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Investigation of Fire and Explosion Accidents in the Drainage Systems Related to Process Industries

by

Muhammad Aizat bin Abd Wahi

Dissertation submitted in partial fulfilment 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 or done by unspecified sources or persons.

(MUHAMMAD AIZAT BIN ABD WAHI)

ABSTRACT

The study of fire and explosion in the process related to oil industries has been a significant scope in the oil and gas business. In this work, oily mixture liquid samples have been taken from PETRONAS Refinery Malacca (PPMSB) drainage system. The aim of the study is to investigate the root causes of the fire incident in the drainage system and to provide engineering approach system to prevent from the likelihood of the similar case recurrence. The result of this study may contribute to minimizing the loss of properties, business and life due to fire or explosion. The liquid samples are first going through distillation process to extract the oil in the liquid. The oily liquid then is analyzed experimentally to indicate the components via Gas Chromatography (GC) as well as the gases that formed when the liquid sample is vaporized. Among the components that have been detected are components from alkane, alkene, arene, alcohol and haloalkane group. The liquid sample contains large numbers of hydrocarbon components (CH-) ranging from C_7 to C_{28}. From the GC result, several parameters such as average flash point, vapor pressure, boiling point, heat of vaporization and molecular weight for the mixture can be estimated. The calculated value of average flash point is 88.58°C and the molecular weight of 188.01 g/mol. Average enthalpy of vaporization of the sample is 44.81 kJ/mol, vapor pressure of 0.62 mmHg at 25°C while the sample's boiling point is 232.65°C. The heat of combustion is measured using bomb calorimeter which gives 45.7 kJ/g. These results lead to the determination of several parameters such as ignitability, evaporation rate and flash point of the samples. The parameters are analyzed using GC, bomb calorimeter, hydrocarbon gas detector and closed cup apparatus. Since the first element from alkane group detected in the liquid sample is nonane (C_9H_{20}), the gas sample is suspected to contain alkane ranging from methane (CH4) to octane (C_8H_{18}). From the GC result, it has been found that the gases presences in the sample are ranging between C_5H_{12} and C_8H_{18}.

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Last, but certainly not least, I would like to apologize if any party was inadvertently excluded from being mentioned above and would like to thank all parties that were involved in making this project a success.

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CHAPTER 1
INTRODUCTION

1.1 Background Of Study

Drainage system in a process plant is a system that will treat all of the effluent discharges so that they are safe to the plant operation as well as meeting the limit of the environmental regulations when discharged into public water. Theoretically, this can be achieved by ensuring proper segregation of the different effluent categories and proper estimation of the drainage rates with provisions for upset conditions such as fire and flooding (SOGT, 2008).

In normal practice, contaminated water will be treated according to its source and the level of oil contamination in it. Normally they are segregated into two types (SOGT, 2008):

- Continuously Oil Contaminated (COC) water
- Accidentally Oil Contaminated (AOC) water

COC water comes directly from the process, specifically from the draining of the equipment's process liquid while AOC water is the water that comes from the firefighting and rain. AOC water is contained with a smaller amount of oil inside it compared to the COC water.

The presence of hydrocarbons in the drainage system exposes the system to the possibility of fire and explosion event. Fire triangle indicates that three elements necessary to ignite ordinary burning and fires are fuel, oxygen and heat. Hydrocarbons fall in the fuel category. Fire might end up in explosion, provided that certain parameters, i.e. the Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL) of the hydrocarbon are met. The liquid waste in the drainage system contains hydrocarbons and oil and they can cause fire and explosion when this mixture vaporizes. In this study, investigation of fire and explosion will be studied for a sample taken from the drainage system of one refinery plant in Malaysia.

1.2 Problem Statement

A refinery plant is a plant that produces various products such as Liquefied Petroleum Gas (LPG), petrochemical naphtha, motor gasoline, kerosene/Jet A1 and diesel. Drainage system in this plant contains various type of wastewater collected from all processes involved with different chemicals and process conditions. The waste in the drainage 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 drainage system if all three elements – oxygen, heat and fuel present in the system. Based on the previous fire incidents in a plant, an investigation will be made on the sample taken from a refinery's drainage system. This will determine the type of elements presented in the sample that might be the fuel for the fire event to occur as well as the presence of oxygen and heat. By doing this investigation, necessary actions will be suggested to minimize the fire and explosion from occurring.

1.3 Objectives Of Study

Upon completing the project, a few objectives need to be achieved. The objectives of the study are as follows:

i. To investigate the root causes of fire and explosion incidents in the drainage systems related to process industries.
ii. To investigate fire and explosion characteristics in the petrochemical drainage systems including LEL, UEL, maximum explosion overpressure (MEO) and minimum oxygen concentration (MOC).
iii. To predict dangerous concentration level and to propose method for fire and explosion precaution.

1.4 Scope Of Study

This study is limited to below considerations only:

i. System

From all of the systems involved in a plant, only drainage and waste water treatment system are taken into consideration for fire and explosion investigation.

ii. Types of Hazards

Consideration only made on the fire and explosion hazards.

iii. Equipment Limitation

All calculations are solely based on the measurable data gathered by available equipment only. They are gas chromatography for combustible liquid and hydrocarbon gas detector for combustible gases.

iv. Analysis of Results

Results obtained from the tests will be analyzed and interpreted. The risk assessment for each model will be conducted according to the tests results.

v. Process Industry

The drainage system of a refinery plant is selected to be studied.

CHAPTER 2

LITERATURE REVIEW

For the literature review, in this beginning stage, focus will be given in identifying past incidents in refinery plants as well as properties of liquid and gas that are significant in the ignition of fire that may also result in explosion. These properties will be useful in the later stage of investigation, after getting the composition of gas and liquid from the sample.

2.1 Past Fire And Explosion Incidents In Refineries

As mentioned earlier, a refinery plant produces various types of products. Refineries possess a large inventory of hazardous material, which exceed the threshold quantities and, therefore, are classified as major hazard installations (Shaluf et al, 2003). Typically, system accidents occur because of unanticipated interactions among multiple failures. One component's failure triggers failures in other components or subsystems. Due to the high complexity and level of interaction among subsystems, designers and operators are unable to predict failures or their mutual interactions. Table 2.1 summarizes several reported accidents in refineries in the world up to year 2003.

From Table 2.1, fires and explosions contributed to total 103 fatalities and 100 injuries. From the table, it is also shown that there are various products in refinery involved in the accident which means that fire and explosion accidents happened in a particular system or equipment in a refinery, not the whole plant. It is suggested that poor project management, poor design, modifications, poor operation procedure, poor communication and coordination were the main causes that led to the incident (Shaluf et al, 2003).

In the drainage system of any petroleum-related plant, large quantities of water may be used to fight fires in facilities handling chemicals. Since most flammable materials float on water there is the potential for fire protection water to spread the fire. In addition, many chemicals have the potential to contaminate the soil and groundwater. Water used for firefighting can disperse these chemicals thus spreading the pollution. As a result there is a need for drainage system to control water runoff. An equally important point to make is that drainage systems can control the flammable liquid spills.

Table 2.1: Fire and Explosion Accidents in the World

Origin of Accident	Date	Location	Product Involved	No. of		
				Dead	Injured	Evacuated
Explosion at refinery	13.04.91	USA, Sweeny	Petroleum	-	2	-
Explosion at refinery	24.07.94	UK, Pembork		-	26	-
Explosion at refinery	03.11.90	USA, Chalmette	Cloud of flammable gases	-	-	-
Explosion at refinery	22.01.88	China, Shanghai	Petrochemicals	25	17	-
Fire at refinery	03.11.91	USA, Beaumont	Hydrocarbons	-	-	-
Fire at refinery	12.01.91	USA, Port Arthur	Petroleum	-	-	-
Fire at refinery	30.11.90	Saudi Arabia, Ras Tan	Kerosene and benzene	1	2	-
Fire at refinery	09.11.88	India, Bombay	Oil	35	16	-
Fire and explosion at refinery	24.01.95	Indonesia, Cilacap	Gas	-	-	-
Vapor cloud fire explosion	2003	Rosharon, Texas		3	4	-
Decomposed hydroxylamine	1999	Allentown, Pennsylvania	Hydroxylamine	5	2	-
Refinery fire	14.09.97	India, Vishakapatnam		34	31	150 000
Total				**103**	**100**	**150 000**

2.2 Petroleum Refinery

A petroleum refinery plant separates crude oil into liquefied petroleum gas, naphtha (used to produce gasoline by blending with octane boosters), kerosene/aviation turbine fuel, diesel oil, and residual fuel oil. Catalytic cracking and reforming, thermal cracking, and other secondary processes are used to achieve the desired product specifications. Certain refineries also produce feed stocks for the manufacture of lubricating oils and bitumen (Dikshit et al, 2005).

2.2.1 Liquid Waste in Refineries

Petroleum refineries use relatively large volumes of water, especially for cooling systems. Surface water runoff and sanitary wastewaters are also generated. The quantity of wastewaters generated and their characteristics depend on the process configuration. As a general guide, approximately 3.5 to 5 m^3 of wastewater per ton of crude are generated when cooling water is recycled (World Bank, 1998). Wastewater from the refinery plant contains petroleum hydrocarbons, heavy metals, sulfur and ammonia (Al-Haddad et al, 2007). Petroleum refineries eliminate salts in their feedstock since these corrode and foul process equipment. The first refining step is desalting where a hot water wash extracts the salts. If feedstock contains aromatics then some will be in the desalter effluent and this is a major source of refinery wastewater containing Volatile Organic Compounds (VOCs). Usually the desalter is the major source of contaminated process wastewater and typically also has the highest benzene, toluene, ethylbenzene, and xylenes (BTEX) content. At several refineries, the desalter effluent flow has been as high as 50% of the total wastewater flow and over 70% of total BTEX discharge. The effluent also is poor in Nitrogen (N_2) concentration (Russel, 2006).

2.3 Drainage Facilities

Drainage facilities should be designed to simultaneously carry flammable liquid and fire protection water away from buildings, structures, storage tanks, pipe racks and process equipment. Drainage system should not be expose adjacent plant facilities to burning or toxic materials during an incident. This may require diversionary curb, trenches, collection sumps, skimmers and holding ponds or basins.

In many cases, the water and chemicals collected during an incident will need to be pretreated prior to disposal in a waste water treatment facility, or the rate that these materials are introduced to the treatment process controlled. Small holding basins for specific process areas should be sized to hold 30-60 minutes of discharge as a minimum. There is potential for fires of long duration such as in petrochemical and oil refining facilities, special precautions may be necessary. It may be possible to separate organics from fire water prior to disposal, thus reducing the size of the required holding area. It is noted that the potential for soil and water contamination should not be used as a reason to avoid providing fire protection or drainage system (Bellinger et al, 1996)

2.4 Properties Of Combustible Gases And Liquids

2.4.1 Flash Point

This is the lowest temperature at which a liquid gives off sufficient vapor at its surface to form a flammable or an explosive mixture (Crowl and Louvar, 2002). Many hazardous liquids have flash points at or below room temperature and are covered by a layer of flammable vapors that will ignite immediately if exposed to an ignition source. Vaporization increases as temperature rises and consequently they are more hazardous at elevated temperatures.

2.4.2 Auto Ignition Temperature

This is the minimum temperature for self-sustained combustion of a substance, independent of the heating or heated element (Crowl and Louvar, 2002). This temperature is generally well above the open-cup flash point, minimum temperature at which the liquid gives off sufficient vapor to form an ignitable mixture with air.

2.4.3 Lower Explosive Limit (LEL) or Lower Flammable Limit (LFL)

This is the minimum concentration of a flammable gas or vapor that will propagate flame when exposed to a source of ignition (General Monitors). Commonly abbreviated LEL or LFL, a mixture below this concentration level is considered too “lean” to burn. An increase in atmospheric temperature or pressure will decrease the LEL of a gas or vapor.

2.4.4 Explosive Range

This includes all concentrations (measured as a percent of volume in air) of a flammable gas or vapor that will propagate flame when exposed to a source of ignition (General Monitors). Many common flammable liquids have very wide explosive ranges. The explosive range of all flammable gases and vapors will vary with temperature and pressure.

2.4.5 Upper Explosive Limit (UEL) or Upper Flammable Limit (UFL)

This is the maximum concentration of gas in air that will combust (Crowl and Louvar, 2002). Any higher percentage of combustible gas or lower amount of oxygen in the mixture of the two, and the mixture will be too "rich" to sustain combustion.

2.4.6 Vapor Density

This is the relative density of the vapor as compared with air. It is calculated as the ratio of the molecular weight of the vapor to the molecular weight of air (General Monitors). A vapor density less than one indicates that a substance lighter than air; conversely, densities greater than one indicate a substance heavier than air. All flammable liquid vapors are heavier than air and can travel along a gradient for considerable distances to an ignition source.

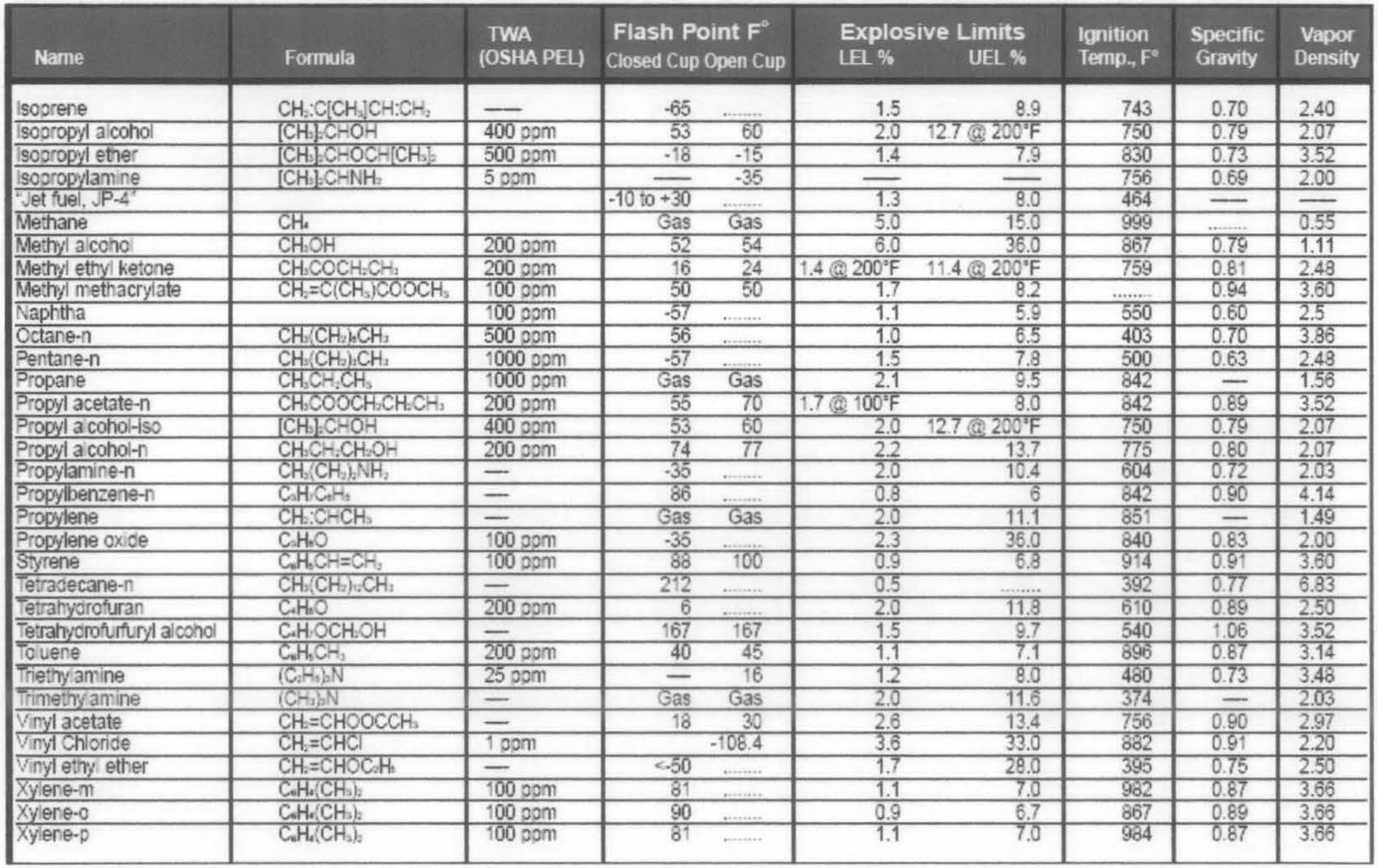
2.5 PETROLEUM GASES

Petroleum gases generally consist of more than 70% methane (CH_4) and less than 10% carbon dioxide (CO_2) (Doyle, 2001). Ethane concentrations are commonly less than 10% and rarely exceed 20%. In most cases, propane concentrations are less than 5% and n-butane concentrations are less than 2%. Methane, the most presence gas in petroleum is combustible in air in concentrations from 5 % (LEL) to 15 % (UEL) by volume. A combustible concentration of methane can be ignited by weak spark (electrical, frictional or static), which produces a high temperature for a short duration. It can also be ignited by a hot surface or an open flame. Methane's autoignition temperature is about 537°C, its combustion is highly exothermic and once initiated are self propagating (Doyle, 2001). Table 2.2 shows the properties of several gases and liquids that are related with the fire and explosion analysis (General Monitors).

