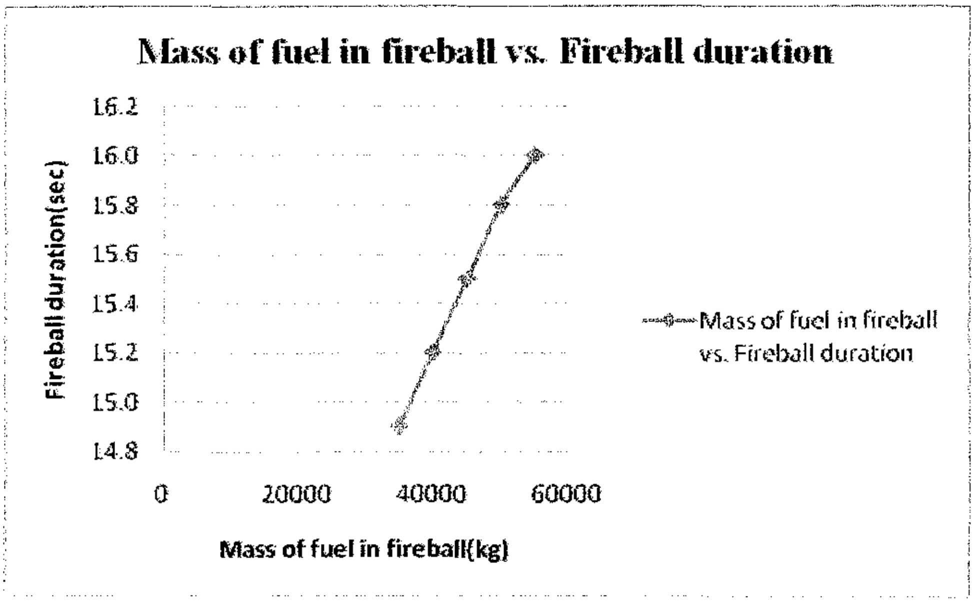

Figure 4.18: Mass of fuel in fireball vs. the fireball duration for sample 1.

For sample 2 that contain 38354 kJ/kg heat of combustion, with the same value of consideration for the initial flammable mass which is 30000 kg and water partial pressure in air which is 2810 pascals. It has radiation fraction of 0.3 and having a distance of 100m from fireball center on ground. From the BLEVE thermal flux calculation, it gives the same results for the maximum fireball diameter which is 189.7

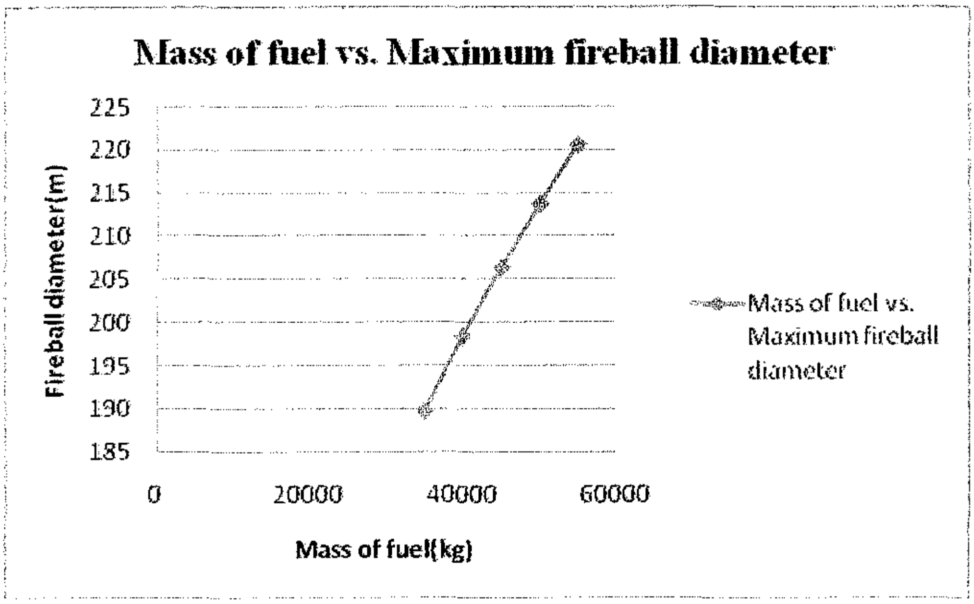

Figure 4.17: Mass of fuel vs. the maximum fireball diameter for sample 1.

