Flammability Characteristics of Combustible Vapor Mixtures from Bio Oil

By

Nurul Amirah Hanim Binti Umar

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

SEPTEMBER 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Flammability Characteristics of Combustible Vapor Mixtures from Bio Oil

by

Nurul Amirah Hanim Binti Umar

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

DR. MOHANAD EL-HARBAWI
Senior Lecturer
Chemical Engineering Department
Universiti Teknologi PETRONAS

(Dr. Mohanad El-Harbawi)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

SEPTEMBER 2011

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.

NURUL AMIRAH HANIM BINTI UMAR

ABSTRACT

Study of fire and explosion is very important mainly in industrial activities 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 bio oil sample. In this study, bio oil liquid sample containing mixtures of hydrocarbon products were produced by fast pyrolysis process using palm oil kernel shell as the main biomass source. The bio oil-liquid phase was analysed using Gas Chromatography Mass Spectrometry (GC-MS) and Gas Chromatography Flame Ionization Detector (GC-FID) to examine the compositions of the sample Mole fractions of components in the liquid phase were obtained from the GC-FID analysis while the mole fractions of the components in gas phase were calculated via modified Raoult's law. In this study, the gas mixture is considered as a real solution. The activity coefficients were calculated using Universal Functional Activity Coefficient (UNIFAC) method; while the fugacity coefficients were obtained by using Peng-Robinson method, which is implemented in ThermoSolver software. LFL and UFL values for mixture (LFL_{mix} and UFL_{mix}) were calculated according to Le Chatelier equation. The LFL_{mix} and UFL_{mix} values were used to construct the flammability diagram and subsequently used to determine the flammability of the mixture. In this study, the LFL_{mix} for the mixture is calculated at 3.89vol% and 12.4vol% for UFL_{mix}. Meanwhile, the Limiting Oxygen Concentration (LOC) for the mixture is 10.69vol%. The findings of this study can be used to propose suitable inherent safer methods to prevent the flammable mixture from occurring and to minimizing the loss of properties, business and life due to fire accidents in bio oil production. The findings of this study also may assist in minimizing fire hazards associated with presence of hydrocarbon vapours derived from bio oil storage system.

ACKNOWLEDGEMENT

Throughout the whole period of conducting the Final Year Project, many have provided immeasurable amount of guidance, ideas, assistance, support and advice. Foremost, I am indebted to my supervisor, Dr Mohanad El-Harbawi for the continuous support of my final year project, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this thesis.

Also to the Final Year Project Coordinator, Dr. Lukman Ismail for providing all the necessary information required to conduct the project.I also want to thanks the lecturers and staffs of Chemical Engineering Department, Universiti Teknologi PETRONAS for their cooperation, suggestions and guidance in the compilation and preparation this final year project thesis. Special thanks goes to UTP research centre for providing me with bio oil sample and assisting in the components identification process.

Deepest thanks and appreciation to my parents, family, and others for their cooperation, encouragement, constructive suggestion and full of support for the thesis completion, from the beginning till the end. Also thanks to all of my friends and everyone, that has been contributed by supporting my work and helps myself during the final year project progress till it is fully completed.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Background of study

In the developed and modern society, energy sources play a significant role in human's life. People rely on the energy resources for homes, business and transportations. The global demand for energy supply is keeping increasing. According to Sharma and Singh (2008), the World Energy Forum has predicted that fossil-based oil, coal and gas reserves will be exhausted in less than another 10 decades. Therefore, recent development in bio oil production as a renewable energy source seems to be an ideal solution for global energy demands.

Bio oil is mainly derived from biological carbon fixation or from biomass conversion. In general, bio oil is considered to be much safer than other petroleum fuels, due to their high flash point. Bio oil is much less flammable than other petroleum fuels. However, that does not mean all bio oil materials are not flammable materials. Some components of bio oil are similar to hydrocarbon components; therefore it can vaporize and turn into vapor mixture form at the ambient temperature and atmospheric pressure. If this mixture is exposed to heat or ignition source or if the concentration of the mixture is within the flammability range then, this may cause fire.

The presence of hydrocarbon components in bio oil mixtures exposes bio oil storage 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. Hydrocarbons fall into the fuel category. 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 bio oil storage system 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. Flammable gas 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.

In general, an inherent safer design is an approach to address safety issues in the design and operation of chemical plants (Dennis, 2006). The design will identify ways to eliminate or significantly reduce hazard. Bio oil storage system and production process should therefore be design as a friendly user and this is applied to all chemical and hydrocarbon industry, where hazardous materials are handled. In the past there have been many bio oil fire and explosion accidents. Probably the most serious disaster is the explosion occurred at biodiesel plant in Ohio in 2009, which injured thirteen people and heavily damaged a processing plant.

1.2 Problem Statement

As bio oil possesses more advantages compared to the fossil fuels, various raw materials have been utilized for biodiesels production in a large scale. Therefore, safety concern has arisen due to the availability of flammable components in the bio oil. There is high potential of fires and explosion occurs in the storage system of bio oil due to the availability of flammable components. Those flammable components such as Phenol, Cyclohexanol and Acetic Acid can vaporize and turn into vapour mixture form at the ambient temperature and atmospheric pressure. If this mixture is exposed to heat or ignition source or if the concentration of the mixture is within the flammability range then, this may cause a fire. This project is aiming to investigate the flammability of bio oil products and propose a systematic approach on inherent safer design in the bio oil storage system.

1.3 Objectives

The objectives of this project are:

- To estimate the flammability limits of bio oil vapor
- To investigate the possibility for the occurrence of fire incidents due to the vaporization of bio oil components
- To identify and recommend suitable inherently safety methods to prevent fire and explosion incidents from occurring

1.4 Scope of Study

Existence of flammable components in bio oil can be dangerous and generate flammable mixtures, which may cause fire and lead to property damage and life threat. The flammability limits are widely used index for representing flammability of gases and vapours. The study focuses on real solution of bio oil. The mole fractions of the components in the gas phase will be calculated according to modified Raoult's law. Then, LFL_{mix}, and UFL_{mix} will be used to predict the zone of a bio oil vapour mixture. Furthermore, this study will examine if the bio oil vapour mixture occupied in the storage container is flammable or not by using flammability diagram method. Finally the results from this work will be used to propose suitable inherent safety methods to prevent the flammable mixture from occurring in storage system. Furthermore, it can contribute to minimizing the loss of properties, business and life due to fire accidents.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

For the past few decades, the global industrial revolution has led to a steep rise for the demand of petroleum-based fuels (Nigam & Anoop, 2011). Currently, fossil fuel takes up almost 80% of the primary global energy consumption. The sources of these fossil fuels are becoming exhausted and also lead to many negative impacts including climate change, receding of glaciers, rise in sea levels and loss of biodiversity. In addition, for the past few years, the crude oil price is reported to be increased exponentially. Therefore, recent development in bio oil production as a renewable energy source seems to be an ideal solution for global energy demands. According to Kumar (2011), global production of bio oil increased 17% in 2010 to reach an all-time high of 105 billion liters, up from 90 billion liters in 2001. In general, bio oil is considered as a safer fuel compared to petroleum fuels due to high flash point. It means that bio oil will not easily ignite or produce fire at low temperature. In other word, bio oil is considered much less flammable than petroleum fuels. However, due to the presence of hydrocarbon components in the bio oil, it turns out to be flammable materials. At ambient temperature and atmospheric pressure, bio oil with the presence of hydrocarbon components could vaporize and forming vapor mixture. If this mixture is exposed to heat or ignition source or if the concentration of the mixture is within the flammability range then, this may cause a fire.

There are innumerable situations where gases, liquids, and hazardous chemicals are produced, stored, or used in a process which are having high risk and if released, could potentially result in a hazardous fire and explosive incident. Thus, it is important to analyse all materials and reactions associated with a particular process in bio oil production, including process reaction, manufacturing, storage, or treatment facilities in order to minimize the opportunity for 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. 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 shows a summary of the major incidents in the bio oil process industries related to fire cases only.

Table 2-1: Summary of the major incidents in biofuels process industries (Kenneth Pete Moss, 2009)

Year	Location	Chemical	Death/Injury
2006	American Biofuels, Bakersfield, Calif	Methanol	2
2006	Sun Break Biofuels, Canby	Ethanol	1
2006	Blue Sky Biodiesel, Idaho	Biodiesel	1
2007	Agri Biofuels Dayton, Texas	Methanol	1
2007	Better Biodiesel Spanish Fork, Utah	Methanol	11
2007	Farmers & Truckers Biodiesel	Methanol	3
2008	American Ag Fuels Defiance, Ohio	Glycerin	13
2008	Biofuels of Tennessee Decaturville	Acetone	1
2009	Columbus Foods Company Chicago	Sulphuric acid/glycerin	2
2009	New Eden Energy St Cloud	Multiple chemicals	1
2008	Biofuels of Tennessee Decaturville	Acetone	2

The understanding of the flammable material properties is necessary especially when we deal or handle dangerous substances. Fires and explosions in industries can be prevented by understanding the flammable limits of gases. Thus, knowing flammability limits and related information are crucial in the process industries where serious hazards may be encountered within the flammability limits.

2.2 Hazardous Material

Basically there are three categories of hazardous materials in process industries; flammable, toxic and reactive materials. The flammable materials are those that can be ignited to give a number of possible hazardous effects, depending on the actual materials and conditions. Major hazards result in thermal radiation of combustion and overpressure. Other hazards could be suffocation caused by the smoke of combustion. The release of toxic materials can give rise to dispersing clouds in atmosphere, which cloud harm man and animals through inhalation or absorption through skin. The materials are classified into water-reactive materials, air reactive materials, oxidizers, unstable materials and incompatible materials (Mustapha and Mc Donnell, 2001).

There are many organizations that have developed classifications related to flammable chemicals, including Department of Transportation (DOT), National Fire Protection Association (NFPA), Occupational Safety and Health Administration (OSHA), and Environmental Protection Agency (EPA). Some organizations establish their classifications with qualitative descriptions but most classifications are based on physical/chemical properties such as flash point and boiling point (Vázquez, 2005). Both NFPA and DOT defined combustible liquids as having a flash point of 100°F (38°C) or higher. On the other hand, OSHA defined combustible liquids as any liquid with a flash point at or above 100°F (38°C) but below 200°F (39.3°C) (Lee, 2005). NFPA have adopted the flash point as a criterion in enforcing the safe handling, storing, and transporting of flammable compounds (Fujii and Hermann, 1982).

2.2.1 Flammable Mixture

A mixture of fuel-air will only burn if the fuel concentration is between the UFL and LFL. Figure 2.2 shows the flammable range for some fuel-air mixtures (Bjerketvedt et al., 1997).

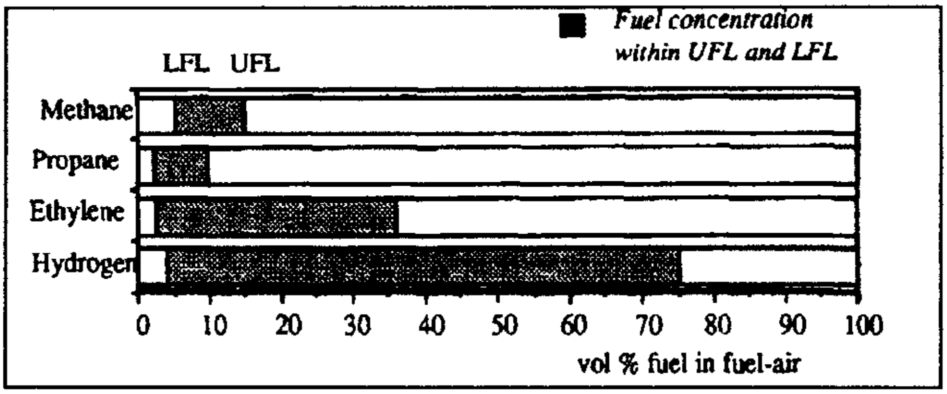


Figure 2-1: Flammability range for fuel-air mixtures at 1 atm. and 25°C.

The flammability in air is the most important safety characteristic of gases and gas mixtures (Volkmar and Maria, 2005). The flammability characteristics of chemical substances are important to prevent accidental explosions during industrial processes and handling flammable gasses. The gas mixture is classified as flammable if it is in between the explosion range. Thus, the explosion limits have to be measured as it is interchangeable with the term flammability limit. The flammable mixture may form either by accident or design. The combustible concentration can be reduced by adding enough air or inert gas to produce non flammable mixtures when they are formed by accident. However, there are certain conditions to increase the combustible concentrations to produce a non flammable mixture. Flammable mixtures may encounter in production of many chemicals and physical operations. Thus, special precautions must be taken to assure no rapid formation of flammable mixture in the industry (Zabetakis, 1965). Flammable mixtures are composed of two or more flammable compounds. There will be different behaviours can be expected from the mixtures but it is depending whether the mixture is ideal or non-ideal (Vazquez, 2005).

Le Chatelier, (1891) proposed empirical models to calculate the LFL and UFL of multiple fuel mixtures. This method is still widely used today. Hustad and Sønju, (1988) found a good agreement between their experiments and Le Chatelier's law for LFL at elevated temperature and pressure for fuel mixtures. Flammability limits for a mixture can be also estimated using the Calculated Adiabatic Flame Temperature (CAFT) methods (Hansel et al., 1991; Melhem, 1997; Crowl, 2003). Zhao (2008) has developed CFT-V (Calculated Flame Temperature at constant Volume) modelling to estimate the LFLs of binary hydrocarbon mixtures. CAFT modelling is based on a comprehensive energy conservation analysis. The energy loss is related to the fuel combustion chamber setup. Zhao (2008) also described that CFT-V modelling is sensitive to the experimental configuration because it is the application of heat balance. Thus, by keeping all data sources which are consistent with CFT-V modelling will give higher accuracy.

