STUDY OF EVAPORATION RATE AND IGNITION OF VAPORS ABOVE REFINERY WASTEWATER CONTAMINATED WITH A MIXTURE OF HYDROCARBONS

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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.

NUR IZZATI BINTI BOHER @ BUJANG AMRI

ABSTRACT

Study of fire and explosion is very important mainly in refineries and industries due to several accidents which have been reported in the past and present. This study investigates the possibility of the occurrence of fire accident occasioned by the vaporization of hydrocarbon components derived from refinery wastewater drainage systems.

In this study, liquid sample containing mixtures of hydrocarbon products and water were collected from a refinery's drainage systems and subjected to a distillation process to separate the water contents. The oil-liquid phase was analyzed using Gas Chromatography Mass Spectrometry (GC-MS) to examine the compositions of the sample. The results obtained indicate that there are 77 hydrocarbon components ranging from C_9 to C_{22}. Mole fractions of components in the liquid phase were obtained from the GC results, while the mole fractions of gas components in gas phase were calculated via modified Raoult's Law.

The evaporation rate and ignition of vapour above refinery wastewater contaminated by mixture of hydrocarbon were assessed. Evaporation Rate, Q_m of each hydrocarbon was estimated by using generalized expression as proposed by Crowl and Louvar, (2002) and the Minimum Ignition Energy, MIE of each component was determine by interpolating the graph of MIE versus Mass Transfer Number, B as introduced by Ballal (1938b).

From the calculations, 2-methyl-octane at peak number 53 has been identified to have the fastest Q_m which is equal to 27.04 g/min and 1, 7-dimethyl-naphtalene at peak number 63 has been identified to have the lowest MIE. 1-nonadecanol at peak number 40 has been identified to have the slowest Q_m that is equal to 0.0000157 g/min and largest MIE value that is equal to 2.620 mJ. This calculation indirectly indicates that 1-nonadecanol is hard to be ignited and takes longer time to vapourized. The results also shows that evaporation rate of components presented in the drainage system is affected by its flash point, volume percent and vapour pressure. Minimum ignition energy of the components is affected by its flash point, volume percent and the number of carbons that make up the structural of the components.

The findings of this study can be used to minimize fire hazards associated with presence of hydrocarbon vapours derived from refinery wastewater streams.

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CHAPTER 1
INTRODUCTION

1.1 Background Study

According to Polprasert and Liyanage (1996), waste is considered hazardous if it exhibits ignitability, corrosively, reactivity and toxicity. Anyhow, the liquid waste is the most abundance waste either in quality or quantities. Rate of water consumptions by petroleum refinery is depends on the size, crude oil, products and complexity of operations.

Refinery is producing various types of products. At the same time, it can generate large volumes of wastewaters containing various petroleum hydrocarbons, heavy metals, sulphur and ammonia at concentrations that typically require treatment prior to final discharge (Al-Haddad et al., 2007). Liquid waste produced in the industrial process contains hydrocarbon and oil. Hydrocarbon containing refinery wastewaters may be composed of flammable substances and some of these compounds may create flammable mixtures with air due to the evaporation occurs at ambient temperature and atmospheric pressure. As for petroleum hydrocarbons, the fuels may contain hundreds of individual constituents of several different chemical classes (Kostecki and Calabrese, 1991).

With respect to hydrocarbon components, highly flammable compounds such as benzene, toluene, ethylbenzene and xylenes may be present and they pose significant threat of fire hazard. Hydrocarbon compounds from these drainage flows can vary widely in compositions from day-to-day due to operational activities such as storage of waste liquids from drains, equipment cleaning and spills. The presence of flammable mixtures exposes drainage system to the possibility of fire and explosion events. Fire triangle indicates that the three elements necessary to ignite ordinary burning and fires are; fuel, oxygen and heat and these hydrocarbons fall under fuel category.

Drainage systems in plants contain various types of wastewater collected from all processes involved with different chemicals and processing conditions. Thus, the design of drainage system should take account of the processes in the plant and the chemicals likely to be present (Vince, 2008). It 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 prior to discharge into public water. In order to meet this requirement, a proper segregation of different effluent categories is needed and the effluent is treated according to its source and type of contaminants.

Fire might result in explosion, provided that certain parameters, i.e. the Lower Flammability Limit (LFL) and Upper Flammability Limit (UFL) of the hydrocarbon are met. It is necessary to understand the properties of flammable materials, when we deal or handle dangerous substances. Fires and explosions in industries can be prevented by understanding the flammable limits of gases. Therefore, flammability limits and related information are crucial in the industrial processes where serious hazards may be encountered within the flammability limits.

There are innumerable situations where gases, liquids, and hazardous chemicals are produced, stored, or used in a process that, if released, could potentially result in hazardous fire and/or explosive incident. It is therefore imperative to analyse all materials and reactions associated with a particular process, including production, manufacturing, storage, or treatment facilities in order to minimize the chances of an undesirable situation. Each process needs to be analysed with respect to the potential for the occurrence of fire and explosion in the work place. Evaporation and ignition characterization can be useful to evaluate the hazards of the gases/vapour during handling, storing, and transporting. Furthermore, it can help in determining corrective actions to prevent accidents.

The sources of ignition are numerous; consequently it is impossible to identify and eliminate them all (Crowl and Louvar, 2002). However, it is still a must to identify and eliminate them in order to have a safer operation of chemical plants. A thorough safety analysis is vital in order to eliminate all possible ignition sources in each of the units where there is possibility of flammable gas present. Elimination of ignition sources with the greatest probability of occurrence shall be given the greatest attention since the possibility of a fire or explosion increases rapidly as the number of ignition sources increases. In the past there have been many tunnel and underground fire and explosion accidents. Probably the most serious tunnel explosion occurred in the United Kingdom

(UK) in 1984, which killed 16 people, and was attributed to accumulated methane beneath a petrol station.

1.2 Problem Statement

Generally, flammable material or flammable vapour is among the major factor that contributes towards major accident such as fire in oil and gas industries. Refineries can generate large volumes of polluted wastewaters containing various petroleum hydrocarbons, heavy metals, sulfur and ammonia. Hydrocarbon containing refinery wastewaters may be composed of flammable substances such as: benzene, toluene, ethylbenzene and xylenes. Over the time, the mixture of water and hydrocarbon in drainage system at certain conditions will naturally separate and form distinct liquid phases, based on density and polarity of the material. However, some compounds can evaporate and turn into vapour form at ambient temperature and atmospheric pressure, which may create flammable mixtures with air. The presence of flammable mixtures exposes drainage system to the possibility of fire and explosion events due to any source of heat, spark, or external factor such as static electricity. Therefore, it is important to estimate the evaporation rate and to determine the other parameters such as the auto ignition temperature (AIT), heat of combustion (H_c), and the Minimum Ignition Energy (MIE) of each component that may form the vapour-air mixture. The outcomes of study can contribute to minimizing the loss of properties, business and life due to fire accidents by providing the best method.

1.3 Objectives of the Study

The objectives of this study are:

1) To estimate the evaporation rate and concentration of the volatile substances derived from refinery wastewater in the drainage system.
2) To estimate the minimum ignition energy required to initiate combustion of the vapour mixture.
3) To identify and recommend suitable inherent safety methods to be applied to prevent fire and explosion incidents from occurring.

1.4 Scope of Study

This study is limited to the following:

1) Process industry.

This study is limited to refinery industry.

2) System.

For this study, only drainage system will be taken into consideration.

3) Types of hazards.

This study only considered hazards that related to the vapour hydrocarbons in the refinery drainage system that can lead to fire and explosion to happen.

4) Analysis of results.

All calculations are solely based on measurable data obtained from previous related research on this topic. Some of the parameters are assumed to be in atmospheric pressure and ambient temperature.

1.5 Significance and Relevancy of Study

This project is basically focusing on the evaporation rate of the liquid hydrocarbons in the refinery's drainage system that may form a flammable mixture with air during evaporation at atmospheric pressure and ambient temperature. By estimating the evaporation rate of liquid hydrocarbons in the refinery's drain, the relative concentration of the hydrocarbons in the vapour form can be estimated as well. From this estimation, the ventilation rate, which is part of chemical plant control techniques, can be calculated prior to determine the appropriate control methods in order to reduce the possibility of accidents such as fire and explosion from occurs. Apart from this, the MIE required to ignite the mixture to start the fire can also be determine as well.

The finding from this study can help in:

1) Suggesting the most applicable chemical plant control techniques depending on types of hydrocarbons.
2) Reducing the probability of the compounds that can lead to flammable mixtures once the suitable control techniques are provided.

3) Reducing the possibility of the drainage system from accidents such as fire and explosion.

CHAPTER 2
LITERATURE REVIEW

2.1 Hazardous Materials

A hazardous material is any item or agent (biological, chemical, physical) which has the potential to cause harm to humans, animals, or the environment, either by it or through interaction with other factors (Institute of Hazardous Materials Management, 2010). There are basically three categories of hazardous materials in process industries; flammable, toxic and reactive materials.

Any materials that can be ignited to give a number of possible hazardous effects, depending on the actual materials and conditions are fall under flammable materials. Other hazards caused by the smoke of combustion could be suffocated as well. As for toxic materials, the release of it can give rise to dispersing clouds in atmosphere, which can be harmful to men and animals through inhalation or absorption through skin. According to Mustapha and Mc Donnell (2001), reactive materials can be classified into water-reactive materials, air reactive materials, oxidizers, unstable materials and incompatible material.

In order for the fire to occur, three elements which are fuel, heat and oxygen must exist. In the event of one element not present, the fire will not occur. In lieu to this, most fire protection and prevention efforts concentrate on removing one or more elements in the fire triangle in order to prevent fire. An understanding of fire characteristics and behavior of flammable materials both when contained and when released is necessary so that correct responses may be designed into a facility or planned action to be taken (Nolan, 1996).

2.2 Flammable and Combustible Liquid

Flammable liquids will ignite and burn more easily than combustible liquids at normal working temperatures while combustible liquids can burn when their temperatures increasing above working temperatures. Thus, the flammables liquids are considered to be more hazardous as compared to the combustible liquids. However, a flammable mixture can also form at temperatures below the flash point of the liquid combustible either if the latter is sprayed into the air, or if a mist or foam forms (Zabetakis, 1924). Basically, flammable liquid does not burn itself. It will form vapor that will burn, and the vaporization of a liquid depends on its temperature and vapor pressure. As the liquid becomes warmer, it will become more potentially hazardous. The flammability of a liquid depends on the degree to which the liquid forms flammable vapors. In an atmosphere that has a greater amount of oxygen (>21%), the flammable liquids can burn readily and fiercely as compared to the atmosphere that have a normal composition of oxygen (21%).

Although in general the combustible liquids seem to be less hazardous as compared to flammable liquids, it also can release enough vapor to form burnable mixtures with air at temperatures above their flash point. At high temperature, the combustible liquids can be as hazardous as flammable liquids to cause fire.

Precautions through the control of ignition sources such as open flames, lightning, hot surfaces, radiant heat, smoking, cutting and welding, static electricity, electrical sparks and stray currents, heating equipment shall be taken in order to prevent the ignition of flammable mixtures. Elimination of ignition sources and proper ventilation are examples of recommendations that can be made in order to prevent fire occurring from flammable mixtures.

2.3 Refinery

Generally, refinery is a production facility composed of a group of chemical engineering unit processes and unit operations refining certain materials or converting raw material into valuable products. According to (Shaluf et al, 2003), a refinery possesses a large inventory of hazardous materials, which exceed the threshold quantities and, therefore, are classified as major hazard installations. In addition, the hydrocarbon content in the drains of the refinery could vary widely in composition from day-to-day due to nature of the process itself (i.e., storage of waste liquids from drains, equipment cleaning and spills). Due to this variation, there are innumerable conditions exist from the production, storing and usage of these gases, liquids and hazardous chemicals that can result in fire and explosion accident due to leakage and accidental release.

Basically, study of fire and explosion is very important mainly in refineries and industries due to several accidents which have been reported in the past and present (Shaaran, 2009). Table 1 summarized the reported major accidents in chemical process industries from the year of 1943 to 2010.

Table 2.1: Summary of Reported Major Accidents in Chemical Process Industries.

(Source: Khan and Abbasi, 1999; BBC, 2001; BBC, 2005; The New Straits Times, 2008; Maykuth, 2009)

Year	**Location**	**Chemical**	**Death/Injury**
1943	Los Angeles, CA	Butane	5/ > 25
1944	Denison, TX	Butane	10/45
1949	Perth, NJ	Hydrocarbons	4/26
1954	Bitburg, Germany	Kerosene	32/16
1958	Signal Hills, CA	Oil forth	2/34
1962	RasTaruna, Saudi Arabia	Propane	1/111
1966	Larsoe, LA	NGL	7/20
1969	Teeside, UK	Cyclohexane	2/23
1972	Lynchburg, VA	Propane	2/3
1973	Kingman, AZ	Propane	13/89
1973	Austin, TX	NGL	6/21
1973	Staten Island, NY	LNG	40
1975	Eagle Pass, TX	Propane	16/7
1976	Los Angles, CA	Gasoline	6/35
1976	Gadsden, AL	Gasoline	3/24
1977	Umm Said, Qatar	LPG	7/87
1978	Santa Cruz, Mexico	Propylene	52/88
1978	Texas City, TX	Butane	7/11
1986	Mont Belyieu, TX	Propane	18/56
1986	Pascagoula, MS	Aniline	7/119
1988	Maharastra, India	Naphtha	15/21
1990	Channeiview, TX	Waste oil	23/130
1994	Dronka, Egypt	Fuel	3/25
1995	Ukhta, Russia	Gas	410/500
1996	Bombay, India	Hydrocarbon	12/20
1997	Chennai, India	LPG	2/45
2004	Snoqualmie, USA	Propane	0/0
2005	Shively, KY	Fuel	0/2
2008	TanjungLangsat, Malaysia	Petrol	0/0
2009	Sunoco, Philadelphia	Hydrogen Fluoride	0/13
2010	Gulf of Mexico	Crude	11

2.4 Evaporation Rate

In general, evaporation can be defined as a type of vaporization of a liquid that occurs only on the surface of a liquid. There are another two types of vaporization, which are boiling and sublimation. Boiling occurs on the entire mass of the liquid and also part of the water cycle, while sublimation is a direct phase transition from the solid phase to the gas phase, skipping the intermediate liquid phase.

Liquid with high saturation vapour pressure evaporate faster. As a result, the evaporation rate (mass/time) is expected to be part of the saturation vapour pressure (Crowl and Louvar, 2002). Evaporation rate is basically used to estimate the concentration (in ppm) of a volatile in an enclosure resulting from evaporation of a liquid.

The ability for a molecule of a liquid to evaporate is based largely on the amount of kinetic energy of an individual particle may possess. Individual molecules of liquid still can evaporate at a lower temperature with a condition that they have more than the minimum amount of kinetic energy for vaporization.

2.5 Formation of Flammable Mixture

Generally, flammable mixtures composed of two or more flammable compounds. According to (Vazquez, 2005), there will be different behaviors can be expected from the mixtures but it is depending whether the mixture is ideal or non-ideal. The mixtures that are initially above the upper limit of flammability may become flammable and in lieu to this, a special precaution must be taken to assure no rapid formation of flammable mixture in the industry (Zabetakis, 1965). Moreover, flammable mixtures may encounter in production of many chemicals and physical operations as well.