The number of carbons in a hydrocarbon molecule determines its burning characteristic. However, a simple rule of thumb can be used in determining using hydrocarbon formula, whether it is a flammable gas or liquid or semi solid or solid. The number of carbon atoms in a hydrocarbon molecule gives the molecule its vapor density which influences the vapor pressure and the color of the flame. From these factors the approximate boiling point, flash point, vapor density and vapor pressure can be calculated. Thus, the kind of substance that is burning can be determined.

Table 2.2: Properties of Flammable Gases and Liquids

Name	Formula	TWA (OSHA PEL)	Flash Point F°		Explosive Limits		Ignition Temp., F°	Specific Gravity	Vapor Density
			Closed Cup	Open Cup	LEL %	UEL %			
1,3- Butadiene	$CH_2=CHCH=CH_2$	1 ppm	Gas	Gas	2.0	12.0	788	—	1.90
Acetaldehyde	CH_3CHO	200 ppm	-38	....	4.0	60.0	347	0.78	1.52
Acetic Acid (glacial)	CH_3COOH	10 ppm	103	110	4.0	19.9	867	1.05	2.07
Acetone	CH_3COCH_3	1000 ppm	-4	15	2.5	13.0	869	0.79	2.00
Acetonitrile	CH_3CN	40 ppm	....	42	3	16	975	0.78	1.42
Acrylonitrile	$CH_2=CHCN$	2 ppm	30	32	3.0	17.0	898	0.80	1.83
Ammonia (anhydrous)	NH_3	50 ppm	Gas	Gas	15.0	28.0	1204	——	0.60
Amyl acetate-n	$CH_3COO[CH_2]_4CH_3$	100 ppm	77	....	1.1	7.5	714	0.88	4.49
Amylamine (mono)	$C_5H_{11}NH_2$		30	45	2.2	22	....	0.75	3.01
Benzene	C_6H_6	1 ppm	12	....	1.2	7.8	928	0.88	2.77
Butane-n	$CH_3CH_2CH_2CH_3$	——	-76	Gas	1.9	8.5	550	0.60	2.06
Butene-1	$CH_3CH_2CH:CH_2$	——	Gas	Gas	1.6	10.0	725	——	1.94
Butyl acetate-n	$CH_3COO[CH_2]_3CH_3$	150 ppm	72	98	1.7	7.6	797	0.88	4.00
Butyl alcohol-n	$CH_3CH_2CH_2CH_2OH$	100 ppm	98	110	1.4	11.2	650	0.81	2.55
Butyl alcohol-sec	$CH_3CH(OH)CH_2CH_3$	150 ppm	75	85	1.7 @ 212°F	9.8 @ 212°F	761	0.81	2.55
Butyl alcohol-tert	$(CH_3)_3COH$	100 ppm	52	60	2.4	8.0	892	0.79	2.55
Cyclohexane	C_6H_{12}	300 ppm	-4	....	1.3	8	473	0.80	2.90
Decane-n	$CH_3(CH_2)_8CH_3$	——	115	....	0.8	5.4	410	0.70	4.90
Diethyl ether	$C_2H_5OC_2H_5$	400 ppm	-49	....	1.9	36.0	356	0.72	2.55
Dimethylformamide	$HCON(CH_3)_2$	10 ppm	136	155	2.2 @ 212° F	15.2	833	0.90	2.52
Dimethylamine, anhydrous	$(CH_3)_2NH$	10 ppm	Gas	Gas	2.8	14.4	752	——	1.60
Dioxane-p	$C_4H_8O_2$	100 ppm	54	65	2	22	356	1.0+	3.00
Dodecane-n	$CH_3(CH_2)_{10}CH_3$	——	165	....	0.6	....	397	0.75	5.86
Ethane	CH_3CH_3	——	Gas	Gas	3.0	12.5	882	....	1.04
Ethyl alcohol	CH_3CH_2OH	1000 ppm	55	71	3.3	19.0	685	0.79	1.59
Ethyl benzene	$CH_3CH_2C_6H_5$	100 ppm	70	75	0.8	6.7	810	0.87	3.66
Ethyl ether	$C_2H_5OC_2H_5$	400 ppm	-49	....	1.9	36.0	356	0.72	2.55
Ethylamine	$CH_3CH_2NH_2$	10 ppm	1	....	3.5	14.0	725	0.80	1.60
Ethylene	$H_2C:CH_2$	——	Gas	Gas	2.7	36.0	842		0.98
Ethylene oxide	C_2H_4O	1 ppm	-20	-4	3.0	100.0	1058	0.89	1.52
Formaldehyde gas	HCHO	.75 ppm	Gas	Gas	7.0	73.0	795	....	1.00
Gasoline, aviation-commercial	——	....	-50	....	1.3	7.1	824	....	....
Gasoline, aviation-military	——	....	-50	....	1.2	7.1	880	....	....
Heptane-n	$CH_3[CH_2]_5CH_3$	500 ppm	25	30	1.1	6.7	399	0.70	3.50
Hexane-n	$CH_3[CH_2]_4CH_3$	500 ppm	-7	-14	1.1	7.5	437	0.70	3.00
Hydrogen	H_2	——	Gas	Gas	4.0	75.0	932	....	0.10



Name	Formula	TWA (OSHA PEL)	Flash Point F°		Explosive Limits		Ignition Temp., F°	Specific Gravity	Vapor Density
			Closed Cup	Open Cup	LEL %	UEL %			
Isoprene	$CH_2:C[CH_3]CH:CH_2$	——	-65	....	1.5	8.9	743	0.70	2.40
Isopropyl alcohol	$[CH_3]_2CHOH$	400 ppm	53	60	2.0	12.7 @ 200°F	750	0.79	2.07
Isopropyl ether	$[CH_3]_2CHOCH[CH_3]_2$	500 ppm	-18	-15	1.4	7.9	830	0.73	3.52
Isopropylamine	$[CH_3]_2CHNH_2$	5 ppm	——	-35	——	——	756	0.69	2.00
"Jet fuel, JP-4"			-10 to +30	....	1.3	8.0	464	——	——
Methane	CH_4		Gas	Gas	5.0	15.0	999	....	0.55
Methyl alcohol	CH_3OH	200 ppm	52	54	6.0	36.0	867	0.79	1.11
Methyl ethyl ketone	$CH_3COCH_2CH_3$	200 ppm	16	24	1.4 @ 200°F	11.4 @ 200°F	759	0.81	2.48
Methyl methacrylate	$CH_2=C(CH_3)COOCH_3$	100 ppm	50	50	1.7	8.2	....	0.94	3.60
Naphtha		100 ppm	-57	....	1.1	5.9	550	0.60	2.5
Octane-n	$CH_3(CH_2)_6CH_3$	500 ppm	56	....	1.0	6.5	403	0.70	3.86
Pentane-n	$CH_3(CH_2)_3CH_3$	1000 ppm	-57	....	1.5	7.8	500	0.63	2.48
Propane	$CH_3CH_2CH_3$	1000 ppm	Gas	Gas	2.1	9.5	842	—	1.56
Propyl acetate-n	$CH_3COOCH_2CH_2CH_3$	200 ppm	55	70	1.7 @ 100°F	8.0	842	0.89	3.52
Propyl alcohol-iso	$[CH_3]_2CHOH$	400 ppm	53	60	2.0	12.7 @ 200°F	750	0.79	2.07
Propyl alcohol-n	$CH_3CH_2CH_2OH$	200 ppm	74	77	2.2	13.7	775	0.80	2.07
Propylamine-n	$CH_3(CH_2)_2NH_2$	—	-35	....	2.0	10.4	604	0.72	2.03
Propylbenzene-n	$C_3H_7C_6H_5$	—	86	....	0.8	6	842	0.90	4.14
Propylene	$CH_2:CHCH_3$	—	Gas	Gas	2.0	11.1	851	—	1.49
Propylene oxide	C_3H_6O	100 ppm	-35	....	2.3	36.0	840	0.83	2.00
Styrene	$C_6H_5CH=CH_2$	100 ppm	88	100	0.9	6.8	914	0.91	3.60
Tetradecane-n	$CH_3(CH_2)_{12}CH_3$	—	212	....	0.5	....	392	0.77	6.83
Tetrahydrofuran	C_4H_8O	200 ppm	6	....	2.0	11.8	610	0.89	2.50
Tetrahydrofurfuryl alcohol	$C_4H_7OCH_2OH$	—	167	167	1.5	9.7	540	1.06	3.52
Toluene	$C_6H_5CH_3$	200 ppm	40	45	1.1	7.1	896	0.87	3.14
Triethylamine	$(C_2H_5)_3N$	25 ppm	—	16	1.2	8.0	480	0.73	3.48
Trimethylamine	$(CH_3)_3N$	—	Gas	Gas	2.0	11.6	374	—	2.03
Vinyl acetate	$CH_2=CHOOCCH_3$	—	18	30	2.6	13.4	756	0.90	2.97
Vinyl Chloride	$CH_2=CHCl$	1 ppm		-108.4	3.6	33.0	882	0.91	2.20
Vinyl ethyl ether	$CH_2=CHOC_2H_5$	—	<-50	....	1.7	28.0	395	0.75	2.50
Xylene-m	$C_6H_4(CH_3)_2$	100 ppm	81	....	1.1	7.0	982	0.87	3.66
Xylene-o	$C_6H_4(CH_3)_2$	100 ppm	90	....	0.9	6.7	867	0.89	3.66
Xylene-p	$C_6H_4(CH_3)_2$	100 ppm	81	....	1.1	7.0	984	0.87	3.66

2.6 Liquid Evaporation

The flammable gas mixture accumulated at the top side of the drainage system origins from the evaporation of the liquid inside the drain. The initial stage of vaporization is usually controlled by the heat transfer from the ground (Crowl and Louvar, 2002). This is especially true for a spill of liquid with a normal boiling point below ambient temperature or ground temperature (i.e., boiling liquid). The heat transfer from the ground is modelled with a simple one-dimensional heat conduction equation given by

$$q_g = \frac{k_s(T_g - T)}{(\pi \alpha_s t)^{1/2}} \tag{2-1}$$

where:

q_g is the heat flux from the ground (J/s-m^2),
ks is the thermal conductivity of the soil (J/ms°C),
T_g is the temperature of the soil (°C),
T is the temperature of liquid pool (°C),
α_s is the thermal diffusivity of the soil (m^2/s),
t is the time after spill (s).

At later times, solar heat fluxes and convective heat transfer from the atmosphere become important. Evaporation rate due to the solar radiation is given by the following formula

$$m_{sol} = \frac{Q_{sol} M A}{H_v} \tag{2-2}$$

where:
m_{mass} = evaporation rate (kg/s),
Q_{sol} = solar radiation (kJ/s-m^2),
M = molecular weight (kg/kgmol),
A = area of the pool (m^2),
H_v = heat of vaporization of the liquid (kJ/mol).

Correlations regarding liquid evaporation due to several factors (i.e. pool evaporation and solar radiation) has been the subject of study for CCPS (1999), Crowl and Louvar (2002) and Casal (2008).

2.7 Flammability Characteristics Of Vapor Mixtures

Theoretically Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) for the vapor mixture are needed. These mixture limits are computed using the Le Chatelier equation:

$$UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{UFL_i}} \tag{2-3}$$

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \frac{y_i}{LFL_i}} \tag{2-4}$$

where:

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

This simple method of calculation can be used, provided that the experimental data i.e. volume percentage for all of the components in the mixture are known (Crowl and Louvar, 2002). If the volume percentage (vol %) for total combustible components is between the calculated LFL_{mix} and UFL_{mix}, then the mixture is combustible. There are several documented works that illustrate the hazards of flammability and explosiveness (or volatility) of hydrocarbons. These include the works of Zabetakis (1965), Sax (1984) and Kuchta (1985).

2.8 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. It is important to basically know the ignition sources because in most of the situations in the process facilities, it is impossible to avoid flammable mixtures as well as the presence of oxygen. The elimination of the ignition sources with the greatest probability of occurrence should be given the greatest attention (Crowl and Louvar, 2002). Table 2.3 shows the ignition sources over 25 000 major fire cases all over the world.

Table 2.3: 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%

Lennard, (2002) made a combustion studies on various heat sources of fires such as electrical fires, non-electrical fires, vehicle fires and spontaneous combustion as well as the laboratory analysis of fire debris samples. The study is conducted based on hundreds of journals.

2.9 Fire Prevention By Design

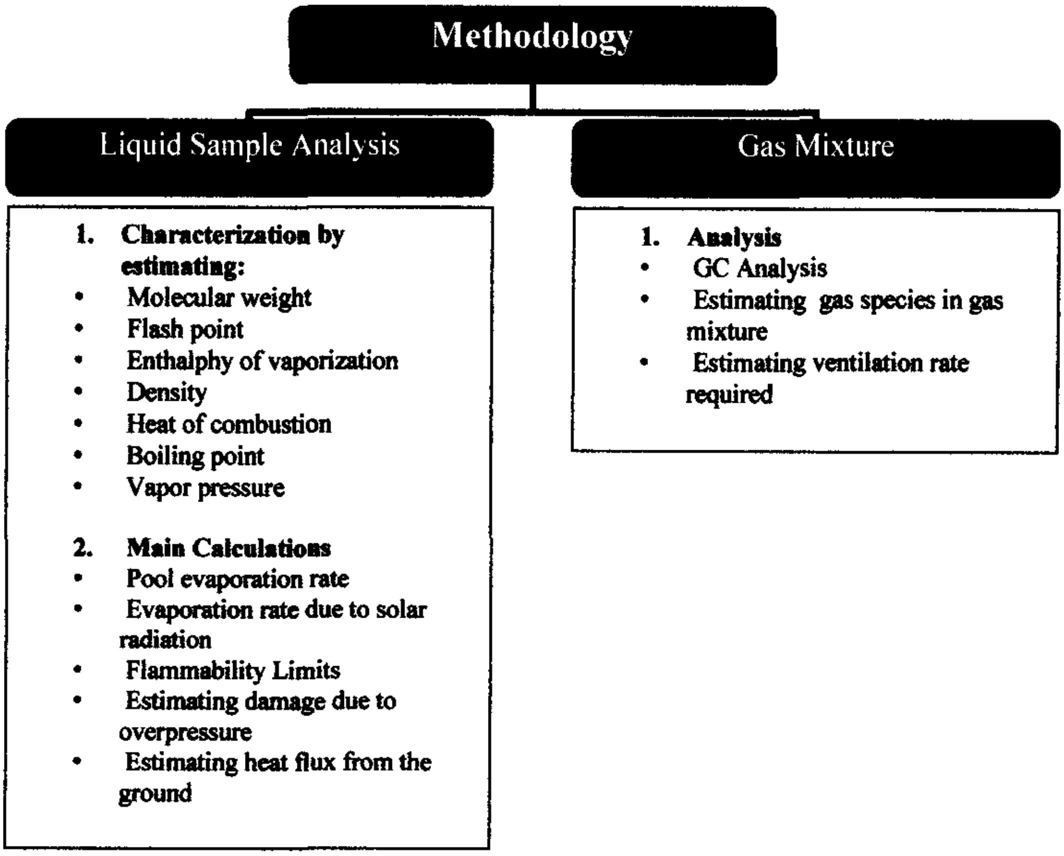
The reported fire and explosion cases in the drainage and wastewater treatment system of the studied plant occurred in the closed area of the drain. Even though most of the sections of the plant's drain are opened type, there is also several closed section. Fire and explosion might happen because of the accumulating vapor in the upper side of the closed space. The most basic practice in the system design is all hydrocarbon areas should be provided with maximum ventilation capability. Enclosed spaces are to be avoided while the installation of walls and roofs are used only when necessary. Attention must also be given in the air circulation. Only open drain can provide the air circulation and reduces the vapor concentration. Sources that may lead to the heat energy, one of the causes for fire and explosion to occur must also be eliminated. For an instance, any works involving the presence of fire such as welding and works with sparks should be avoided. As a summary, among the control measures that can be taken to minimize fire and explosion risks are as the following (Egypt Oil & Gas Web Portal):

- Reduce the quantity of dangerous substances to a minimum
- Avoid or minimize releases
- Control releases at source
- Prevent the formation of an explosive atmosphere
- Collect, contain and remove any releases to a safe place (e.g. by ventilation)
- Avoid ignition sources
- Avoid adverse conditions (e.g. exceeding the limits of temperature or control settings) that could lead to danger
- Keep incompatible substances apart

CHAPTER 3

METHODOLOGY

The methodology in doing the analysis for the sample is divided into two parts, for liquid sample analysis and gas mixture analysis. Combustible gas mixture formed by the evaporation of the liquid and for the liquid, apart from its combustible parameters, the rate of evaporation and factors affecting the evaporation must be in consideration. The gas species that might be evaporated and forms combustible gas mixture must be identified and finally, recommendations in minimizing the fire and explosion risk are proposed. Figure 3.1 shows the summary of the methodology.