There were several experimental work have been conducted to measure the flammability of gas mixtures. For example, Bolk et al., (1996) constructed a large pilot plant to study the UFL of ethene-air-nitrogen mixtures under conditions of flow. Experiments were performed at pressures of 5 and 10 bar, with gas temperatures between 25 and 300°C. Liekhus et al., (2000) conducted some experiments to predict the flammability of gas mixtures containing hydrogen and flammable or non-flammable volatile organic compounds (VOCs) in air. Kondo et al., (2007) have experimentally measured the flammability limits of isobutane and five kinds of binary mixtures of isobutene using ASHRAE method.

2.2.2 Flammability Limits of Liquid Solutions

The liquid hydrocarbon will vaporize some components at ambient temperature or if it is exposed to some heat. Consequently, it is necessary to estimate the vapour compositions, which contribute to the flammable mixture. Liquid mixtures can be divided into two categories: ideal solutions and non-ideal solutions;

- Ideal Solution

An ideal solution can be defined as a solution with thermodynamic properties similar to those of a mixture of ideal gases. In an ideal solution, both interactions between both chemicals are equal. These mixtures follow Raoult's law behaviour. The activity coefficient for an ideal solution is 1. These solutions result from mixing two similar materials and no differential energies of interaction are encountered between the components. However, most solutions are not ideal.

- Real Solution

It should be noted that Raoult's Law only works for ideal mixtures. Thermodynamically, the relation between an ideal vapour and a non-ideal liquid is represented by the equilibrium condition. A combination of Raoult's and Dalton's laws can be used to estimate the amount of vapour mixture formed about any hydrocarbon solution.

Non-ideal solutions have an activity coefficient value smaller or greater than 1. Real mixture is also known as non-ideal mixture. The mixture is positive deviations from Roult's law if more molecules than ideal mixtures will escapes to the vapour phase and raises the vapour pressure. Thus, a higher vapour pressure will results in a lower flash point value to reach LFL if both chemicals are flammable. However, the mixture is negative deviations from Roults law if the mixture vapour pressure is lower than the vapour pressure of the individual component. Therefore, mixture flash point values are expected to be higher than the pure component flash points (Vazquez, 2005).

2.2.3 Flammability Diagram

Application of flammability diagram is the safest method to prevent fires and explosions of flammable mixtures in the first place (Mashuga and Crowl, 1998). The most useful tool to display the flammability region, and to determine if a flammable mixture is present during plant operations is a triangular flammability diagram (Mashuga and Crowl, 2004) Each apex of triangle represent 100% fuel, oxygen or nitrogen. Concentrations of fuel, oxygen, and inert material (in volume or mole %) are required to plot the flammability diagram. All possible combinations of fuel plus air will represent as air line. Meanwhile, the stoichiometric line represents all stoichiometric combinations of fuel plus oxygen. In the diagram, the UFL and LFL are shown as the intersection of the flammability zone boundary with the air line. Any gas mixture containing oxygen below the LOC is not flammable. Flammability diagram is dependable with fuel type, temperature, pressure and inert species (Crowl and Louvar, 2002). The flammability zone is a region on a flammability diagram in which all mixtures are flammable. Those mixtures outside of the region are considered non flammable. There are several ways to construct a flammability zone with limited literature data. These data include UFL, LFL, and LOC, and the flammability limits in pure (Mashuga and Crowl, 1998). Flammability diagram was used by number of researchers. This is including work of Zabetakis, (1965), who used flammability diagram to study the flammability of various mixtures at different pressures and temperatures. Mashuga and Crowl, (1998) used flammability apparatus to acquire the data necessary to define the complete flammability zone in a triangular flammability. Shu and Wen, (2002) used 20-litter spherical explosion vessel to study the safety-related properties of o-xylene (flammability limits, minimum oxygen concentration, maximum explosion overpressure, and flammability zone). Ohtani, (2004) examined the flammability of perfluorocarbon/fluorine/nitrogen mixtures using explosion vessel.

The results of the flammability were revealed quantitatively as triangular flammability diagrams. Chang et al., (2007) used 20-litter spherical explosion vessel to investigate the flammability characteristics of the 3-picoline/water mixtures. The results presented the possible mixture ratios in a triangular flammability diagram. Brooks and Crowl, (2007) conducted experiment to study the flammability of vapours above aqueous solutions of ethanol and acetonitrile using a 20-L combustion apparatus. The results were presented in flammability diagram using LabVIEW program. More recently, Mao et al., (2011) utilized the standard flammability diagram to study backdraught in tunnel fires. The flammability envelope plotted for the mass fraction of the volatilized unburnt fuel (n-heptane), oxygen, and nitrogen.

2.3 Hazard Assessment

Hazard assessment can be defined as thorough, orderly, and systematic approach for identifying, evaluating, and controlling hazards of processes involving chemicals. Absolutely safety can never be achieved but risk can be reduced to an acceptable level (Vázquez, 2005). The major hazards with which the chemical industry is concerned are fire, explosion and toxic release. Of these three, fire is most common but explosion is more significant in terms of its damage potential, often leading to serious danger to human health and/or to the environment.

The first step in conducting process flammability hazard analysis has to involve characterizing the crucial flammability properties of chemicals that might potentially incur a fire/explosion in a plant. Further consideration must be given to the reciprocal influence of the important working conditions such as the operating temperature, pressure, or loading fuel/oxygen concentration. It is imperative to recognize the degree of danger of the used substances' explosion limits and pressure under their surrounding scenarios, and then to conduct data interpretation to determine the safe operating envelope for the process, even for a large-scale one (Zabetakis, 1965; Lautenberger et al., 2006).Prediction of explosion/flammability limits is of great practical significance to safety decision making. The fire triangle indicates that the three elements; fuel, oxygen and heat, are necessary to enable ignition and sustain ordinary burning and fires.

Flammable and combustible liquids are liquids that can burn at certain conditions. They are classified, or grouped, as either flammable or combustible by their flash point temperatures. OSHA classified liquids into two type; flammable and combustible liquids. A flammable liquid is any liquid having a flash point below 100°F (37.8°C). Flammable liquids are categorized into three groups, which are:

- Class IA Flammable Liquid

Any liquid having a flash point below 73°F (22.8°C) and having boiling point below 100°F (37.8°C).

- Class IB Flammable Liquid

Any liquid having a flash point below 73°F (22.8C) and having boiling point at or above 100°F (37.8°C).

- Class IC Flammable Liquid

Any liquid having a flash point at or above 73°F (22.8C) and below 100°F (37.8°C).

On the other hand, a combustible liquid is any liquid having a flash point at or above 100°F (37.8°C). Combustible liquids are divided into two classes:

- Class II Combustible Liquid

Any liquid having a flash point at or above 100°F (37.8°C) and below 140°F (60°C).

- Class III Combustible Liquid

Any liquid having a flash point at or above 140°F (60°C). Class III liquids are subdivided into two subclasses:

- Class IIIA Combustible Liquid

Any liquid having a flash point at or above 140°F (60°C) and below 200°F.

- Class IIIB Combustible Liquid

Any liquid having a flash point at or above 200°F (93.3°C).

2.4 Flammability Characteristics

There is not a single parameter that defines flammability, but some of the relevant properties are: flash point (FP), lower flammable limit (LFL), upper flammable limit (UFL), and auto ignition temperature (AIT). LFL and UFL is the lowest and highest concentrations (percentage) of a vapour in air capable of producing a flash of fire in presence of an ignition source. The AIT is the minimum temperature required to cause self-sustained combustion (NFPA, 1994). The flash point is the lowest temperature at which it can vaporize to form an ignitable mixture in air. The flash point criterion is used by regulatory authorities to rate the flammability hazards of chemicals (Vázquez, 2005).

Table 2-2:Classification of flammability according to DOT (Vázquez, 2005)

Purpose	Flammability Definition	Classification
Transportation	Flammable liquid is any liquid with $T_f < 141$ °F (60.5 °C) Combustible liquid is any liquid with 141 °F (60.5 °C) $< T_f <$ 200 °F (93.3 °C).	Class 3 flammable liquids are defined as liquids having a T_f of not more than 141 °F (60.5 °C) or any material in a liquid phase with a T_f at or above 100 °F (37.8 °C)

Table 2-3: Classification of flammability according to NFPA (Vázquez, 2005)

Purpose	Flammability Definition	Classification	Hazard Rating	Liquid Definition	Hazard Description
Fire-fighting and fire Protection	A liquid is classified as flammable if it has a T_f of 100°F or lower, when tested by closed cup methods. Combustible liquids are those with T_f higher than 100 °F (37.8 °C)	IA	4	$T_f < 73$ °F (22.8 °C) ; $T_b < 100$ °F (37.8 °C)	Flammable Materials will rapidly vaporize at atmospheric pressure and normal temperatures, or are readily dispersed in air and which burn readily.
		IB, IC	3	$T_f < 73$ °F (22.8 °C); $T_b \geq 100$ °F (37.8 °C) 100 °F (37.8 °C) $> T_f \geq$ 73 °F (22.8 °C)	Flammable Liquids and solids can ignite under almost all temperature conditions.
		II	2	140 °F (60 °C) $> T_f \geq$ 100 °F (37.8 °C)	Combustible Materials must be moderately heated or exposed to relatively high ambient temperatures before they will ignite.
		IIIA	2	200 °F (93.3 °C) $\leq T_f \geq$ 140 °F (60 °C)	
		IIIB	1	$T_f >$ 200 °F (93.3 °C)	Combustible Materials must be preheated before they will ignite

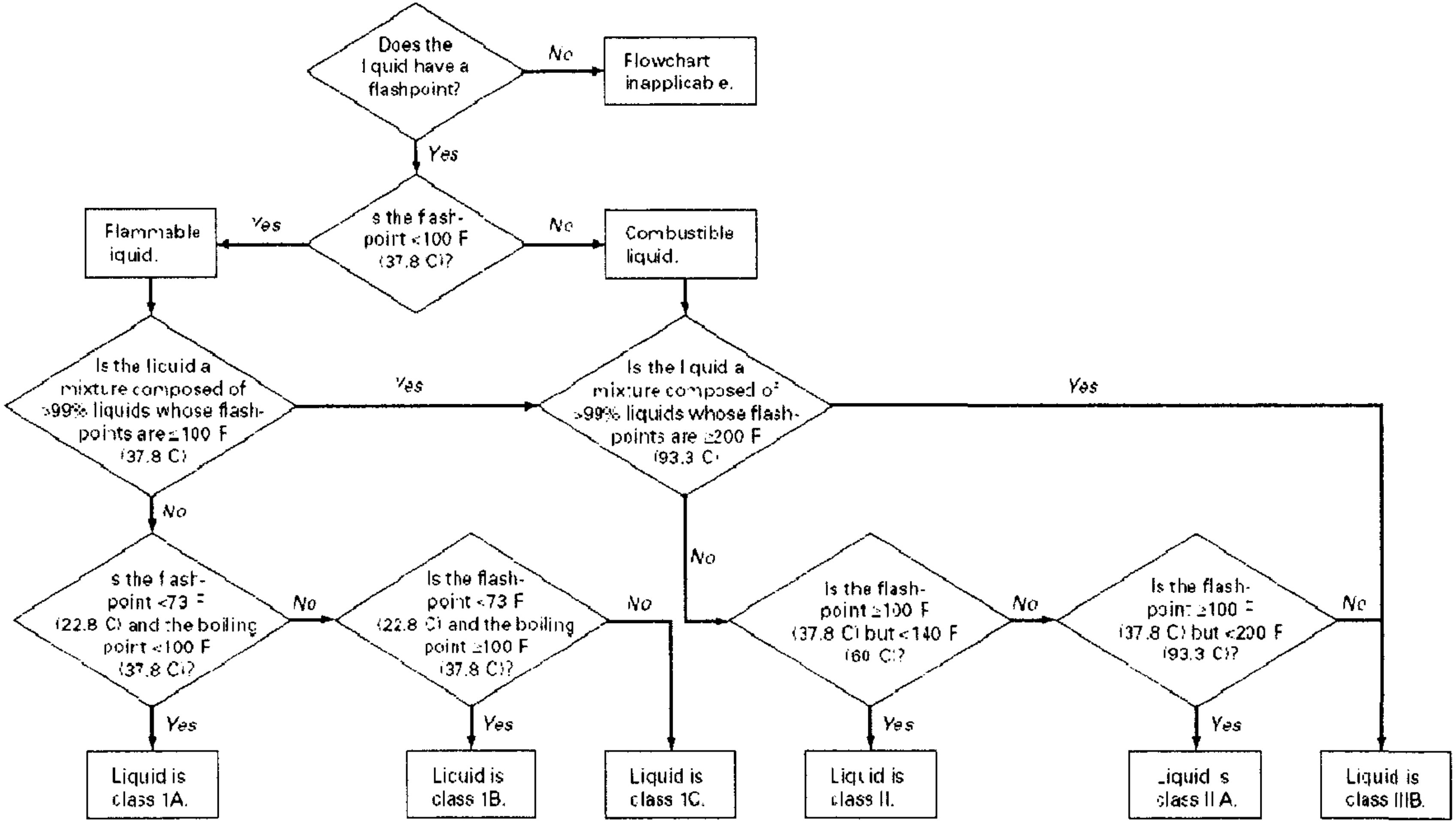


Figure 2-2:OSHA/NFPA classes of flammable and combustible liquids (Meyer, 2005).