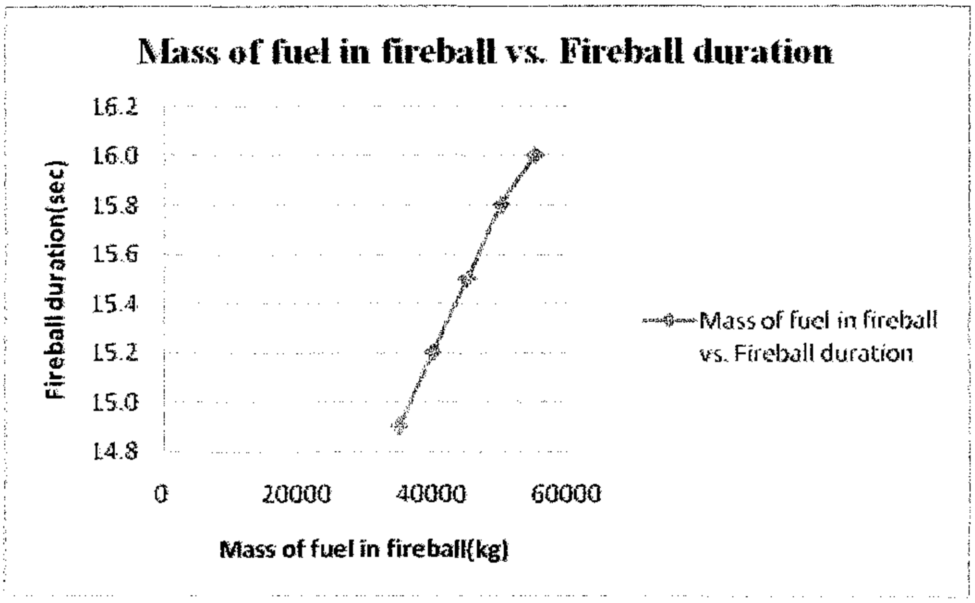

Figure 4.18: Mass of fuel in fireball vs. the fireball duration for sample 1.

For sample 2 that contain 38354 kJ/kg heat of combustion, with the same value of consideration for the initial flammable mass which is 30000 kg and water partial pressure in air which is 2810 pascals. It has radiation fraction of 0.3 and having a distance of 100m from fireball center on ground. From the BLEVE thermal flux calculation, it gives the same results for the maximum fireball diameter which is 189.7

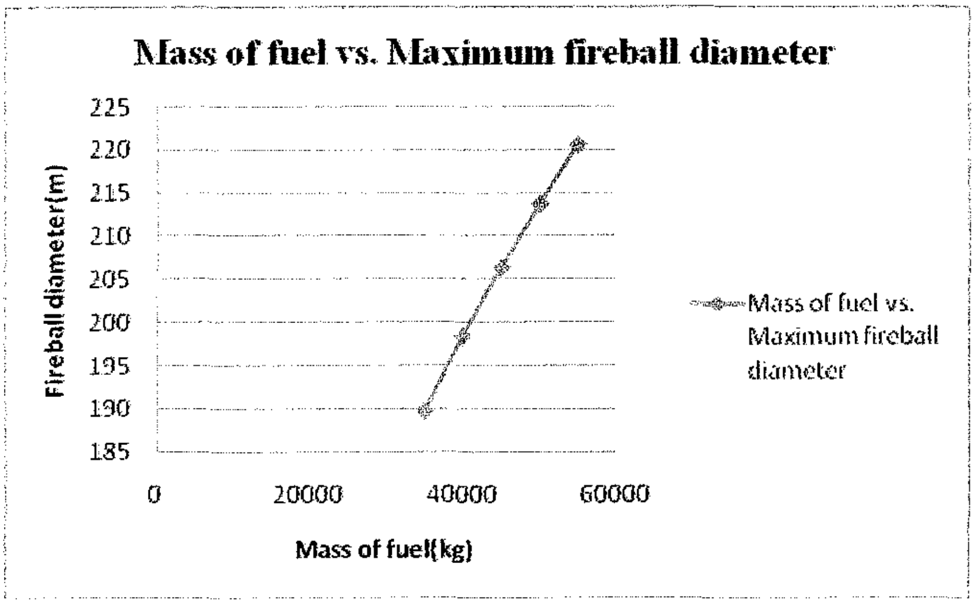

Figure 4.17: Mass of fuel vs. the maximum fireball diameter for sample 1.