1. **Characterization by estimating:**
- Molecular weight
- Flash point
- Enthalpy of vaporization
- Density
- Heat of combustion
- Boiling point
- Vapor pressure

2. **Main Calculations**
- Pool evaporation rate
- Evaporation rate due to solar radiation
- Flammability Limits
- Estimating damage due to overpressure
- Estimating heat flux from the ground

1. **Analysis**
- GC Analysis
- Estimating gas species in gas mixture
- Estimating ventilation rate required

Figure 3.1: Methodology for liquid sample and gas mixture analysis.

3.1 Liquid Sample

The liquid sample (Figure 3.2) is collected from the drainage line by using a pump and transferred into a tightly closed bottle to avoid small molecules from the sample to escape. The sample is then stored under the temperature of $5^{o}C$ to ensure that the sample will not vaporize out of the bottle. Then, the sample will be analyzed to measure the composition of all combustible species inside. Once the composition being identified, the flash point of the sample will be calculated using the open cup experiment and the possibilities of the sample to be caught by fire will be determined.

Figure 3.2: Liquid sample taken from a refinery

3.1.1 Distillation

In the beginning part, it was suspected that the liquid sample contain a small amount of water. Even though the sample collected does not show any distinctive layers as expected, the sample was taken from the drainage and wastewater treatment system which might also contain water. 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.

Below are the steps to set up the simple distillation apparatus:

1. Round bottom flask is held in place in the set-up with a small three-pronged clamp with holder .
2. 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.
3. Secure the round bottom flask to the ring stand using the three pronged clamp.
4. The Y-adaptor is then placed on top of the round bottom flask.
5. Next, a condenser is added to the Y-adaptor and the connection is secured with clip.
6. The vacuum adaptor is connected to the condenser by using a clip.
7. After that, a stemmed funnel is placed on top of the Y-adaptor and the liquid sample is poured so that it goes into the round bottom flask. The liquid volume needed is 200 mL.
8. 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.
9. The next items to be added are the thermometer adaptor and thermometer.
10. The thermometer and thermometer adaptor are connected on top of the Y-adaptor.
11. 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.
12. Cooling water is then turned on and the distillation can be started.

Figure 3.3 shows the simple distillation set up as a summary of step 1 to step 12.

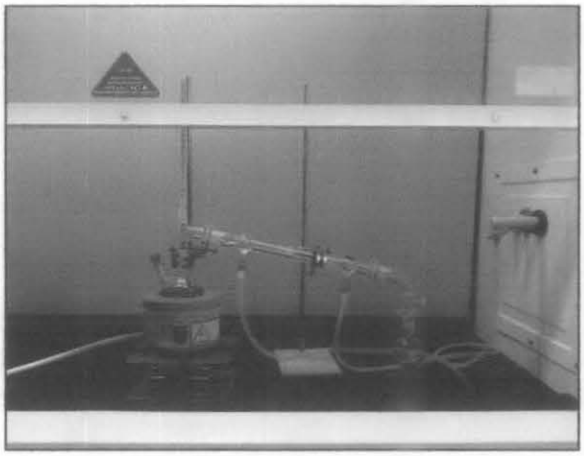


Figure 3.3: Full simple distillation set up

The distillation was done without specifying any condition on the experiment. From the observation made, the product (clear in colour) starts to be produced at the temperature of 184°C and continuously be produced up to the temperature of 218°C. The liquid sample's temperature changes between these two temperatures are fluctuating and they did not happen in uniform pattern. After one hour and fifteen minutes, the distillation was stopped since there is no significant change happens. The products are as in the figure below:

Figure 3.4: Original sample (200 mL)

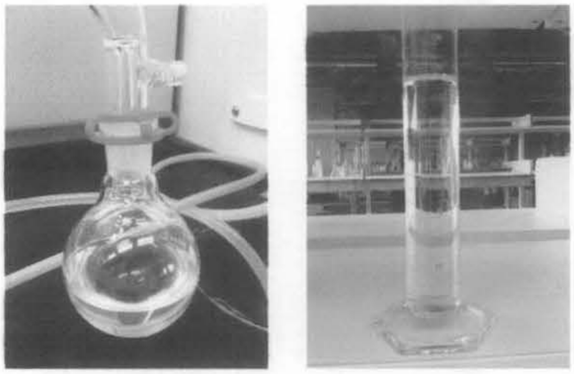


Figure 3.5: Distillation product (170 mL)

Figure 3.6: Distillate (30 mL)

The black colored liquid contains heavier hydrocarbons compared to the clear one. It is expected that water might be in the clear colored product, or the lighter component one. All samples then are then sent to be analyzed by using GC/MS. For the clear colored sample, purge and trap method has been used by the technician because prior to the hydrocarbon identification, water presence will be removed by purge and trap. However there is no water found in the sample, meaning that all of the incoming tests can be made only to the original sample.

3.1.2 Determining the Composition

The composition of a liquid sample can be determined by using the gas chromatography (GC) which is Shimadzu GCMS-QP5050 type. The GC is used to separate volatile components of a mixture. First, before using the GC, water-oil mixture sample collected must be extracted to separate the oil from water. A small amount of the oil sample to be analyzed is drawn up into a GC syringe. The syringe needle is placed into a hot injector port of the gas chromatograph, and the sample is 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, such as helium, 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 has been used to identify the hydrocarbons in the liquid sample. The sample was handed to the GC technical staff and was attached with studied settings. The GC settings are as the following: Electron impact ionization, electron energy 70 eV, scan range 40 to 500 amu at 1 scan/s. Helium is at a flow rate of 1.5 cm^3/min. Samples were injected on-column onto a 30 m HP5 fused silica capillary column, 0.25 mm i.d, and the temperature held at 55 °C for 2 min, then increased from 55 to 300 °C at 5°C/min, thereafter held at 300 °C for 40 minutes.

The full result of the GC analysis is shown in Figure 3.7 and Figure 3.8. All of the component presences are shown in Table 3.1. Gas Chromatography analysis shows that the liquid sample contains large numbers of hydrocarbon components (CH-) from C_7 to C_{28}. From the analysis, majority components are in the alkane and alkene group with some species from the haloalkane and arene are also in. Out of four peaks (peaks no. 21, 34, 47 and 59) that each made up more than 5 % from the sample, three (peaks no. 21,

34, and 59) contains species from alkane group. It can be concluded that the liquid sample taken contain heavy hydrocarbon and most of them are from the alkane group.

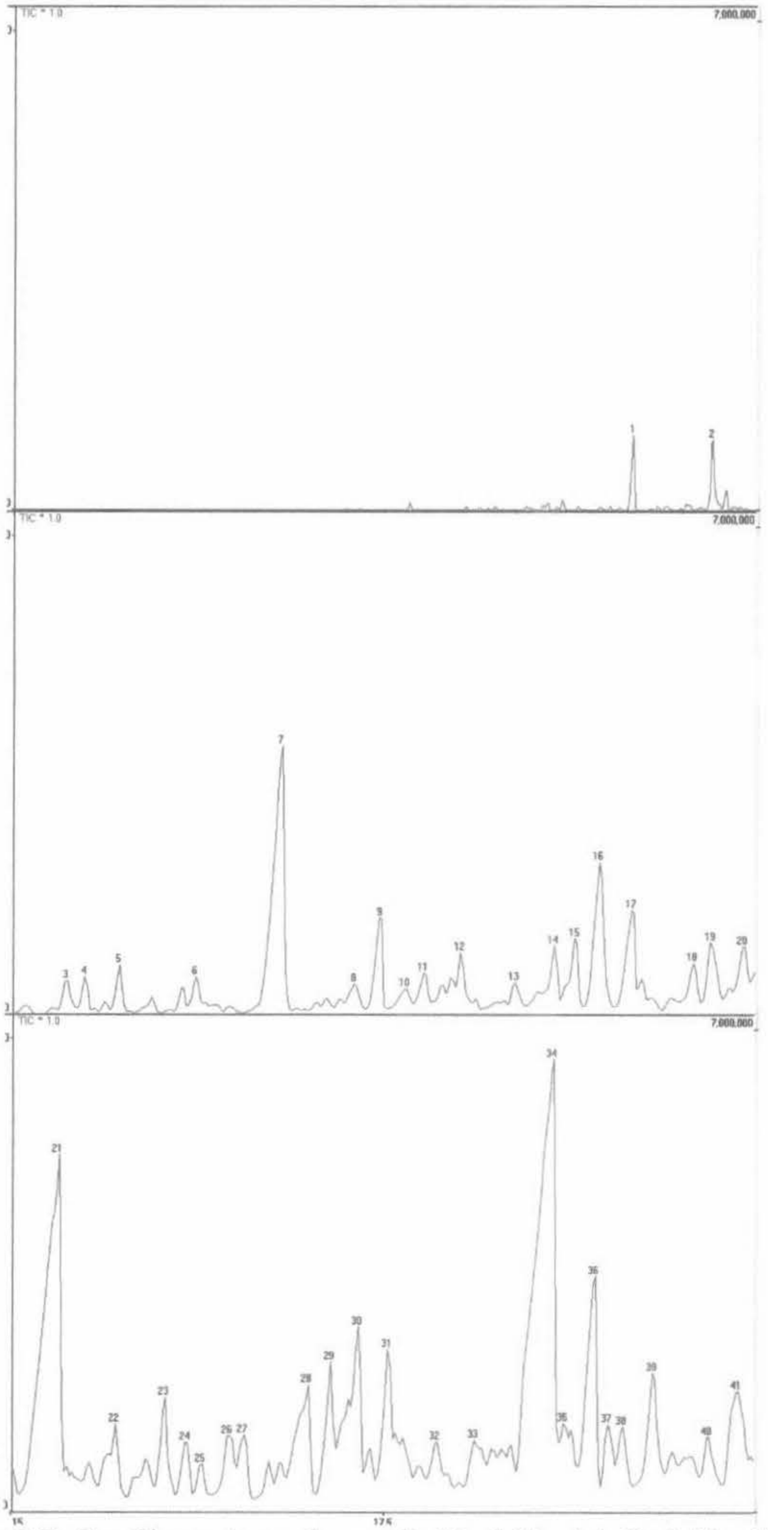


Figure 3.7: Gas Chromatography results (Peak No. 1 to Peak No. 41)

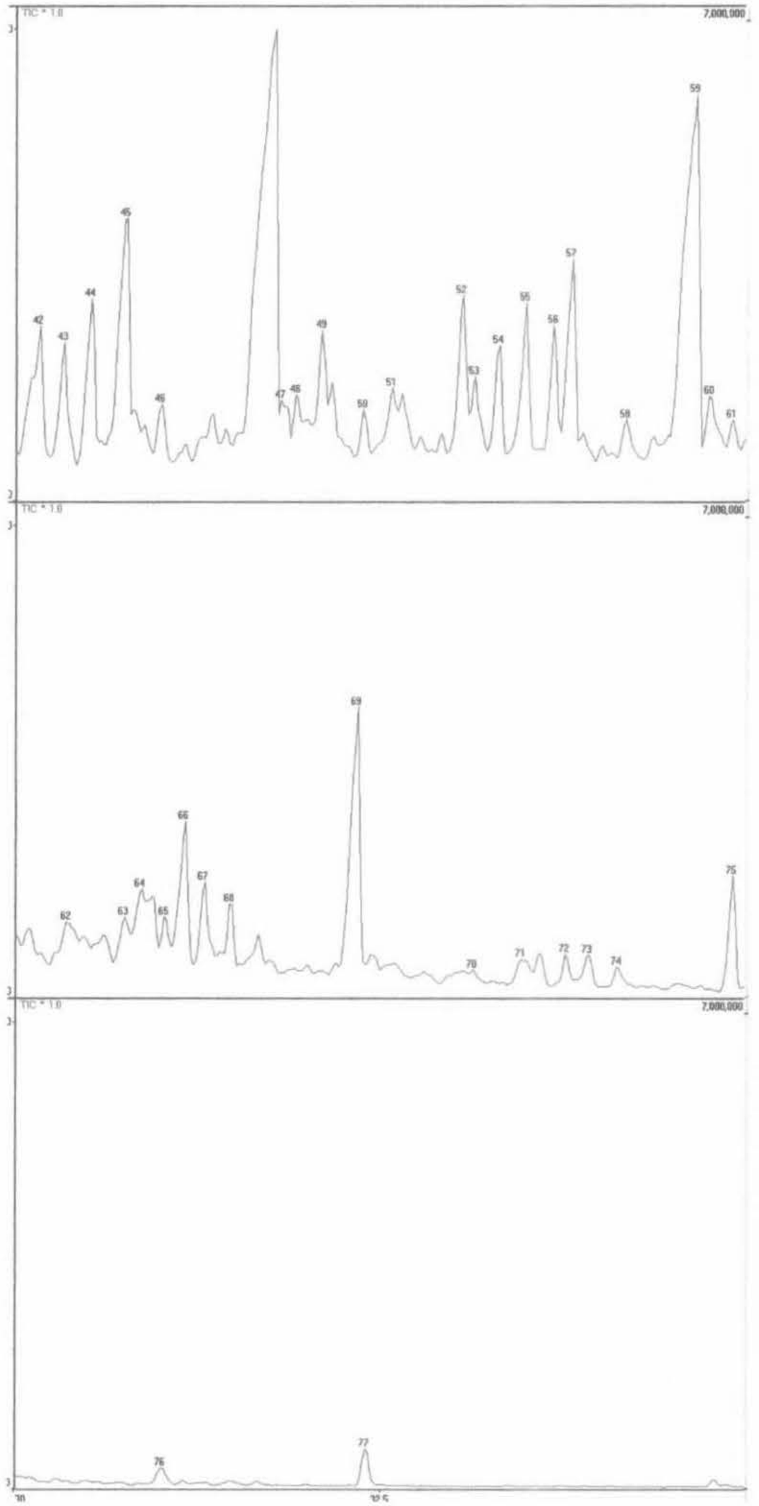


Figure 3.8: Gas Chromatography results (Peak No. 42 to Peak No. 77)