In practice, heterogeneous mixtures are always formed when two gases or vapors are first brought together. It may be formed either by accident or design. It is usually desirable to reduce the combustible concentration quickly by adding enough air or inert gas to produce nonflammable mixtures when they are formed by accident. Under certain conditions, it may be possible to increase the combustible concentration so as to produce a non-flammable mixture.

A flammable mixture can also form at temperature below the flash point of the liquid combustible either if the latter is sprayed into the air, or if a mist or foam forms. A mixture of fuel-air will only burn if the fuel concentration is between the UFL and LFL while the gas mixture is classified as flammable if it is in between the explosion range. Figure 1 showed the flammable range for some fuel-air mixtures according to (Bjerketvedt et al., 1997).

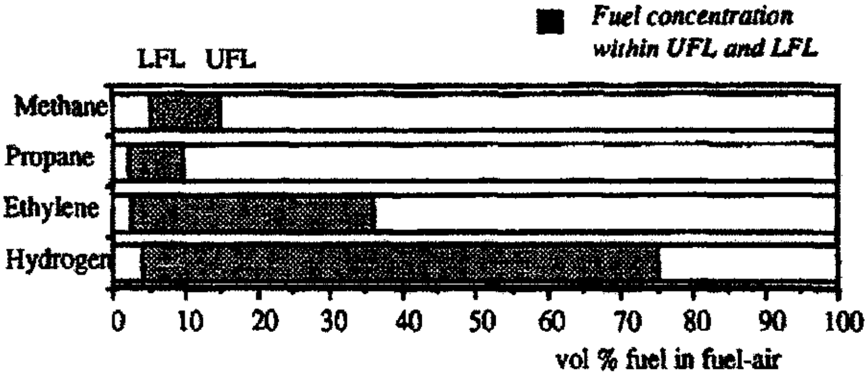

Fig. 2.1: Flammability range for fuel-air mixtures at 1 atm. and 25°C.

2.6 Auto Ignition Temperature (AIT)

Sometimes called as spontaneous ignition temperature (SIT), the auto ignition temperature of a vapor is the temperature at which the vapor ignites spontaneously from the energy to the environment. (Crowl and Louvar, 2002) define AIT as a fixed temperature above which adequate energy is available in the environment to provide an ignition source. The auto ignition temperature is basically a function of concentration of vapor, volume of vapor, pressure of the system, presence of catalytic material, and flow conditions. According to (Norman, 2008), AIT for vapour mixture can influence by number of factors, which are: pressure, fuel type, fuel concentration, influence of additives and oxidiser. In lieu to this, it is essential to determine experimentally the AITs at conditions as close as possible to process conditions.

Auto ignition temperatures of different hydrocarbons are generally different when they are in air and oxygen. Composition affects the AIT; rich or lean mixtures have higher AITs. Larger system volumes decrease AITs; an increase in pressure decreases AITs; and increases in oxygen concentration decrease AITs. This string dependence on conditions illustrates the importance of exercising caution when using AIT data. Based on (Zabetakis, 1924), an increase in pressure generally decreases the AIT of a combustible in a given oxidant. Accordingly, the AIT values obtained at atmospheric pressure should not be used to assess ignition hazards at high pressure.

There are two types of auto ignition data can be obtained, depending upon the objectives. For the first type, the ignition delay is relatively short and usually obtained at high temperatures. These are not normally used for safety purposes, unless there is some assurance that the contact time of combustible and air is less than the ignition delay at the temperature of the hot zone. As for the second type, it is usually the quantity of interest in safety work, especially when combustible and air can remain in contact for an indefinite period. It is called as minimum AIT.

Most of the time, AIT is used to determine the maximum operating temperature of other hot surface in a classified area, such as utilities or process pipelines. In a reactive chemical, AIT is lowered by rusty surface and as for liquid, the AIT is influenced by four factors as follow (Britton et. al., 2005):

a) Size, shape and surface material of an enclosure.
b) Convictive conditions and residence time.
c) Composition and pressure of reacting mixture.
d) Relative rates of heat generation and removal.

2.7 Ignition Energy

The minimum energy input required to initiate combustion is called as minimum ignition energy (MIE). In general, many flammable mixtures can bi ignited by sparks giving relatively small energy content (1 to 100mJ) but a large power density (greater than 1 megawatt/cm^3). However, when the source energy is diffuse, as in a sheet discharge, even the total energy requirements for ignition may be extremely large (Zabetakis, 1924). Basically, MIE depends on the specific chemical or mixture, the concentration, pressure and temperature and all flammable materials (including dust) have its own MIE.

Based on Crowl and Louvar (2002), the experimental data have indicated that:

a) MIE decreases with an increase in pressure.
b) MIE of dusts is, in general, at energy levels somewhat higher than combustible gases.
c) Increase in the nitrogen concentration increases the MIE.

Most of the times, human can only sense discharges of 0.6 mJ or more, which means that discharges we cannot detect might carry enough energy to ignite a flammable mixture. Many hydrocarbons have MIEs of about 0.25 mJ and this is low as compared to the sources of ignition. In addition, electrostatic discharges from the fluid flow also have energy levels exceeding the MIEs of flammable materials. Hence, it can provide an ignition source, which may leads to plant explosions.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The methodology of this work will be developing a systematic method to analyze the possible ignition sources that can cause fire and may leads explosion. It incorporates both experimental and theoretical assessments as described by the following sections. Fig. 3.1 shows the methodology of this work incorporates experimental and theoretical assessments.

3.2 Experimental and Theoretical Methods

3.2.1 Composition

The liquid sample was collected from the drainage lines of one of the refineries in Malaysia. The water content was removed from the sample using a simple distillation technique. The composition of the samples was taken from previous research done by (Wahi, 2010) regarding investigation of fire and explosion in the drainage system related to process industries and also (Ahamad@Ahmad, 2011) who had proposed inherently safer design for hazardous waste contaminated in industrial drains.

3.2.2 Evaporation Rate

In reality, for vaporization into stagnant air, the vaporization rate is proportional to the difference between the saturation vapor pressure and the partial pressure of the vapor in stagnant air. The more generalized expression for the evaporation rate is as follow (Crowl and Louvar, 2002):

$$Q_m = \frac{MKA(P^{sat} - p)}{R_g T_L} \tag{3.1}$$

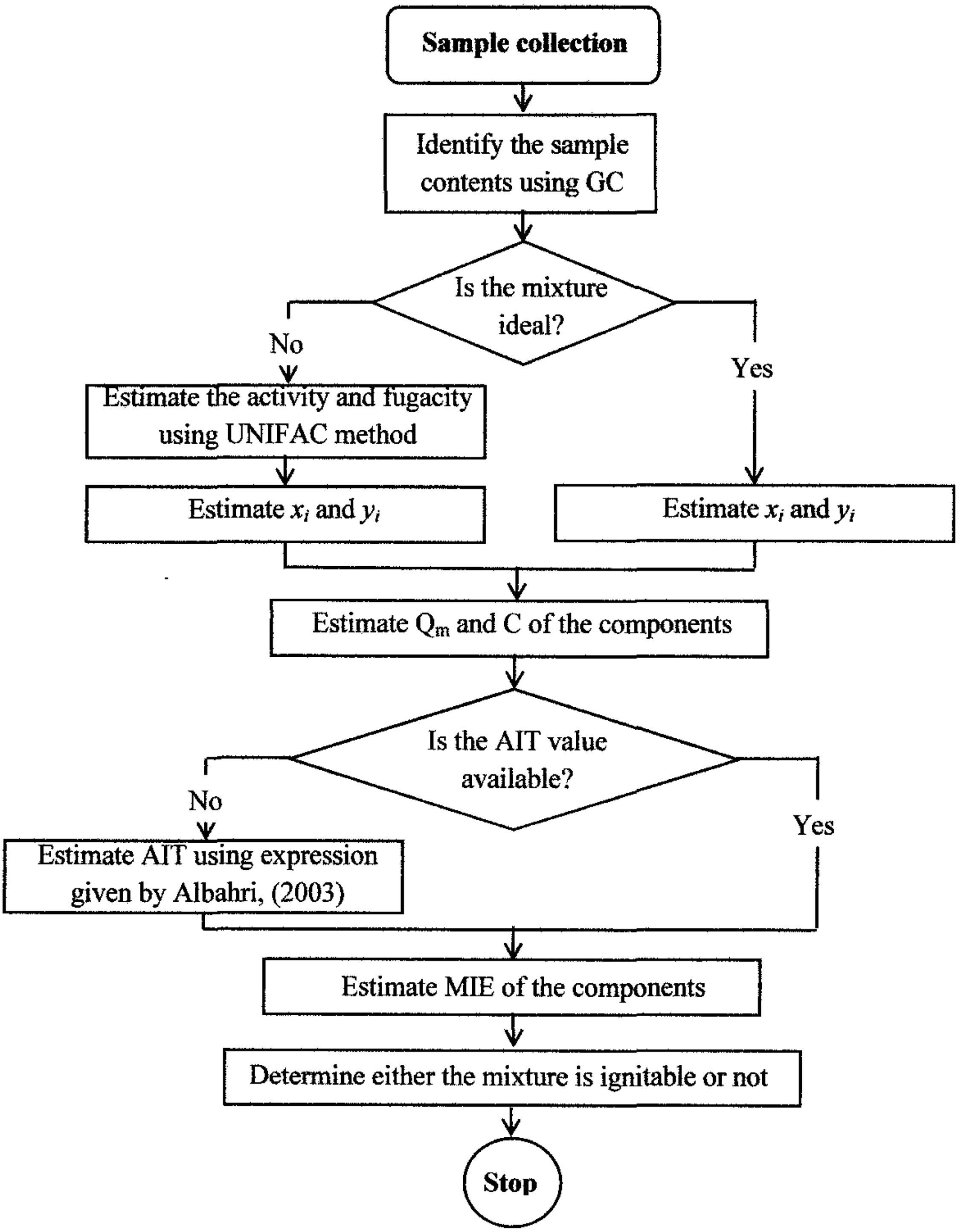

Fig. 3.1: Flowchart describes the methodology steps.

where,

Q_m is the evaporation rate (mass/time),

M is the molecular weight of the volatile substance,

K is a mass transfer coefficient (length/time) for an area A,

R_g is the ideal gas constant, and

T_L is the absolute temperature of the liquid.

The mass transfer coefficient for an area, K in eq. (3.1) is determined from the question as follow,

$$K = K_o \frac{M_o}{M} \tag{3.2}$$

where,

K_o is the reference substance and water is most frequently used, 0.83 cm/s,

M_o is the molecular weight of reference substance, and

M is the molecular weight of the volatile substance.

3.2.3 Concentration of a Volatile in an Enclosure

The concentration (in ppm) of a volatile enclosure resulting from evaporation of liquid is calculated using following equation (Crowl and Louvar, 200),

$$C_{ppm} = C(kg/m^3)\frac{RT}{PM}\times 10^6 \tag{3.3}$$

where,

T is the absolute ambient temperature,

M is the molecular weight of the volatile species,

P is absolute pressure, and

R is the ideal gas constant.

In order to get the concentration in kg/m^3, the following equation is used,

$$C(kg/m^3) = \frac{MP^{sat}}{RT} \times x_i \qquad (3.4)$$

where,

P^{sat} is the vapour pressure of the respective compound.

3.2.4 Auto Ignition Temperature (AIT) and Minimum Ignition Energy (MIE)

In section 2.6, it was mentioned that auto ignition temperature is affected by four factors. In addition, the AIT values of the respective components are varied when they are in air and in oxygen. Some of the AIT values are obtained from the work of Shoib (2011), while the other unavailable AIT values will be calculated according to nonlinear form equation which has been developed by Albahri (2003).

$$\Phi = [a. + b(\Sigma(\Phi)i) + c((\Sigma(\Phi)i)^2 + d((\Sigma(\Phi)i)^3 + e((\Sigma(\Phi)i)^4]$$

(3.5)

where,

ϕ is the AIT,

$((\Sigma\ (\phi)i)$ is the sum of the molecular group contribution for the AIT,

a is the specific constant for AIT and equal to 780.42,

b is the specific constant for AIT and equal to 26.78,

c is the specific constant for AIT and equal to -2.5887,

d is the specific constant for AIT and equal to -0.3195, and

e is the specific constant for AIT and equal to -0.007825.

The sum of the group contribution for the AIT is given in (Table A2) Appendix A.

I should be noted that, in some situations, some components can reach their AIT, but there still do not ignite or burn. This is because it does not have enough ignition energy to ignite. Therefore, the determination of MIE for potential sources of fire, explosion and any other accidents is vital in order to know at which temperature and ignition energy that can speed up the risks of the potential accidents to happen due to the ignition. MIE of potential sources are basically determined according to the method of Ballal, (1938b) equation; MIE for a number of mixtures of gases, vapours, liquid droplets and dusts has been correlated with air at atmospheric pressure and the size of the liquids and solid particles being of the order of 50µm. The correlation is given in term of spalding mass transfer number, B.

$$B = \frac{q_{st}H + c_{pa}(T_g - T_b)}{L + C_p(T_b - T_s)} \tag{3.6}$$

where,

B is the mass transfer number,

q_{st} is the mass ratio of fuel into air,

H is the heat of combustion,

C_{pa} is the specific heat of air,

T_g is the AIT of the fuel,

T_b is the boiling point of the fuel,

L is the latent of vaporization,

C_p is the specific heat capacity of the fuel, and

T_s is the surface temperature of the fuel and is taken to be the same as ambient temperature, 298.15K.

The mass ratio of fuel into air, q_{st} were calculated using an expression suggested by Zabetakis, (1924) that is purposely to convert a lower limit value in volume-percent to a fuel-air (weight) ratio.

$$qst = \frac{M}{28.96} \times [\frac{L(vol.pct)}{100 - L(vol.pct)}] \tag{3.7}$$

Once the value of mass transfer numbers are obtained, the MIE value is then obtained by interpolating the graph of MIE (mJ) versus mass transfer number, B (Lees, 1996).

The specific heat capacity of fuels are obtained from Chemspider website (www.chemspider.com) and for hydrocarbons that fall under Alkane group, the C_p value is calculated using the following equation.

$$C_p = a. + bT_r + cT_r^{\ 2} + dT_r^{\ 3} + n(\Delta a + \Delta bT_r + \Delta cT_r^{\ 2} + \Delta dT_r^{\ 3}) \tag{3.8}$$

where,

C_p is the specific heat capacity of the fuel,

a is constant that equal to 0.84167,

b is constant that equal to -1.47040,

c is constant that equal to 1.67165,

d is constant that equal to -0.59198,

T_r is the reduce temperature,

n is the number of the carbon atoms,

Δa is the changes in the constant per carbon atom and equal to -0.003826,

Δb is the changes in the constant per carbon atom and equal to -0.000747,

Δc is the changes in the constant per carbon atom and equal to 0.041126, and

Δd is the changes in the constant per carbon atom and equal to -0.013950.

The reduce temperature for Eq. (3.8) is determine by using the following equation,

$$T_r = \frac{T}{T_b} \tag{3.9}$$

where,

T is the ambient temperature and is taken to be 298.15K, and

T_b is the normal boiling point temperature of the fuel.

The heat of combustion for each hydrocarbon is calculated using heat of combustion and Respiratory Quotient (RQ) using online tool, which is available at; (http://home.fuse.net/clymer/rq/index.html).