Table 2-4:Comparison between standardised methods for the determination of the auto-ignition temperature (Norman, 2008)

method	EN 14522	DIN 51 794	IEC 60079-4	BS 4056-66	ASTM D2155-66	ASTM E 659-78	ASTM D2883-95
scope	$p = 1$ atm $T \leq 923$ K gases/vapours	$p = 1$ atm $T \leq 923$ K gases/vapours	$p = 1$ atm gases/vapours	$p = 1$ atm $T \leq 923$ K gases/vapours	$p = 1$ atm liquids	$p = 1$ atm liquids	$p \leq 0.8$ MPa $T \leq 923$ K liquids/solids
test vessel	borosilicate erlenmeyer $V = 200$ ml open	borosilicate erlenmeyer $V = 200$ ml open	borosilicate/quartz/ metal erlenmeyer $V = 200$ ml open	borosilicate/quartz/ metal erlenmeyer $V = 200$ ml open	borosilicate erlenmeyer $V = 200$ ml open	borosilicate round bottomed $V = 500$ ml open	steel explosion vessel $V = 1$ l closed
auto-ignition criterion	visual flame	visual flame	visual flame	visual flame	visual flame	visual flame	temp./press. recordings
time criterion	$t \leq 5$ min	$t \leq 5$ min	$t \leq 5$ min	$t \leq 5$ min	$t \leq 5$ min	$t \leq 10$ min	$t \leq 10$ min

EN 14522. Determination of the minimum ignition temperature of gases and vapors. British-Adopted European Standard.

IEC 60079-4. Electrical apparatus for explosive gas atmospheres – Part 4: Method of test for ignition temperature. International Electrotechnical Commission.

BS 4056-66. Method of Test for Ignition Temperature of Gases and Vapours. British Standard Institution.

ASTM D2155-66. Method of Test for Autoignition Temperature of Liquid Petroleum Products. American Society for Testing and Materials

ASTM E659-78. Autoignition temperature of liquid chemicals. American Society for Testing and Materials.

ASTM D2883-95. Standard Test Method for Reaction Threshold Temperature of Liquid and Solid Materials. American Society for Testing and Materials.

2.4.1 Flammability Limits

A combustible gas-air mixture can be burned over a wide range of concentrations- when either subjected to temperatures or ignition source (Zabetakis, 1965). Most hydrocarbons are extremely volatile under relatively normal operation conditions. A detailed knowledge of the flammability is needed to prevent workplace explosions of such flammable vapours (Zhao, 2008). Flammable limit values are often provided with material safety datasheets. According to ASTM (American Society for Testing and Materials), flammability limit can be defined as the maximum or minimum concentration of a combustible substance that is capable of propagating flame in a homogenous mixture of the combustible and a gaseous oxidizer under specified conditions of test (Rowley, 2010). Flammability limits are divided into two types: the upper flammable limit (UFL) and the lower flammability limit (LFL).

UFL can be defined as maximum fuel concentration to burn which is deficient in oxygen. Meanwhile, LFL is minimum fuel concentration where is too lean or sufficient in oxygen to be ignited (Zhao, 2008). A mixture is flammable when the composition is between the LFL and UFL and vapour air mixture will only ignite and burn in the specific range of composition.

LFL and UFL data for pure hydrocarbons are available in different literatures. However, hydrocarbon mixtures with different components and different mole fraction are often presented in the industry as having significant contributions to fire and explosion accidents. Vapour-air mixtures ignite and burn only over a well-specified range of compositions. The mixture will not burn when the composition is lower than the lower LFL; that is the mixture is too lean for combustion. The mixture is also not combustible when the composition is too rich; that is, when it is above the UFL. A mixture is flammable only when the composition is between the LFL and the UFL (Crowl and Louvar, 2002).

- Flammability Limits Estimation

Flammability experimental work began in 1816, when Sir Humphrey Davy examined the flammability limits of methane by igniting methane-air mixtures in a narrow necked bottle out of concern for mine safety (Wong, 2006). Large flammability data for pure gases and for some gas mixtures can be found in Bureau of Mines Bulletin publications (Coward and Jones et al., 1952; Zabetakis et al., 1965; and Kuchta et al., 1985). Perhaps currently the best available flammability database is the one published by American Institute of Chemical Engineers (DIPPR project 801) (DIPPR, 2010).

The Bureau of Mines measured the flammability limits using a narrow tube, 2 cm to 7.5 cm in diameter and at least 1 m high is used to perform the test. If the fuel-oxidizer support flame propagation along the tube, the mixture was consider flammable. The method is described in details by Coward and Jones et al., (1952). Another method is ASHRAE (American Society of Heating, Refrigerating and Air-Conditioning Engineers). The method was developed specifically to accommodate halogenated compounds that may be difficult to ignite in smaller vessels and a spherical 12-L flask is used in the experimental work. ASTM also developed numerous, widely used standards dealing chemical hazard properties. For example, a standard test method E 681 to estimate the limits of flammability of Chemicals (vapours and gases) at atmospheric pressure and temperatures up to 150°C (ASTM E681-09). The other standard by ASTM to determine flammability limits of chemicals at elevated temperature and pressure is the test method E 918-83 (ASTM E918-83). Europe has also developed a standard test method (EN 1839) to determine the explosion limits of gases, completely evaporated liquids (vapours) and their mixtures mixed with air.

There are several individual authors, who have done experimental works using 20-L explosion apparatus to estimate the flammability characteristics. For example, Shu and Wen, (2002) conducted experiments to investigate the safety flammability limits, minimum oxygen concentration, maximum explosion overpressure, and flammability zone of o-xylene. These properties were determined with a 20-L-explosion apparatus at operation temperature of 150°C and initial pressures of 760, 1520 mmHg, and 2280 mmHg. Chang et al., (2007) used 20-L explosion vessel to study the flammability characteristics of the 3-picoline/water mixtures. Brooks and Crowl, (2007) utilized a 20-L combustion explosion apparatus to study the flammability of vapours above aqueous solutions of ethanol and acetonitrile. In general, there are many differences between all these methods.

2.4.2 Limiting Oxygen Concentration (LOC)

Limiting oxygen concentration (LOC) is the minimum oxygen concentration required to propagate a flame (Crowl and Louvar, 2002). Fire and explosion can be prevented by reducing the concentration of oxygen. Vapour mixture cannot generate the reaction enough energy if below LOC. LOC can be measured using flammability apparatus (Coward and Jones, 1952; Zabetakis et al., 1965; Kuchta, 1985). ASTM also developed a standard test method E2079 to estimate the LOC of mixtures of oxygen and inert gases with flammable gases and vapours at a specified initial pressure and initial temperature (ASTM E2079-07).

However, in absence of experimental work, LOC value is estimated using stoichiometry of the combustion reaction of hydrocarbon (Crowl and Louvar, 2002). LOC work can be found in different literature. Domnina et al., (2003) also has described a new algorithm to estimate the LOC by using the values of lower explosion limit (LEL) of the fuel mixture and the calculated adiabatic flame temperature (CAFT). Isaac and Gregory (2009) presents data on the limiting (minimum) oxygen concentration (LOC), in the presence of added N_2, of methane (CH_4), propane (C_3H_8), ethylene (C_2H_4), carbon monoxide (CO), and hydrogen (H_2), and some of their binary mixtures. If experimental and literature data are not available, the LOC is estimated by using the stoichiometry from the combustion reaction and the LFL. This procedure works quite well for many different hydrocarbons (Siwek, 1996; Crowl and Louvar, 2002).

LOC can be estimated using the stoichiometry of the combustion reaction and the LFL. Eq. (2-6) can be used to estimate LOC (Crowl and Louvar, 2002):

$$LOC = \left(\frac{moles\ of\ fuel}{total\ moles}\right)\left(\frac{moles\ of\ O_2}{moles\ fuel}\right) = LFL\left(\frac{moles\ of\ O_2}{moles\ fuel}\right) = z(LFL) \qquad (2\text{-}6)$$

LOC for a mixture can be also estimated using a method of Zlochower and Green, 2009).

2.5 Fire and explosion potential in the Bio Oil Storage Container

It should be noted that all hydrocarbon compounds are combustible. However, only the lightest are capable of mixing with air and generate fire or explosion. Doyle, (2001) stated that for liquid hydrocarbon, only gasoline fraction (C_5-C_{10}) is capable of volatilizing in air at normal temperature. Bio oil consists of various hydrocarbon components. At ambient temperature, hydrocarbon components in bio oil could vaporize and lead to fire and explosions. The presence of hydrocarbon components turns bio oil into flammable material. In addition, according to Yu Tian *et.al* bio oil is a good potential source of light aromatics such as benzene, toluene and xylene. The aromatics components are flammable components too. The greatest hazard associated with flammable materials is the creation of a flammable atmosphere by high concentrations of flammable vapours. The potential of a flammable atmosphere increases as the environment temperature increases in areas where flammables are stored or are in use. As the temperature inside the bio oil container rises, the production of vapours at the surface of the bio oil is enhanced, thus increasing the vapour concentration .Each flammable substance has a corresponding flammable range at which concentrations a fire may result if an ignition source is at hand. The flammability range consists of an upper and lower concentration boundary that indicates where the danger lies between the two limits. Therefore, it is important to identify the flammability limits of vapour mixtures of the bio oil in avoiding fire and explosions.

2.6 Inherent Safety

The concept of reducing rather than controlling hazards comes from Kletz, (1978). Now, this concept is widely applied in pursuing the reduction of the hazards in industrial processes. Inherent safety is a design approach useful to remove or reduce hazards at the source instead of controlling them with add-on protective barriers (Vázquez, 2005). Inherent safety, also called primary prevention, consists in the elimination of a hazard (Hansson, 2010). It is not a specific technology or set of tools and activities at this point in its development (Dennis and Scott, 2006). Inherent safer design is a design that eliminates or reduces hazards. Inherently safer design concepts are highly recognized and recommended by safety professionals as a first choice in process design practices for risk reduction. CCPS, (1996) published a well-known book for inherent safety. Inherent safer design concepts can be easily applied to reduce number of accidents in industry, particularly in the design phase of a new or modified process, and may have very powerful benefits at relatively low cost. In industry, there is no chemical process that is without risk, but all chemical process can be made safer (Bollinger et al., 1996).

Inherent safer design will enhance overall risk management by reducing the frequency of potential accident especially causes by fire and explosion. Approaches to inherent safer design have been grouped into four categories (Kletz, 1998):

- Minimize the amount of hazardous material present at any given time.
- Substitute hazardous materials by least hazardous materials.
- Moderate the operating the operating conditions of pressure, temperature and concentrations.
- Simplify the plant since simple process plants are easier to operate and maintain, with fewer chances of things going wrong.

A good practise of inherent safety is, instead of keeping large quantities of hazardous materials under control, we have to try and remove them. Therefore, all portions of process areas where flammable liquid vapours are normally present due to open containers, dispensing these materials should be provided with ventilation as a basic prevention against formulation of flammable liquid vapour concentrations within the explosive range.

CHAPTER 3

METHODOLOGY

3.1 Introduction

The methodology of this work will be developing a systematic method to examine if the vapour mixture occupied from the bio oil is flammable or not. This vapour mixture is formed by vaporization of several components contain in the produced bio oil. Figure 3.1 shows the methodology of this work incorporates experimental and theoretical assessments.

3.2 Experimental and Theoretical Methods

3.2.1 Bio oil production

A few techniques of thermo-chemical processes have been used to convert the biomass into various energy products including combustion, gasification, liquefaction and pyrolysis (Goyal *et.al*, 2008). In the present energy scenario, pyrolysis has received special attention for bio oil production. In this study, Palm Kernell Shell will be utilized for bio-oil production by fast pyrolysis process (Ali & Uemura, 2011). Palm kernel shell is selected for the bio oil production due to its availability in Malaysia. Palm Oil production can be classified as a main industry in Malaysia. Pyrolysis process is a new developed themal decomposition process of biomass into liquid oil. The process will be carried out in a fluidized bed fast pyrolysis unit under nitrogen gas flowrate of 1.35 m^3/h, with reactor temperature ranges from 400°C – 600°C. Fast pyrolysis involves rapid heating of biomass and short vapor residence time. Heating rate is around 300 °C/min and the vapor residence time is below than 2 seconds. Generally, fast pyrolysis is applied to obtain high-grade of bio-oil.

3.2.2 Composition

The liquid sample was obtained from the bio oil produced from Palm kernel shell by fast pyrolisis process (Ali & Uemura, 2011). Then, composition of the organic-phase liquid was analysed using Shimadzu Gas Chromatography (GC). The bio oil sample is injected into Gas Chromatography–Mass Spectrometry (GC-MS). GC-MS analysis of the bio-oil was performed with Agilent Technology 7890A.BPX5 column and MS detector, using 30x250x0.25 mm capillary column. The starting temperature of the oven was 35°C. It was held for 2 min before the temperature was increased to 250 °C at the rate of 20 °C /min and held at its temperature for 20 min. GC-MS was used to identify the compounds in the evaporated fraction of the liquid. GC-MS identifies different compounds at different times (retention times) depending on their chemical structures. The results from the GC-MS show peak areas and retention times. Then, the bio oil sample is also being injected to Gas Chromatography Flame Ionization Detector (GCFID) in order to get more accurate peak areas. The same GC setting and column are applied for GCFID machine. The components are assigned by comparing the retention time results for both GC machines.