Table 3.1: Components in Liquid Sample

PKNO	%Total Area	NAME	Formula	Group	Molecular Weight, M	Flash Point (°C)	Vapor pressure @ 25°C (mmHg)	Enthalpy of Vaporization (kJ/mol)	Boiling Point at 760 mmHg (°C)	$M_{average}$	Average Flash Point (°C)	Average Vapor pressure @ 25°C (mmHg)	Average Enthalpy of Vaporization (kJ/mol)	Average Boiling Point at 760 mmHg (°C)
1	0.66	Nonane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7	0.8448	0.20526	0.030558	0.243606	1.00122
2	0.72	4-methyl-1-Decene	$C_{11}H_{22}$	Alkene	154	48	2.17	38.79	168.1	1.4256	0.6588	0.0078122	0.369972	1.7244
		1,1-oxybis-Octane	$C_{16}H_{34}O$	Alcohol	242	135	5.19E-05	63.98	310.9					
3	0.29	3,5-dimethyl-octane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9	0.3915	0.11194	0.0090045	0.109707	0.47357
		3-ethyl-4-methyl-Hexane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7					
4	0.24	2-methyl-Nonane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9	0.324	0.09264	0.007452	0.090792	0.39192
		Nonane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7					
5	0.35	4-methyl-1-Decene	$C_{11}H_{22}$	Alkene	154	48	2.17	38.79	168.1	0.518	0.164675	0.0065625	0.135695	0.60025
		2,6-dimethyl-octane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9					
6	0.24	1,3,5-trimethyl-benzene	C_9H_{12}	Arene	120	38.3	3.01	38.13	161.1	0.288	0.09192	0.007224	0.091512	0.38664
		2-methyl-3-mthylene-1-hepten-5-yne	C_9H_{12}	Arene	120	38.3	3.01	38.13	161.1					
7	3.99	nonane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7	5.3865	1.54014	0.1238895	1.509417	6.51567
		decane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9					
8	0.25	dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	0.425	0.1805	0.0015146	0.1077417	0.5374167
		tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
		decane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9					
9	0.92	4-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	1.4352	0.552	0.0051888	0.381616	1.80596
		2-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3					
10	0.22	1-chloro-tetradecane	$C_{14}H_{29}Cl$	Haloalkane	232	122.5	0.00313	51.11	292.9	0.5104	0.2695	6.886E-06	0.112442	0.64438
11	0.3	1,3,5-trimethyl-benzene	C_9H_{12}	Arene	120	38.3	3.01	38.13	161.1	0.558	0.3418	0.00301	0.15992	0.887
		E-2-hexenyl benzoate	$C_{13}H_{16}O_2$		204	150.6	2.23E-05	60.61	360.4					
		2-octyl benzoate	$C_{15}H_{22}O_2$		234	152.9	1.57E-05	61.18	365.5					
12	0.22	3-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	0.5925333	0.2788133	0.0001925	0.1121193	0.6366067
		trichlorodocosyl-silane	$C_{22}H_{45}Cl_3Si$	Hydride	442	203	2.97E-06	62.57	400.3					

		4,6,8-trimethyl-1-nonene	$C_{12}H_{24}$	Alkene	168	77.8	0.234	43.18	213.9					
13	0.22	(E)-3-undecene	$C_{11}H_{22}$	Alkene	154	48	2.17	38.79	168.1	0.3696	0.14762	0.0025014	0.091883	0.43758
		(Z)-3-tridecene	$C_{13}H_{26}$	Alkene	182	86.2	0.104	44.74	229.7					
14	0.4	5-methyl-decane	$C_{15}H_{32}$	Alkane	212	132.2	0.0112	48.83	270.6	0.764	0.4066	0.0004404	0.18446	0.9734
		dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
15	0.7	4-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	1.092	0.42	0.003948	0.29036	1.3741
16	1.9	2-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	2.964	1.14	0.010716	0.78812	3.7297
17	0.99	3-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	1.8216	0.95139	0.0028472	0.4470345	2.311155
		2,6,11-trimethyl-dodecane	$C_{15}H_{32}$	Alkane	212	132.2	0.0112	48.83	270.6					
18	0.37	p-cymene	$C_{10}H_{14}$	Arene	134	46.3	1.7	39.29	173.3	0.6684667	0.3158567	0.0021282	0.1683377	0.87579
		5-(1,5-dimethyl-4-hexenyl)-2-methyl-1,3-cyclohexadiene	$C_{15}H_{24}$		204	104.9	0.0128	48.6	268.4					
		6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]heptane	$C_{15}H_{24}$		204	104.9	0.0128	48.6	268.4					
19	0.69	p-cymene	$C_{10}H_{14}$	Arene	134	46.3	1.7	39.29	173.3	0.9246	0.31947	0.01173	0.271101	1.19577
		methyl(1-methylethyl)-benzene	$C_{10}H_{14}$	Arene	134	46.3	1.7	39.29	173.3					
		(1,1-dimethyl)-tert-butylbenzene	$C_{10}H_{14}$	Arene	134	46.3	1.7	39.29	173.3					
20	0.4	6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]heptane	$C_{15}H_{24}$	Arene	204	104.9	0.0128	48.6	268.4	0.816	0.4196	0.0000512	0.1944	1.0736
		5-(1,5-dimethyl-4-hexenyl)-2-methyl-1,3-cyclohexadiene	$C_{15}H_{24}$	Arene	204	104.9	0.0128	48.6	268.4					
21	7.84	undecane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	11.1328	3.5854933	0.1770272	3.0612587	13.66512
		nonane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7					
		decane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9					
22	0.91	2-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	1.9292	1.076985	0.0009544	0.441077	2.42242
		2-methyl-heptadecane	$C_{18}H_{38}$	Alkane	254	165.6	0.000769	53.54	316.3					
23	0.88	tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	1.8656	0.7914133	0.0007439	0.406912	2.1536533
		1-iodo-2-methylnonane	$C_{10}H_{21}I$	Haloalkane	268	99.3	0.0161	48.18	264.2					
		dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
24	0.57	p-cymene	$C_{10}H_{14}$	Arene	134	46.3	1.7	39.29	173.3	0.7638	0.26391	0.00969	0.223953	0.98781

		1,2,4,5-tetramethyl-benzene	$C_{10}H_{14}$	Arene	134	46.3	1.7	39.29	173.3					
25	0.27	n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	0.4968	0.22887	0.0003569	0.121014	0.62226
		n-tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
26	0.52	cyclopentylcyclohexane	$C_{11}H_{20}$	Alkyne	152	65.6	0.479	41.8	199.6	0.7904	0.34112	0.0024908	0.21736	1.03792
		trans-anti-1-methyl-decahydronaphthalene	$C_{11}H_{20}$	Alkyne	152	65.6	0.479	41.8	199.6					
		decahydro-2-methyl-naphthalene	$C_{11}H_{20}$	Alkyne	152	65.6	0.479	41.8	199.6					
27	0.4	(E)-3-undecene	$C_{11}H_{22}$	Alkene	154	48	2.17	38.79	168.1	0.616	0.192	0.00868	0.15516	0.6724
		(Z)-3-undecene	$C_{11}H_{22}$	Alkene	154	48	2.17	38.79	168.1					
28	1.71	2-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3					
29	0.94	4-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	1.7296	0.80135	0.0011163	0.425538	2.209
		4-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
30	1.93	2-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	4.0916	2.284155	0.0020243	0.935471	5.13766
		2-methyl-heptadecane	$C_{18}H_{38}$	Alkane	254	165.6	0.000769	53.54	316.3					
31	2.07	3-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	3.9054	1.86231	0.0018354	0.949992	4.99491
		n-tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
32	0.53	4,8-dimethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	0.9752	0.44414	0.0008427	0.232776	1.17342
Km		2,4-dimethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
33	0.55	E-2-octadecadecene-1-ol	$C_{18}H_{36}O$	Enol	268	120.7	1.00E-05	66.72	333	1.3933333	0.7135333	1.013E-05	0.3392217	1.76165
		Z-10-pentadecenol	$C_{15}H_{30}O$	Enol	226	109.6	0.00551	50.11	283.1					
		E,Z-2,13-octadecadien-1-ol	$C_{18}H_{34}O$		266	158.9	4.06E-06	68.2	344.8					
34	9.94	n-undecane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	14.9864	5.6758933	0.0749811	3.9593573	18.80754
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
		n-decane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9					
35	0.32	2-ethenyl-1,3,5-trimethyl-benzene	$C_{11}H_{14}$		146	79.4	0.161	43.9	221.2	0.4693333	0.2558933	0.0005675	0.139936	0.7022933
		7-isopropyl-bicyclo[4.2.0]octa-1,3,5-triene	$C_{11}H_{14}$		146	79.4	0.161	43.9	221.2					
		2-allyl-4-methylphenol	$C_{10}H_{12}O$		148	81.1	0.21	43.39	216					

36	2.56	2,6-dimethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	4.1728	1.66272	0.0222592	1.058176	5.07264
		3,5-dimethyl-octane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9					
37	0.53	n-decane	$C_{10}H_{22}$	Alkane	142	46.1	1.58	38.75	174.9	0.8268	0.31058	0.0047409	0.2176975	1.03615
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
38	0.43	2-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	0.7611	0.333035	0.0007912	0.187738	0.940625
		n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
39	1.32	1-chloro-octadecane	$C_{18}H_{37}Cl$	Haloalkane	288	157.8	5.04E-05	58.08	359.1	3.1944	1.69752	0.0002129	0.693	4.03062
		1-tetradecene	$C_{14}H_{28}$	Alkene	196	99.4	0.0322	46.92	251.6					
40	0.49	trichlorodocosyl-silane	$C_{22}H_{45}Cl_3Si$	Hydride	442	203	2.97E-06	62.57	400.3	1.8277	0.793065	8.378E-07	0.287875	1.78801
		1-bromo-hexadecane	$C_{16}H_{33}Br$	Haloalkane	304	120.7	0.000339	54.93	329.5					
41	1.65	cyclododecane	$C_{12}H_{24}$	Cycloalkane	168	77.8	0.234	43.18	213.9	3.19	1.2958	0.0025743	0.825385	4.05075
		2-dodecyl-1,3-propanediol	$C_{15}H_{32}O_2$		244	80	6.11E-05	63.71	308.7					
		1-dodecene	$C_{12}H_{24}$	Alkene	168	77.8	0.234	43.18	213.9					
42	2.13	2,4-dimethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	4.8138	1.950015	0.0018648	0.980865	5.17164
		1-iodo-2-methylnonane	$C_{10}H_{21}I$	Haloalkane	268	99.3	0.0161	48.18	264.2					
43	1.44	4-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	2.5824	1.16736	0.0036072	0.636192	3.22368
		2-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3					
		4,8-dimethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
44	1.95	2-methyl-heptadecane	$C_{18}H_{38}$	Alkane	254	165.6	0.000769	53.54	316.3	3.77	1.92855	0.0050295	0.89973	4.73655
		2-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3					
		2-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
45	3.38	2,6-dimethyl-heptadecane	$C_{19}H_{40}$	Alkane	268	140.7	0.0026	51.43	296	7.0078667	3.3304267	0.0041754	1.56325	8.2641
		tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
46	0.56	(E)-3-tetradecene	$C_{14}H_{28}$	Alkene	196	99.4	0.0322	46.92	251.6	1.0584	0.51968	0.0003814	0.256648	1.34764
		(E)-3-tridecene	$C_{13}H_{26}$	Alkene	182	86.2	0.104	44.74	229.7					
47	10.41	1-ethyl-2,3-dihydro-1-methyl-1H-Indene	$C_{12}H_{16}$		160	93.2	0.0524	46.01	242.6	26.1291	16.33329	0.0027275	5.7166515	34.045905
		5-N-pentadecyl-1,2,3,4-tetrahydronaphtalene	$C_{25}H_{42}$		342	220.6	1.32E-06	63.82	411.5					

48	0.28	3-ethyl-5-methyl-heptane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3	0.4368	0.168	0.0015792	0.116144	0.54964
		2,3,7-trimethyl-octane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3					
49	0.68	2,6-dimethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	1.2512	0.56984	0.0010812	0.298656	1.50552
		5-ethyl-undecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
50	0.39	n-hexadecane	$C_{16}H_{34}$	Alkane	226	97.6	0.006	49.95	281.6	0.9256	0.46124	4.492E-05	0.201721	1.16298
		1-chloro-octadecane	$C_{18}H_{37}Cl$	Haloalkane	288	157.8	5.04E-05	58.08	359.1					
		n-tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
51	0.28	3-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	0.5805333	0.27664	0.0000588	0.1346147	0.7367733
		n-tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
		n-hexadecane	$C_{16}H_{34}$	Alkane	226	97.6	0.006	49.95	281.6					
52	1.39	trichlorodocosyl-silane	$C_{22}H_{45}Cl_3Si$	Hydride	442	203	2.97E-06	62.57	400.3	5.1291	2.38524	2.521E-08	0.929076	5.33899
		1-(ethenyloxy)-octadecane	$C_{20}H_{40}O$	Enol	296	140.2	6.57E-07	71.11	367.9					
53	0.4	2-methyl-octane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7	0.512	0.1244	0.01852	0.14764	0.6068
		n-nonane	C_9H_{20}	Alkane	128	31.1	4.63	36.91	151.7					
54	1.06	4-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	1.9504	0.90365	0.0012588	0.479862	2.491
		4-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
55	1.64	2-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	3.0176	1.3981	0.0019475	0.742428	3.854
		2-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
56	1.1	3-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	2.6913333	1.5260667	0.0001115	0.57574	3.3462
		3-methyl-hexadecane	$C_{17}H_{36}$	Alkane	240	148.9	0.00185	52.03	301.8					
		3-methyl-eicosane	$C_{21}H_{44}$	Alkane	296	167.9	5.81E-05	57.85	356.9					
57	1.93	2,6,10,14-tetramethyl-heptadecane	$C_{21}H_{44}$	Alkane	296	167.9	5.81E-05	57.85	356.9	5.4426	2.97799	2.565E-05	1.054552	6.300485
		2,6-dimethyl-heptadecane	$C_{19}H_{40}$	Alkane	268	140.7	0.0026	51.43	296					
58	0.48	(E)-3-Tetradecene	$C_{14}H_{28}$	Alkene	196	99.4	0.0322	46.92	251.6	0.9408	0.47712	0.0001546	0.225216	1.20768
		n-tetradec-1-ene	$C_{14}H_{28}$	Alkene	196	99.4	0.0322	46.92	251.6					
59	7.64	n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	13.5228	5.91718	0.0140576	3.335624	16.7125
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					