The values of latent heat of vaporization and the boiling point temperature for all hydrocarbons are taken from Chemspider website (www.chemspider.com). Once all of the latent heat of vaporization and boiling point temperature data are obtained, possible sources of ignition will be identified and the suitable prevention method to eliminate these sources will be further discussed and suggested. It is expected that from this study, the inherent safer design that is the design that eliminates or reduces hazards can be applied.

Fig. 3.1 gives the relation between MIE and B that is calculated using Eq. 3.6. This graph is introduced by Ballal (1938b) as a method to determine the MIE of a dust cloud which is also applicable to a vapour and an aerosol. It gives an approximate relation between the MIE and B for both homogeneous and two-phase mixtures of vapour, dust cloud and aerosol.

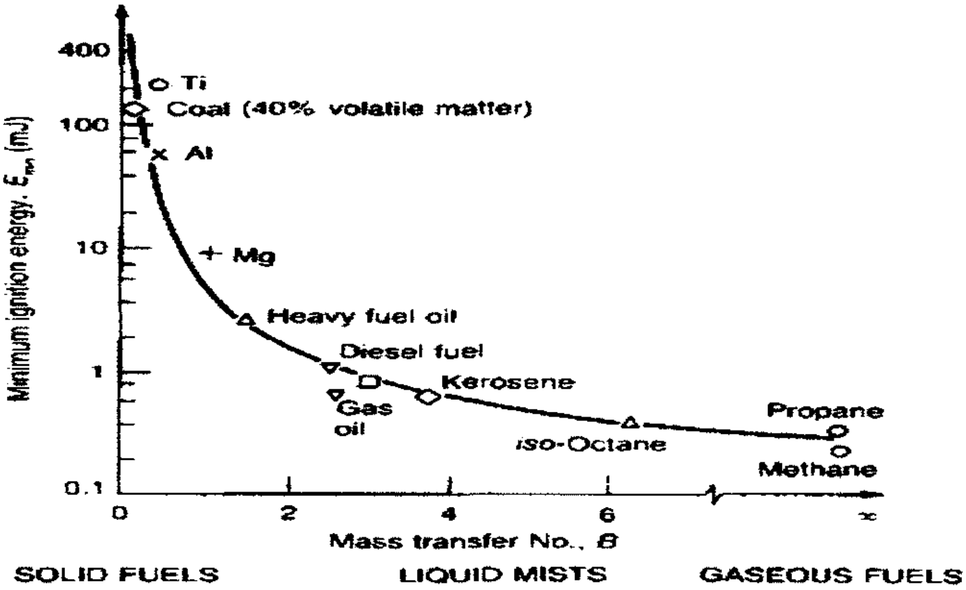

Fig. 3.2: MIE versus Mass Transfer Number, B.

3.3 Key Milestones

There are two semesters in the completion of this project. The two tables below summarized the key milestones for each of the semesters:

Table 3.1: Key Milestone for Semester 1 (May 2011).

No	Activities	Week
1	Information Gathering (Literature Review)	3-10
2	Submission of Extended Proposal	7
3	Proposal Defense	8-9
4	Project Work Continuations	10-12
5	Submission of Interim Draft Report	13
6	Submission of final report	14

Table 3.2: Key Milestone for Semester 2 (September 2011).

No	Activities	Week
1	Project Work Continuations	1-7
2	Submission of Progress Report	8
3	Project Work Continuations	8-12
4	Pre-EDX	11
5	Submission of Draft Report	12
6	Submission of Dissertation (soft bound)	13
7	Submission of Technical Paper	13
8	Oral Presentation	14
9	Submission of Project Dissertation (hard bound)	15

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter will present the results of Q_m and MIE of the 77 components that have been identified using GC-MS. The calculated results of Q_m and MIE are presented in Table 4.2. The factors that can influence the Q_m and MIE also been identified and discussed. Results show that there are three factors that can affect the Q_m; Flash Point (FP), Volume Percent and Vapour Pressure (VP) while for MIE, it is affected by FP, Volume Percent and Number of Carbons of the components. In addition, the significance of finding the average value of certain parameters such as AIT and MIE are also been explained. The potential sources of ignition are also been elaborated based on information obtained from the following website; (http://www.firesandexplosions.ca/).

4.2 Sample Collections and Analysis

4.2.1 Sample Collections

Figure 4.1 shows the retention time and peak abundance data for the 77 components detected in the liquid phase using GC-MS analysis; while Table 4.1 list their properties relevant to this study. The liquid sample contains a large number of hydrocarbon components ranging from C_9 to C_{22}. From the analysis, the predominant hydrocarbon groups are alkane and alkene with relative minor presence of haloalkane and arene.

4.2.2 Mole Fraction in Liquid Phase

Figure 4.2 and Table 4.1 show the result distributions from the GC-MS for the mole fractions in the liquid phase, x_i. Mole fractions of the components were calculated using compositional data determined by the GC analysis. The mole fraction of each component is obtained from calculation done by Ahamad, (2011) .

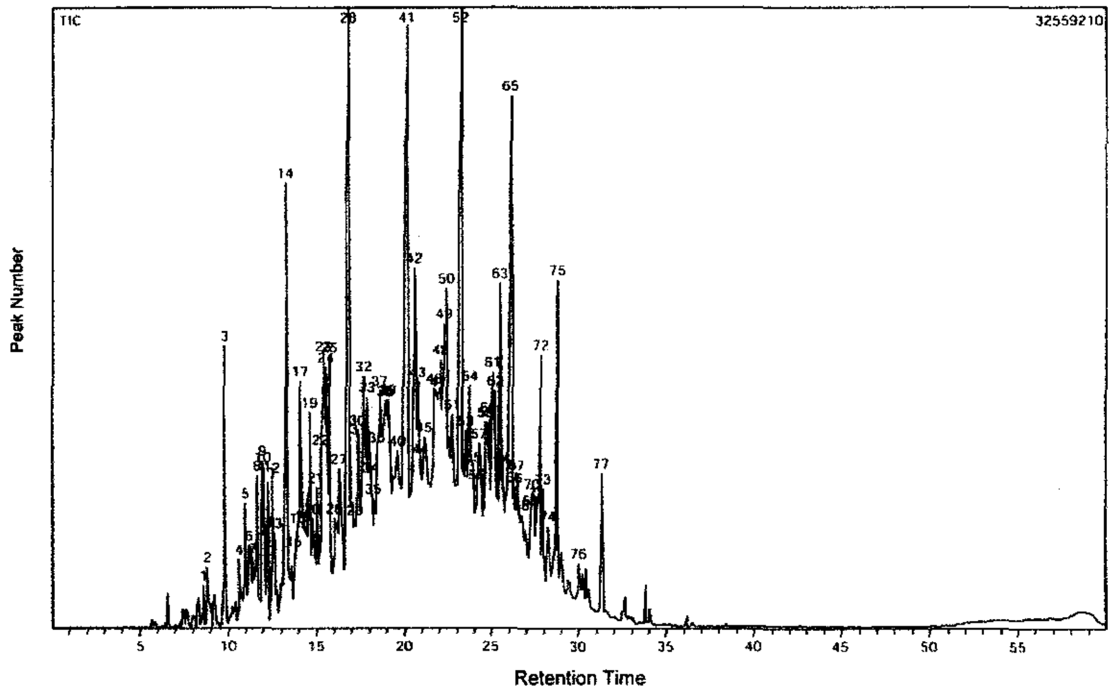

Fig. 4.1: GC-MS analysis for the liquid sample.

4.2.3 Mole Fraction in Vapour Phase

The mole fractions of the components in vapour phase are also obtained from the same work as mentioned in section 4.2.2. The mole fraction of vapour phase existed shown in Fig. 4.3.

Table 4.1: Different Components Present in the Liquid Phase.

Peak No.	Retention Time (min)	Compound	Formula	Area (Abundance)	*xi* (mol fraction)
1	8.33	Nonane	C_9H_{20}	3055018	0.0066447
2	9.402	4-methyl-1-Decene	$C_{11}H_{22}$	3327548	0.0072375
3	10.35	3,5-dimethyl-octane	$C_{10}H_{22}$	1329035	0.0028907
4	10.48	2-methyl-Nonane	$C_{10}H_{22}$	1119080	0.002434
5	10.71	4-methyl-1-Decene	$C_{11}H_{22}$	1608876	0.0034993
6	11.23	1,3,5-trimethyl-benzene	C_9H_{12}	1126189	0.0024495
7	11.8	Nonane	C_9H_{20}	18335941	0.0398811
8	12.29	Dodecane	$C_{12}H_{26}$	1171259	0.0025475
9	12.47	4-methyl-decane	$C_{11}H_{24}$	4242572	0.0092277
10	12.64	1-chloro-tetradecane	$C_{14}H_{29}Cl$	1025678	0.0022309
11	12.77	1,3,5-trimethyl-benzene	C_9H_{12}	1380997	0.0030037
12	13.01	3-methyl-tridecane	$C_{14}H_{30}$	1028112	0.0022362
13	13.37	(E)-3-undecene	$C_{11}H_{22}$	1000315	0.0021757
14	13.64	5-methyl-decane	$C_{11}H_{24}$	1820173	0.0039589
15	13.78	4-methyl-decane	$C_{11}H_{24}$	3223257	0.0070107
16	13.94	2-methyl-decane	$C_{11}H_{24}$	8740434	0.0190107
17	14.16	3-methyl-decane	$C_{11}H_{24}$	4536250	0.0098665
18	14.58	P-cymene	$C_{10}H_{14}$	1697549	0.0036922
19	14.7	P-cymene	$C_{10}H_{14}$	3178322	0.0069129
20	14.92	6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]heptane	$C_{15}H_{24}$	1826975	0.0039737
21	15.3	Undecane	$C_{11}H_{24}$	36062976	0.0784379
22	15.69	2-methyl-undecane	$C_{12}H_{26}$	4204657	0.0091452
23	16.02	Tetradecane	$C_{14}H_{30}$	4036588	0.0087797
24	16.17	P-cymene	$C_{10}H_{14}$	2601861	0.0056591
25	16.27	N-tridecane	$C_{13}H_{28}$	1263105	0.0027473
26	16.45	Cyclopentylcyclohexane	$C_{11}H_{20}$	2390780	0.0052
27	16.55	(E)-3-undecene	$C_{11}H_{22}$	1852337	0.0040289
28	16.99	2-methyl-decane	$C_{11}H_{24}$	7843749	0.0170604
29	17.14	4-methyl-undecane	$C_{12}H_{26}$	4343063	0.0094463
30	17.32	2-methyl-undecane	$C_{12}H_{26}$	8862907	0.019277
31	17.53	3-methyl-tridecane	$C_{14}H_{30}$	9509116	0.0206826
32	17.85	4,8-dimethyl-undecane	$C_{13}H_{28}$	2449357	0.0053274
33	18.11	Cyclododecane	$C_{12}H_{24}$	2543041	0.0055312
34	18.63	Undecane	$C_{11}H_{24}$	45698889	0.0993962
35	18.71	2-ethenyl-1,3,5-trimethyl-benzene	$C_{11}H_{14}$	1490898	0.0032427
36	18.92	2,6-dimethyl-undecane	$C_{13}H_{28}$	11773241	0.0256071

37	19.01	N-decane	$C_{10}H_{22}$	2439808	0.0053066
38	19.11	2-methyl-undecane	$C_{12}H_{26}$	1972392	0.00429
39	19.31	1-tetradecene	$C_{14}H_{28}$	6088869	0.0132434
40	19.68	1-nonadecanol	$C_{19}H_{40}O$	2260369	0.0049164
41	19.88	Cyclododecane	$C_{12}H_{24}$	7600609	0.0165315
42	20.15	2,4-dimethyl-undecane	$C_{13}H_{28}$	9785074	0.0212828
43	20.32	4-methyl-tridecane	$C_{14}H_{30}$	6599976	0.0143551
44	20.51	2-methyl-heptadecane	$C_{18}H_{38}$	8970517	0.0195111
45	20.75	Tridecane	$C_{13}H_{28}$	15525484	0.0337683
46	20.99	(E)-3-tetradecene	$C_{14}H_{28}$	2570346	0.0055906
47	21.81	4-tert-butylstyrene	$C_{12}H_{16}$	47882114	0.1041448
48	21.91	Octane, 2,3,7-trimethyl-	$C_{11}H_{24}$	1307611	0.0028441
49	22.09	2,6-dimethyl-undecane	$C_{13}H_{28}$	3135032	0.0068188
50	22.38	N-hexadecane	$C_{16}H_{34}$	1774350	0.0038593
51	22.57	3-methyl-tridecane	$C_{14}H_{30}$	1306920	0.0028426
52	23.05	1-Octanol, 2-butyl-	$C_{12}H_{26}O$	6403693	0.0139282
53	23.14	2-methyl-octane	C_9H_{20}	1861100	0.0040479
54	23.3	4-methyl-tridecane	$C_{14}H_{30}$	4886210	0.0106276
55	23.49	2-methyl-tridecane	$C_{14}H_{30}$	7543765	0.0164079
56	23.68	3-methyl-tridecane	$C_{14}H_{30}$	5069859	0.0110271
57	23.81	2,6,10,14-tetramethyl-heptadecane	$C_{21}H_{44}$	8877187	0.0193081
58	24.17	(E)-3-Tetradecene	$C_{14}H_{28}$	2186729	0.0047562
59	24.65	N-tridecane	$C_{13}H_{28}$	35111234	0.0763678
60	24.75	2,3,6,7-tetramethyl-octane	$C_{12}H_{26}$	3178423	0.0069131
61	24.9	N-hexadecane	$C_{16}H_{34}$	1106927	0.0024076
62	25.35	2,6-dimethyl-naphthalene	$C_{12}H_{12}$	2452874	0.0053351
63	25.74	1,7-dimethyl-naphthalene	$C_{12}H_{12}$	1312510	0.0028547
64	25.85	1,6-dimethyl-naphthalene	$C_{12}H_{12}$	4979460	0.0108305
65	26.02	Decyl-cyclopentane	$C_{15}H_{30}$	1126078	0.0024492
66	26.15	Heptadecane	$C_{17}H_{36}$	6962273	0.0151431
67	26.29	2-methyl-heptadecane	$C_{18}H_{38}$	3673329	0.0079896
68	26.47	3-methyl-tridecane	$C_{14}H_{30}$	1973326	0.004292
69	27.34	N-tridecane	$C_{13}H_{28}$	15112884	0.0328709
70	28.13	1-Decanol, 2,2-dimethyl-	$C_{12}H_{26}O$	2137606	0.0046493
71	28.46	4-Octanone	$C_8H_{16}O$	1423098	0.0030953
72	28.76	4-methyl-undecane	$C_{12}H_{26}$	1060248	0.0023061
73	28.92	2-methyl-pentadecane	$C_{16}H_{34}$	1356363	0.0029501
74	29.12	3-methyl-hexadecane	$C_{17}H_{36}$	1171790	0.0025487
75	29.91	N-tridecane	$C_{13}H_{28}$	5076982	0.0110426
76	31	N-tetradecane	$C_{14}H_{30}$	1042962	0.0022685
77	32.4	N-pentadecane	$C_{15}H_{32}$	1758278	0.0038243
Total				459764804	1