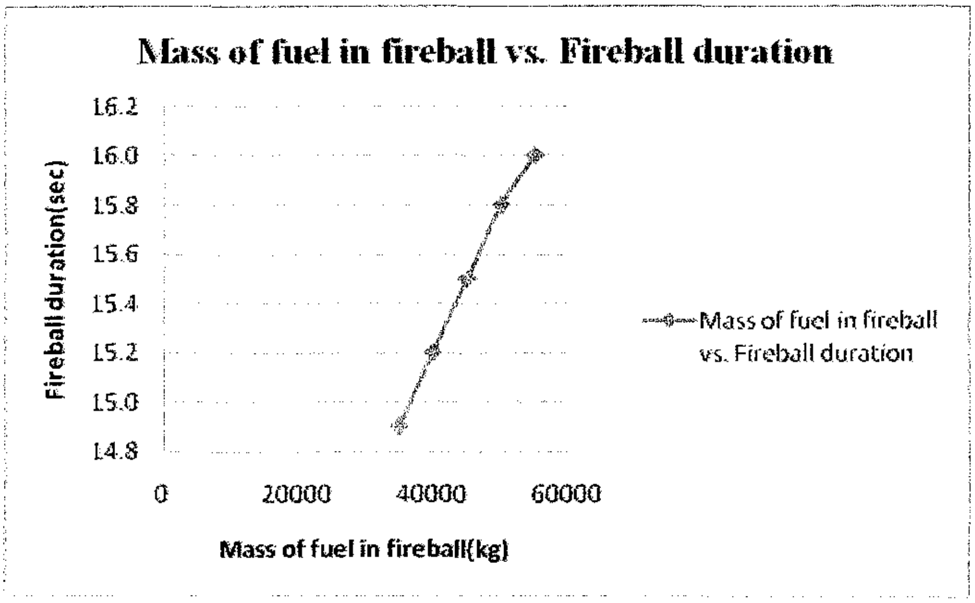

Figure 4.18: Mass of fuel in fireball vs. the fireball duration for sample 1.

For sample 2 that contain 38354 kJ/kg heat of combustion, with the same value of consideration for the initial flammable mass which is 30000 kg and water partial pressure in air which is 2810 pascals. It has radiation fraction of 0.3 and having a distance of 100m from fireball center on ground. From the BLEVE thermal flux calculation, it gives the same results for the maximum fireball diameter which is 189.7

Table 4.7: Area of pool and evaporation rate for sample 2

Area of pool(m2)	Evaporation rate(kg/s)
0.10	0.00010
0.26	0.00027
0.30	0.00031
0.40	0.00042
0.50	0.00052