60	0.69	2,3,6,7-tetramethyl-octane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	1.9182	0.99222	0.0007211	0.3851925	2.30115
		(2-decyldodecyl)-benzene	$C_{28}H_{50}$		386	216.5	6.79E-08	68.25	450.9					
61	0.24	n-hexadecane	$C_{16}H_{34}$	Alkane	226	97.6	0.006	49.95	281.6	0.4864	0.22464	0.0001548	0.112808	0.60552
		n-tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
		n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
62	0.53	2,6-dimethyl-naphthalene	$C_{12}H_{12}$	Arene	156	109.4	0.0165	48.13	263.7	0.8268	0.57982	8.745E-05	0.255089	1.39761
		1,5-dimethyl-naphthalene	$C_{12}H_{12}$	Arene	156	109.4	0.0165	48.13	263.7					
63	0.29	1,7-dimethyl-naphthalene	$C_{12}H_{12}$	Arene	156	109.4	0.0165	48.13	263.7	0.4524	0.31726	4.785E-05	0.139577	0.76473
		1,5-dimethyl-naphthalene	$C_{12}H_{12}$	Arene	156	109.4	0.0165	48.13	263.7					
		1,8-dimethyl-naphthalene	$C_{12}H_{12}$	Arene	156	109.4	0.0165	48.13	263.7					
64	1.08	1,6-dimethyl-naphthalene	$C_{12}H_{12}$	Arene	156	109.4	0.0165	48.13	263.7	2.3904	1.12896	0.0001022	0.533052	2.97828
		1-iodo-undecane	$C_{11}H_{23}I$	Haloalkane	282	106.6	0.00589	49.99	282					
		6,9-dimethyl-tetradecane	$C_{16}H_{34}$	Alkane	226	97.6	0.006	49.95	281.6					
65	0.24	decyl-cyclopentane	$C_{15}H_{30}$	Cycloalkane	210	111.1	0.0114	48.81	270.4					
66	1.51	heptadecane	$C_{17}H_{36}$	Alkane	240	148.9	0.00185	52.03	301.8	3.2012	1.756885	0.0012144	0.7244225	3.95016
		n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4					
67	0.8	2-methyl-heptadecane	$C_{18}H_{38}$	Alkane	254	165.6	0.000769	53.54	316.3	1.64	0.9024	0.0022591	0.38008	2.0504
		2-methyl-decane	$C_{11}H_{24}$	Alkane	156	60	0.564	41.48	196.3					
68	0.43	3-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	1.0922	0.53664	4.398E-05	0.2209053	1.2690733
		3-methyl-hexadecane	$C_{17}H_{36}$	Alkane	240	148.9	0.00185	52.03	301.8					
		1-iodo-tetradecane	$C_{14}H_{29}I$	Haloalkane	324	126.1	0.000335	54.95	329.7					
69	3.29	n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	6.2071333	3.14853	0.0041586	1.4931117	7.7654967
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
		n-pentadecane	$C_{15}H_{32}$	Alkane	212	132.2	0.0112	48.83	270.6					

70	0.46	trichlorodecyl-silane	$C_{10}H_{21}Cl_3Si$	Hydride	274	123.7	0.0208	47.72	259.6	1.173	0.54924	0.0004195	0.22287	1.1970733
		n-tetradecyltrichlorosilane	$C_{14}H_{29}Cl_3Si$	Hydride	330	156.5	0.000794	53.48	315.8					
		butyl-o-ethylester of carbamothioic acid	$C_7H_{15}NOS$	Carboxylic Acid	161	78	0.252	44.15	205.3					
71	0.31	n-tetradecyltrichlorosilane	$C_{14}H_{29}Cl_3Si$	Hydride	330	156.5	0.000794	53.48	315.8	0.7099	0.31062	0.0037832	0.1443515	0.737335
		4-octanone	$C_8H_{16}O$	Enol	128	43.9	2.44	39.65	159.9					
72	0.23	4-methyl-undecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1	0.391	0.16353	0.0004807	0.09982	0.49703
73	0.3	2-methyl-pentadecane	$C_{16}H_{34}$	Alkane	226	97.6	0.006	49.95	281.6	0.636	0.2955	5.175E-05	0.145635	0.80325
		2-methyl-tridecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9					
74	0.25	3-methyl-hexadecane	$C_{17}H_{36}$	Alkane	240	148.9	0.00185	52.03	301.8	0.5825	0.308125	9.813E-06	0.127475	0.72925
		6,9-dimethyl-tetradecane	$C_{16}H_{34}$	Alkane	226	97.6	0.006	49.95	281.6					
75	1.1	n-tridecane	$C_{13}H_{28}$	Alkane	184	83.8	0.159	43.92	221.4	2.0753333	1.0527	0.0013904	0.4992167	2.5963667
		n-pentadecane	$C_{15}H_{32}$	Alkane	212	132.2	0.0112	48.83	270.6					
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
76	0.23	n-tetradecane	$C_{14}H_{30}$	Alkane	198	99.4	0.0285	47.14	253.9	0.4983333	0.2917167	3.186E-05	0.1134667	0.6334967
		heptadecane	$C_{17}H_{36}$	Alkane	240	148.9	0.00185	52.03	301.8					
		n-pentadecane	$C_{15}H_{32}$	Alkane	212	132.2	0.0112	48.83	270.6					
77	0.38	n-pentadecane	$C_{15}H_{32}$	Alkane	212	132.2	0.0112	48.83	270.6	0.7258	0.38627	0.0004184	0.175237	0.92473
		n-dodecane	$C_{12}H_{26}$	Alkane	170	71.1	0.209	43.4	216.1					
										188.00	88.57816	0.620678	44.80605	232.646

Summary: Average Molecular Weight: 188 g/mol
Average Flash Point: 88.57°C
Average Vapor Pressure: 0.62 mmHg at 25°C
Average Enthalpy of Vaporization: 44.81 kJ/mol
Average Boiling Point: 232.65 °C

3.1.3 Determining the Density

The steps to determine the density of the liquid sample are as the following:

1. The volume of the pycnometer,V is first recorded.
2. Determine the weight of empty, dry pycnometer, m_{empty}.
3. The pycnometer is then filled with the liquid sample from the drainage system until it is almost full.
4. The pycnometer is then closed by using a capillary hole until the entire excess liquid spill out of the pycnometer.
5. The weight of pycnometer from step 4, m_{filled} is then measured. Density is then calculated using the mass/volume relation.

Figure 3.9: Density determination using pycnometer

By using $\rho=m/v$ where ρ = density, m = mass and v = volume, the density of the liquid can be determined. The density of the liquid sample is determined as 0.807 g/mL or 807 kg/m^3.

Table 3.2: Density of the liquid sample

	Volume (mL)	m_{empty} (g)	m_{filled} (g)	m_{liquid} (g)	Density (g/mL)
Original Sample	24.996	19.179	39.358	20.179	0.807

3.1.4 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 3.10 shows the picture of the bomb calorimeter.

Figure 3.10: Bomb Calorimeter

The experiment has been done for two runs on the same sample and the results are as in the Table 3.3 below:

Table 3.3: Heat of combustion for liquid sample.

	Heat of Combustion for the 1st Run ($J\ g^{-1}$)	Heat of Combustion for the 2nd Run ($J\ g^{-1}$)
Original Sample	45,752	45,737

Average Heat of Combustion = 45,745 $J\ g^{-1}$

3.1.5 Determining the Flash Point

Mixtures of flammable and non-flammable liquids, for example alcohol-water mixture are classified by the definition of flammable liquids based on a closed cup method (Wray, 1992). Open cup method can only determine the ability of a liquid mixture to sustain burning. For this apparatus, a small, manually opened shutter is provided at the top of the cup. The liquid is placed in a preheated cup and allowed to sit for a fixed time period. The shutter is then opened and the liquid is exposed to the flame. The temperature when the momentary flame occurs is called the flash point temperature. Closed cup method typically result in lower flash point because more of the vapor produced are contained inside the cup (Campbell and Mnizsewski, 1998).

3.1.6 Evaporation Rate

Prior to the evaporation rate calculation, oil must be extracted out from the oil water mixture. The oil layer on the water surface has the tendency to evaporate. Liquids with high saturation vapor pressures evaporate faster. Evaporation of volatile components from a liquid pool is given by the following equation (Crowl and Louvar, 2002):

$$m_{mass} = \frac{Mk_g AP^{sat}}{R_g T_L} \tag{3-1}$$

where:
m_{mass} = mass evaporation rate (kg/s),
M = molecular weight (kg/kgmol),
k_g = mass transfer coefficient (m/s),
A = area of the pool (m^2),
P^{sat} = saturation vapour pressure (atm),
R_g = ideal gas constant (m^3 atm/kmol K),
T_L = temperature of the liquid (K).

For the evaporation rate due to the solar radiation, equation 2-2 is applicable.

Further calculations are presented in Chapter 4.

3.1.7 Determining the Flammability Limitshj

Crowl and Louvar (2002) introducing a method to correlate the flammability limits as a function of the heat of combustion of a fuel. A good fit was obtained for 123 organic materials containing hydrogen, oxygen, nitrogen and sulfur. For lower flammability limit, the correlations are as the following:

$$LFL = \frac{-3.42}{\Delta H_c} + 0.569\Delta H_c + 0.0538\Delta H_c^2 + 1.80 \tag{3-2}$$

While for the upper flammability limit, the following correlations are applicable:

$$UFL = 6.30\Delta H_c + 0.567\Delta H_c^2 + 23.5 \tag{3-3}$$

Further calculations are made in Chapter 4.

3.1.8 Estimating Damage Due to Overpressure

The explosion of a dust or gas results in a reaction front moving outward from the ignition source preceded by a shock wave or pressure front. After the combustible material is consumed, the reaction front terminates, but the pressure wave continues its outward movement. A blast wave is composed of the pressure wave and subsequent wind. It is the blast wave that causes most of the damage (Crowl and Louvar, 2002). The formula to estimate overpressure is as the following:

$$p_o = \frac{1616\left[1+\left(\frac{z_e}{4.5}\right)^2\right]}{\sqrt{1+\left(\frac{z_e}{0.048}\right)^2}\sqrt{1+\left(\frac{z_e}{0.32}\right)^2}\sqrt{1+\left(\frac{z_e}{1.35}\right)^2}} \times p_a \tag{3-4}$$

where:

p_o = overpressure (kPa),
z_e = scale distance (12.07 m/kg$^{1/3}$),
p_a = ambient pressure (kPa).

All calculations are shown in Chapter 4 and the possible damages caused by overpressure can be found in Appendix A.

3.2 Gas Sample

Combustible gases are normally formed by several combustible elements that have the lower vapor pressure than the operating pressure. As a result, they vaporize and accumulate at the top side inside the pipeline. For the combustible gases, once the volume concentration has been measured by the hydrocarbon gas detector, flammability and explosion limit will be calculated using the Le Chatelier's equation. Combustible gases are normally formed by several combustible elements that have the lower vapor pressure than the operating pressure. As a result, they vaporize and accumulate at the top side inside the pipeline. When all of the analyses are already performed, designs to prevent fires and explosions should be suggested. Drainage systems in the refinery have many sections, some are closed drain and some are opened drain. The gases that vaporize from the liquid sample must be known so that the LFL and UFL can be measured. For the closed drain, it is expected to contain more combustible gases than the open ones.

3.2.1 Gas Component Testing

Vapor in the drainage system formed when the liquid vaporizes into gas at certain temperature. The liquid sample is filled half the volume of a small bottle. The bottle cover must be sealed tightly using a parafilm and the top of the bottle must be made from rubber so that the sample can be easily collected by using syringe. From the storage temperature (5°C), the bottle is heated to the room temperature by submerging it into a heated beaker filled by water where the temperature of water is about 28°C. Next, by using a syringe, the gas sample is taken from the upper part (or the empty part) of the bottle and injected into the Gas Chromatography (GC). The GC used to analyze the gas sample is Agilent GCPID G-1540A model. This GC is competent in detecting 22 types of hydrocarbon (CH) gases from C_1 (methane) up to C_6 (n-hexane). The full list of gases that can be detected is as in Table 3.4 below. This is also called standard, where the gas species is pre determined with its retention time. If the tested samples' retention time is matched with standard's retention time, the presence of a species can be known. Each run will take 30 minutes.

From Table 3.4, for example if the result given by the GC shows that there is peak at the retention time of 12.476 minutes, n-Pentane is presence in the sample. If the retention time is 13.000 minutes, a species between n-Pentane (C_5) and 1,3-Butadiene (C_6) is one of the components for the gas mixture.

Table 3.4: Standard Set for GC-PID

Retention Time (min)	Name
1.160	Methane
1.367	Ethane
1.651	Ethylene
2.410	Propane
4.305	Propylene
5.592	Acetylene
5.922	iso-butane
6.089	1,2-Propadiene
6.216	n-Butane
9.081	trans-2-Butene
9.260	1-Butene
9.846	iso-Butane
10.306	cis-2-Butene
11.345	Iso-Pentane
11.966	Methyl acetylene
12.476	n-Pentane
13.035	1,3-Butadiene
14.481	Trans-2-Pentene
15.051	2-Methyl-2-butene + 1-Pentene
15.670	Cis-2-Pentene
17.979	n-Hexane

CHAPTER 4

RESULT AND DISCUSSION

4.1 LIQUID SAMPLE

4.1.1 Pool Evaporation Rate

The pool evaporation rate is determined using Equation 3-1,

T_L is assumed to be 23°C (temperature of the liquid at open air condition).
First, the value of kg must be determined using this correlation:

$$k_g = k_g{}^o\left(\frac{M_o}{M}\right)^{1/3}$$

where:
k_g = mass transfer coefficient
$k_g{}^o$ = reference mass transfer coefficient
M_o = reference molecular weight
M = molecular weight

The reference used is water with M_o value of 18 g/mol and $k_g{}^o$ of 0.83 cm/s (Crowl and Louvar, 2002). Hence,

$$k_g = 0.83\left(\frac{18}{188.01}\right)^{1/3}$$

$$k_g = 0.3797cm/s = 0.003797m/s$$

Then, k_g value is substituted into Equation 3-1:

$$m_{mass} = \frac{(188.01kg/kmol)(0.003797m/s)Am^2(0.0082atm)}{(0.082057m^3atm/kmol.K)(296K)}$$

Since the exact area of the pool is unknown, a correlation between mass evaporation rate and pool area is presented in Figure 4.1. From the figure, for pool area of 3500 m^2, the mass evaporation rate is 0.085 kg/s.

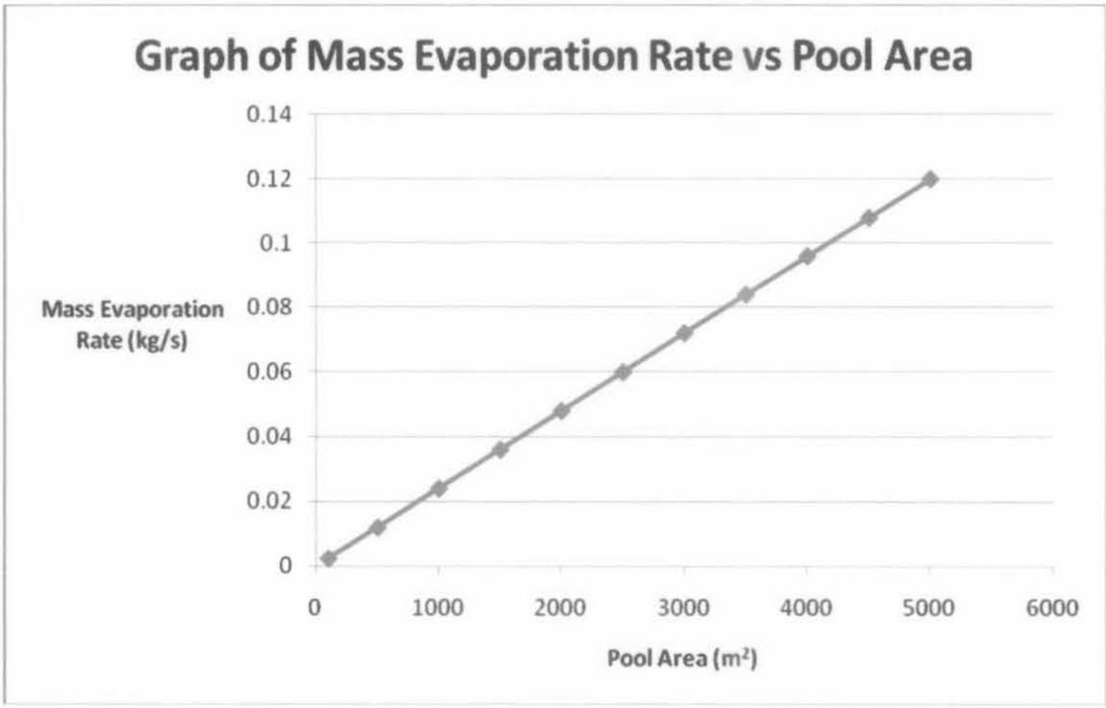


Figure 4.1: Correlation between pool area and mass evaporation rate for pool evaporation

4.1.2 Evaporation Rate Due to Solar Radiation

For mass evaporation due to the solar radiation, Equation 2-2 takes place.