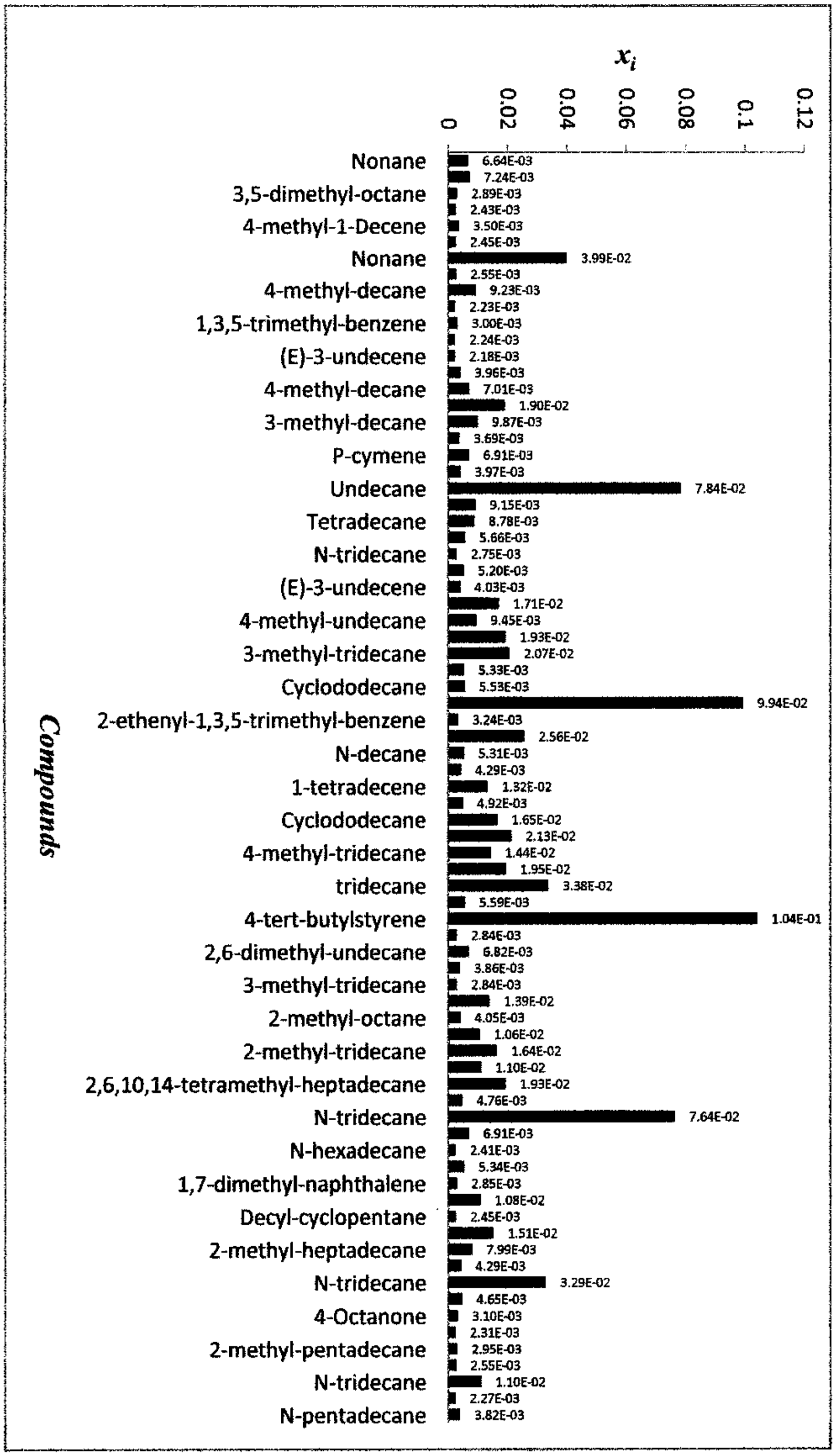

Fig. 4.2: Mole fractions of hydrocarbon components in the liquid phase.

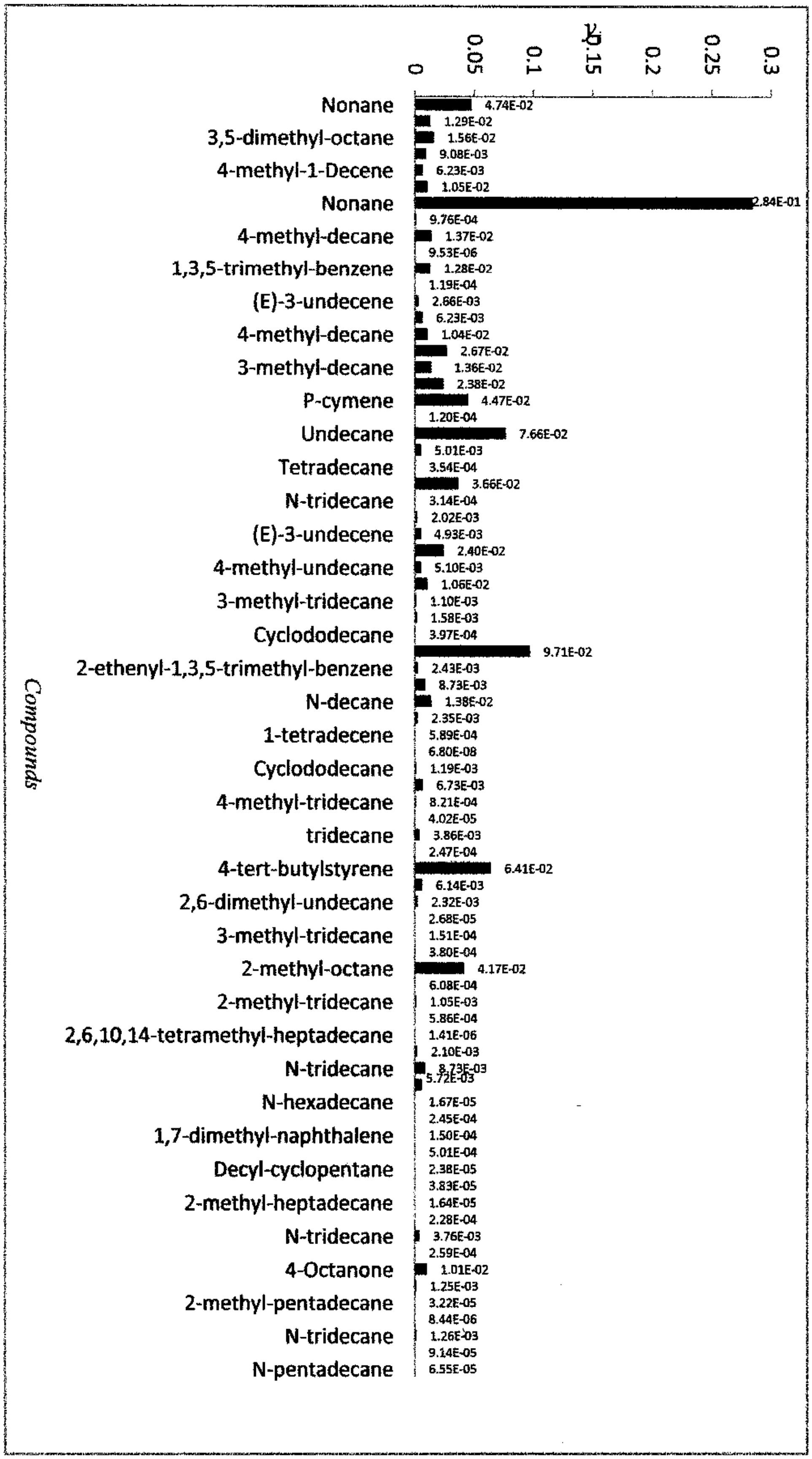

Fig. 4.3: Mole fractions of hydrocarbon components in the vapour phase.

Table 4.2: Compounds Name and Their Relevant Properties to Analyze Their Ignition Behaviours.

Peak No.	Compound	Formula	Mwt	Fraction, x_i	Activity, γ_i	Fugacity, Øi	y_i	P^{sat} (mmHg)	Volume Percent (%)	Bp (K)	Reduce Temp. (T_R)	Qm (g/min)	C(kg/m^3)	Qv (m^3/min)	Fuel - Air Weight Ratio (q)	Heat of Combustion (kJ/kg)	Heat of Vaporization, L (kJ/kg)	Specific Heat Capacity (kJ/kg.K)	Flash Point (K)	AIT (K)	Spalding Mass Transfer Number (B)	Minimum Ignition Energy (mJ)
1	Nonane	C_9H_{20}	128.3	0.6645	0.975573	0.8735	4.74E-02	4.630	0.834	424.9	0.702	18.6011	0.021243	2.9187	0.037258	44310.6	287.69	2.21919	304.3	478.2	2.997	0.964
2	4-methyl-1-Decene	$C_{11}H_{22}$	154.3	0.7238	1.011648	0.8147	1.29E-02	1.040	0.693	456.9	0.653	4.1782	0.006251	2.2281	0.037206	47213.22	251.39	1.94533	346.9	573.2	3.346	1.780
3	3,5-dimethyl-octane	$C_{10}H_{22}$	142.3	0.2891	0.998869	0.8611	1.56E-02	3.380	0.752	431.8	0.691	13.5792	0.007483	6.0491	0.037227	47638.79	272.31	2.24844	354.2	755.9	3.668	0.769
4	2-methyl-Nonane	$C_{10}H_{22}$	142.3	0.2434	0.999133	0.8496	9.08E-03	2.300	0.752	440.1	0.678	9.2403	0.004287	7.1840	0.037227	47638.79	272.31	2.22931	311.5	755.9	3.554	0.769
5	4-methyl-1-Decene	$C_{11}H_{22}$	154.3	0.3499	1.011648	0.8147	6.23E-03	1.040	0.693	456.9	0.653	4.1782	0.003022	4.6083	0.037206	47213.22	251.39	1.94533	346.9	573.2	3.346	1.780
6	1,3,5-trimethyl-benzene	C_9H_{12}	120.2	0.2449	1.187247	0.8911	1.05E-02	2.324	0.890	439.8	0.678	9.3367	0.003683	8.4512	0.037279	45224.63	317.22	1.57421	317.6	743.2	3.687	0.794
7	Nonane	C_9H_{20}	128.3	3.9881	0.975573	0.8735	2.84E-01	4.630	0.834	424.9	0.702	18.6011	0.127501	0.4863	0.037258	44310.6	287.69	2.21919	304.3	478.2	2.997	0.964
8	Dodecane	$C_{12}H_{26}$	170.3	0.2548	1.024267	0.7701	9.76E-04	0.209	0.628	489.3	0.609	0.8397	0.000488	5.7354	0.037181	47507.93	254.84	2.20962	344.3	476.2	2.589	1.360
9	4-methyl-decane	$C_{11}H_{24}$	156.3	0.9228	1.015104	0.8170	1.37E-02	0.869	0.685	460.6	0.647	3.4912	0.006745	1.7252	0.037202	47549.58	265.39	2.2266	322.6	477.8	2.849	0.982
10	1-chloro-tetradecane	$C_{14}H_{29}Cl$	232.8	0.2231	0.989566	1.0000	9.53E-06	0.003	0.460	566.1	0.527	0.0126	0.000009	4.7911	0.037118	40021.48	219.54	1.74514	395.7	503.2	2.070	2.200
11	1,3,5-trimethyl-benzene	C_9H_{12}	120.2	0.3004	1.187247	0.8911	1.28E-02	2.324	0.890	439.8	0.678	9.3367	0.004516	6.8919	0.037279	45224.63	317.22	1.57421	317.6	743.2	3.687	0.794
12	3-methyl-tridecane	$C_{14}H_{30}$	198.4	0.2236	1.024724	1.0000	1.19E-04	0.038	0.539	521.9	0.571	0.1511	0.000090	5.6086	0.037148	47328.63	237.6	2.2187	354.5	473.2	2.329	1.660
13	(E)-3-undecene	$C_{11}H_{22}$	154.3	0.2176	1.002320	0.8183	2.66E-03	0.725	0.693	464.4	0.642	2.9127	0.001310	7.4119	0.037206	47213.22	251.39	1.57667	333.0	481.6	3.455	0.807
14	5-methyl-decane	$C_{11}H_{24}$	156.3	0.3959	1.015104	0.8227	6.23E-03	0.925	0.685	459.3	0.649	3.7162	0.003080	4.0213	0.037202	47549.58	312.41	2.22922	322.0	474.2	2.657	1.360
15	4-methyl-decane	$C_{11}H_{24}$	156.3	0.7011	1.015104	0.8170	1.04E-02	0.869	0.685	460.6	0.647	3.4912	0.005125	2.2708	0.037202	47549.58	265.39	2.2266	322.6	474.2	2.843	0.982
16	2-methyl-decane	$C_{11}H_{24}$	156.3	1.9011	1.015104	0.8152	2.67E-02	0.818	0.685	461.9	0.646	3.2863	0.013081	0.8374	0.037202	47549.58	265.39	2.22402	323.3	474.2	2.830	1.000
17	3-methyl-decane	$C_{11}H_{24}$	156.3	0.9866	1.015104	0.8143	1.36E-02	0.800	0.685	462.3	0.645	3.2140	0.006640	1.6135	0.037202	47549.58	265.39	2.22323	323.6	474.2	2.826	1.000
18	P-cymene	$C_{10}H_{14}$	134.2	0.3692	1.223279	0.8748	2.38E-02	1.550	0.797	450.3	0.662	6.2271	0.004134	5.0210	0.037244	45365.82	292.73	1.61466	320.2	709.2	3.624	0.743
19	P-cymene	$C_{10}H_{14}$	134.2	0.6913	1.223279	0.8748	4.47E-02	1.550	0.797	450.3	0.662	6.2271	0.007740	2.6817	0.037244	45365.82	292.73	1.61466	320.2	709.2	3.624	0.743
20	6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]heptane	$C_{15}H_{24}$	204.4	0.3974	1.087607	1.0000	1.20E-04	0.020	0.523	533.3	0.559	0.0812	0.000088	3.0635	0.037142	45763.21	237.77	1.36962	374.0	792.0	3.593	0.794
21	Undecane	$C_{11}H_{24}$	156.3	7.8438	1.015311	0.8082	7.66E-02	0.564	0.685	469.5	0.635	2.2659	0.037214	0.2030	0.037202	47513.76	265.39	2.20957	333.2	477.8	2.758	1.060
22	2-methyl-undecane	$C_{12}H_{26}$	170.3	0.9145	1.024118	0.7754	5.01E-03	0.301	0.628	482.1	0.619	1.2093	0.002523	1.5977	0.037181	47469.17	254.84	2.22204	334.0	476.2	2.651	1.360
23	Tetradecane	$C_{14}H_{30}$	198.4	0.8780	1.024778	1.0000	3.54E-04	0.029	0.539	527.1	0.566	0.1145	0.000267	1.4285	0.037148	47346.27	237.6	2.21124	372.6	508.2	2.339	1.540
24	P-cymene	$C_{10}H_{14}$	134.2	0.5659	1.223279	0.8748	3.66E-02	1.550	0.797	450.3	0.662	6.2271	0.006336	3.2759	0.037244	45365.82	292.73	1.61466	320.2	709.2	3.624	0.743
25	N-tridecane	$C_{13}H_{28}$	184.4	0.2747	1.027158	1.0000	3.14E-04	0.081	0.580	507.7	0.587	0.3242	0.000220	4.9117	0.037163	47395.34	238.18	2.21146	374.9	475.0	2.464	1.360