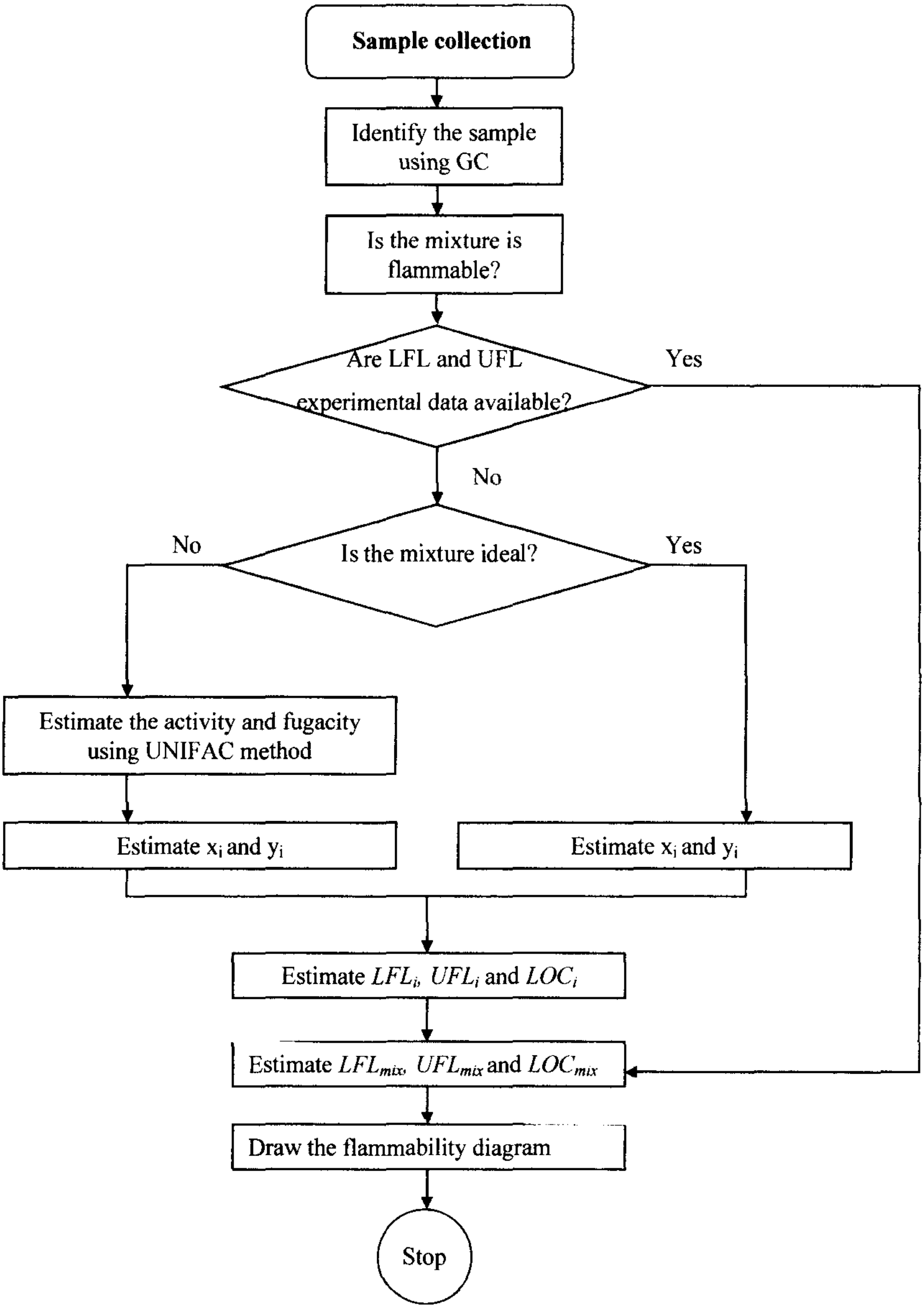


Figure 3-1: Flowchart describes the methodology steps

- Mole Fraction in Liquid Phase

The mole fraction of each component in the bio oil sample can be calculated from GC data. The mole fraction in the liquid phase can be found from the calculation below. GC-MS only give the name of components that are present in the bio oil sample and ignore peaks with small areas. Therefore, in order to obtain the exact peak area of identified components, the bio oil sample is injected into GC-FID. Unlike GC-MS, GC-FID indentifies all peaks of components in the sample. The retention times for each identified components is being compared. A detected component should give similar retention time for both equipments. Then, the peak areas from GC-FID result were taken into mol fraction calculation.

Firstly, the ratio of peak area of individual components to the total peak areas is calculated in order to obtain the mass fraction of the components.

$$x_i = \frac{A_i}{A_T} \qquad (3\text{-}1)$$

where,

x_i is the mass fraction of component *i*,

A_i is the peak area of component *i*, and

A_T is the peak area of all components

Then, the mole fraction in liquid phase is obtained by applying the below formula:

$$\psi_i = \frac{x_i/M_i}{\sum x_i/M_i} \qquad (3\text{-}2)$$

M_i is the molecular weight of component *i*

ψ_i is the mole fraction in liquid phase of component *i*

- Mole Fraction in Vapour Phase

The liquid bio oil will vaporize some hydrocarbon components at ambient temperature or if it is exposed to some heat. Consequently, it is necessary to estimate the concentrations of components in the vapour phase, which contribute to the flammable mixture. It should be noted that liquid solutions can be divided into two categories: ideal solutions and non-ideal solutions. Therefore, the liquid solution should be identified first if it's ideal or non-ideal solution.

- Ideal Solution

In an ideal solution, both interactions between both chemicals are equal. These mixtures follow Raoult's law, in which the equilibrium condition between the vapour and liquid phase is represented by Eq. (3-3):

$$x_i P_i^{sat} = y_i P_t \tag{3-3}$$

where,

P_i^{sat} is the vapour pressure of compound i as a pure component,

y_i is the mole fraction of component i in the vapour phase,

x_i is the mole fraction of component i in liquid phase and

P_t is the total pressure.

- Non-ideal Solution

Raoult's Law can be only used for ideal solutions. However, Raoult's Law can be extended or modified to be suitable for non-ideal solution by incorporating two factors, which are; the fugacity coefficient (φ_i) and the activity coefficient (γ_i).

Eq. (3-4) (modified/extended Raoult's law) can be used to estimate the amount of liquid vaporized to the atmosphere at ambient temperature:

$$\gamma_i x_i P_i^{sat} = \varphi_i y_i P_t \tag{3-4}$$

where,

γ_i is the activity coefficient for component i,

x_i is the mole fraction of component i in liquid phase,

P_i^{sat} is the vapour pressure of compound i as a pure component,

φ_i is the fugacity coefficient for component i, and

y_i is the mole fraction of component i in the vapour phase.

The activity coefficient, γ_i for an ideal solution is equal to 1. However, in this study, the mixture is considered non-ideal. Therefore, the activity coefficient can be calculated using established methods. The Universal Functional Activity Coefficient (UNIFAC) method can be used to estimate the activity for real mixture.

The UNIFAC method expresses the activity coefficient as the sum of a combinatorial part, $\ln \gamma_i^C$ and a residual part, $\ln \gamma_i^R$ (Eq. 3-5) (Fredenslund et al., 1975):

$$ln\gamma_i = ln\gamma_i^C + ln\gamma_i^R \tag{3-5}$$

The configurational, $ln\,\gamma_i^C$ is given by Eq. (3-6):

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \,.\, \ln \frac{\theta_i}{\Phi_i} + l_i + \frac{\Phi_i}{x_i} \sum_{j=1}^{M} x_j l_j \tag{3-6}$$

$$l_j \equiv \frac{z}{2}(r_j - q_j) - (r_j - 1) \tag{3-7}$$

Where, z is the average number of nearest neighbours around a group in solution (constant value is used which is $z = 10$).

The segment fraction, Φ_i and surface area fraction, θ_i are defined respectively by Eq. (3-8) and Eq. (3-9):

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{M} r_j x_j} \tag{3-8}$$

$$\theta_i = \frac{q_i x_i}{\sum_{k=1}^{M} q_j x_j} \tag{3-9}$$

In Eq. (3-8), the molecular volume, r_j, is defined by the sum of its constituent group given by Eq. (3-10):

$$r_j = \sum_{k=1}^{N} v_k^j . R_k \qquad (3\text{-}10)$$

where,

v_k^j is the number of k groups in molecule j, and

R_k is the volume of group k.

The molecular surface area, q_j, is found by summing the individual group areas in the molecules as given by Eq. (3-11):

$$q_j = \sum_{k=1}^{N} v_k^j \cdot Q_k \qquad (3\text{-}11)$$

where, Q_k is the group surface area.

The residual part $\ln \gamma_i^R$ can be calculated by solution-of-group concept Eq. (3-12):

$$\ln \gamma_i^R = \sum_{k=1}^{N} v_k^i \left[\ln \Gamma_k - \ln \Gamma_k^i\right] \qquad (3\text{-}12)$$

Where Γ_k^i is the group residual activity coefficient of group k in a reference solution containing only molecules of type i. Meanwhile, Γ_k is the group residual activity coefficient and can be calculated using Eq. (3.13):

$$\ln \Gamma_k = Q_k \left\{ 1 - \ln\left(\sum_{m=1}^{N} \Theta_m . \psi_{mk} \right) - \sum_{m=1}^{N} \left[\frac{\Theta_m . \psi_{km}}{\sum_{n=1}^{N} \Theta_n . \psi_{nm}} \right] \right\} \qquad (3\text{-}13)$$

In Eq. (3-13), the group interaction parameters, ψ_{mk} are defined by Eq. (3-14):

$$\psi_{mn} = e^{-\frac{a_{mn}}{T}}, \quad a_{mn} \neq a_{nm} \qquad (3\text{-}14)$$

The surface contribution, Θ_m and the mole fraction of the group, X_m are defined by Eq. (3-15) and Eq. (3-16) respectively.

$$\Theta_m \equiv \frac{Q_m . X_m}{\sum_{n=1}^{N} Q_n . X_n} \qquad (3\text{-}15)$$

$$X_m \equiv \frac{\sum_{j=1}^{M} v_m^j . x_j}{\sum_{j=1}^{M} \sum_{n=1}^{N} v_n^j . x_j} \qquad (3\text{-}16)$$

The fugacity coefficient, φ_i have calculated by using ThermoSolver Software based on Engineering and Chemical Thermodynamic. The software used Peng Robinson equation and based on Lewis fugacity rule to calculate the fugacity coefficient for each component. This rule allows the fugacity coefficient of isolated species i to be substituted as an approximation for the proper fugacity in a mixture. The fugacity coefficient can be calculated by using Eq. (3-17).

$$\ln \varphi_i = Z_i - 1 - \ln(Z_i - B_i) - \frac{A_i}{2.8284 B_i} \ln\left(\frac{Z + 2.414 B_i}{Z - 2.414 B_i} \right) \qquad (3\text{-}17)$$

where,

φ_i is the fugacity coefficient,

Z_i is the compressibility factor defined by Eq. (3-18),

B_i is a constant defined by Eq. (3-19),

A_i is a constant defined by Eq. (3-20),

$$Z_i = \frac{P v}{RT} \qquad (3\text{-}18)$$

$$B_i = \frac{b_i P}{RT} \qquad (3\text{-}19)$$

$$A_i = \frac{a_i \alpha_i P}{R^2 T^2} \qquad (3\text{-}20)$$

where,

P is the pressure,

T is the temperature,

v is the molar volume,

R is the universal gas constant,

a_i is defined by Eq. (3-21),

α_i is defined by Eq. (3-22),

b_i is defined by Eq. (3-23)

$$a_i = 0.45724\frac{(RT_{c,i})^2}{P_{c,i}} \tag{3-21}$$

$$\alpha_i = [1 + (0.37464 + 1{,}54226\omega_i - 0.26992\omega_i^2)(1 - \sqrt{T_{r,i}})]^2 \tag{3-22}$$

$$b_i = 0.07780\frac{RT_{c,i}}{P_{c,i}} \tag{3-23}$$

where, ω_i is the acentric factor of the species.

The vapour pressures of the components were calculated according to the Antoine equation Eq. (3-24) and extended Antoine equation Eq. (3-25):

$$\log_{10} P^{sat} = A - \frac{B}{C+T} \tag{3-24}$$

$$\log_{10} P^{sat} = A - \frac{B}{T} + C\log_{10} T + DT + ET^2 \tag{3-25}$$

Where *A*, *B*, *C*, and *D* are the component-specific constants. These constants were collected from different sources (Dykyj et al., 1999; Yaws et al., 2009; www.webbook.nist.gov).

3.2.2 LFL and UFL for Individual Components

It should be noted that the *LFL* and *UFL* will be calculated in the vapour phase. Jones, (1938), found that for many hydrocarbon vapours, the *LFL* and *UFL* are functions of the stoichiometric concentration of fuel (C_{st}) Eq. (3-26) and Eq. (3-27):

$$LFL = 0.55C_{st} \tag{3-26}$$

$$UFL = 3.5C_{st} \tag{3-27}$$

where,

C_{st} is the stoichiometric concentration expressed by Eq. (3-30).

The stoichiometric concentration for most organic compounds was determined using the general combustion reaction Eq. (3-28).

$$C_mH_xO_y + zO_2 \rightarrow mCO_2 + \left(\frac{x}{2}\right)H_2O \tag{3-28}$$

z is equivalent moles O_2/moles fuel and can be found from Eq. (3-29):

$$z = m + \frac{x}{4} - \frac{y}{2} \tag{3-29}$$

The stoichiometric concentration (C_{st}) can be found as a function of z by Eq. (3-30):

C_{st} = [moles fuel/ (moles fuel + moles air)] ×100

$$= \frac{100}{[1 + (z/0.21)]} \tag{3-30}$$

Substituting Eq. (3-30) into Eq. (3-29) and by applying Eq. (3-26) and Eq. (3-27), will yield Eq. (3-31) and Eq. (3-32):

$$LFL = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1} \tag{3-31}$$

$$UFL = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1} \tag{3-32}$$

3.2.3 Limiting Oxygen Concentration (LOC)

LOC for a mixture can be estimated using, Eq. (3-33) can also be used to estimate LOC for a vapour mixture (Zlochower and Green, 2009):

$$LOC_{mix} = \sum y_i R_i / \sum y_i / L_i^* = \sum y_i R_i / \sum y_i R_i / LOC_i \tag{3-33}$$

$$L_i^* = LOC_i / R_i \tag{3-34}$$

where,

LOC_{mix} is the limiting oxygen concentration for the vapour mixture,

R_i is the stoichiometric molar ratio of oxygen to compound i in the vapour phase,

and LOC_i is the limiting oxygen concentration for individual compound.