According to Exxon's Design Instruction Manuals (DIM), in Malaysia solar radiation,Q_{sol} is assumed to be 0.79 kW/m^2

$$m_{sol} = \frac{(0.79kJ/s.m^2)(188.01g/mol)Am^2}{44.81kJ/mol}$$

Since the exact area of the pool is unknown, a correlation between mass evaporation rate and pool area is presented in Figure 4.2. From the figure, for a pool area of 3500 m^2, the mass evaporation rate due to solar radiation is 11.60 kg/s.

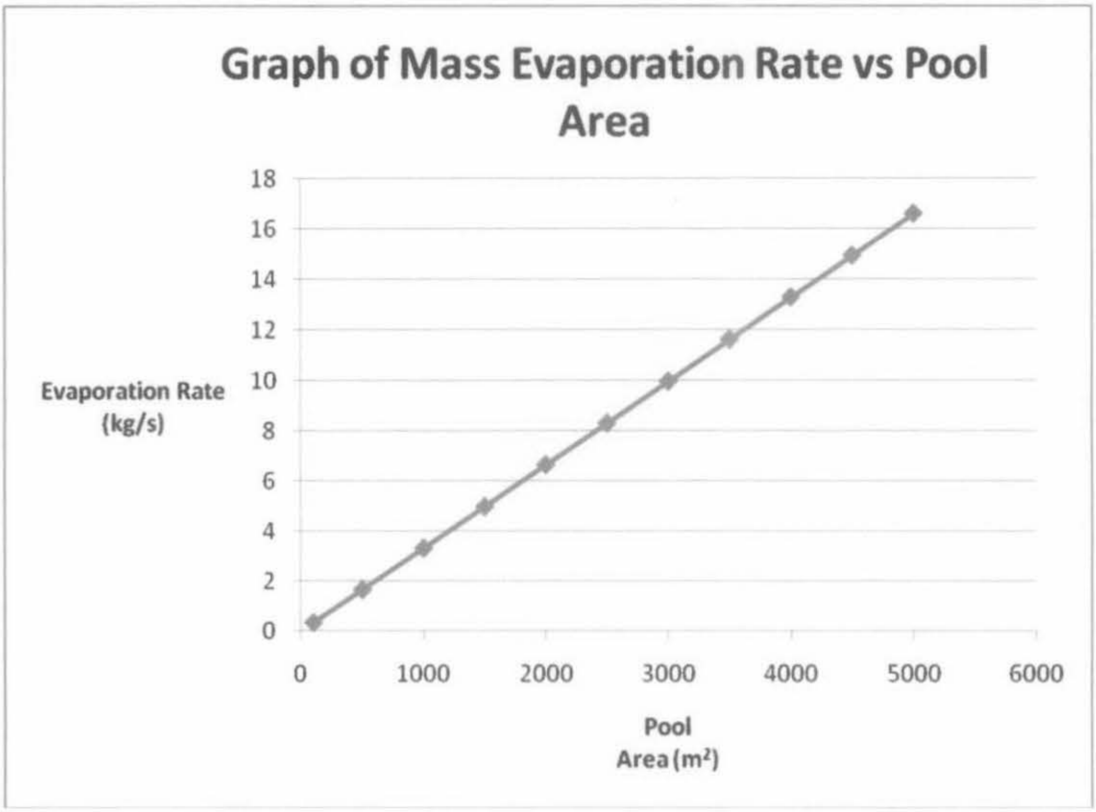


Figure 4.2: Correlation between pool area and mass evaporation rate due to solar radiation

4.1.3 Estimating Heat Flux from the Ground

Based on the equation 2-1, heat flux from the ground, q_g which control the heat transfer in the initial stage can be determined. With assumptions of thermal diffusivity of soil, α_s value of 4.16 x 10-7 m^2/s, thermal conductivity of soil, k_s of 0.92 W/m K and soil temperature, T_g of 30°C (CCPS, 1999), the correlation between q_g and time after spill, t is as the following and shown graphically in Figure 4.3.

$$q_g = \frac{0.92(30-23)}{(\pi(4.16\times10^{-7})t)^{1/2}}$$

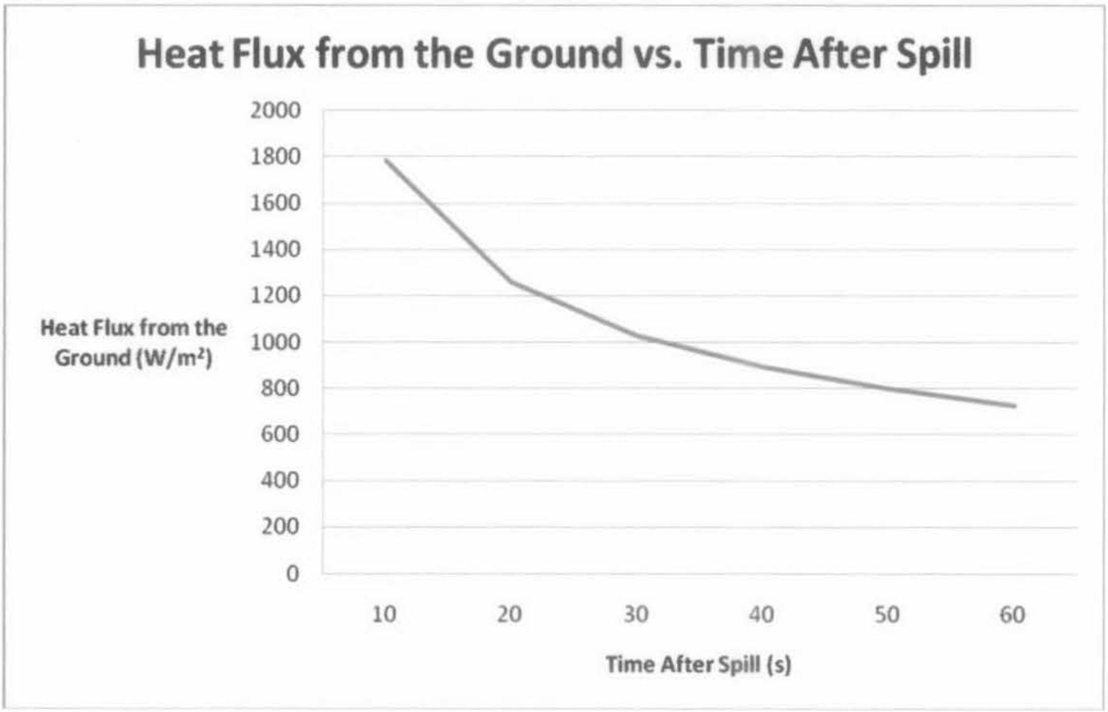


Figure 4.3: Correlations between heat flux from the ground and time after spill

At the beginning of the spillage, the heat flux from the ground is high. Taking at 10 seconds after the spill, the heat flux is 1782 W/m^2 and it decreases with time. After one minute of the spill, the amount of heat flux decreasing to 727.44 W/m^2. This is because as the time goes by, the temperature gradients or the temperature difference, ΔT decreases because of the heat transfer that continuously happen between the ground and the liquid. As a result, heat flux amount will decrease.

4.1.4 Estimating Flammability Limits of the Sample

By using Equation 3-2, lower flammability limit can be estimated if the heat of combustion value for the sample is known,

where:

ΔH_c must be in 10^3 kJ/mol unit.

The value ΔH_c from the bomb calorimeter is 45 745 J/g.

Hence, the calculated ΔH_c value is 8600.38 kJ/mol or 8.60038 x 10^3 kJ/mol.

$$LFL = \frac{-3.42}{8.60038} + 0.569(8.60038) + 0.0538(8.60038)^2 + 1.80$$

$$LFL = 10.28\%$$

While for the upper flammability limit, Equation 3-3 is applicable:

$$UFL = 6.30(8.60038) + 0.567(8.60038)^2 + 23.5$$

$$UFL = 119.62$$

$$UFL = 100\%$$

For the gas, if the Explosive Limit lies between 10.28% and 100%, it is flammable.

4.1.5 Damage Due to Overpressure

Overpressure can be obtained from Equation 3-4.

To get p_o, first equivalent mass of TNT, m_{TNT} must be known first. It can be calculated from the following formula:

$$m_{TNT} = \frac{\eta m \Delta H_c}{E_{TNT}} \qquad (4\text{-}1)$$

where:
m_{TNT} = is the equivalent mass of TNT
η = the empirical explosion efficiency
m = is the mass of hydrocarbon
ΔH_c = energy of explosion of the flammable gas
E_{TNT} = energy of explosion of TNT

Assuming $\eta = 0.02$, m=1000 kg and E_{TNT} is a constant of 4686 kJ/kg into Equation 4-1,

$$m_{TNT} = \frac{0.02(1000kg)(8600.38kJ/mol)}{4686kJ/kg(0.18801kg/mol)}$$

$$m_{TNT} = 195.24 kgTNT$$

Next, the value of scale distance, z_e is calculated using the m_{TNT} value,

$$z_e = \frac{r}{m_{TNT}^{1/3}}$$

where:

m_{TNT} = is the equivalent mass of TNT
r = ground-zero point of the exposion

Assuming r = 70 m,

$$z_e = \frac{70}{195.24^{1/3}}$$

$$z_e = 12.07 m/kg^{1/3}$$

z_e value is then inserted into Equation 3-5,

$$p_o = \frac{1616\left[1+\left(\frac{12.07}{4.5}\right)^2\right]}{\sqrt{1+\left(\frac{12.07}{0.048}\right)^2}\sqrt{1+\left(\frac{12.07}{0.32}\right)^2}\sqrt{1+\left(\frac{12.07}{1.35}\right)^2}} \times 101.3kPa$$

$$p_o = 15.72kPa$$

From the overpressure value, damage can be checked from table in Appendix A.

As for p_o = 15.72 kPa, the damage are:

→Concrete or cinder block walls, not reinforced, shatter and

→Lower limit of serious structural damage.

4.2 GAS MIXTURE

From the liquid sample identification by using GC, the first alkane to be found in the sample is nonane (C_9H_{20}). Nonane and heavier alkanes (e.g. decane, dodecane, tetradecane) are found in a very large amount in the liquid sample. It shows that there is possibility that lighter alkanes such as pentane, hexane and heptanes already vaporized prior to the identification. Table 4.1 shows the boiling point of alkanes between methane (C_1) and decane (C_{10}) together with their respective state at 25°C.

Table 4.1: Boiling Point for Alkanes

Name	Molecular Formula	Boiling Point (°C)	State at 25°C
Methane	CH_4	-164	Gas
Ethane	C_2H_6	-89	Gas
Propane	C_3H_8	-42	Gas
Butane	C_4H_{10}	-0.5	Gas
Pentane	C_5H_{12}	36	Liquid
Hexane	C_6H_{14}	69	Liquid
Heptane	C_7H_{16}	98	Liquid
Octane	C_8H_{18}	125	Liquid
Nonane	C_9H_{20}	151	Liquid
Decane	$C_{10}H_{22}$	174	Liquid

From Table 4.1, methane, ethane, propane and butane are all expected to be vaporized in the plant due to their respective low boiling point. The possible gases from the sample are expected to be pentane (C_5), hexane (C_6), heptane (C_7) and octane (C_8) as from nonane and other heavier alkanes already found in the liquid sample.

4.2.1 Gas Sample Analysis

From the steps of gas mixture identification explained in Section 3.2, GC analysis has been done on the sample at five different temperatures. The result for the first run, where the temperature of water is 28°C is as in the Figure 4.3 and Table 4.2 below.

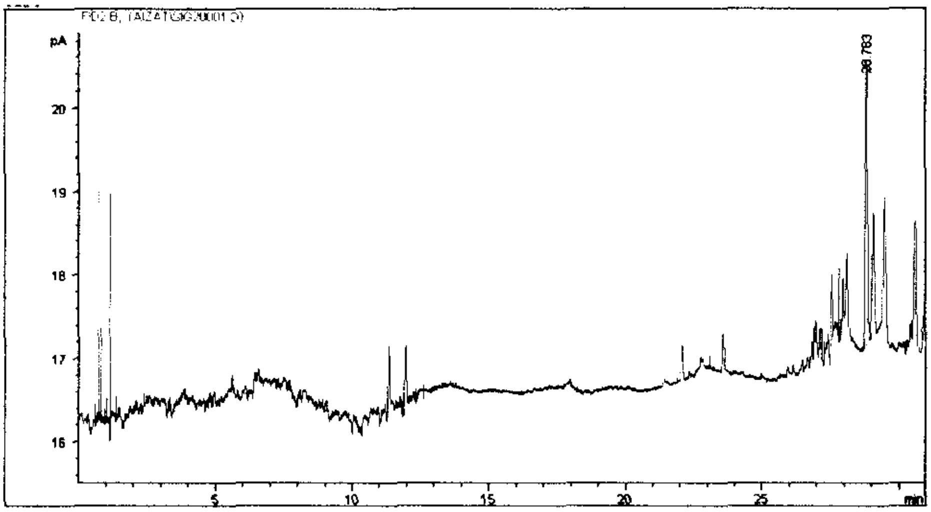


Figure 4.3: GC Result (Peak) at 28°C

Table 4.2: GC Result at 28°C

Peak No.	Retention Time (min)	Width (min)	Area (pA*s)	Area %	Name
1	1.160	0	0	0	Methane
2	1.367	0	0	0	Ethane
3	1.651	0	0	0	Ethylene
4	2.410	0	0	0	Propane
5	4.305	0	0	0	Propylene
6	5.592	0	0	0	Acetylene
7	5.922	0	0	0	iso-butane
8	6.089	0	0	0	1,2-Propadiene
9	6.216	0	0	0	n-Butane
10	9.081	0	0	0	trans-2-Butene
11	9.260	0	0	0	1-Butene
12	9.846	0	0	0	iso-Butane
13	10.306	0	0	0	cis-2-Butene
14	11.345	0	0	0	Iso-Pentane
15	11.966	0	0	0	Methyl acetylene
16	12.476	0	0	0	n-Pentane
17	13.035	0	0	0	1,3-Butadiene
18	14.481	0	0	0	Trans-2-Pentene
19	15.051	0	0	0	2-Methyl-2-butene + 1-Pentene
20	15.670	0	0	0	Cis-2-Pentene
21	17.979	0	0	0	*n*-Hexane
22	28.783	0.0692	15.13636	100	?

From the above table, the gas that presence in the sample is only detected when the retention time is 28.783 minutes. The gas detected is heavier than n-Hexane (C_6) gas and the gas should be one of the gases containing C_7 and C_8. The sample does not have any light gases such as methane, ethane and butane. The test is then repeated by heating the sample at different water temperature: 30°C, 35°C, 40°C and 45°C.

For the temperature of 30°C, Figure 4.4 and Table 4.3 show the results.