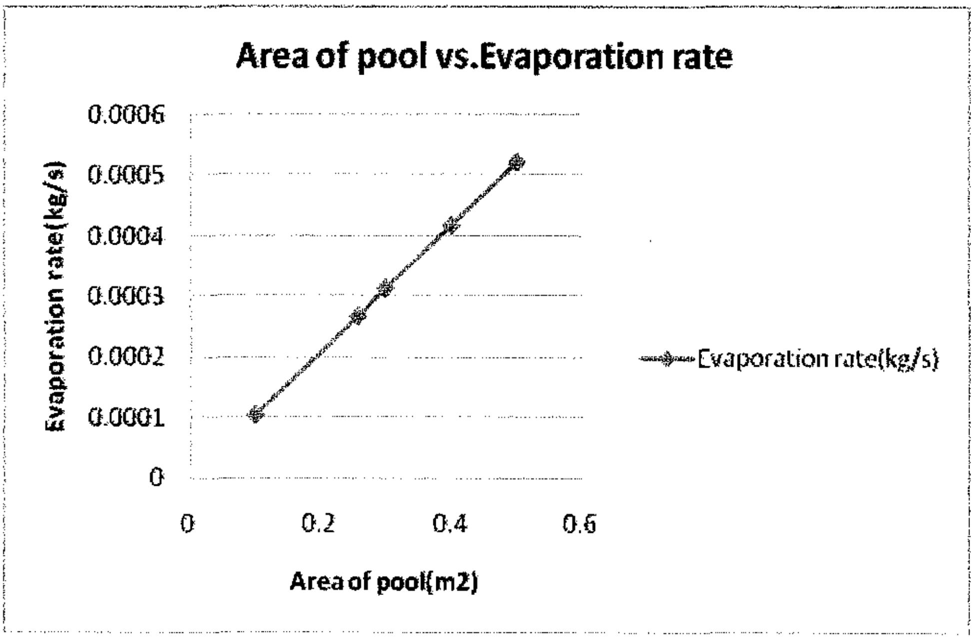

Figure 4.22: Area of pool vs. the evaporation rate for sample 2.

Sample 2 is having 119.14 molecular weight of liquid. For the area of pool of 0.257 m^2, the ambient temperature of 298 K and at saturation vapor pressure is 36.71 mmHg, the calculated results obtain for mass transfer coefficient is 0.004421 m/s and the evaporation rate is 0.000267 kg/s.

The characteristics of a pool fire depend on the pool diameter. The evaporation rate increases with increasing the area of pool.

4.9 FLAMMABILITY DIAGRAM

It is assume that the vapor is an ideal gas mixture. An analogous situation is arrived at for a system at constant pressure. Raoult's law by Francois-Marie Roult, (1882) states that the partial pressures must always sum to this total pressure:

$$P = p_1 + p_2 = y_1P + y_2P = x_1P^o{}_1 + x_2P^o{}_2 \tag{16}$$

Value of $P^o{}_1$ and $P^o{}_2$ is can be getting from equation (17) and (18):

$$\ln P^o{}_1 = A_1 - B_1/(T' + C_1) \tag{17}$$

$$\ln P^o{}_2 = A_2 - B_2/(T' + C_2) \tag{18}$$

where the value of coefficient A_1, A_2, B_1, B_2, C_1, and C_2 can be getting inside the Handbook of Vapor Pressure : Antoine Coefficient, (2007).

The stoichiometric concentration for most organic compound is determined using the general combustion reaction:

$$C_mH_xO_y + zCO_2 + x/2H_2O \tag{19}$$

For estimating flammability limits:

$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1} \tag{20}$$

$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1} \tag{21}$$

The limiting oxygen concentration (LOC) is estimated using the stoichiometry of the combustion reaction and the LFL.

$$LOC = z(LFL) \tag{22}$$

The stoichiometric line represents all stoichiometric combinations of fuel plus oxygen. The intersection of the stoichiometric line with the oxygen axis (in volume % oxygen) is given by:

$$100\left(\frac{z}{1+z}\right) \tag{23}$$

Table 4.8: LFL, UFL and LOC of components presences in waste sample 1

PKNO	NAME	Formula	AREA	Fraction,xi	VAPOR PRESSURE @ 25OC (mmHg)	xi*Poi	yi=xi*Pisat/Pt	LFLi	yi/LFLi	UFLi	yi/UFLi	z	LOC	100(z/(1+z))
1	water	H_2O	13540849	0.0122	24.5	0.2989	0.0097							
2	Diisopropyl ether	$C_6H_{14}O$	170582857	0.1537	152	23.3584	0.7611	1.2546	0.6066	7.9836	0.0953	9.5	11.9183	90.4762
3	2-Propanol, 1-methoxy-	$C_4H_{10}O_2$	857940	0.0008	8.15	0.0063	0.0002							
4	Toluene	C_7H_8	1662168	0.0015	27.7	0.0415	0.0014	1.2546	0.0011	7.9836	0.0002	9.0	11.2911	90.0000
5	Cyclohexane, ethyl-(CAS) Ethylcyclohexane	C_8H_{16}	1144916	0.0010	12.4	0.0128	0.0004							
6	Ethylbenzene	C_8H_{10}	384232374	0.3461	9.21	3.1880	0.1039	1.0789	0.0963	6.8654	0.0151	10.5	11.3280	91.3043
7	Benzene, 1,4-dimethyl-(CAS) p-Xylene	C_8H_{10}	378445611	0.3409	7.94	2.7070	0.0882	1.0789	0.0818	6.8654	0.0128	10.5	11.3280	91.3043
8	Octane, 2-methyl-	C_9H_{20}	1326642	0.0012	6.73	0.0080	0.0003							
9	Octane, 3-methyl-	C_9H_{20}	568961	0.0005	6.69	0.0034	0.0001							
10	p-Xylene	C_8H_{10}	144507416	0.1302	7.94	1.0337	0.0337	1.0789	0.0312	6.8654	0.0049	10.5	11.3280	91.3043
11	Ethanol, 2-butoxy-	$C_6H_{14}O_2$	1910311	0.0017	0.552	0.0009	0.0000							
12	Nonane	C_9H_{20}	857529	0.0008	4.63	0.0036	0.0001							
13	Benzene, (1-methylethyl)-	C_9H_{12}	3620961	0.0033	4.48	0.0146	0.0005							
14	Benzene, propyl-	C_9H_{12}	3828200	0.0034	3.09	0.0107	0.0003							
15	Benzene, 1-ethyl-3-methyl-	C_9H_{12}	1612644	0.0015	3.01	0.0044	0.0001							
16	Benzenemethanol (CAS) Benzyl alcohol	C_7H_8O	455777	0.0004	0.158	0.0001	0.0000							
17	1-.alpha.-Terpineol	$C_{10}H_{18}O$	875696	0.0008	0.0283	0.0000	0.0000							
		TOTAL	1.11E+09	1	279.208	30.6923	1		0.8170		0.1284		57.1933	454.3892

Table 4.9: Liquid mixture value of LFL, UFL, LOC and stoichiometry in sample 1

Data	
LFLmix(vol. %)	1.2241
UFLmix(vol. %)	7.7895
LOC	11.439
Stoichiometry	90.878

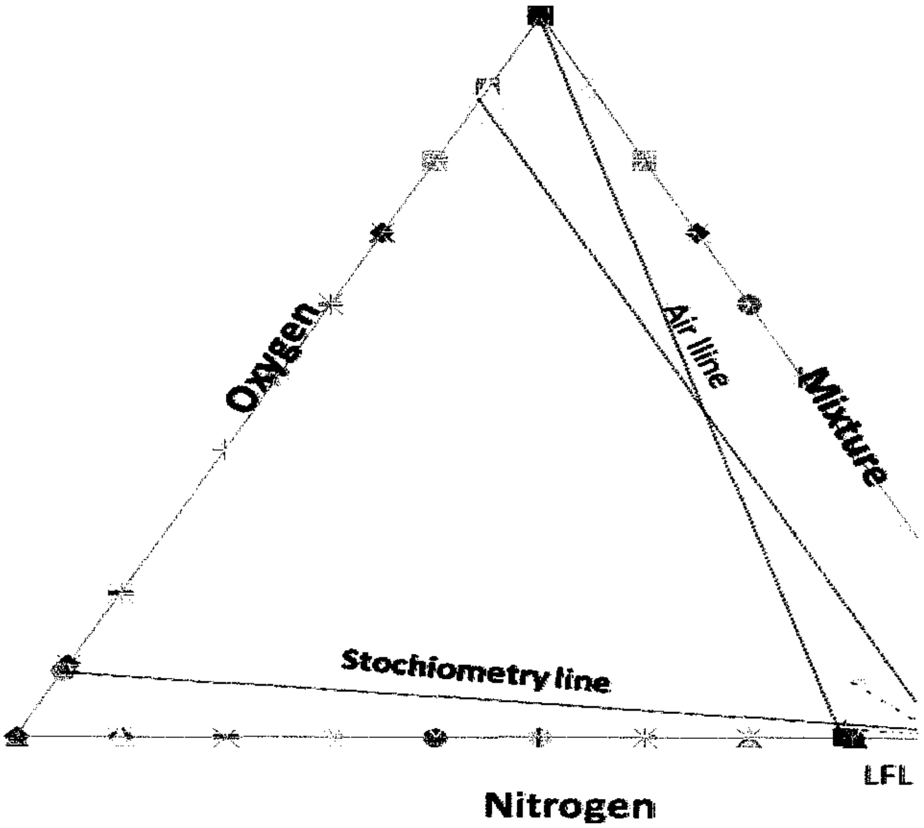

Figure 4.23: Flammability diagram of waste sample 1.