Peak No.	Compound	Formula	Mwt	Fraction, x_i	Activity, Υ_i	Fugacity, Øi	y_i	P^{sat} (mmHg)	Volume Percent (%)	Bp (K)	Reduce Temp. (T_R)	Qm (g/min)	C(kg/m^3)	Qv (m^3/min)	Fuel - Air Weight Ratio (q)	Heat of Combustion (kJ/kg)	Heat of Vaporization, L (kJ/kg)	Specific Heat Capacity (kJ/kg.K)	Flash Point (K)	AIT (K)	Spalding Mass Transfer Number (B)	Minimum Ignition Energy (mJ)
26	Cyclopentylcyclohexane	$C_{11}H_{20}$	152.3	0.5200	1.067922	0.8328	2.02E-03	0.220	0.703	488.3	0.611	0.8839	0.000938	3.1419	0.037209	45677.61	274.46	1.65863	340.1	490.2	2.885	0.928
27	(E)-3-undecene	$C_{11}H_{22}$	154.3	0.4029	1.002320	0.8183	4.93E-03	0.725	0.693	464.4	0.642	2.9127	0.002426	4.0026	0.037206	47213.22	251.39	1.57667	333.0	481.6	3.455	0.807
28	2-methyl-decane	$C_{11}H_{24}$	156.3	1.7060	1.015104	0.8152	2.40E-02	0.818	0.685	461.9	0.646	3.2863	0.011739	0.9331	0.037202	47549.58	265.39	2.22402	323.3	474.2	2.830	1.000
29	4-methyl-undecane	$C_{12}H_{26}$	170.3	0.9446	1.024118	0.7767	5.10E-03	0.297	0.628	482.4	0.618	1.1932	0.002571	1.5468	0.037181	47469.17	254.84	2.2215	334.2	755.9	3.074	0.874
30	2-methyl-undecane	$C_{12}H_{26}$	170.3	1.9277	1.024118	0.7754	1.06E-02	0.301	0.628	482.1	0.619	1.2093	0.005318	0.7580	0.037181	47469.17	254.84	2.22204	334.0	755.9	3.077	0.874
31	3-methyl-tridecane	$C_{14}H_{30}$	198.4	2.0683	1.024724	1.0000	1.10E-03	0.038	0.539	521.9	0.571	0.1511	0.000830	0.6064	0.037148	47328.63	237.6	2.2187	354.5	473.2	2.329	1.660
32	4,8-dimethyl-undecane	$C_{12}H_{28}$	184.4	0.5327	1.026969	0.7521	1.58E-03	0.158	0.580	494.7	0.603	0.6348	0.000835	2.5329	0.037163	47380.69	238.18	2.23273	428.3	473.2	2.569	1.000
33	Cyclododecane	$C_{12}H_{24}$	168.3	0.5531	1.029996	0.8112	3.97E-04	0.041	0.636	520.1	0.573	0.1647	0.000205	2.6730	0.037184	47165.78	261.91	1.67647	360.7	474.0	2.692	1.240
34	Undecane	$C_{11}H_{24}$	156.3	9.9396	1.015311	0.8082	9.71E-02	0.564	0.685	469.5	0.635	2.2659	0.047157	0.1602	0.037202	47513.76	265.39	2.20957	333.2	477.8	2.758	1.060
35	2-ethenyl-1,3,5-trimethyl-benzene	$C_{11}H_{14}$	146.2	0.3243	1.391318	0.8411	2.43E-03	0.329	0.732	480.4	0.621	1.3218	0.000839	5.2485	0.03722	45116.28	300.27	2.19072	345.0	722.7	2.750	1.060
36	2,6-dimethyl-undecane	$C_{13}H_{28}$	184.4	2.5607	1.026969	0.7521	8.73E-03	0.181	0.580	492.1	0.606	0.7272	0.004600	0.5270	0.037163	47380.69	238.18	2.23732	425.2	473.2	2.592	1.300
37	N-decane	$C_{10}H_{22}$	142.3	0.5307	0.999407	0.8418	1.38E-02	1.583	0.752	448	0.665	6.3597	0.006433	3.2951	0.037227	47633.87	272.31	2.21236	319.3	483.2	2.995	0.892
38	2-methyl-undecane	$C_{12}H_{26}$	170.3	0.4290	1.024118	0.7754	2.35E-03	0.301	0.628	482.1	0.619	1.2093	0.001184	3.4058	0.037181	47469.17	254.84	2.22204	334.0	755.9	3.077	0.874
39	1-tetradecene	$C_{14}H_{28}$	196.4	1.3243	0.999164	1.0000	5.89E-04	0.032	0.545	524.8	0.568	0.1298	0.000452	0.9567	0.03715	47067.21	238.9	1.5881	388.8	508.2	2.892	0.946
40	1-nonadecanol	$C_{19}H_{40}O$	284.5	0.4916	2.558601	1.0000	6.80E-08	0.000	0.376	618.5	0.482	0.0000	0.000000	1.7789	0.037087	43944.19	239.91	1.91701	413.6	550.0	1.828	2.620
41	Cyclododecane	$C_{12}H_{24}$	168.3	1.6532	1.029996	0.8112	1.19E-03	0.041	0.636	520.1	0.573	0.1647	0.000614	0.8943	0.037184	47165.78	256.57	1.67647	360.7	474.0	2.715	1.240
42	2,4-dimethyl-undecane	$C_{13}H_{28}$	184.4	2.1283	1.026969	0.7521	6.73E-03	0.168	0.580	493.5	0.604	0.6749	0.003548	0.6342	0.037163	47390.97	238.23	2.23483	426.9	473.2	2.580	1.228
43	4-methyl-tridecane	$C_{14}H_{30}$	198.4	1.4355	1.024724	1.0000	8.21E-04	0.041	0.539	520.6	0.573	0.1627	0.000621	0.8737	0.037148	47332.68	257.62	2.22063	353.8	755.9	2.728	1.180
44	2-methyl-heptadecane	$C_{18}H_{38}$	254.5	1.9511	0.975824	1.0000	4.02E-05	0.002	0.420	578.1	0.516	0.0061	0.000041	0.5011	0.037104	47160.19	210.38	2.23682	382.1	755.9	2.306	1.720
45	tridecane	$C_{13}H_{28}$	184.4	3.3768	1.027158	1.0000	3.86E-03	0.081	0.580	507.7	0.587	0.3242	0.002704	0.3997	0.037163	47405.26	238.23	2.21146	374.9	475.0	2.464	1.360
46	(E)-3-tetradecene	$C_{14}H_{28}$	196.4	0.5591	0.994520	1.0000	2.47E-04	0.032	0.545	524.8	0.568	0.1294	0.000190	2.2665	0.03715	47073.9	238.93	1.58844	373.5	512.7	2.900	0.982
47	4-tert-butylstyrene	$C_{12}H_{16}$	160.3	10.4145	1.456988	0.8154	6.41E-02	0.250	0.668	485.8	0.614	1.0044	0.022456	0.1491	0.037196	49801.75	287.1	1.63057	348.6	707.2	3.501	0.807
48	Octane, 2,3,7-trimethyl-	$C_{11}H_{24}$	156.3	0.2844	1.014714	0.8298	6.14E-03	1.280	0.685	452.5	0.659	5.1424	0.003062	5.5972	0.037202	47547.06	265.37	2.24347	329.5	522.3	3.008	0.892
49	2,6-dimethyl-undecane	$C_{12}H_{28}$	184.4	0.6819	1.026969	0.7521	2.32E-03	0.181	0.580	492.1	0.606	0.7272	0.001225	1.9793	0.037163	47390.61	238.23	2.23732	425.2	473.2	2.592	1.300
50	N-hexadecane	$C_{16}H_{34}$	226.4	0.3859	1.006983	1.0000	2.68E-05	0.005	0.473	559.7	0.533	0.0201	0.000024	2.8473	0.037123	47248.91	220.59	2.21722	408.2	475.2	2.084	2.200
51	3-methyl-tridecane	$C_{14}H_{30}$	198.4	0.2843	1.024724	1.0000	1.51E-04	0.038	0.539	521.9	0.571	0.1511	0.000114	4.4121	0.037148	47328.63	237.6	2.2187	354.5	473.2	2.329	1.660
52	1-Octanol, 2-butyl-	$C_{12}H_{26}O$	186.3	1.3928	4.157893	1.0000	3.80E-04	0.005	0.574	518.7	0.575	0.0191	0.000066	0.9589	0.037161	41921.63	294.04	1.57641	373.3	738.0	2.773	1.180
53	2-methyl-octane	C_9H_{20}	128.3	0.4048	0.975225	0.8790	4.17E-02	6.730	0.834	416.5	0.716	27.0378	0.018811	4.7911	0.037258	47747.47	287.69	2.23946	298.7	478.2	3.332	0.820

Peak No.	Compound	Formula	Mwt	Fraction, x_i	Activity, γ_i	Fugacity, Øi	y_i	P^{sat} (mmHg)	Volume Percent (%)	Bp (K)	Reduce Temp. (T_R)	Qm (g/min)	C(kg/m^3)	Qv (m^3/min)	Fuel - Air Weight Ratio (q)	Heat of Combustion (kJ/kg)	Heat of Vaporization, L (kJ/kg)	Specific Heat Capacity (kJ/kg.K)	Flash Point (K)	AIT (K)	Spalding Mass Transfer Number (B)	Minimum Ignition Energy (mJ)
54	4-methyl-tridecane	$C_{14}H_{30}$	198.4	1.0628	1.024724	1.0000	6.08E-04	0.041	0.539	520.6	0.573	0.1627	0.000460	1.1801	0.037148	47328.63	237.6	2.22063	353.8	755.9	2.728	1.180
55	2-methyl-tridecane	$C_{14}H_{30}$	198.4	1.6408	1.024724	1.0000	1.05E-03	0.046	0.539	518.4	0.575	0.1828	0.000797	0.7644	0.037148	47328.63	237.6	2.22394	352.7	755.9	2.747	1.060
56	3-methyl-tridecane	$C_{14}H_{30}$	198.4	1.1027	1.024724	1.0000	5.86E-04	0.038	0.539	521.9	0.571	0.1511	0.000443	1.1374	0.037148	47328.63	237.6	2.2187	354.5	755.9	2.717	1.240
57	2,6,10,14-tetramethyl-heptadecane	$C_{21}H_{44}$	296.6	1.9308	0.912543	1.0000	1.41E-06	0.000	0.361	630.1	0.473	0.0002	0.000002	0.4345	0.037081	46156.44	195.04	2.23026	441.1	755.9	1.966	2.380
58	(E)-3-tetradecene	$C_{14}H_{28}$	196.4	0.4756	0.994520	1.0000	2.10E-03	0.032	0.545	524.8	0.568	0.1294	0.000162	2.6638	0.03715	46542.77	238.9	1.58844	373.5	512.7	2.867	0.982
59	N-tridecane	$C_{13}H_{28}$	184.4	7.6368	1.027158	1.0000	8.73E-03	0.081	0.580	507.7	0.587	0.3242	0.006116	0.1767	0.037163	47395.34	238.18	2.21146	374.9	475.2	2.464	1.360
60	2,3,6,7-tetramethyl-octane	$C_{12}H_{26}$	170.3	0.6913	1.023718	0.7998	5.72E-03	0.469	0.628	473.2	0.63	1.8842	0.002972	2.1135	0.037181	47469.17	254.84	2.23867	343.3	755.9	3.171	0.874
61	N-hexadecane	$C_{16}H_{34}$	226.4	0.2408	1.006983	1.0000	1.67E-05	0.005	0.473	559.8	0.533	0.0201	0.000015	4.5650	0.037123	47257.51	220.63	2.21718	408.2	475.2	2.085	2.200
62	2,6-dimethyl-naphthalene	$C_{12}H_{12}$	156.2	0.5335	1.706912	0.8186	2.45E-04	0.016	0.685	537.6	0.555	0.0643	0.000072	2.9859	0.037202	43866.84	308.13	1.15749	383.7	825.6	3.285	0.820
63	1,7-dimethyl-naphthalene	$C_{12}H_{12}$	156.2	0.2855	1.706912	0.8087	1.50E-04	0.018	0.685	535.2	0.557	0.0727	0.000043	5.5802	0.037202	43866.84	308.13	0.78374	381.9	822.1	3.891	0.717
64	1,6-dimethyl-naphthalene	$C_{12}H_{12}$	156.2	1.0830	1.706912	0.8087	5.01E-04	0.016	0.685	537.6	0.555	0.0639	0.000145	1.4709	0.037202	43866.84	308.13	0.78374	383.7	781.1	3.787	0.730
65	Decyl-cyclopentane	$C_{15}H_{30}$	210.4	0.2449	1.039542	1.0000	2.38E-05	0.007	0.509	552.7	0.539	0.0272	0.000019	4.8286	0.037136	46549.43	231.99	1.60692	388.6	746.4	3.002	0.964
66	Heptadecane	$C_{17}H_{36}$	240.5	1.5143	0.992783	1.0000	3.83E-05	0.002	0.445	575	0.519	0.0074	0.000036	0.6832	0.037113	47198.34	216.34	2.22026	422.1	475.0	1.987	2.380
67	2-methyl-heptadecane	$C_{18}H_{38}$	254.5	0.7990	0.973824	1.0000	1.64E-05	0.002	0.420	578.1	0.516	0.0061	0.000017	1.2237	0.037104	47159.14	210.37	2.23682	382.1	755.9	2.306	1.720
68	3-methyl-tridecane	$C_{14}H_{30}$	198.4	0.4292	1.024724	1.0000	2.28E-04	0.038	0.539	521.9	0.571	0.1511	0.000172	2.9221	0.037148	47328.63	237.6	2.2187	354.5	755.9	2.717	1.240
69	N-tridecane	$C_{13}H_{28}$	184.4	3.2871	1.027158	1.0000	3.76E-03	0.081	0.580	507.7	0.587	0.3242	0.002633	0.4105	0.037163	47395.34	238.18	2.21146	374.9	475.0	2.464	1.360
70	1-decanol, 2,2-dimethyl-	$C_{12}H_{26}O$	186.3	0.4649	4.192033	1.0000	2.59E-04	0.010	0.574	507.8	0.587	0.0387	0.000045	2.8727	0.037161	42442.3	294.04	1.57407	372.5	738.0	2.900	0.928
71	4-Octanone	$C_8H_{16}O$	128.2	0.3095	0.972291	0.8674	1.01E-02	2.110	0.835	436.2	0.684	8.4769	0.004506	6.2706	0.037258	39196.57	309.28	1.76888	326.9	620.0	2.974	0.892
72	4-methyl-undecane	$C_{12}H_{26}$	170.3	0.2306	1.024118	0.7767	1.25E-03	0.297	0.628	482.4	0.618	1.1932	0.000628	6.3359	0.037181	47469.17	254.84	2.2215	334.2	755.9	3.074	0.874
73	2-methyl-pentadecane	$C_{16}H_{34}$	226.4	0.2950	1.007003	1.0000	3.22E-05	0.008	0.473	550.1	0.542	0.0315	0.000028	3.7255	0.037123	47243.82	220.63	2.22976	368.5	755.9	2.507	1.120
74	3-methyl-hexadecane	$C_{17}H_{36}$	240.5	0.2549	0.992831	1.0000	8.44E-06	0.002	0.445	570.4	0.523	0.0097	0.000008	4.0595	0.037113	47189.19	216.34	2.22579	378.4	755.9	2.358	1.780
75	N-tridecane	$C_{13}H_{28}$	184.4	1.1043	1.027158	1.0000	1.26E-03	0.081	0.580	507.7	0.587	0.3242	0.000884	1.2220	0.037163	47395.34	238.18	2.21146	374.9	475.2	2.464	1.360
76	N-tetradecane	$C_{14}H_{30}$	198.4	0.2268	1.024778	1.0000	9.14E-05	0.029	0.539	527.1	0.566	0.1145	0.000069	5.5287	0.037148	47346.27	237.6	2.21124	372.6	493.2	2.319	1.720
77	N-pentadecane	$C_{15}H_{32}$	212.4	0.3824	1.017840	1.0000	6.55E-05	0.012	0.504	543.8	0.548	0.0490	0.000053	3.0633	0.037135	47774.48	229.9	2.21419	405.4	475.0	2.203	1.960

From Table 4.2, the results can be summarized are as follow:

Results Summary	
Vapour mixture	0.0954 %
Air	99.9046 %
N_2 = (79%*99.9046)	78.9246 %
O_2 = (21%*99.9046)	20.9799 %
Average Flash Point	358.10K
Average Auto Ignition Temperature (AIT)	595.81K
Average Minimum Ignition Energy (MIE)	1.219mJ

From the summary, the average AIT and MIE for the mixing hydrocarbon is 598.81 K and 1.219mJ. This indicates that at this temperature with this amount of ignition energy, there is potential for the contaminated wastewater to initiate combustion due to the various hydrocarbons presented in the drainage system. The components that have the minimum ignition energy close to this value will be easily ignited and once it ignited, it can spread the combustion to the whole system.