3.2.4 LFL and UFL for the vapor mixture

Le Chatelier, (1891) proposed empirical models to calculate the LFL and UFL of multiple fuel mixtures. The models are giving by Eq. (3-35) and Eq. (3-36):

$$LFL_{mix} = \frac{1}{\sum_{i=1}^{n} \left(y_i / LFL_i\right)} \tag{3-35}$$

$$UFL_{mix} = \frac{1}{\sum_{i=1}^{n} \left(y_i / UFL_i\right)} \tag{3-36}$$

where,

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

UFL_i, is the upper flammable limit for component *i* (in volume %) of component *i* in fuel and air

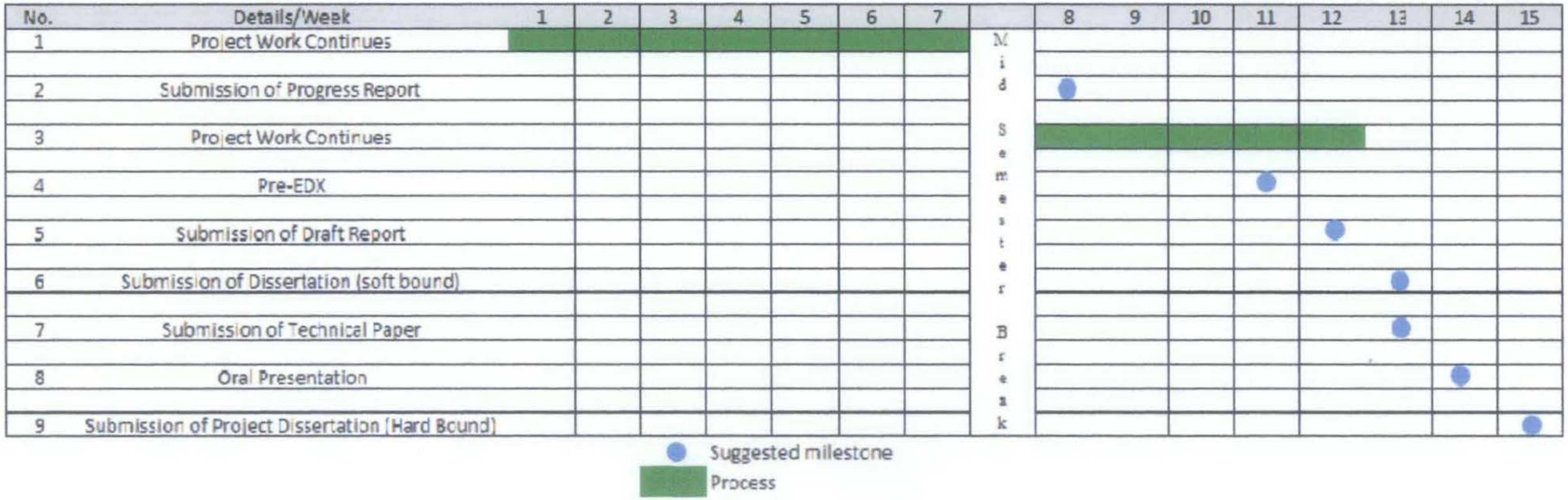
y_i is the mole fraction of component i on a combustible basis and

n is the number of combustible species.

3.3 Generating the flammability diagram

As mentioned earlier, this study made to investigate the possibility of fire occurrence in the storage of biofuels due to the formation of vapour mixtures. The flammability diagram is a general way to represent the flammability of mixture of gases. The flammability diagram is represented by three axes, which are: fuel (hydrocarbon vapour mixture in this study), inert material and oxygen. There are three methods to generate the flammability diagram described in detail by Crowl and Louvar, (2002). It should be noted flammability limits and LOC for the vapour mixture is enough to generate the flammability diagram.

3.4 Key Milestone & Gantt Chart



No.	Details/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	Project Work Continues	🟩	🟩	🟩	🟩	🟩	🟩	🟩	Mid Semester Break								
2	Submission of Progress Report									●							
3	Project Work Continues									🟩	🟩	🟩	🟩	🟩			
4	Pre-EDX												●				
5	Submission of Draft Report													●			
6	Submission of Dissertation (soft bound)														●		
7	Submission of Technical Paper														●		
8	Oral Presentation															●	
9	Submission of Project Dissertation (Hard Bound)																●

● Suggested milestone
🟩 Process

Figure 3-2: Ganchartt of FYP II

Tool & Equipment

- Gas Chromatography Mass Spectrometry (GC-MS)
- Gas Chromatography Flame Ionization Detector (GC-FID)
- Thermosolver Software
- Microsoft Excel

CHAPTER 4

RESULT & DISCUSSION

4.1 Introduction

This chapter presents and discusses the results obtained from the flammability assessment of bio oil vapour mixture. The results from this study have been integrated together and inherent safety recommendations have been proposed and discussed in preventing fire accidents due to accumulating of flammable vapours of bio oil.

4.2 Composition

Table 4.1 summarized all the components in bio oil sample given by GC-MS library excluding components for unnecessary peaks. The unnecessary peak refers to the peak with no exact component representing it. Table 4.1 shows 12 identified components in the bio oil sample that will be used for bio oil flammability analysis. The identified components were ranging from C_2 to C_{17}. GC-MS results show that, the predominant components are Phenol and Acetic Acid. Identification of the components of the bio oil sample was performed using the retention indices, which were calculated in relation to a homologous series of hydrocarbons, and by comparing the mass spectrum to reference spectra registered in mass spectral libraries.

Table 4-1: GC-MS components for bio oil sample

No	RT (min) GC-MS	RT (min) GC-FID	Component
1	2.81	3.674	Acetic acid
2	5.084	5.923	Furfural
3	6.678	7.492	Phenol
4	7.375	7.697	2-Methylphenol
5	7.623	7.944	2-Methoxyphenol
6	7.872	8.309	2,4-Dimethylphenol
7	8.46	8.47	2-Methoxy-4-methylphenol
8	9.103	9.354	4-Ethyl-2-methoxyphenol
9	9.865	9.857	4-Methoxybenzoic acid
10	10.092	10.634	Vanillin
11	10.967	10.917	Dodecanoic acid
12	12.944	13.141	Hexadecanoic acid, methyl ester

4.2.1 Mole Fraction in Liquid Phase

Mass fraction in Table 4-1 is gathered from GC-FID data. The mass fraction is calculated using Eq. (3-1) based on the peak areas of the components in the bio oil sample. Then, the mass fractions are converted to mole fractions using Eq. (3-2). Figure 4.1 shows the result distributions of mole fractions in the liquid phase.

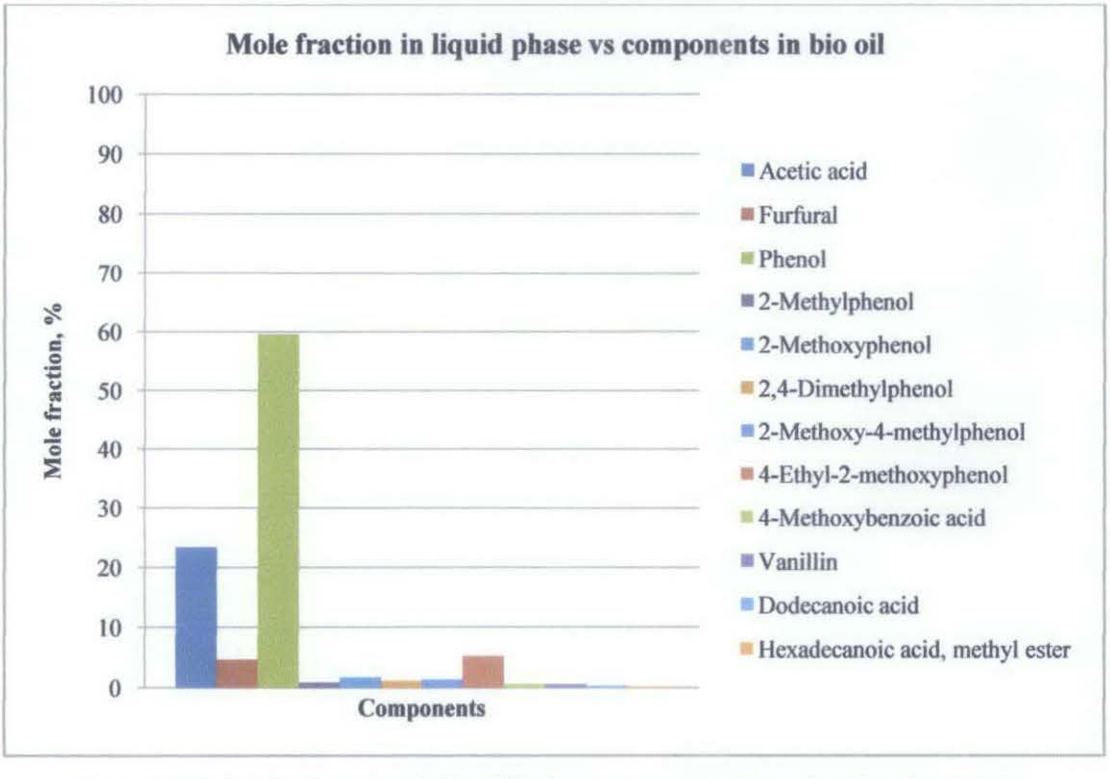


Figure 4-1: Mole fraction in liquid phase vs components in bio oil sample

4.2.2 Mole Fraction in Vapor Phase

Mole fractions in the vapour phase are calculated using the modified Raoult's law (Eq. 3-3). Vapour pressure, the activity coefficient and the fugacity coefficient of each component are required to estimate the mole fraction in the vapour phase. Vapour pressure for each component was calculated using the Antoine equation (Eq. 3-24) .It should be noted that the vapour pressure for some components were obtained from ChemSpider website (www.chemspider.com). The activity coefficients were calculated using UNIFAC method, described by Eq. (3-5) to Eq. (3-16). The activity coefficients calculations were performed using an Excel spreadsheet and the results are illustrated in Table 4.2. A snap shot of Excel spreadsheet is included in Appendix A (Table A1). The average activity coefficient for the vapour mixture was found equal to 1.29. Hence, the fugacity coefficient for each component was calculated using ThermoSolver software which follows the Peng Robinson method, described by Eq. (3-17) to Eq. (3-23). The average fugacity coefficient for the vapour mixture was estimated equal to 0.88. Figure 4.2 displays the mole fraction of each component in the vapour phase, y_i (combustible basis).