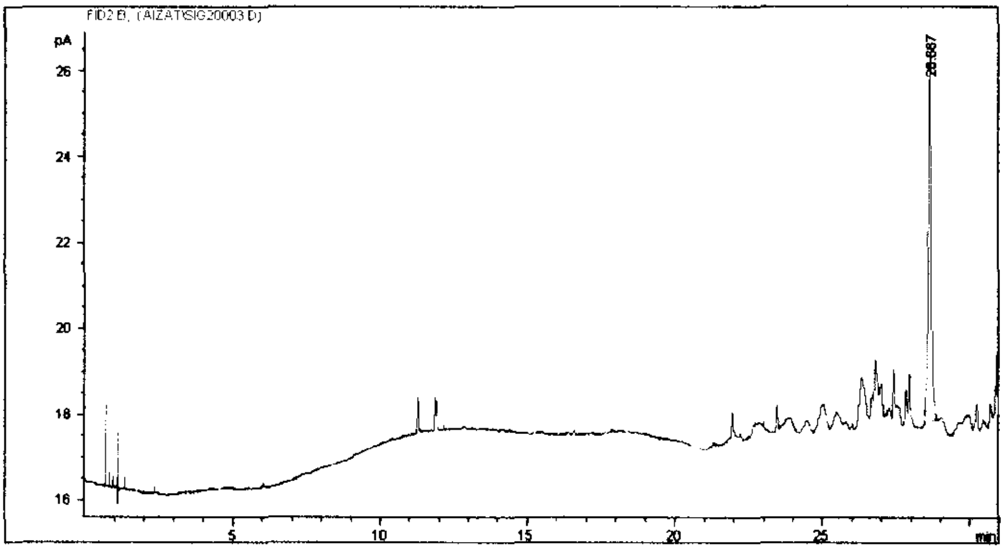


Figure 4.4: GC Result (Peak) at 30°C

Table 4.3: GC Result at 30°C

Peak No.	Retention Time (min)	Width (min)	Area (pA*s)	Area %	Name
1	1.160	0	0	0	Methane
2	1.367	0	0	0	Ethane
3	1.651	0	0	0	Ethylene
4	2.410	0	0	0	Propane
5	4.305	0	0	0	Propylene
6	5.592	0	0	0	Acetylene
7	5.922	0	0	0	iso-butane
8	6.089	0	0	0	1,2-Propadiene
9	6.216	0	0	0	n-Butane
10	9.081	0	0	0	trans-2-Butene
11	9.260	0	0	0	1-Butene
12	9.846	0	0	0	iso-Butane
13	10.306	0	0	0	cis-2-Butene
14	11.345	0	0	0	Iso-Pentane
15	11.966	0	0	0	Methyl acetylene
16	12.476	0	0	0	n-Pentane
17	13.035	0	0	0	1,3-Butadiene
18	14.481	0	0	0	Trans-2-Pentene
19	15.051	0	0	0	2-Methyl-2-butene + 1-Pentene
20	15.670	0	0	0	Cis-2-Pentene
21	17.979	0	0	0	n-Hexane
22	28.667	0.1062	65.30811	100	?

For this sample, the first peak detected is when the retention time is 28.667 minutes, does not show any significant deviation with the previous run (water temperature at 28°C). This is because the temperature difference is small, that is 2°C. The species is heavier than the n-hexane and cannot be specifically detected. It is expected the gas detected is between heptane (C_7) and octane (C_8)

The GC result for the water temperature of 35°C is as in the Figure 4.5 and Table 4.4.

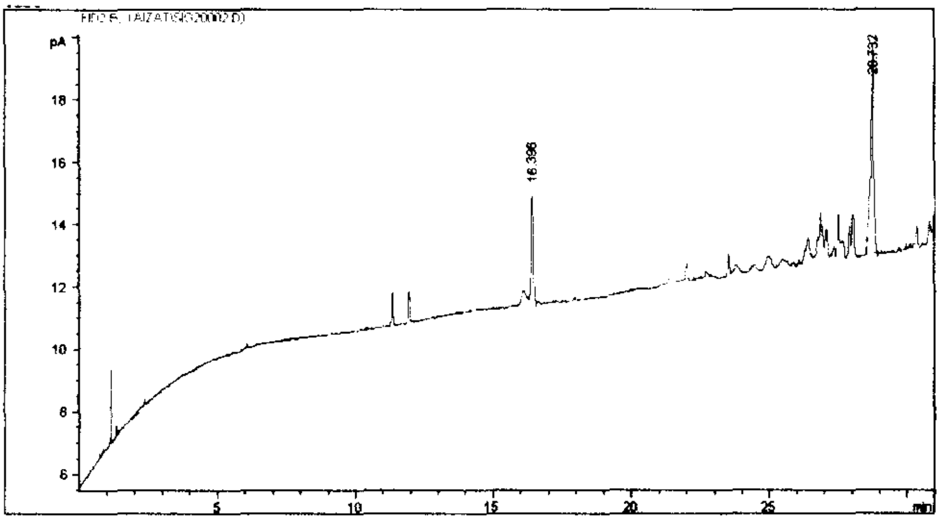


Figure 4.5: GC Result (Peak) at 35°C

When the liquid sample is heated by using water at the temperature of 35°C, the GC result on the gas formed shows the presence of a hydrocarbon gas between cis-2-Pentene (C_5) and n-Hexane (C_6). It means that the gas contain either 5 carbons (C_5) or 6 carbons (C_6) in its molecule. The other peak formed at 28.732 minutes, almost similar to the previous temperatures which indicate the presence of gas from either C_7 or C_8 type.

Table 4.4: GC Result at 35°C

Peak No.	Retention Time (min)	Width (min)	Area (pA*s)	Area %	Name
1	1.160	0	0	0	Methane
2	1.367	0	0	0	Ethane
3	1.651	0	0	0	Ethylene
4	2.410	0	0	0	Propane
5	4.305	0	0	0	Propylene
6	5.592	0	0	0	Acetylene
7	5.922	0	0	0	iso-butane
8	6.089	0	0	0	1,2-Propadiene
9	6.216	0	0	0	n-Butane
10	9.081	0	0	0	trans-2-Butene
11	9.260	0	0	0	1-Butene
12	9.846	0	0	0	iso-Butane
13	10.306	0	0	0	cis-2-Butene
14	11.345	0	0	0	Iso-Pentane
15	11.966	0	0	0	Methyl acetylene
16	12.476	0	0	0	n-Pentane
17	13.035	0	0	0	1,3-Butadiene
18	14.481	0	0	0	Trans-2-Pentene
19	15.051	0	0	0	2-Methyl-2-butene + 1-Pentene
20	15.670	0	0	0	Cis-2-Pentene
21	16.396	0.0792	19.30603	27.42713	?
22	17.979	0	0	0	n-Hexane
23	28.732	0.1061	51.08426	72.57287	?

The results obtained when the liquid sample is submerged into 40°C water are shown in Figure 4.6 and Table 4.5.

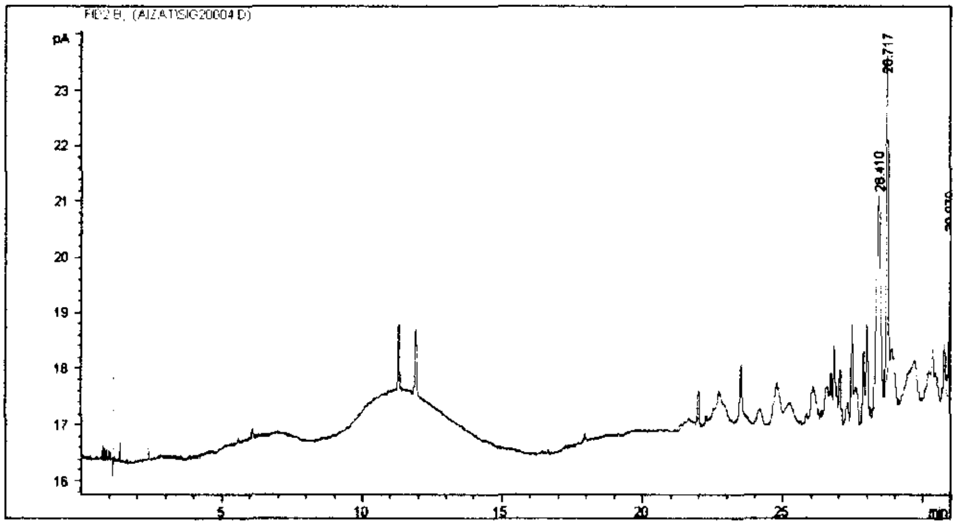


Figure 4.6: GC Result (Peak) at 40°C

The result shows that all three peaks detected are heavier gases than n-hexane and cannot be precisely detected. The retention time when the first and the second peak formed is very close to the first three runs, that is in the region of 28 minutes. This shows that there is a presence of a stable gas in that region. At 30.970 minutes, new gas has been detected, with a probability of its vaporization due to the higher temperature compared to prior runs. All three types of gases detected must be from species containing seven or eight carbons in its molecule (C_7 or C_8)

Table 4.5: GC Result at 40°C

Peak No.	Retention Time (min)	Width (min)	Area (pA*s)	Area %	Name
1	1.160	0	0	0	Methane
2	1.367	0	0	0	Ethane
3	1.651	0	0	0	Ethylene
4	2.410	0	0	0	Propane
5	4.305	0	0	0	Propylene
6	5.592	0	0	0	Acetylene
7	5.922	0	0	0	iso-butane
8	6.089	0	0	0	1,2-Propadiene
9	6.216	0	0	0	n-Butane
10	9.081	0	0	0	trans-2-Butene
11	9.260	0	0	0	1-Butene
12	9.846	0	0	0	iso-Butane
13	10.306	0	0	0	cis-2-Butene
14	11.345	0	0	0	Iso-Pentane
15	11.966	0	0	0	Methyl acetylene
16	12.476	0	0	0	n-Pentane
17	13.035	0	0	0	1,3-Butadiene
18	14.481	0	0	0	Trans-2-Pentene
19	15.051	0	0	0	2-Methyl-2-butene + 1-Pentene
20	15.670	0	0	0	Cis-2-Pentene
21	17.979	0	0	0	n-Hexane
22	28.410	0.1411	39.95757	51.3445	?
23	28.717	0.0652	24.50401	31.46863	?
24	30.970	0.0700	13.40648	17.21692	?

Finally are the results for the water temperature of 45°C, interpreted in Figure 4.7 and Table 4.6.

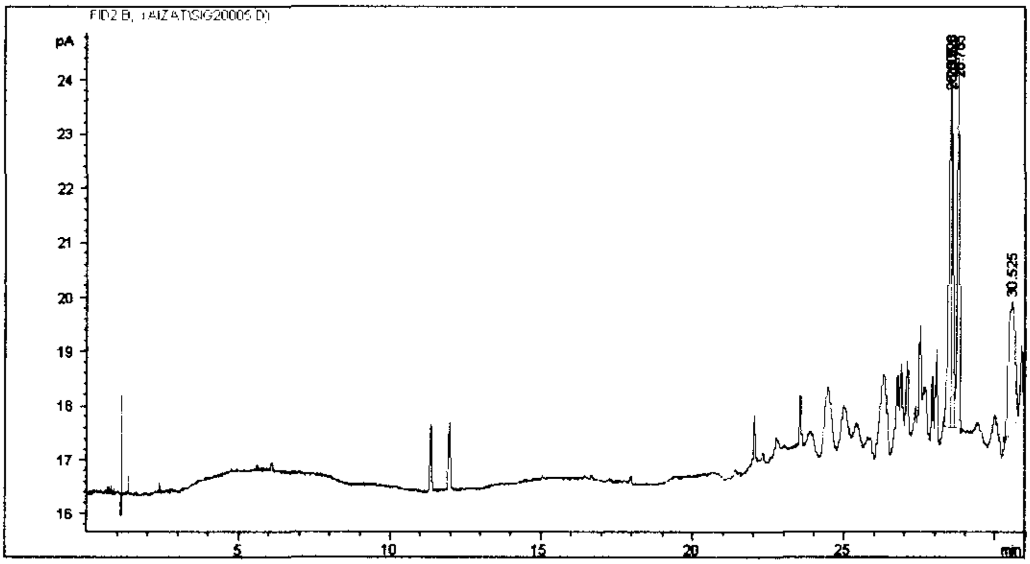


Figure 4.7: GC Result (Peak) at 45°C

Table 4.6: GC Result at 45°C

Peak No.	Retention Time (min)	Width (min)	Area (pA*s)	Area %	Name
1	1.160	0	0	0	Methane
2	1.367	0	0	0	Ethane
3	1.651	0	0	0	Ethylene
4	2.410	0	0	0	Propane
5	4.305	0	0	0	Propylene
6	5.592	0	0	0	Acetylene
7	5.922	0	0	0	iso-butane
8	6.089	0	0	0	1,2-Propadiene
9	6.216	0	0	0	n-Butane
10	9.081	0	0	0	trans-2-Butene
11	9.260	0	0	0	1-Butene
12	9.846	0	0	0	iso-Butane
13	10.306	0	0	0	cis-2-Butene
14	11.345	0	0	0	Iso-Pentane
15	11.966	0	0	0	Methyl acetylene
16	12.476	0	0	0	n-Pentane
17	13.035	0	0	0	1,3-Butadiene
18	14.481	0	0	0	Trans-2-Pentene
19	15.051	0	0	0	2-Methyl-2-butene + 1-Pentene
20	15.670	0	0	0	Cis-2-Pentene
21	17.979	0	0	0	n-Hexane
22	28.505	0.0683	31.11252	23.25667	?
23	28.528	0.0778	33.87212	25.31948	?
24	28.765	0.0699	30.86661	23.07286	?
25	30.525	0.1885	37.92763	28.35098	?

Four types of gases are detected in this run, shows that increase in the water temperature evaporates the liquid sample into gases faster. The time retention between all four peaks is close, which is between 28.505 minutes and 30.525 minutes and the number of carbons in molecule of each species detected is either C_7 or C_8.

4.2.2 Ventilation Rate

For a closed drainage system, with temperature of the liquid inside is 23°C, ventilation rate must be provided to reduce the concentration of cumulated gas mixture inside the system. The concentration must not exceed the Permissible Exposure Level (PEL) of

OSHA to ensure a safe workplace. The correlation between the concentrations of the possible gas formed (between pentane and decane) with ventilation rate can be produced via the following formula

$$kC_{ppm} = \frac{KAP^{sat}}{Q_v P} \times 10^6 \tag{4-2}$$

where

C_{ppm} is the gas concentration (ppm),
k is the non ideal mixing factor = 1 (unitless),
A is the area of the pool (m^2),
P^{sat} is the saturation vapour pressure (mmHg),
P is the pressure of the surrounding (mmHg)
Q_v *is the ventilation rate* (m^3/s).

Saturation vapor pressure for each gas can be obtained by using Antoine equation. All of the calculations made on this section are limited to several assumptions which are:

- The temperature of the gas is at 23°C.
- *k* value is equal to 1, assumed it is a perfect mixing.
- Area of the drainage is 50 m x 0.5 m = 25 m^2.

Table 4.7 shows all necessary data needed to relate the concentration of each gas to the ventilation rate required based on equation 4-2.

Table 4.7: Properties for Ventilation Rate Determination

Name	Molecular Formula	Boiling Point (°C)	State at 25°C	MW (kg/kgmol)	K (m/s)	Antoine Parameters			T (°C)	$\log_{10}p^*$	p^* (mmHg)
						A	B	C			
methane	CH_4	-164	gas	16	0.0086	-	-	-	23	-	-
ethane	C_2H_6	-89	gas	30	0.0070	-	-	-	23	-	-
propane	C_3H_8	-42	gas	44	0.0062	-	-	-	23	-	-
butane	C_4H_{10}	-0.5	gas	58	0.0056	-	-	-	23	-	-
pentane	C_5H_{12}	36	liquid	72	0.0052	6.84471	1060.793	231.541	23	2.677236	475.5936
hexane	C_6H_{14}	69	liquid	86	0.0049	6.88555	1175.817	224.867	23	2.141808	138.6144
heptane	C_7H_{16}	98	liquid	100	0.0047	6.90253	1267.828	216.823	23	1.616015	41.30613
octane	C_8H_{18}	125	liquid	114	0.0045	6.91874	1351.756	209.1	23	1.094716	12.43701
nonane	C_9H_{20}	151	liquid	128	0.0043	6.93764	1430.459	201.808	23	0.574615	3.755041
decane	$C_{10}H_{22}$	174	liquid	142	0.0042	6.95707	1503.568	194.738	23	0.05167	1.126341

For pentane, hexane, heptane and octane that have the possibility to be found in the gas mixture, the PEL of each of the gas as stated by OSHA are as in Table 4.8. The data in the table are extracted from Crowl and Louvar (2002).

Table 4.8: OSHA PELs for possible gases in gas mixtures

Gas	OSHA Permissible Exposure Level (PEL) (ppm)
Pentane	1000
Hexane	500
Heptane	500
Octane	500

The PEL indicates the dose that the body is able to detoxify and eliminate the agent without any detectable effects. For example, from the table, a body can stand to be exposed to a release of pentane below 1000 ppm without giving bad effects to his body. From equation 4-2 and the data in Table 4.7, the following correlation in Figure 4.8 between concentration and required ventilation rate is developed for pentane.