The average flash point tells us the conditions under which we can expect the fuel vapor to be created, but it is the explosive range which tells us that a certain mixture of fuel vapor and air is required for the vapor to become ignitable. To have the ability to categorize a liquid correctly when it is not so identified, it is only necessary to know its flash point. By definition, the flash point of a liquid determines whether a liquid is flammable or combustible.

At the average flash point of 358.10K, the evaporation rate of most hydrocarbon components is getting higher and the ignition energy required to initiate combustion is getting lower. It should be noted that the combustible components can become flammable if they exist at temperature higher than the flash point (Cheremisinoff, 1999).

It is important to note that a combustible liquid at or above its flash point will behave in the same manner that a flammable liquid would in a similar emergency. Combustible liquid category is those materials with a flash point above 100°F and it is considered less hazardous than flammable liquids because of their higher flash points.

However, this statement can be misleading since there are circumstances when it is not a valid assumption such as during hot summer sun that striking the metal container for some time or during transportation of some combustible products.

4.3 Effect of Flash Point, Volume Percentage and Vapor Pressure of Components to the Evaporation Rate

The evaporation rate of each component was calculated using a generalized expression given by Eq. (3.1). The results are tabulated in Table 4.2.

For calculation purpose, the area of the drainage system is assumed to be $25m^2$, with the length of 50 m and width of 0.5m. The temperature of the wastewater is assumed to be the same as ambient temperature and the pressure is assumed to be the same as atmospheric pressure.

From the analysis, it shows that the evaporation rate is inversely proportional to the components' flash point but proportional to the volume percent and the vapour pressure of the components. These correlations are shown by Fig. 4.4, Fig. 4.5 and Fig. 4.6.

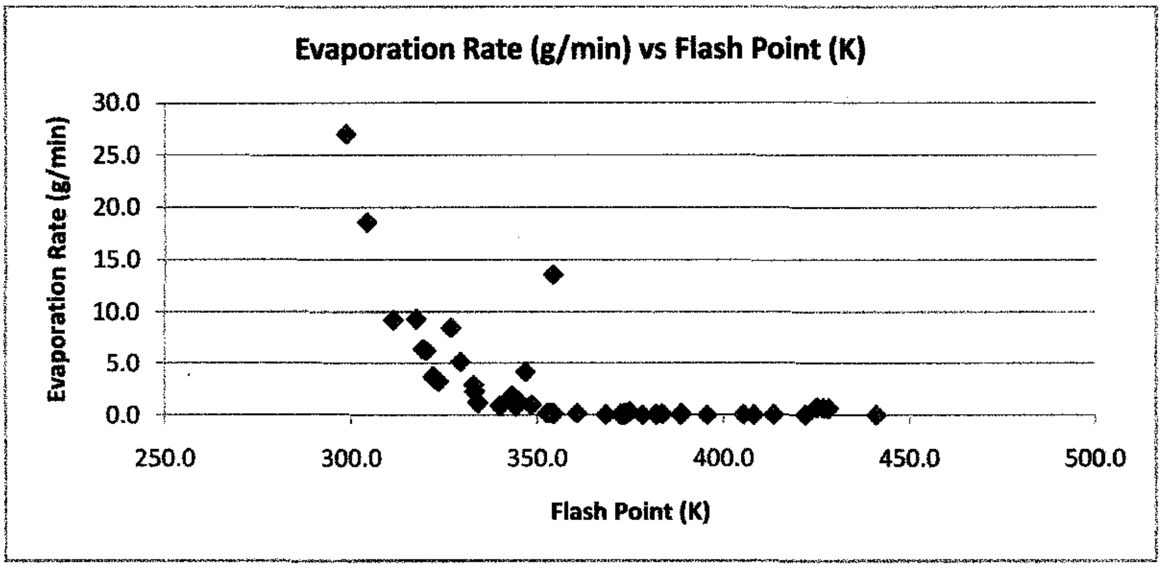

Fig. 4.4: Evaporation rate (g/min) versus flash point (K).

From Fig. 4.4, it can be seen that in general, the rate of evaporation of the compounds is faster for the components with lower flash point. The reason of this finding can be related to the definition of the flash point itself, which is the lowest temperature of a liquid at which it gives off enough vapor to form an ignitable mixture (Cheremisinoff, 1999) and thus, for components with lower flash point, they will vaporize at lower temperature and as a result, the evaporation will also occurred at high rate and lower temperature. In addition, according to (Cheremisinoff, 1999), most of hydrocarbons tend to vaporize easily at room temperature and this justify the significance of high evaporation rate as the flash point of the components are getting lower.

However, there is one point at Fig. 4.4 that is deviated from the general pattern of the graph (354.2, 13. 58). This happened due to the high percent volume of the respective component (3,5-dimethyl-octane) as compared to the other components that have almost similar flash point value with this component.

The components which are the organic compounds generally tend to burn easily because they can volatilize easily at room temperature and possess relatively low specific heat and low ignition temperature. Moreover, organic vapors often have high heats of combustion which, upon ignition, facilitate the ignition of surrounding chemicals, thus compounding the severity of the hazard.

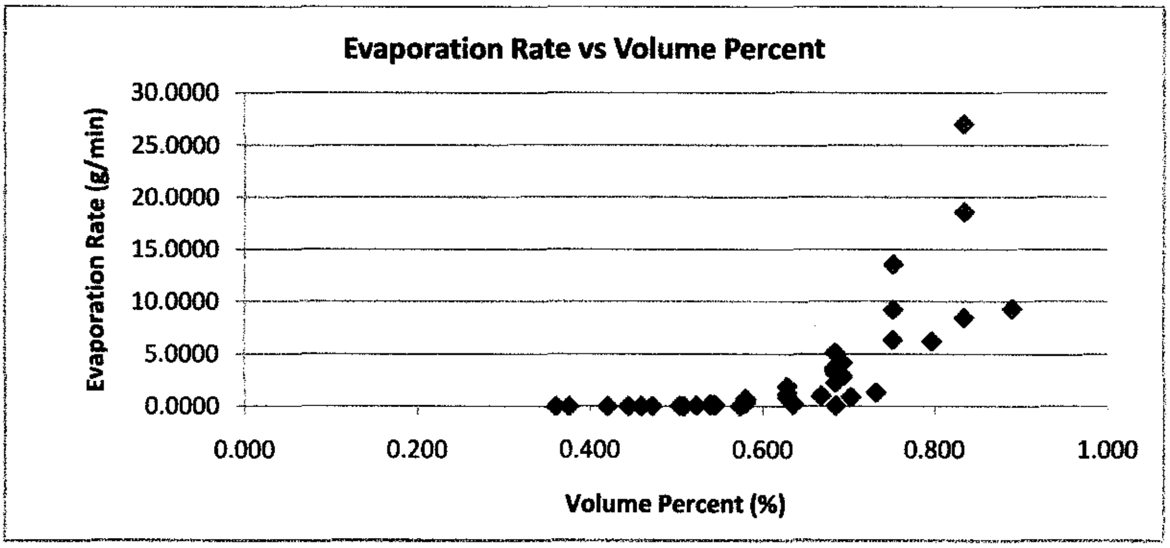

Fig. 4.5: Evaporation rate (g/min) versus volume percent (%).

In Fig. 4.5, the evaporation rate increases as the volume percentage of the component increases. Since the components are mixed with the wastewater in the same drainage system, the evaporation rate is faster for higher volume percentage of components since the higher volume components have the higher possibility to be exposed on the surface of the drainage system that indirectly increase the evaporation rate. It should be noted that evaporation only occurs on the surface of a liquid.

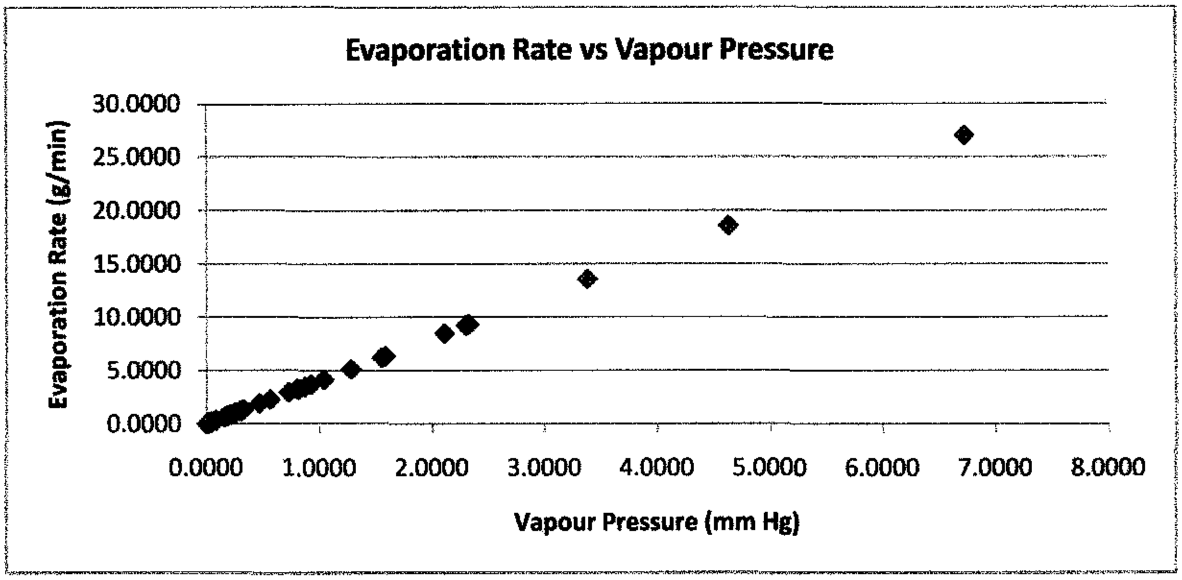

Fig. 4.6: Evaporation rate (g/min) versus vapour pressure (mm Hg).

Fig. 4.6 shows a proportional correlation between the evaporation rate and the vapour pressure of each component. According to Cheremisinoff (1999), the vapour pressure is among the factors that controlled the evaporation rate, instead of temperature, aid material interfacial surface area and the action of active mass transfer agents such as wind. According to Crowl and Louvar (2002), the relation between evaporation rate and the vapour pressure is given by the following correlation;

$$Q_m \alpha (P^{sat} - P) \qquad (4.1)$$

where,

P^{sat} is the saturation vapour pressure of the pure liquid at the temperature of the liquid, and

P is the partial pressure of the vapour in the bulk stagnant gas above the liquid.

It should be noted that liquids with high vapor pressures generally represent a greater fire hazard than those with lower vapor pressures (Cheremisinoff, 1999). As a safety precaution, drummed materials with high vapor pressures in particular should not be stored in direct sunlight, as overheating of the materials and resultant increases in vapor pressures could result in "pregnant" drums with failed or weakened seams.

It should be noted that properties such as saturated vapour pressure is important to determine the flammable hazards since vapours are more easily ignited and more readily transportable as compared to the liquids (they may disperse, or when heavier than air, flow to a source of ignition and flash back).

4.4 Minimum Ignition Energy (MIE)

The MIEs for each component are obtained through interpolation on graph of MIE versus mass transfer number, B (Lees, 1996) as presented in Figure 3.1. The mass transfer number can be calculated using Eq. (3.6). The results of calculated mass transfer number and the corresponding MIE values of each compound are presented in Table 4.2. Fig. 4.7 shows the MIE values for each hydrocarbon at specific peak number.

From Fig. 4.7, 1-nonadecanol has the highest MIE value and this is in line with Cheremisinoff (1999) who stated that molecular weight effect is the reason for the increasing melting and boiling points, the increasing flash points, and the decreasing ignition temperatures. It should be noted that 1-nonadecanol is belongs to alcohol group and it also have high molecular weight (284.5).

Component at Peak Number 63 which is 1,7-dimethyl-naphtalene has the lowest ignition energy with the value of 0.717 mJ. Based on Crowl and Louvar, (2002), human can only sense discharges of 0.6 mJ or more, and the results of this case study indicates that human or people around the drainage system can sense the discharges that have the potential to ignite the component that have the lowest value of MIE.

From Fig. 4.7, the three lowest MIEs are 1, 7-dimethyl-naphthalene (peak number 63), 3, 5-dimethyl-octane (peak number 3) and 1, 3, 5-trimethyl-benzene (peak number 6). The components that have the three highest MIEs are 1-nonadecanol (peak number 40), heptadecane (peak number 66) and 2-methyl-heptadecane (peak number 67).

4.5 Effect of Number of Carbons, Flash Point and Volume Percentage of Components to the Minimum Ignition Energy (MIE)

Fig. 4.8 shows the correlation between the MIE values of each component and their number of carbons. In general, within any group of hydrocarbons, the larger molecules are less volatile than the smaller ones (Cheremisinoff, 1999). This low volatility indirectly indicates that larger molecules should have higher MIE since it needs more energy and higher temperature to be ignited. This is the main reason on why it takes only the first four or five of the straight-chain hydrocarbons are important in the study of hazardous materials since they are flammable as compared to the long-chain hydrocarbons (Cheremisinoff, 1999). The structure of the molecule clearly plays part in the properties of the compounds.