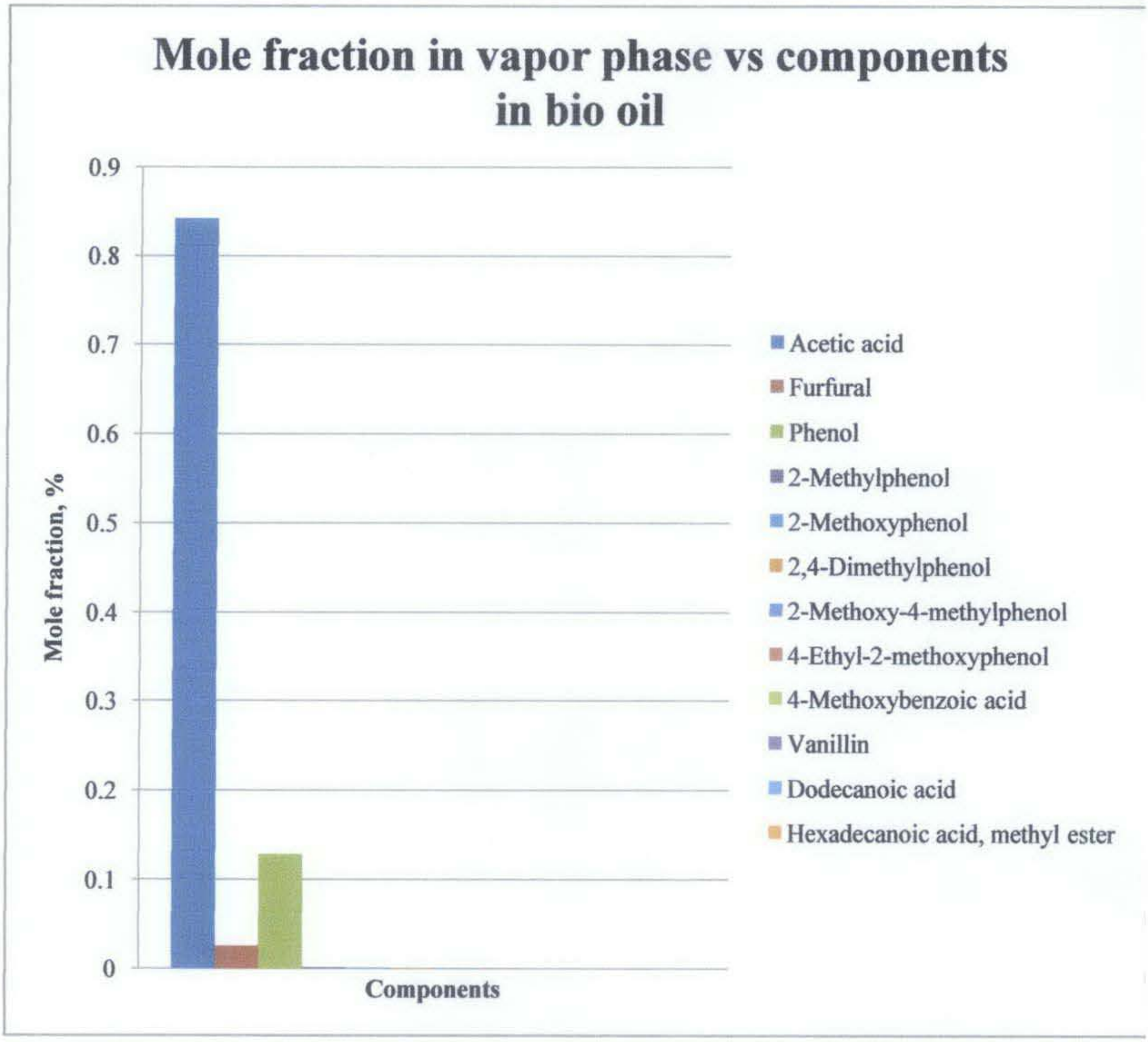


Figure 4-2: Mole fraction in vapor phase vs components of bio oil sample

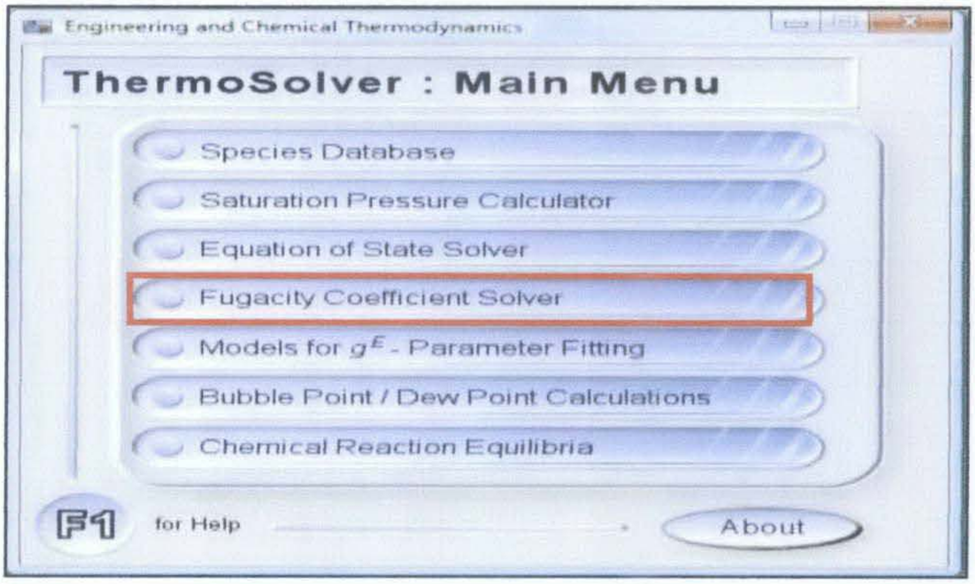


Figure 4-3: ThermoSolver software interface

4.3 LFL and UFL

The *LFL* and *UFL* for each component in the mixture are obtained from literature values. However, there are three components are not available in literature or experimental work values for LFL and UFL. The components are 2-Methoxy-4-methylphenol, 4-Ethyl-2-methoxyphenol and 4-Methoxybenzoic acid. The LFL and UFL of the three components has been calculated in accordance to the stoichiometric concentration method proposed by Jones, (1938) and given by Eq. (3-26) and Eq. (3-27). The results are summarized in Table 4.2. LFL_{mix} and UFL_{mix} for the mixtures are calculated according to the Le Chatelier equations (Eq. 3-35 and Eq. 3-36) and their values were obtained as 3.89vol% and 12.4vol% respectively.

4.4 Limiting Oxygen Concentration (LOC)

LOC for each component mixture is calculated using Eq. (3-33) and presented in Table 4.2. The LOC_{mix} value was found to be 10.69vol%. The LOC_{mix} value is important in drawing the flammability diagram.

4.5 Flammability Diagram

A flammability diagram is a conventional method used to assess the flammability of mixture of gases. The flammability diagram is represented by three axes, namely, (i) fuel (hydrocarbon vapour mixture), (ii) inert material, and (iii) oxygen. In order to plot the flammability diagram, concentrations of the fuel, oxygen, and inert material (in volume or mole %) are required. Air line is plotted by taking the compositions of air (78.5 % nitrogen and 20.87% oxygen). The intersection of the stoichiometric line with the oxygen axis is given by $100(z/1+z)$ (Crowl and Louvar, 2002). The LOC_{mix} line can be drawn by locating the LOC_{mix} value (10.69%) on the air axis and then drawing a parallel line until it intersects with the stoichiometric line. To construct the flammability zone, the values of LFL_{mix} and UFL_{mix} are required and they are located on the air line while the flammability zone is the area to the right of the air line. Figure 4.4 represents the triangular flammability diagram for the hydrocarbon mixture. It can be clearly seen that the stoichiometric line does not cross the flammable zone. The line is below the LFL line. Therefore, it can be inferred that the vapour mixtureof bio oi is not flammable.

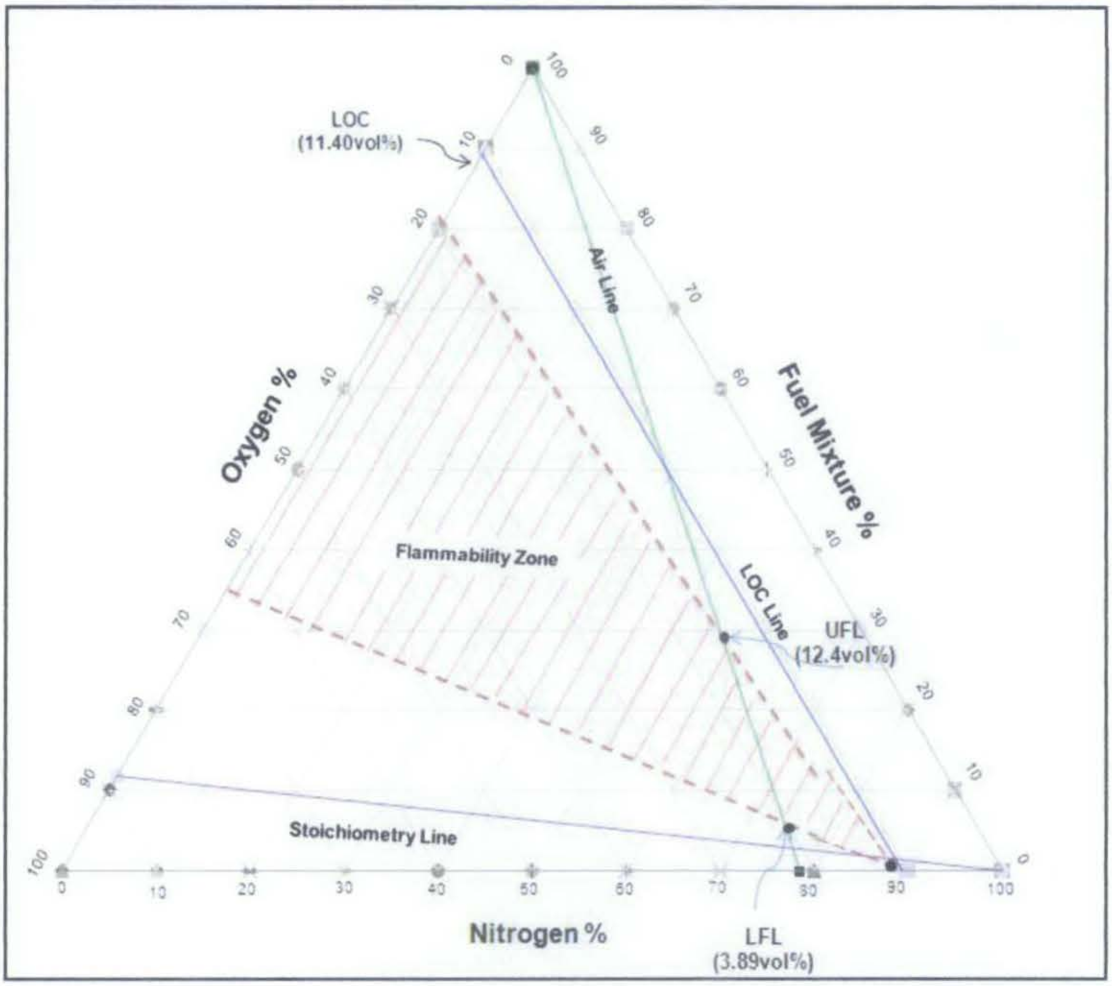


Figure 4-4: Triangular flammability diagram of the biofuel

Table 4-2: Compound names and their relevant properties to estimate the flammability properties

No.	Compound	Formula	Database match %	Verified by standard	Bp °C	M_i	Mass Fraction, x_i	Mole Fraction x_i (vol%)	$LFL_{Lit.}$ (vol.%)	$UFL_{Lit.}$ (vol.%)	P^{sat} (mmHg)	Activity Y_i	Fugacity Φi	z	LOC_i (vol%)
1	Acetic acid	$C_2H_4O_2$	91	/	117.1	60.0	0.152	23.41	5.4	19.9	13.87	1.18479	0.950	2	10.80
2	Furfural	$C_5H_4O_2$	96	/	161.8	96.0	0.049	4.69	2.1	19.3	2.23	1.11172	0.934	5	10.50
3	Phenol	C_6H_6O	96	/	181.8	94.0	0.607	59.61	1.5	9.1	0.61	1.56641	0.930	7	10.50
4	2-Methylphenol	C_7H_8O	98	×	191.0	108.1	0.011	0.90	1.4	7.6	0.38	1.72871	0.909	8.5	11.90
5	2-Methoxyphenol	$C_7H_8O_2$	97	×	205.0	124.1	0.023	1.70	1.3	9.6	0.18	1.66077	0.900	8	10.40
6	2,4-Dimethylphenol	$C_8H_{10}O$	95	×	210.9	122.1	0.016	1.19	1.1	6.4	0.13	2.11455	0.892	10	11.00
7	2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	96	×	220.0	138.1	0.021	1.41	n/a	n/a	0.08	1.83036	0.889	9.5	11.30
8	4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	96	×	246.5	152.1	0.086	5.23	n/a	n/a	0.02	1.99872	0.880	11	11.33
9	4-Methoxybenzoic acid	$C_8H_8O_3$	96	×	278.3	152.0	0.011	0.70	n/a	n/a	2.0E-3	1.93154	0.878	8.5	11.27
10	Vanillin	$C_8H_8O_3$	95	×	282.6	152.0	0.011	0.64	1.2	8.8	2.0E-3	1.83993	0.823	8.5	10.20
11	Dodecanoic acid	$C_{12}H_{24}O_2$	97	×	296.1	200.2	0.007	0.32	0.6	5.1	1.0E-3	2.16179	0.811	17	10.20
12	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	95	×	332.1	270.3	0.006	0.21	0.03	3.2	1.5E-4	4.07348	0.803	24.5	11.45
Total							**1**	**100**			**17.51**	**23.20**	**10.60**		**130.86**
Average												**1.29**	**0.88**		**10.90**

Results Summary	**(vol. %)**
LFL_{mix}	3.89
UFL_{mix}	12.4
LOC_{mix}	10.69
Stoichiometry	88.2
Air	99.37
N_2 = (79%*99.37)	78.5
O_2 = (21%*99.37)	20.87

4.6 Inherent Safety

Flammable liquids will ignite and burn easily than combustible liquids at normal working temperatures. On the other hand, combustible liquids can burn when their temperatures increasing above working temperatures. This indicates that the flammables liquids are considered to be more hazardous than the combustible liquids. Accident histories show that most cases of fire involve flammable liquids. A flammable liquid does not burn itself. It will form a vapour, which will burn. The vaporization of a liquid depends on its temperature and vapour pressure. The warmer the liquid, the more potentially hazardous becomes. The flammability of a liquid depends on the degree to which the liquid forms flammable vapours. It should be noted that flammable liquids burn more readily and fiercely in an atmosphere that has a greater amount of oxygen (>21%) than that in the air.

At room temperatures, flammable liquids can give off enough vapour to form burnable mixtures with air. Therefore, the flammable components need extra precautions to be taken to minimize the possibility of fire. On the other hand, combustible liquids at temperatures above their flash point will also release enough vapour to form burnable mixtures with air. Combustible liquids at high temperature can be as serious as flammable liquids to cause fire. Precautions need to be taken to prevent ignition of flammable vapours in the bio oil storage system 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. Furthermore, storage systems should be designed in such a way to avoid flammable liquids accumulation.

From the results presented in this study, the following recommendations can be made to prevent fire from occurring by flammable vapours:

- Ensure low storage conditions. The recommended conditions are at atmospheric pressure and ambient temperature.
- It is recommended to have storage temperature at below LFL point for bio oil.

- Eliminate ignition sources from the storage container areas where flammable vapours may be present.
- Implement systematic hazardous material inventory especially for bulk storage of bio oil material. Ensure that the storage amount is proportional to the demand in avoiding the hazard potential.
- Design a proper layout of bio oil storage. The good design should have adequate spacing and separation for the arrangement of bio oil tanks and containers.
- Design a proper earthing, grounding and bonding system to avoid electrostatic hazards to the bio oil storage

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

This study shows that bio oil can generate flammable mixtures at ambient temperature and atmospheric pressure, which may cause fire. The results from the study indicate that several components were presented in the bio oil sample. The study discussed and proposed a procedure on how to assist the flammability hazards due to the formation of vapor mixture in the industrial storage of bio oil.

The methodology in this study covered both experimental and theoretical works. The experimental work covered the collection of bio oil sample, and then analyzing the sample using GC-MS and GC-FID to identify the compositions of the sample. The GC analyses have shown that the sample contained light components ranged from C_3 to C_7. The theoretical work included thermodynamic fundamentals and flammability calculations were applied in order to estimate the flammability limits and examine if the mixture is flammable or not.