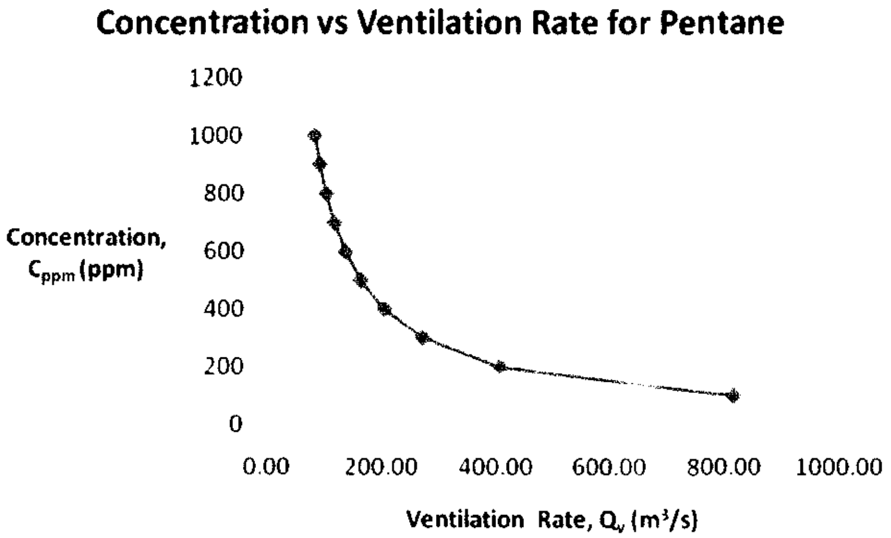


Figure 4.8: Correlation between pentane concentration and required ventilation rate.

From Figure 4.8, if the pentane concentration is at the PEL which is 1000 ppm, the ventilation rate required is 81.35 m^3/s. Figure 4.9 shows the same correlation for hexane gas.

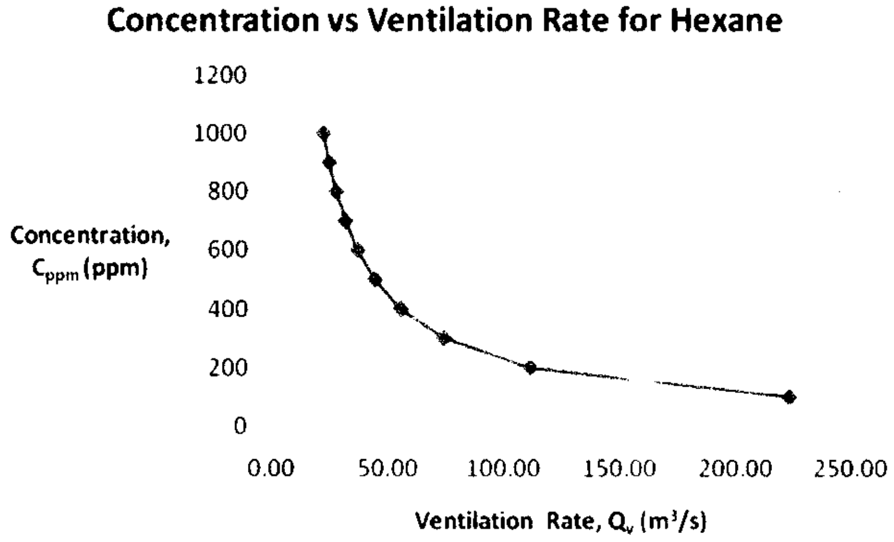


Figure 4.9: Correlation between hexane concentration and required ventilation rate.

When the concentration of hexane is at the PEL of 500 ppm, the ventilation rate required is 44.68 m^3/s. Figure 4.10 represents the correlation between heptane concentration to the required ventilation rate.

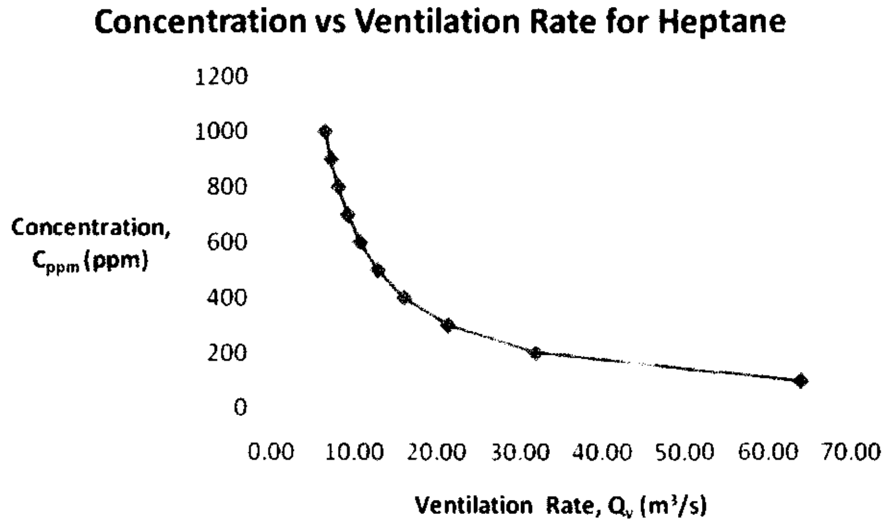


Figure 4.10: Correlation between heptane concentration and required ventilation rate.

The PEL of heptane is the same as hexane, which is at 500 ppm. Thus, from the correlation, 12.77 m^3/s of ventilation rate is required once the PEL value is met. Finally, Figure 4.11 shows the correlation of concentration to the ventilation rate required for the last possible alkane that might present in the gas mixture, the octane.

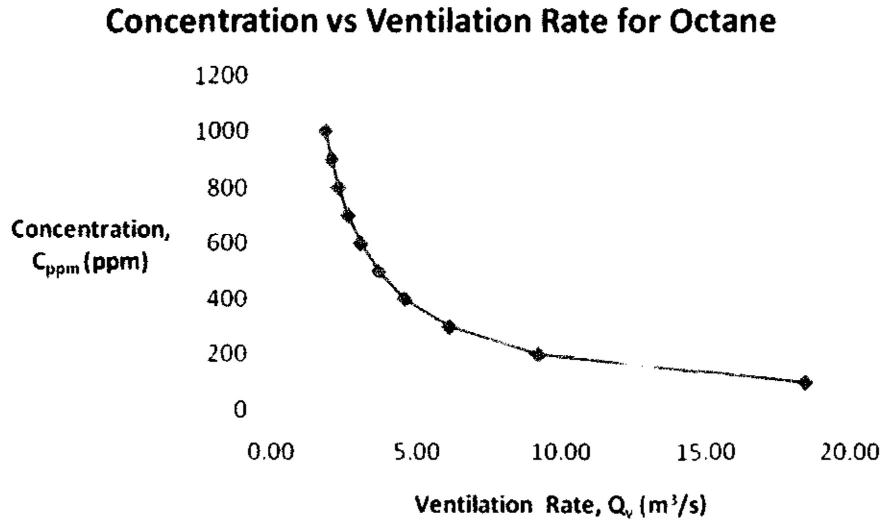


Figure 4.11: Correlation between octane concentration and required ventilation rate.

The required ventilation rate for PEL of octane, which is at 500 ppm is only 3.68 m^3/s.

4.3 FIRE PREVENTION

From the study that has been made, it has been found that two types of fire prevention methods are suitable to be applied. First is the fire prevention by design. All of the liquid waste must be either pre treated or screened before being sent to the drainage system. This is due to the high concentration of hydrocarbons inside the liquid sample that can cause fire and explosion. Another solution is to send the liquid waste directly to the waste management company. The design of the drainage system also must include more ventilation area. As explained in Section 4.2.2, ventilation rate is vital in ensuring that the concentration of flammable gases is under control. Closed drain area must be minimized and several closed sections in the plant must be replaced with open cover. This will ensure that the flammable gases will be ventilated away from accumulating in the drainage system. Another type of fire prevention is by safety precautions taken by the personnel. Apart from the suitable outfit, the personnel inside the plant must not do any action that can cause fire. For example, ignition source must be taken away from the plant area, including the drainage system. Work like welding which involves heat and fire must be avoided near the drainage system area because of the possibility that the accumulated flammable gas will react and caught in fire. Another way is by having personnel who will do the regular check on the gas concentration inside the drainage system so that the concentration is under the permissible limit and has very minimum possibility to be caught in fire.

CHAPTER 5

CONCLUSION

5.1 RECOMMENDATIONS

By current technology, fire and explosion analysis to the flammable gas mixture inside the drainage system can be done directly on the plant. The data collected will be the most precise one. The use of hydrocarbon detector for example can detect hundreds of gases and gives several parameters needed such as the concentration of gases and flammability limits immediately. Other latest explosion apparatus such as Cone Calorimeter and LIFT apparatus can be used in the analysis especially in determining the flame propagation or burning rate of the liquid sample. Cone calorimeter cannot be found in Malaysia currently and the cost to test the sample by using cone calorimeter oversea is expensive. Since the study is made on the liquid sample of wastewater from a refinery, it is suggested for the study to be done on other type of plant in petroleum industry such as an oil distribution plant, oil and gas terminal or other petrochemical plant.

5.2 CONCLUSION

Drainage system is often missed in the fire and explosion analysis prior to a plant's operation. Drainage system of a refinery plant consists of flammable materials that can evaporate and forms flammable gases. Risks of fire and explosion are always there, in case of the presence of ignition source and oxygen. For the liquid sample, the parameter that must be concerned about is the evaporation rate. Evaporation possibly happens by natural evaporation or evaporation due to solar radiation. Heat flux from the ground must also be taken into consideration. When they are in the gaseous form and ignition source is provided at the upper part of the drainage system where the vapor exists, fire and explosion can happen. Besides that, the impact of the explosion might as well be estimated from the data gathered by determining its overpressure value. For the gas formed when the liquid sample is heated, the analysis shows that the components in the liquid sample evaporate faster at higher temperature. The most suitable methods to minimize fire and explosion risks in this study are by design and personnel safety precautions. The liquid waste that is rich in hydrocarbons must be either pretreated before sent to the drainage system or handed directly to the waste management company. Sufficient ventilation rate must also be provided in the drainage system so as the concentration of combustible gases inside the drainage is under control. In this study, knowledge in process safety, specifically in fire and explosion analysis has been applied. In each of the possibilities, the causes have been determined thoroughly and the best possible solution was taken. The study also emphasis on having a save working environment and at the same time minimize lost for the company due to accidents involving fire and explosion.

REFERENCES

Al-Haddad A., Chmielewská E. and Al-Radwan S., A Brief Comparable Lab Examination for Oil Refinery Wastewater Treatment Using The Zeolitic and Cabonaceous Adsorbents, 2007.

Beard A. N., Fire Safety in Tunnels, Fire Safety Journal 44 (2009) 276-278.

Beard A. N., Cope D., Assessment of the Safety of Tunnels. Commissioned by the European Parliament via the committee on Science and Technology Options Assessment (STOA); report IP/A/STOA/FWC/2005-28/SC22/29.

Bellinger, R., Clark, D., Dowell III, A., Ewbank, R., Hendershot, D., Lutz, W., Meszaros, S., Park, D., and Wixom, E., Inherently Safer Chemical Processes, A Life Cycle Approach, AIChemE, Center for Chemical Process Safety, 1996.

Brooks M. R., Crowl D. A., Vapor Flammability Above Aqueous Solutions of Flammable Liquids, March 2007.

Campbell J. A., Mnizsewski K. R., on Flash Point for Safety Bulletin of Triodyne Inc. (1998)

Casal J., Evaluation of the Effects and Consequences of major Accidents in Industrial Plants, 2008.

Center for Chemical Process Safety (CCPS), Guidelines for Consequence Analysis of Chemical Releases, 1999.

Crowl D. A., Louvar J.F., Chemical Process Safety – Fundamentals with Application, 2nd Edition (2002) 225 – 265

Dikshit A. K., Amit Dutta, Ray S., Least Cost SO2 Emission Minimization for a Petroleum Refinery by Optimum Use of Source Reduction, Tail Gas Treatment and Flue Gas Desulphurization, 2005.

Doyle B. R., Hazardous Gas Underground, Applications to Tunnel Engineering (2001)

General Monitors' Technical Staffs, Fundamentals of Combustible Gas Detection - A Guide to the Characteristics of Combustible Gases and Applicable Detection Technologies, California.

Kuchta, J. M. (1985). Investigation of fire and explosion accidents in the chemical, mining, and fuel-related industries-A manual, 1959.

Lennard C., Fire Cause & Fire Debris Analysis - A Review: 1998 to 2001 (2001)

Owens K. A. and Hazeldean J. A., Fires, Explosions and Related Incidents at Work in 1992-1993, 1995.

PETRONAS' Sabah Oil and Gas Terminal (SOGT) Front-End Engineering Design (FEED) Improvement Study - Drainage Philosophy Report (Document no. SOGT(F)-PR-RP-2001) (2008).

Russell D. L., Practical Wastewater Treatment, Wiley InterScience, 2006.

Sax, N. I., (1984). Dangerous properties of industrial materials (6th ed). New York: Van Nostrand Reinhold Co.

Shaluf I. M., Ahmadun F. R., Aini M. S., Fire incident at a refinery in West Malaysia: The Causes and Lessons Learned, Journal of Loss Prevention in the Process Industries 16 (2003) 297–30

World Bank Group, Petroleum Refinery: Pollution Prevention and Abatement Handbook, July 1998.

Wray H. A., Manual on Flash Point Standards and Their Use: Methods and Regulations by American Society for Testing and Materials (1992)

Zabetakis, M. G., (1965). Flammability characteristics of combustible gases and vapors. Bulletin 627, Bureau of Mines, US Department of Interior, Washington, DC, 1965.

Websites:

http://www.egyptoil-gas.com/read_article_issues.php?MID=58&arch=true&AID=317

www.chemspider.com

http://www.elmhurst.edu/~chm/vchembook/501hcboilingpts.html

APPENDIX A

Table 6-9 Damage Estimates for Common Structures Based on Overpressure (these values are approximations)[1]

Pressure		
psig	**kPa**	**Damage**
0.02	0.14	Annoying noise (137 dB if of low frequency, 10–15 Hz)
0.03	0.21	Occasional breaking of large glass windows already under strain
0.04	0.28	Loud noise (143 dB), sonic boom, glass failure
0.1	0.69	Breakage of small windows under strain
0.15	1.03	Typical pressure for glass breakage
0.3	2.07	"Safe distance" (probability 0.95 of no serious damage below this value); projectile limit; some damage to house ceilings; 10% window glass broken
0.4	2.76	Limited minor structural damage
0.5–1.0	3.4–6.9	Large and small windows usually shatter; occasional damage to window frames
0.7	4.8	Minor damage to house structures
1.0	6.9	Partial demolition of houses, made uninhabitable
1–2	6.9–13.8	Corrugated asbestos shatters; corrugated steel or aluminum panels, fastenings fail, followed by buckling; wood panels (standard housing), fastenings fail, panels blow in
1.3	9.0	Steel frame of clad building slightly distorted
2	13.8	Partial collapse of walls and roofs of houses
2–3	13.8–20.7	Concrete or cinder block walls, not reinforced, shatter
2.3	15.8	Lower limit of serious structural damage
2.5	17.2	50% destruction of brickwork of houses
3	20.7	Heavy machines (3000 lb) in industrial buildings suffer little damage; steel frame buildings distort and pull away from foundations
3–4	20.7–27.6	Frameless, self-framing steel panel buildings demolished; rupture of oil storage tanks
4	27.6	Cladding of light industrial buildings ruptures
5	34.5	Wooden utility poles snap; tall hydraulic presses (40,000 lb) in buildings slightly damaged
5–7	34.5–48.2	Nearly complete destruction of houses
7	48.2	Loaded train wagons overturned
7–8	48.2–55.1	Brick panels, 8–12 in thick, not reinforced, fail by shearing or flexure
9	62.0	Loaded train boxcars completely demolished
10	68.9	Probable total destruction of buildings; heavy machine tools (7000 lb) moved and badly damaged, very heavy machine tools (12,000 lb) survive
300	2068	Limit of crater lip