Table 4.10: LFL, UFL and LOC of components presences in waste sample 2

PKNO	NAME	Formula	AREA	Fraction,xi	VAPOR PRESSURE @ 25OC (mmHg)	xi*Poi	yi=xi*Pisat/Pt	LFLi	yi/LFLi	UFLi	yi/UFLi	z	LOC	100(z/(1+z))
1	Water	H_2O	13747345	0.0137	24.5	0.3369	0.0092							
2	Diisopropyl ether	$C_6H_{14}O$	170464809	0.1705	152	25.9144	0.7058	1.2546	0.5626	7.9836	0.0884	9.5	11.9183	90.4762
3	2-Propanol, 1-methoxy-	$C_4H_{10}O_2$	30045647	0.0300	8.15	0.2449	0.0067	2.0235	0.0033	12.8771	0.0005	6.5	13.1531	86.6667
4	Pentane, 2,2,4-trimethyl-	C_8H_{18}	7542635	0.0075	45.2	0.3410	0.0093	0.9091	0.0102	5.7851	0.0016	12.5	11.3636	92.5926
5	Hexane, 2,4-dimethyl-	C_8H_{18}	48959183	0.0490	29.4	1.4396	0.0392	0.9091	0.0431	5.7851	0.0068	12.5	11.3636	92.5926
6	Pentane, 2,3,4-trimethyl-	C_8H_{18}	104445739	0.1045	24.5	2.5593	0.0697	0.9091	0.0767	5.7851	0.0120	12.5	11.3636	92.5926
7	Pentane, 2,3,3-trimethyl-	C_8H_{18}	131994154	0.1320	23.1	3.0495	0.0831	0.9091	0.0914	5.7851	0.0144	12.5	11.3636	92.5926
8	Hexane, 2,3-dimethyl-	C_8H_{18}	30634396	0.0306	23.1	0.7078	0.0193	0.9091	0.0212	5.7851	0.0033	12.5	11.3636	92.5926
9	Hexane, 3,4-dimethyl-	C_8H_{18}	9939970	0.0099	21.5	0.2137	0.0058	0.9091	0.0064	5.7851	0.0010	12.5	11.3636	92.5926
10	Hexane, 2,2,5-trimethyl-	C_9H_{20}	83981983	0.0840	16	1.3439	0.0366	0.8131	0.0450	5.1745	0.0071	14.0	11.3838	93.3333
11	Hexane, 2,3,5-trimethyl-	C_9H_{20}	16243479	0.0162	11.2	0.1820	0.0050	0.8131	0.0061	5.1745	0.0010	14.0	11.3838	93.3333
12	Heptane, 2,5-dimethyl-	C_9H_{20}	8638861	0.0086	9.42	0.0814	0.0022	0.8131	0.0027	5.1745	0.0004	14.0	11.3838	93.3333
13	Heptane, 2,2,4-trimethyl- (CAS) 2,2,4-Trimethylheptane	$C_{10}H_{22}$	7755124	0.0078	5.17	0.0401	0.0011	0.7355	0.0015	4.6804	0.0002	15.5	11.4001	93.9394
14	Heptane, 2,2,4-trimethyl- (CAS) 2,2,4-Trimethylheptane	$C_{10}H_{22}$	12262029	0.0123	5.17	0.0634	0.0017	0.7355	0.0023	4.6804	0.0004	15.5	11.4001	93.9394
15	Heptane, 2,2,4-trimethyl-	$C_{10}H_{22}$	15787650	0.0158	5.17	0.0816	0.0022	0.7355	0.0030	4.6804	0.0005	15.5	11.4001	93.9394
16	Tetrahydrofurfurylacetate	$C_7H_{12}O_3$	153362964	0.1534	0.0031	0.0005	0.0000							
17	Ethanol, 2-butoxy-	$C_6H_{14}O_2$	109925700	0.1099	0.552	0.0607	0.0017	1.3266	0.0012	8.4419	0.0002	9.5	12.6025	90.4762
18	Decane (CAS) n-Decane	$C_{10}H_{22}$	28522546	0.0285	1.58	0.0451	0.0012	0.7355	0.0017	4.6804	0.0003	15.5	11.4001	93.9394
19	Undecane	$C_{11}H_{24}$	15600971	0.0156	0.564	0.0088	0.0002							
		TOTAL	999855185	1	406.2791	36.7145	1		0.8785		0.1381		185.6075	1478.9322