The liquid mixture in this study found to be non-ideal and therefore, modified Raoult's law have been used to estimate the amount of liquid vaporized to the atmosphere at ambient temperature. All calculations including UNIFAC method to find activity coefficient, flammability limits for the vapour mixture, flammability diagram method to draw the region of flammable mixture were performed in Excel spreadsheets.

Based on the results obtained, inherent safety recommendations were suggested and discussed. These recommendations can provide useful guidelines to prevent buildup of flammable mixtures that could lead to fires and explosions.

5.2 Recommendations

It should be noted that when all the necessary actions have been taken to evaluate the root cause of fire and explosion incident, the hazards shall be controlled and minimized accordingly as 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) Proper Storage Layout Design

   Safe storage layout designed based on standard design and local regulation. The right spacing of storage containers are important in avoiding any spillage occurs from the adjacent container.

2) Elimination of ignition sources

   Ignition source such as welding shall not be conducted near the storage tanks or containers. Moreover, avoid hot works to be done in the storage area.

REFERENCES

Affens, W. A., (1966). Flammability Properties of Hydrocarbon Fuels. Interrelations of Flammability Properties of *n*-Alkanes in Air. *J. Chem. Eng. Data* 11(2), 197-202.

Affens, W. A., and Mclaren, G., W., (1972). Flammability Properties of Hydrocarbon Solutions in Air. Journal of Chemical and Engineering Data, 17 (4): 482-488.

Albahri, T. A., (2003). Flammability characteristics of pure hydrocarbons. Chemical Engineering Science 58, 3629–3641.

ASTM E2079-07. Standard Test Methods for Limiting Oxygen (Oxidant) Concentration in Gases and Vapors. American Society for Testing and Materials.

ASTM E681-09. Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases). American Society for Testing and Materials.

BAM, TUD, (2005). Report on Experimentally Determined Self-Ignition Temperature and the Ignition Delay Time, SAFEKINEX, Deliverable No. 5, Federal Institute for Materials Research and Testing (BAM).

BBC, (2001). Test explosions at a former RAF base in Lincolnshire reached unreasonable and unacceptable noise levels, environmental health officers said.

BBC, (2005). Toxic leak threat to Chinese city, BBC, 23 November 2005.

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

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

Bodurtha, F. T., (1980). Industrial Explosion Prevention and Protection. New York: McGraw-Hill. 167.

Britton, L. G., (2002). Using Heats of Oxidation to Evaluate Flammability Hazards. Process Saf. Prog. 21 (1), 31-54.

Britton, L. G., Frurip, D. J., (2003). Further Uses of the Heat of Oxidation in Chemical Hazard Assessment. Process Saf. Prog. 21(1), 1-19.

Britton, L., G., (1999). Avoiding Static Ignition Hazards in Chemical Operations. Centre For Chemical Process Safety/the American Institute of Chemical Engineers.

Brooks, M., Crowl, D., (2007a). Vapor flammability above aqueous solutions of flammable liquids. Journal of Loss Prevention in the Process Industries 20: 477–485.

Brooks, M., Crowl, D., (2007b). Flammability Envelopes for Methanol, Ethanol, Acetonitrile and Toluene. Journal of Loss Prevention in the Process Industries 20: 144–150.

Butler, R. M. Cooke, G. M. Lukk, G. G. and Jameson B. G., (1956). Prediction of Flash Points of Middle Distillates. Industrial and Engineering Chemistry, 48 (4), 808-812.

Caron, M., Goethals, M., De Smedt, G., Berghmans, J., Vliegen, S., Van't Oost, E. and van den Aarssen, A., (1999). Pressure dependence of the auto ignition temperature of methane/air mixtures. Journal of Hazardous Materials, 65, 233–244.

Catoire, L., and Paulmier, S., (2006). Estimation of Closed Cup Flash Points of Combustible Solvent Blends. J. Phys. Chem. Ref. Data, 35, (1), 9-14.

Catoire, L., Naudet, V., (2005). Estimation of Temperature-Dependent Lower Flammability Limit of Pure Organic Compounds in Air at Atmospheric Pressure. *Process Saf. Prog.*, 24(2), 130-137.

CCPS, (1996). Inherently Safer Chemical Processes-A Life Cycle Approach, AIChE, New York.

Chang Y. M., Yun R. L., Wan T. J. and Shu C. M., (2007). Experimental Study of Flammability Characteristics of 3-picoline/water under Various Initial Conditions. Chemical Engineering Research and Design, 85 (A7) 1020–1026.

Chang Yi-Min, Tseng Jo-Ming, Shu Chi-Min, and Hu Kwan-Hua, (2005). Flammability Studies of Benzene and Methanol with Various Vapor Mixing Ratios at 150°C. Korean J. Chem. Eng., 22(6): 803-812.

Chatterjee, S., Hadi, A.S., (2006). Regression Analysis by Example, 4th edition. John Wiley, New York.

Coward H. F., and Jones G.W., (1939). Limits of Inflammability of Gases and Vapors. U.S. Bureau of Mines, Bulletin 279.

Coward, H. F., Jones, G. W., (1952). Limits of Flammability of Gases and Vapors. US Bureau of Mines Bulletin, Bulletin 503, Washington, DC.

Crowl D., A, Louvar J. F., (2002). Chemical Process Safety: fundamentals with applications. Prentice-Hall.

Crowl, D. A., (2003). Understanding Explosion. Center for Chemical Process Safety (American Institute of Chemical Engineers), New York.

Dalmazzone, D., Laforest, J. C., Petit, J. M., (2001).Application of Thermochemical Energy Hazard Criteria to the Prediction of Lower Flammability Limits of Hydrocarbons in Air. *Oil Gas Sci. Technol.* 56(4), 365-372.

Doyle B. R., (2001). Hazardous Gases Underground: Application to Tunnel Engineering. Marcel Dekker, Inc.

Dykyj J., Svoboda J., Wilhoit R., Frenkel M., Hall K., (1999). Vapor Pressure of Chemicals. *Springer*, Vol. 20.

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.

Fujiia, A., and Hermann, E., (1982). Correlation between flash points and vapor pressure of organic compounds. Journal of Safety Research, 13 (4), 163-175.

Funk, F., (1974). Calculation of the Lower Explosivity Limit of Combustible Gases and Vapors. *Chem. Tech.* 26(12), 779-780.

Gharagheizi F., (2011). An accurate model for prediction of autoignition temperature of pure compounds. Journal of Hazardous Materials 189, 211–221.

Gharagheizi, F., (2009a). Prediction of upper flammability limit percent of pure compounds from their molecular structures. Journal of Hazardous Materials, 167, 507–510.

Goto, R., and Hirai, N., (1952). Theory of Limit of Flammability. *Bull. Inst. Chem. Res., Kyoto University* 30, 32-34.

H. B. Goyal, D. Seal and R. C. Saxena. Bio-fuels from Thermochemical Conversion of Renewable Resources: A Review. Renewable and Sustainable Energy Reviews 12 (2008) 504 – 517.

Hansel, J. G., Mitchell, J. W., Klotz, H. C., (1991). Predicting and Control ling Flammability of Multiple Fuel and Multiple Inert Mixtures. AIChE Loss Prevention Symposium, Pittsburgh. New York: American Institute of Chemical Engineers.

Hansson, S., O., (2010). Promoting inherent safety. Process Safety and Environmental Protection 88, 168–172.

Hilado, C. J., (1975). A Method for Estimating Limits of Flammability. *J. Fire Flammability*, 6, 130-139.

Hshieh, F. Y., (1999). Predicting Heats of Combustion and Lower Flammability Limits of Organosilicon Compounds. *Fire Mater.*, 23(2), 78-89.

Hustad J.E., Sønju O.K., (1988). Experimental studies of lower flammability limits of gases and mixtures of gases at elevated temperatures, Combustion and Flame, 71 (3), 283-294.

Industrial Operations. *Chemical Reviews*, 22 (1): 1-26.

Jones, G. W., (1938). Inflammation Limits and their Practical Application in Hazardous

Jones, G. W., Kennedy, R. E. and Spolan I., (1949). Effect of High Pressures on the Flammability of Natural Gas-Air-Nitrogen Mixtures. BuMines Rept. of Inv. 4557, 16.

Kenneth Pete Moss (2009). Biodiesel Plant Safety: Reported Accidents. Biodiesel Magazine.

Kletz, T., A., (1998). Process plants: a handbook for inherently safer design. Taylor & Francis.

Kletz, T.A., (1978). What you don't have, Can't leak. Chem. Ind. 6, 287–292.

Kondo S., Takahashi A., Tokuhashi K., (2003). Experimental Exploration of Discrepencies in F-number Correlation of Flammability Limits. *J. Hazard. Mater.* A100 (1-3), 27-36.

Kondo S., Takahashi A., Tokuhashi K., Sekiya A., (2002). RF Number as a New Index for Assessing Combustion Hazard of Flammable Gases. *J. Hazard. Mater.* A93 (3), 259-267.

Kondo S., Takizawa K., Takahashi A., Tokuhashi K., (2011). On the temperature dependence of flammability limits of gases. Journal of Hazardous Materials, 187 (1-3): 585-590.

Kondo S., Urano Y., Tokuhashi K., Takahashi A., Tanaka K., (2001).Prediction of Flammability of Gases by Using F-number Analysis. *J. Hazard. Mater.*A82 (2), 113-128.

Kondo, S., Takizawa, K., Takahashi, A., Tokuhashi, K., Sekiya, A., (2007). Flammability limits of isobutane and its mixtures with various gases. Journal of Hazardous Materials 148: 640–647.

Kong D., am Ende D. J., Brenek S. J., Weston N. P., (2003). Determination of flash point in air and pure oxygen using an equilibrium closed bomb apparatus. Journal of Hazardous Materials A102, 155–165.

Kong D., Eckhoff R. K., Alfert F., (1995). Autoignition of CH_4/air, C_3H_8/air, CH_4/C_3H_8/air and CH_4/CO_2/air using 1l ignition bomb. Journal of Hazardous Materials, 40, 69–84.

Kuchta, J. M., (1985). Investigation of Fire and Explosion Accidents in the Chemical, Mining, and Fuel-Related Industries – a Manual.Bureau of Mines Bulletin 680.

Kumar, (2011). Biofuels Make a Comeback Despite Tough Economy. Worldwatch Institute. Washington DC

Lautenberger, C., Torero, J. L. Fernandez-Pello, A.C., (2006). "Understanding Materials Flammability," in Flammability Testing of Materials Used in Construction, Transport and Mining, Edited by V. Apte, Woodhead Publishing, Cambridge.

Le Chatelier H., (1891). Estimation of Firedamp by Flammability Limits. *Ann. Mines*, ser. 8, 19: 388-395.

Lee, C. C., (2005). Environmental engineering dictionary.4th Edition, Government Institutes.

Lewis, Bernard, and Guenther von Elbe, (1961). Combustion, Flames and Explosions of Gases.2nd edition.Academic Press, Inc., New York.

Liaw H.-J., Tang C.-L., Lai J.-S., (2004). A model for predicting the flash point of ternary flammable solutions of liquid. Combust. Flame 138, 308-319.

Lihou, D. A. (1993). Prediction of flammable limits for inerting and vacuum. Journal of Loss Prevention in the Process Industries, 6(4), 265–266.

M.G. Zabetakis, J. K. Richmond, (1953). The determination and graphic presentation of the limits of flammability of complex hydrocarbon fuels at low temperature and pressure. 4thsymp. (internat.) on combustion, Williams & Wilkins Co., Baltimore, Md.,
121-126.

Mack, E., Boord, C. E., Barham, H. N., (1923). Calculation of flash points for pure organic substances. Ind. Eng. Chem., 9, 963–965.

Mao J., Xi Y.H., Bai G., Fan H.M., Ji H.Z., (2011). A model experimental study on backdraught in tunnel fires. Fire Safety Journal 46: 164–177.

Mashuga, C. V. and Crowl, D. A., (1998). Application of the flammability diagram for evaluation of fire and explosion hazards of flammable vapors. Process Safety Progress, 17 (3): 176-183.

Mathieu, D., (2010). Inductive modeling of physico-chemical properties: Flash point of alkanes. Journal of Hazardous Materials 179 (2010) 1161–1164.

Maykuth A., (2009). Deadly acid poses a safety issue for Sunoco. Philadelphia Inquirer.

Melhem, G.A., (1997). A detailed method for estimating mixture flammability limits using chemical equilibrium, Process Safety Progress, 16: 203-218.

Meyer, E., (2005). Chemistry of Hazardous Materials. Brady Publishing.

Miloshev, M., Vulchev, D., Zdravchev, Z., (1982). Relation Between the Concentration Limits of Flammability and Physicochemical Indexes of Hydrocarbons. *God. Vissh.Khim.-Tekhnol Inst.* 27(3), 92-107.

Mitchell J. W., Vratsanos M. S., Hanley B. F., and Parekh V. S., (1999). Experimental Flash Points of Industrial Amines. J. Chem. Eng. Data, 44, 209-211.

National Fire Protection Association, NFPA 325, (1994). Guide to Fire Hazards Properties of Flammable Liquids, Gases, and Volatile Solids, NFPA, Quincy, MA.

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

Norizan Ali & Yoshimitsu Uemura (2011). Bio-Oil Production by Oil Palm Residue by Fluidized Bed Fast Pyrolisis and Its Characterization. Universiti Teknologi PETRONAS.

Norman F., Van den Schoor F., Verplaetsen F., (2006). Auto-ignition and upper explosion limit of rich propane–air mixtures at elevated pressures. Journal of Hazardous Materials A137, 666–671.

Norman, (2008). Influence of Process Conditions on the Auto-Ignition Temperature of Gas Mixtures. PhD thesis, Katholieke Universiteit Leuven.