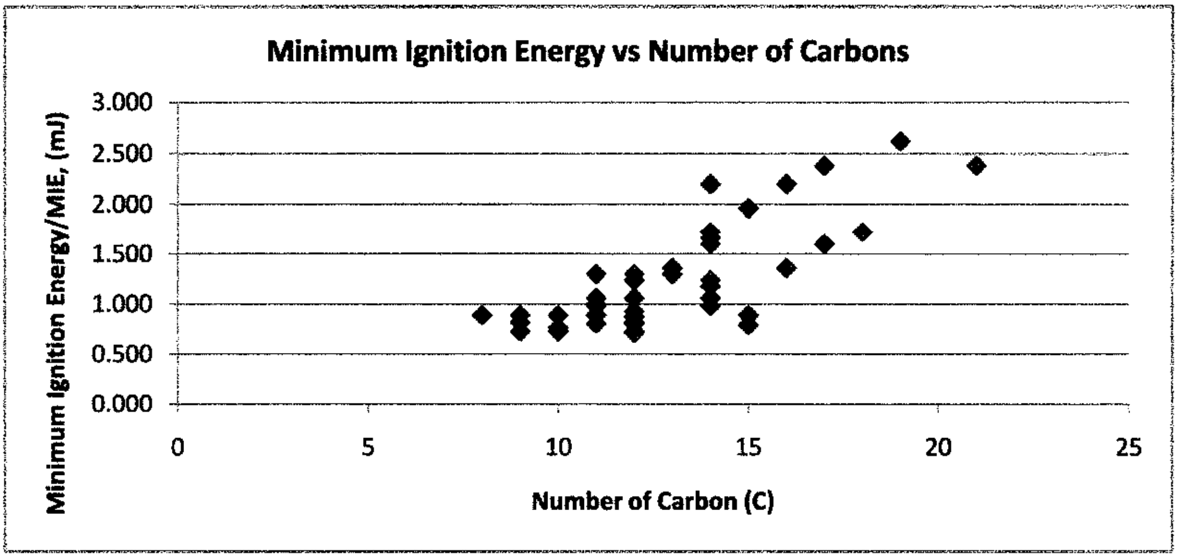

Fig. 4.8: Minimum ignition energy (mJ) versus number of carbon.

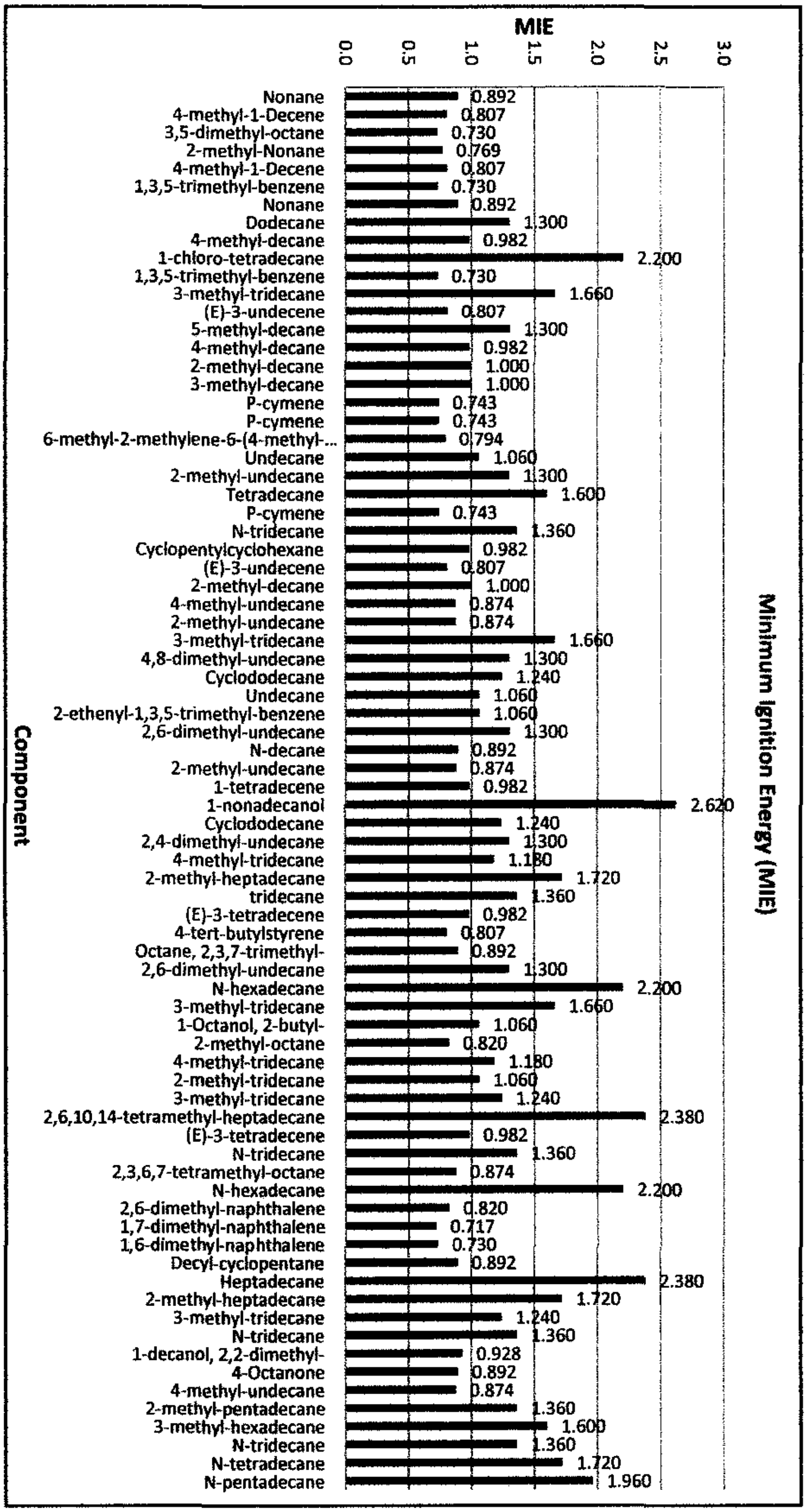

Fig. 4.7: Minimum Ignition Energy (MIE) for hydrocarbon components

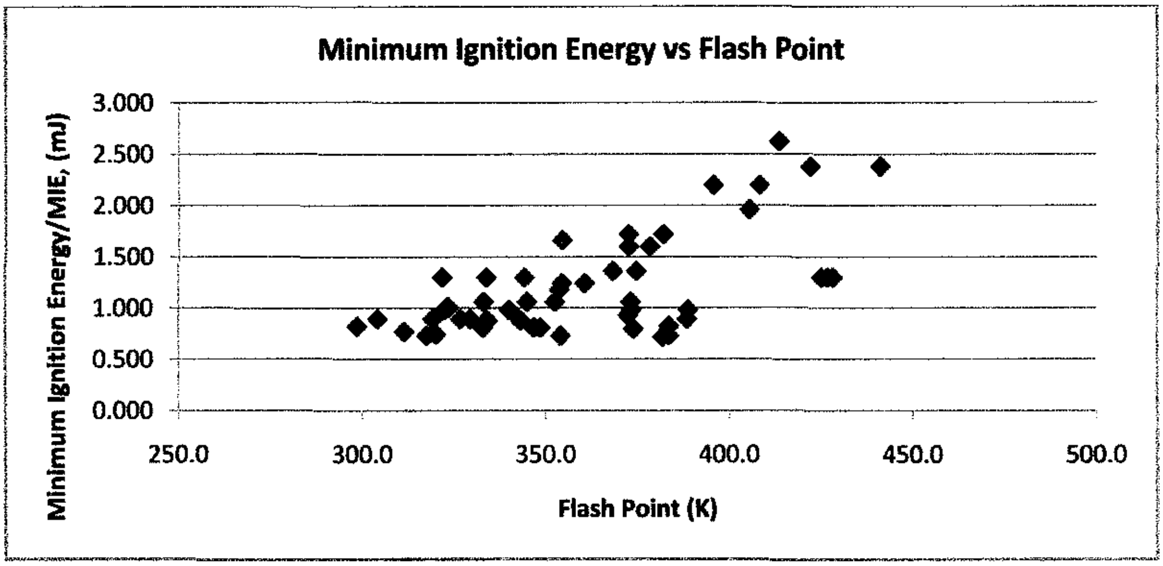

Fig. 4.9: Minimum Ignition Energy (mJ) versus flash point (K).

Most organic compounds are flammable. They tend to melt and boil at lower temperatures than most inorganic substances. Moreover, organic vapors often have high heats of combustion which, upon ignition, facilitate the ignition of surrounding chemicals, thus compounding the severity of the hazard (Cheremisinoff, 1999).

The term flash point basically referring to the temperature that liquid fuel must achieved in order to vapourize so that spontaneous combustion can occur. From Fig. 4.9, the relation between the MIE and the flash point is proportional to each other since the MIE increases as the flash point increases. This correlation is in line with Cheremisinoff (1999) finding that stated the flash point as the lowest temperature a liquid may be and still have the ability to liberate flammable vapor at a sufficient rate that, when mixed with the proper amounts of air, the air-fuel mixture will flash in the presence of a source of energy or ignition source.

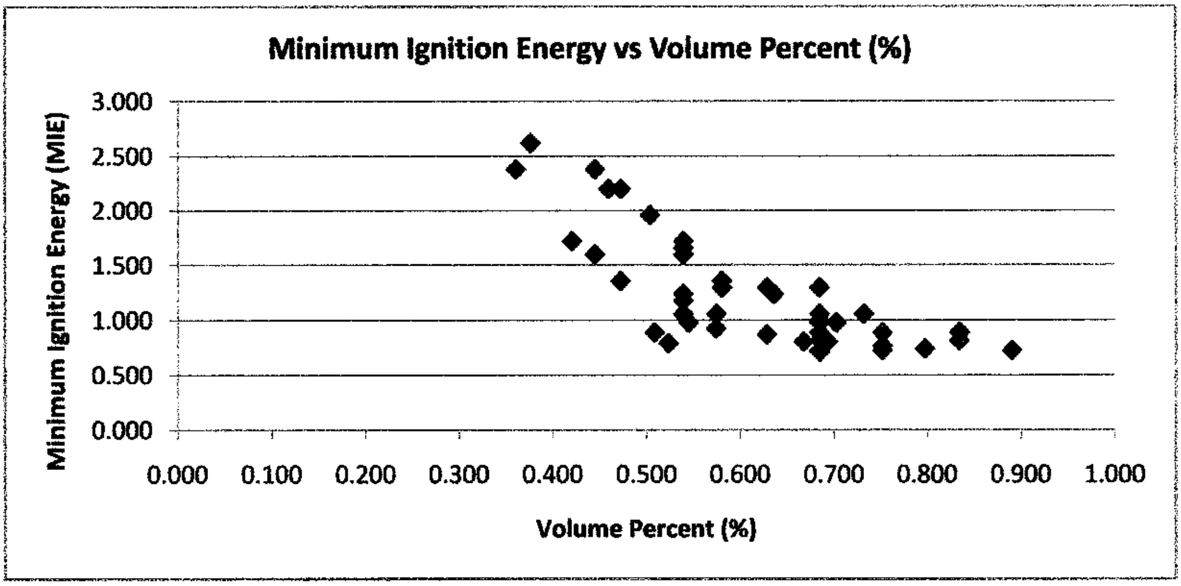

Fig. 4.10: Minimum ignition energy (mJ) versus volume percent (%).

The explanation for correlation in Fig. 4.10 can be related to the explanation given for Fig. 4.5. In Fig. 4.5, the evaporation rate is higher for larger volume percent of components and as for MIE, the correlation is opposite. The MIE for components with higher volume percent is lower because it vapourize faster and thus it require less ignition energy to initiate combustion since most of it converts from liquid to vapour phase easily.

4.6 Sources of Ignition

Identification of ignition sources is vital for safety precaution purpose. Some of the sources are well-understood and readily identified while there are some ignition sources that still need further examination. Basically, this ignition source plays the role to complete the fire triangle. In general, the hydrocarbons can be ignited in two ways:

1) When an external ignition source with sufficient energy to ignite the fuel-oxygen mixture is available (e.g., flames, sparks).
2) When the temperature is raised above the auto-ignition temperature (e.g., the compression ignition of a diesel engine).

The pie chart below shows the outlines of the common ignition sources in oil and gas industries taken from (http://www.firesandexplosions.ca/).

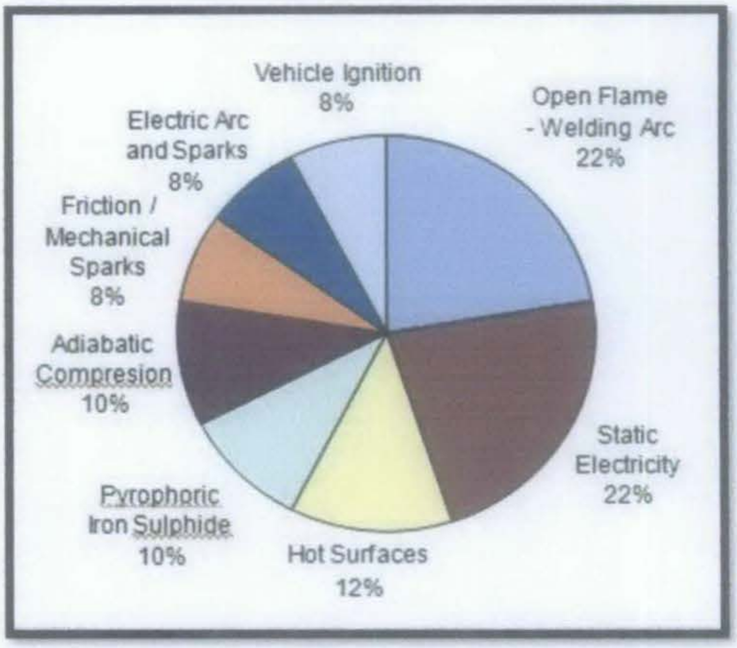

Fig. 4.11: The common ignition sources in oil and gas industry.

From Fig. 4.11, it can be seen that welding activity and static electricity are the main ignition sources that make up the total of 44% out of all potential ignition sources available, each contributes 22%.

Welding is one of the hot work activities that can produce enough heat from flame and spark that can provide sufficient energy to ignite flammable vapours, gases, or dust (Institute, 2002). According to Crowl and Louvar, (2002), the range for MIE of spark is from 0.001 mJ until 10, 000 mJ. Minimization of welding activity at the location near to the drainage system can be one of the best approaches to minimize the possibility of fire hazards. In a fire, chemical energy is converted to heat, and if this heat is converted at a rate faster than the rate of heat loss from the fire, the heat of the fire increases and therefore, the reaction will proceed faster, producing more heat faster than it can be carried away from the fire, thus increasing the rate of reaction even more (Cheremisinoff, 1999).

As for static electricity, it is originally referred to physical phenomena associated with charges at rest, such as on charged, isolated conductors. Due to this, it is important to appreciate mechanisms for production of static discharges and more important is to recognize the factors influencing flammability and ease of ignition (Britton, 1999). Static electricity is one of the causes of electrostatic discharge and it should be noted that the MIE of electrostatic discharge can be as low as 0.001 mJ and can reach up to 100, 000 mJ (Crowl and Louvar, 2002). Since the lowest MIE of the component is 0.717 mJ, a great attention shall be given to this source since it can potentially contributes to fire hazards due to its MIE range.

It is potentially high that vapours can be ignited in the event of the hot surfaces temperature exceeded the minimum AIT of the hydrocarbons. It should be noted that from Table 4.2, the lowest AIT for the hydrocarbons is 473.15 K and due to this, the hot surfaces temperature should be ensure to not exceeding this temperature in order to avoid the ignition. Although the MIE for the hydrocarbon that have the lowest AIT is still higher as compared to the MIE of many hydrocarbons as stated in Crowl and Louvar, (2002), which is equivalent to 0.25 mJ, minimization of ignition sources is still the best solution since the probability of fire and explosion increases rapidly as the number of ignition sources increases (Crowl and Louvar, 2002). However, it is not only the surfaces temperature that may leads to the ignition of hydrocarbon vapours, but in general the refineries itself frequently operate the processing equipment that contains a liquid above its respective ignition temperature (Cheremisinoff, 1999).