Table 4.11: Liquid mixture value of LFL, UFL, LOC and stoichiometry in sample 2

Data	
LFLmix(vol. %)	1.138
UFLmix(vol. %)	7.244
LOC	11.6
Stoichiometry	92.43

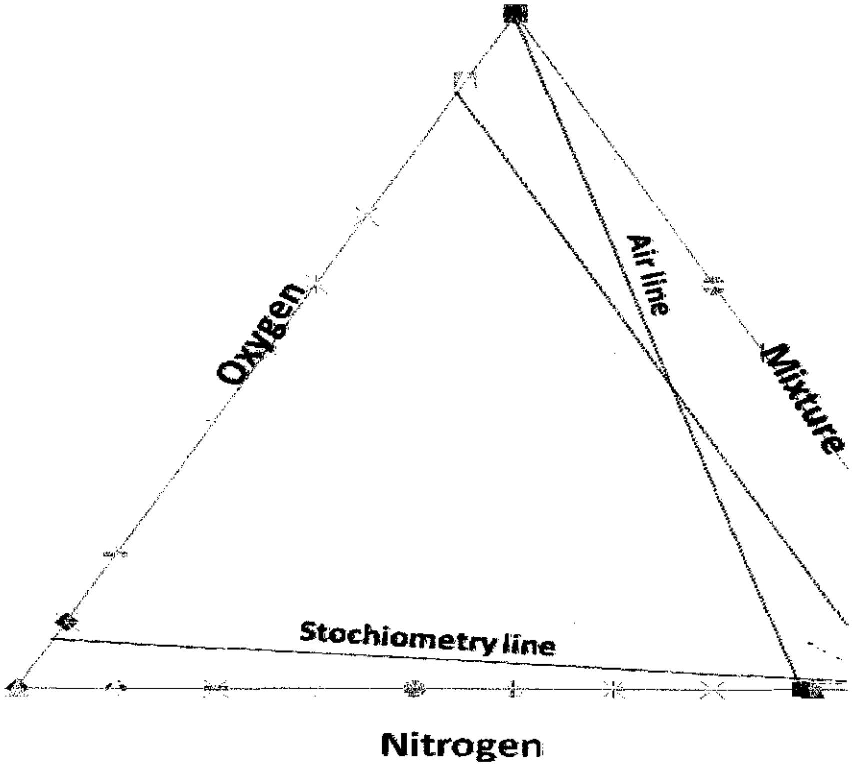

Figure 4.24: Flammability diagram of waste sample 2.

CHAPTER 5
CONCLUSION

This project is basically an investigation of fire and explosion assessment of the waste from industries. The flammability of a waste material is dependent on many parameters, such as its chemical composition, physical properties, geometric configuration, and combustion products. As a result, flammability is really a characterization of multiple fire hazards. The essential elements for combustion are fuel, an oxidizer and an ignition sources.

The heat of combustion of the liquid sample was measured using bomb calorimeter. The heat of combustion indicates the amount of heat released per unit mass or unit volume of a substance when the substance is completely burned.

The consequences of the flash fire, pool fire, boiling expanding vapor cloud explosion (BLEVE), fireball and evaporation rate have been studied. Furthermore, the damage due to overpressure has been estimated. This project provides information and methods, which can help people who are dealing with some flammable waste of industries.

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