Nuzdha, L. I., Glinkin, M. A., Rafales-Lamarka, E. E., Tyupalo, N. F., (1979). A System for Determining the Upper Explosive Limit. *Sov. Chem. Ind.,* 11(4), 209-212.

Ohtani H., (2004). Experimental study on flammability limits of perfluorocarbons in a fluorine atmosphere. Journal of Loss Prevention in the Process Industries 17, 377–379.

Peng, D. Y., and Robinson, D. B. (1976). A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.,* 15 (1): 59-64.

Poonam Singh Nigam & Anoop Singh, (2010). Progress in Energy and Combustion Science: Production of Liquid Biofuels from Renewable Resources. Elsevier article.

Pintar, A. J., (1999). Predicting Lower and Upper Flammability Limits. *28th International Conference on Fire Safety.*

Rowley J., (2010). Flammability Limits, Flash Points, and their Consanguinity: Critical Analysis, Experimental Exploration, and Prediction Jef Rowley. PhD. thesis, Brigham Young University.

Rowley, J. R., Rowley, R. L., Wilding, W.V., (2011). Estimation of the lower flammability limit of organic compounds as a function of temperature. Journal of Hazardous Materials, 18 (1), 551-557.

Satyanarayana K., and Krishna D., (2006). Estimation of Flash Points for Silane Group Organic Compounds. Indian Chemical Engr. Section B, 48, 2.

Semenov, N. N., (1959). Some Problems in Chemical Kinetics and Reactivity. Prince University Press, Princeton, ver.2, 1959, 331.

Shebeko, Y. N., Ivanov, A. V., Dmitrieva, T. M., (1983).Methods of Calculation of Lower Concentration Limits of Combustion of Gases and Vapors in Air.*Sov. Chem. Ind.*, 15(3), 311-314.

Shu Chi-Min, Wen Po-Jiun, (2002). Investigation of the flammability zone of o-xylene under various pressures and oxygen concentrations at 150 °C. Journal of Loss Prevention in the Process Industries 15, 253–263.

Spakowski, A. E., (1955) RM E52H15, Natl. Advisory Committee Aeronautics (NACA).
Valenzuela, E.M., Vázquez-Román, R., Patel, S., Sam Mannan, M., (2011). Prediction Models for the Flash point of Pure Components. Journal of Loss Prevention in the Process Industries (in press).

Van den Schoor F., Verplaetsen F., (2006). The upper explosion limit of lower alkanes and alkenes in air at elevated pressures and temperatures. Journal of Hazardous Materials A128, 1–9.

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

Vidal, M., Rogers, W.J., Holste, J.C., Mannan, M.S., (2004). A review of estimations method for flash points and flammability limits. Process Saf. Progress, 23, 47-55.

Walsham J. G., (1973). Prediction of Flash Points for Solvent Mixtures. Solvents Theory and Practice, Chapter 5, pp 56–69.

Wen Po-Jiun, Shu Chi-Min, Zhi-Cheng Chang, Shu-Ching Chen, and Mei-Ling Shyu, (2001). Effects of Initial Pressure on the Flammability Limit of OX-Air Mixture with 20-L-Appartus. Proceedings of the 17th Asia Pacific Occupational Safety & Health Organization (APOSHO-17) Conference, pp. 443-465, September 24-29, 2001, Taipei, Taiwan.

White, J., F., (2005). Flammability characterization of fat and oil Derived phase change materials. Master thesis, University of Missouri- Columbia.

Wong, W., K., (2006). Measurement of Flammability in a Closed Cylindrical Vessel with Thermal Criteria. PhD. Thesis, Texas A&M University.

Woodward, J., (1998). Estimating the Flammable Mass of a Vapor Cloud. Center for Chemical Process Safety of the American Institute of Chemical Engineers.

Xinshuai Liu and Zhenyi Liu. (2010). Research Progress on Flash Point Prediction. J. Chem. Eng. Data, 55, 2943-2950.

Yaws, C. L., Narasimhan, P. K., Gabbula Chaitanya, (2009). Yaws' Handbook of Antoine Coefficients for Vapor Pressure. *Knovel library.*

Yaws, C., L., Sheth, S., D., and Mei Han, (1999). Chemical Properties Handbook: Physical, Thermodynamics, Environmental Transport, Safety & Health Related Properties for Organic & Inorganic Chemical. McGraw-Hill Professional.

Y.C.Sharma, B.Singh, (2008). Renewable and Sustainable Energy Reviews: Development of Biodiesel (Current Scenario). Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, India.

Yong Pan, Juncheng Jiang, Xiaoye Ding, Rui Wang, and Jiajia Jiang. Prediction of Flammability Characteristics of Pure Hydrocarbons from Molecular Structures. AIChE Journal, 56, 3, 690-701.

Tian, Y., Zuoa, W., Rena, Z., Chen, D., (2011). Estimation of a Novel Method to produce bio-oil from sewage sludge by microwave pyrolysis with the consideration of efficiency and safety. Bioresource Technology, 102 (2): 2053-2061.

Zabetakis M.G., Lambiris S. Scott G.S., (1958). Flame temperatures of limit mixtures, in: Proceedings of the Seventh Symposium on Combustion. The Combustion Institute, 1958, 484–488.

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

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

Zalosh R., Casey J., (2010). Autoignition temperature data and scaling for amide solvents. Journal of Loss Prevention in the Process Industries 23, 71–76.

Zatsepin, V. M., Iopa, R. F., Sorokin, Y. M., (1986).A Generalized Method and Its Application to the Calculation of the Lower Concentration Limit for the Ignition of Organic Compounds. *Russ. J. Phys. Chem.*,60(8), 2018-2021.

Zhao, F., (2008). Experimental measurements and Modeling prediction of flammability Limits of binary hydrocarbon mixtures. PhD. Thesis, ,Texas A&M University.

Zlochower, I., Green, G., (2009). The Limiting Oxygen Concentration and Flammability Limits of Gases and Gas mixtures. Journal of Loss Prevention in the Process Industries 22: 499-50

APPENDICES

APPENDIX A

		1	2	3	4	5	6	7
		$C_2H_4O_2$	$C_5H_4O_2$	C_6H_6O	C_7H_8O	$C_7H_8O_2$	$C_8H_{10}O$	$C_8H_{10}O_2$
		Acetic Acid	Furfural	Phenol	2-Methylphenol	2-Methoxyphenol	2,4-Dimethylphenol	2-Methoxy-4-methylphenol
	x	0.234	0.047	0.596	0.009	0.017	0.012	0.014
SubGroup	[illegible]	1.185	1.112	1.556	1.729	1.551	2.115	1.830
[illegible]	CH3	1			1	1	2	2
[illegible]	CH2							
[illegible]	CH							
4	C							
[illegible]	CH2=C							
[illegible]	CH=C			3	2	2	1	1
[illegible]	C=C							
[illegible]	ACH		4					
14	OH			1	1	1	1	1
[illegible]	CH3OH							
[illegible]	H2O							
[illegible]	CH2CO	1						
[illegible]	CHO		1					
[illegible]	CH2COO							
[illegible]	HCOO							
[illegible]	CH2O							
[illegible]	COOH	1						
[illegible]	CH2CL							
[illegible]	CCL3							
[illegible]	CH2OCH2		1			1		1
	Σ[illegible] x	0.70235029	0.281545	2.3842106	0.036155083	0.08490331	0.047459589	0.070555732
	N groups	3	5	4	4	5	4	5

		8	9	10	11	12
		$C_9H_{12}O_2$	$C_8H_8O_3$	$C_8H_8O_3$	$C_{12}H_{24}O_2$	$C_{17}H_{34}O_2$
		4-Ethyl-2-methoxyphenol	4-Methoxybenzoic acid	Vanillin	Dodecanoic acid	Hexadecanoic acid, methyl ester
	x	0.052	0.007	0.006	0.003	0.002
SubGroup	[illegible]	1.999	1.932	1.840	2.162	4.073
1	CH3	2	1	1	1	2
2	CH2	1			10	14
3	CH					
4	C					
7	CH2=C					
8	CH=C	1	2	1		
70	C=C					
9	ACH					
14	OH	1		1		
15	CH3OH					
16	H2O					
19	CH2CO				1	1
20	CHO			1		
22	CH2COO				1	1
23	HCOO					
25	CH2O					
[illegible]	COOH		1		1	1
44	CH2CL					
51	CCL3					
109	CH2OCH2	1		1		
	Σ[illegible]x	0.313841938	0.02781562	0.0318808	0.044344236	0.039591119
	N groups	6	4	5	14	19

Table 7-1: UNIFAC group specifications

Group Numbers		**Name**	**Volume, R**	**Surface Area, Q**
Main	**Secondary**			
1	1	CH_3	0.9011	0.848
	2	CH_2	0.6744	0.540
	3	CH	0.4469	0.228
	4	C	0.2195	0.000
2	5	$CH_2{=}CH$	1.3454	1.176
	6	CH=CH	1.1167	0.867
	7	$CH_2{=}C$	1.1173	0.988
	8	CH=C	0.8886	0.676
	70	C=C	0.6605	0.485
3	9	ACH	0.5313	0.400
	10	AC	0.3652	0.120
4	11	$ACCH_3$	1.2663	0.968
	12	$ACCH_2$	1.0396	0.660
	13	ACCH	0.8121	0.348
5	14	OH	1.0000	1.200
6	15	CH_3OH	1.4311	1.432
7	16	H_2O	0.9200	1.400
8	17	ACOH	0.8952	0.680
9	18	CH_3CO	1.6724	1.488
	19	CH_2CO	1.4457	1.180
10	20	CHO	0.9980	0.948
11	21	CH_3COO	1.9031	1.728
	22	CH_2COO	1.6764	1.420
12	23	HCOO	1.2420	1.188
13	24	CH_3O	1.1450	1.088
	25	CH_2O	0.9183	0.780
	26	CHO	0.6908	0.468
	27	THF	0.9183	1.100
14	28	CH_3NH_2	1.5959	1.544
	29	CH_2NH_2	1.3692	1.236
	30	$CHNH_2$	1.1417	0.924
15	31	CH_3NH	1.4337	1.244
	32	CH_2NH	1.2070	0.936
	33	CHNH	0.9795	0.624
16	34	CH_3N	1.1865	0.940
	35	CH_2N	0.9597	0.632
17	36	$ACNH_2$	1.0600	0.816
18	37	C_5H_5N	2.9993	2.113
	38	C_5H_4N	2.8332	1.833
	39	C_5H_3N	2.6670	1.553
19	40	CH_3CN	1.8701	1.724
	41	CH_2CN	1.6434	1.416
20	42	COOH	1.3013	1.224
	43	HCOOH	1.5280	1.532
21	44	CH_2Cl	1.4654	1.264
	45	CHCl	1.2380	0.952
	46	CCl	1.0106	0.724
22	47	CH_2Cl_2	2.2564	1.988
	48	$CHCl_2$	2.0606	1.684
	49	CCl_2	1.8016	1.448
23	50	$CHCl_3$	2.8700	2.410
	51	CCl_3	2.6401	2.184
24	52	CCl_4	3.3900	2.910
25	53	ACCl	1.1562	0.844
26	54	CH_3NO_2	2.0086	1.868

	55	CH_2NO_2	1.7818	1.560
	56	$CHNO_2$	1.5544	1.248
27	57	$ACNO_2$	1.4199	1.104
28	58	CS_2	2.5070	1.650
29	59	CH_3SH	1.8770	1.676
	60	CH_2SH	1.6510	1.368
30	61	Furfural	3.1680	2.484
31	62	DOH	2.4088	2.248
32	63	I	1.2640	0.992
33	64	Br	0.9492	0.832
34	65	$CH\equiv C$	1.2929	1.088
	66	$C\equiv C$	1.0613	0.784
35	67	DMSO	2.8266	2.472
36	68	Acrylonitrile	2.3144	2.052
37	69	$Cl-(C=C)$	0.7910	0.724
38	71	ACF	0.6948	0.524
39	72	DMF	3.0856	2.736
	73	$HCON(CH_2)_2$	2.6322	2.120
40	74	CF_3	1.4060	1.380
	75	CF_2	1.0105	0.920
	76	CF	0.6150	0.460
41	77	COO	1.3800	1.200
42	78	SiH_3	1.6035	1.263
	79	SiH_2	1.4443	1.006
	80	SiH	1.2853	0.749
	81	Si	1.0470	0.410
43	82	SiH_2O	1.4838	1.062
	83	SiHO	1.3030	0.764
	84	SiO	1.1044	0.466
44	85	NMP	3.9810	3.200
45	86	CCl_3F	3.0356	2.644
	87	CCl_2F	2.2287	1.916
	88	$HCCl_2F$	2.4060	2.116
	89	HCClF	1.6493	1.416
	90	$CClF_2$	1.8174	1.648
	91	$HCClF_2$	1.9670	1.828
	92	$CClF_3$	2.1721	2.100
	93	CCl_2F_2	2.6243	2.376
46	94	$CONH_2$	1.4515	1.248
	95	$CONHCH_3$	2.1905	1.796
	96	$CONHCH_2$	1.9637	1.488
	97	$CON(CH_3)_2$	2.8589	2.428
	98	$CONCH_3CH_2$	2.6322	2.120
	99	$CON(CH_2)_2$	2.4054	1.812
47	100	$C_2H_5O_2$	2.1226	1.904
	101	$C_2H_4O_2$	1.8952	1.592
48	102	CH_3S	1.6130	1.368
	103	CH_2S	1.3863	1.060
	104	CHS	1.1589	0.748
49	105	MORPH	3.4740	2.796
50	106	C_4H_4S	2.8569	2.140
	107	C_4H_3S	2.6908	1.860
	108	C_4H_2S	2.5247	1.580