Other main sources of ignitions are pyrophoric iron sulphides, which are found frequently in vessels, storage tanks and sour gas pipelines (10%), adiabatic compression (10%), friction or mechanical sparks (8%) that usually occur when there is excessive metals or extremely hard substances, electric arcs and sparks (8%) and vehicle ignition (8%). However, according to Crowl and Louvar, (2002), the elimination efforts should give the greatest attention to the sources that have the greatest probability of occurrence.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This study shows that some waste generated by the refineries can be dangerous and can generate flammable mixtures, which may cause fire. The results from the study indicate that several hydrocarbon compounds were presented in the waste sample collected from a refinery's drain. Hydrocarbons are among the most useful materials to mankind, but are also among the most dangerous in terms of their fire potential.

The study discussed the procedure on how to determine the evaporation rate and MIE of substances presented in the drainage system. The significance of determination of the values of these two parameters are also been discussed besides identify the potential sources of ignition that may leads to into accident like fire and explosion.

The methodology in this study covered both experimental and theoretical works. The experimental work covered the collection of a liquid sample from a refinery's drain, and then analyzing the sample using GC to identify the compositions of the sample. The GC analyses have shown that the sample contained heavy hydrocarbon components ranged from C_9 to C_{22}. Even though these components have high boiling points and heavy molecular weights, the results shown that these components can be vaporized at ambient temperature and atmospheric pressure. This is indicating that heavy liquid hydrocarbon can also vaporize and form flammable and explosive mixtures in air.

From the results obtained, most of the hydrocarbons have low MIE, as low as 0.717mJ which indicates that it can be easily been ignited. Therefore, identification of potential ignition sources is vital prior to assist the elimination method of those ignition sources. The preventive strategy such as the concept of inherent safety is then been proposed in recommendation section in order to reduce the possibility of fire and explosion to occur.

5.2 Recommendation

By current technology, fire and explosion analysis to the flammable and ignitable gas mixture inside the drainage system can be done directly on the plant. The data collected will be the most precise one since in any cases when working with ignitable and flammable materials, controlling the source of ignition is often the easiest and safest way to avoid fires or explosions.

In order to ensure the plant operates safely after all safety factors are taken into consideration and all necessary actions have been taken in evaluating and analyzing the possible root causes of the fire and explosion, the hazards shall be controlled and minimized accordingly in order to avoid recurrence. Therefore, industrial should approach more preventive strategy such as the concept of inherent safety methods for their facility as recommended below:

1) Plant Layout Design

Safe plant layout designed based on standard design and local regulation. The right spacing of unit operations are critical so that there is adequate evacuation access in time of emergency especially during maintenance, shut down act and routine operation work which may involved a lot of hot work activities.

2) Elimination of ignition sources

Ignition source such as welding, shall not be conducted near an open space drainage system if there is no O_2 content indication applied prior to hot work activities. As drainage system may contain traces of hydrocarbon which can vaporize to the surrounding.

3) Reduced the leak inventory into the drainage system

It is recommended to have curbed area with a drain at the process equipment area to contain and evacuate the spill as to avoid spillage into the drainage system.

4) Extinguishing techniques

The use of an extinguishing agent such as a foam with the capability of restricting the air from uniting with the vapor. Another technique is to prevent the liquid from having the ability to generate vapor. Usually this is a cooling action and is accomplished with water spray streams.

REFERENCES

Ahamad@Ahmad, N. F. (2011). *Inherently Safer Design for Hazardous Waste Contaminated in Industrial Drains.* Bsc Thesis, Universiti Teknologi PETRONAS.

Albahri, T. A. (2003). *Flammability Characteristics of Pure Hydrocarbons.* Safat: Chemical Engineering Dept, Kuwait University.

Al-Haddad A., Chmielewská E. and Al-Radwan S., (2007). *A Brief Comparable Lab Examination for Oil Refinery Wastewater Treatment Using the Zeolitic and Cabonaceous Adsorbents.* Petroleum & Coal 49 (1): 21-26.

Bjerketvedt D., Bakke J., van Wingerden K., (1997). *Gas Explosion Handbook. Journal of Hazardous Materials* 52, 1-150.

(IHMM), (2010). *Institute of Hazardous Materials Management (IHMM).* Retrieved August 14, 2011, from Institute of Hazardous Materials Management (IHMM), Protecting the Environment and the Public's Health, safety and Security for over 25 Years.: http://www.ihmm.org/index.php?option=com_content&view=article&id=61&Itemid=161

Cheremisinoff, N. P. (1999). *Handbook of Industrial Toxicology and Hazardous Materials.* New York: Marcel Dekker, Inc.

Crowl D., A, Louvar J. F., (2002). *Chemical Process Safety: Fundamentals with Applications.* Prentice-Hall.

EPA, (1998). *EPA Chemical Accident Investigation Report.* United State Environmental Protection Agency.

Fredenslund, A. Jones, R. L. Prausnitz, J. M., (1975). Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures. *AIChE J.* 21: 1086–1099.

Khan F., and Abbasi S., (1999 a). Major Accidents in Process Industries and anAnalysis of causes and Consequences. Journal of Loss Prevention in the Process Industries. 12, 361-378.

L. G. Britton, Kenneth L. C., William Fenlon, David Frurip, John Going, B. Keith Harrison, Jeff Niemeier and Erdem A. Ural. (2005). *The Role of ASTM E27 Methods in Hazard Assessment Part II: Flammability and Ignitability.* West Conshohocken: American Society for Testing and Materials (ASTM).

Lees, F. P. (1996). *Loss Prevention in the Process Industries.* United Kingdom: Reed Educational and Professional Publishing.

Mustapha S. and Mc Donnell R., 2001.*On-Site and Off-Site Emergency Response Plans.*

Nolan, D., (1996). *Handbook of Fire & Explosion Protection Engineering Principles for Oil, Gas, Chemical, & Related Facilities.* Noyes Publications, USA.

Paul T. Kostecki and Edward J. Calabrese. (1991). *Hydrocarbon Contaminated Soils and Groundwater*. Michigan: Lewis Publishers, Inc.

Polprasert, C., Liyanage, L. R. J., (1996). *Hazardous waste generation and processing. Resources, Conservation and Recycling, 16 (1-4), 213-226.*

Shaaran, S. N. (2009). *An Investigation of Fire and Explosions Accidents in the Drainage System Related to process Industries.* Tronoh: Universiti Teknologi Petronas.

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

Shoib, F. A. (2011). *Predictions of Flammability Hazard Properties of Chemical Mixtures Using Computerized Tools.* Tronoh: Universiti Teknologi PETRONAS.

Vázquez, M., (2005).*Binary mixture flammability characteristics for hazard assessment.*PhD. Thesis, Texas A&M University.

Vince, I. (2008). *Major Accidents to The Environments.* Burlington: Elsevier Ltd.

Wahi, M. A. (2010). *Investigation of Fire and Explosion in the Drainage System Related to Process Industries.* Tronoh: Universiti Teknologi PETRONAS.

Zabetakis, M. G. (1924). Flammability Characteristics of Combustible Gases and Vapors. *Bureau of Mines,Bulletin 627,* 6.

Zabetakis, M. G., (1965). Flammability Characteristics of Combustible Gases and Vapors.*Bureau of Mines, Bulletin 627.*

APPENDICES

Table A1: Critical properties and acentric factor

Compound	**Formula**	**Tc(K)**	**Pc(bar)**	**Pc(MPa)**	ω_i
Nonane	C_9H_{20}	595.65	23.06	2.306	0.438
4-methyl-1-Decene	$C_{11}H_{22}$	615.61			
3,5-dimethyl-octane	$C_{10}H_{22}$	606.3	21.89	2.189	0.424
2-methyl-Nonane	$C_{10}H_{22}$	610	21.2	2.12	0.472
4-methyl-1-Decene	$C_{11}H_{22}$				
1,3,5-trimethyl-benzene	C_9H_{12}	637.25	31.27	3.127	0.4016
Nonane	C_9H_{20}	595.65	23.06	2.306	0.438
Dodecane	$C_{12}H_{26}$	658.2	18.24	1.824	0.573
4-methyl-decane	$C_{11}H_{24}$	629.99	19.48	1.948	0.507
1-chloro-tetradecane	$C_{14}H_{29}Cl$	738.54	14.8	1.48	0.694
1,3,5-trimethyl-benzene	C_9H_{12}	637.25	31.27	3.127	0.4016
3-methyl-tridecane	$C_{14}H_{30}$	685.13	15.33	1.533	0.622
(E)-3-undecene	$C_{11}H_{22}$	637.84	20.23	2.023	0.504
5-methyl-decane	$C_{11}H_{24}$	630	19.86	1.986	0.48838
4-methyl-decane	$C_{11}H_{24}$	629.990	19.480	1.948	0.51
2-methyl-decane	$C_{11}H_{24}$	631.760	19.480	1.948	0.51
3-methyl-decane	$C_{11}H_{24}$	632.860	19.480	1.948	0.51
P-cymene	$C_{10}H_{14}$	653.150	28.370	2.837	0.37
P-cymene	$C_{10}H_{14}$	653.150	28.370	2.837	0.37
6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-bicyclo[3.1.1]heptane	$C_{15}H_{24}$				
Undecane	$C_{11}H_{24}$	638.8	19.7	1.966	0.5
2-methyl-undecane	$C_{12}H_{26}$	650.71	17.92	1.792	0.548
Tetradecane	$C_{14}H_{30}$	692.400	16.210	1.621	0.7
P-cymene	$C_{10}H_{14}$	653.150	28.370	2.837	0.37
N-tridecane	$C_{13}H_{28}$	675.800	17.230	1.723	0.618
Cyclopentylcyclohexane	$C_{11}H_{20}$	665.48	23.61	2.361	0.447
(E)-3-undecene	$C_{11}H_{22}$	637.84	20.23	2.023	0.504
2-methyl-decane	$C_{11}H_{24}$	631.76	19.48	1.948	0.507
4-methyl-undecane	$C_{12}H_{26}$	649.36	17.92	1.792	0.548
2-methyl-undecane	$C_{12}H_{26}$	650.71	17.92	1.792	0.548
3-methyl-tridecane	$C_{14}H_{30}$	685.13	15.33	1.533	0.622
4,8-dimethyl-undecane	$C_{13}H_{28}$				
Cyclododecane	$C_{12}H_{24}$	747.23	25.46	2.546	0.313
Undecane	$C_{11}H_{24}$	638.8	19.7	1.966	0.5
2-ethenyl-1,3,5-trimethyl-benzene	$C_{11}H_{14}$	692.36	27.246	2.7246	0.43485
2,6-dimethyl-undecane	$C_{13}H_{28}$				
N-decane	$C_{10}H_{22}$	618.45	21.23	2.123	0.484

2-methyl-undecane	$C_{12}H_{26}$	650.71	17.92	1.792	0.548
1-tetradecene	$C_{14}H_{28}$	692.000	16.600	1.66	0.6
1-nonadecanol	$C_{19}H_{40}O$				
Cyclododecane	$C_{12}H_{24}$	747.23	25.46	2.546	0.313
2,4-dimethyl-undecane	$C_{13}H_{28}$	653.35	16.66	1.666	0.558
4-methyl-tridecane	$C_{14}H_{30}$				
2-methyl-heptadecane	$C_{18}H_{38}$	739.33	11.59	1.159	0.727
tridecane	$C_{13}H_{28}$	675.8	17.23	1.723	0.619
(E)-3-tetradecene	$C_{14}H_{28}$	692.000	16.600	1.66	0.6
4-tert-butylstyrene	$C_{12}H_{16}$	709	24.8	2.48	0.422
Octane, 2,3,7-trimethyl-	$C_{11}H_{24}$	625.29	19.75	1.975	0.449
2,6-dimethyl-undecane	$C_{13}H_{28}$				
N-hexadecane	$C_{16}H_{34}$	720.6	14.19	1.419	0.747
3-methyl-tridecane	$C_{14}H_{30}$	685.13	15.33	1.533	0.622
1-Octanol, 2-butyl-	$C_{12}H_{26}O$	712.9	19.7	1.97	0.635
2-methyl-octane	$C_{9}H_{20}$	582.8	23.1	2.31	0.458
4-methyl-tridecane	$C_{14}H_{30}$				
2-methyl-tridecane	$C_{14}H_{30}$	684.08	15.33	1.533	0.622
3-methyl-tridecane	$C_{14}H_{30}$	685.13	15.33	1.533	0.622
2,6,10,14-tetramethyl-heptadecane	$C_{21}H_{44}$				
(E)-3-Tetradecene	$C_{14}H_{28}$	692.000	16.600	1.66	0.6
N-tridecane	$C_{13}H_{28}$	675.8	17.23	1.723	0.619
2,3,6,7-tetramethyl-octane	$C_{12}H_{26}$	642.6	18.29	1.829	0.462
N-hexadecane	$C_{16}H_{34}$	720.6	14.19	1.419	0.747
2,6-dimethyl-naphthalene	$C_{12}H_{12}$	777	31.7	3.17	0.418
1,7-dimethyl-naphthalene	$C_{12}H_{12}$	770.6	30.06	3.006	0.443
1,6-dimethyl-naphthalene	$C_{12}H_{12}$	770.6	30.06	3.006	0.443
Decyl-cyclopentane	$C_{15}H_{30}$	730.64	16.29	1.629	0.604
Heptadecane	$C_{17}H_{36}$	736	14.1	1.41	0.753
2-methyl-heptadecane	$C_{18}H_{38}$	739.33	11.59	1.159	0.727
3-methyl-tridecane	$C_{14}H_{30}$	685.13	15.33	1.533	0.622
N-tridecane	$C_{13}H_{28}$	675.8	17.23	1.723	0.619
1-Decanol, 2,2-dimethyl-	$C_{12}H_{26}O$				
4-Octanone	$C_{8}H_{16}O$	624	26.4	2.64	0.528
4-methyl-undecane	$C_{12}H_{26}$	649.36	17.92	1.792	0.548
2-methyl-pentadecane	$C_{16}H_{34}$	713.05	13.26	1.326	0.683
3-methyl-hexadecane	$C_{17}H_{36}$	727.5	12.38	1.238	0.708
N-tridecane	$C_{13}H_{28}$	675.8	17.23	1.723	0.619
N-tetradecane	$C_{14}H_{30}$	692.400	16.210	1.621	0.7
N-pentadecane	$C_{15}H_{32}$	706.8	15.2	1.52	0.705

Table A2: Group Contribution for Estimation of the AIT

HC Types	**Serial No.**	**Group**	**$(AIT)_i$**
Paraffins	1	$-CH_3$	-0.8516
	2	$>CH_2$	-1.4207
	3	>CH-	0.0249
	4	>C<	2.3226
Olefins	5	$=CH_2$	0.4682
	6	=CH-	-1.9356
	7	>C=	-2.242
	8	≡CH	-3.118
	9	≡CH-	-1.136
Cyclic	10	$>CH_2$	-1.160
	11	>CH-	0.0372
	12	>C<	8.960
	13	=CH-	0.0037
	14	>CH=	-12.33
Aromatics	15	=CH-	0.4547
	16	>CH= (fused)	0.0246
	17	>CH=	-1.889
	18	>CH= (ortho)	0.9125
	19	>CH= (meta)	2.465
	20	>CH= (para)	2.097