ESTIMATION OF FLAMMABILITY LIMITS AND FLASH POINT

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
CHEMICAL ENGINEERING
(With Specialization in Industrial Safety & Hazards Management)

By

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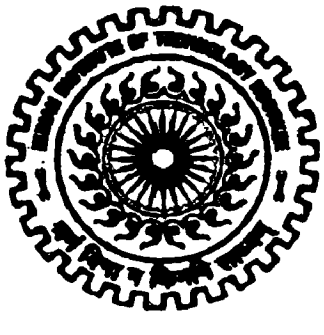

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CANDIDATE'S DECLARATION

I hereby declare that the work, which is being presented in this dissertation work, entitled "**ESTIMATION OF FLAMMABILITY LIMITS AND FLASH POINT**", submitted in partial fulfilment of the requirement for award of the degree of **Master of Technology** in **Chemical Engineering** with the specialization in **INDUSTRIAL SAFETY & HAZARDS MANAGEMENT,** is an authentic record of my own work carried out under the supervision of **Prof. V. K. AGARWAL**, Department of Chemical Engineering, Indian Institute of Technology Roorkee.

The matter embodied in this report has not been submitted for the award of any other degree or any other Institute/University.

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

Flammability limit is a significant safety issue for industrial processes. A certain amount of flammability limit data for pure hydrocarbons are available in the literature, but for industrial applications, there are conditions including different combinations of fuels at standard and non-standard conditions, in which the flammability limit data are scarce and sometimes unavailable.

In this dissertation work a new method of estimating the lower flammability limit (LFL) of general organic compounds is presented using "C". The LFL is predicted at 298K for gases and liquids from structural contributions and the ideal gas heat of formation of the fuel. In this work an equation is proposed for the accurate and user friendly estimation of the lower flammability limit (LFL) & upper flammability limit (UFL) of C/H, C/H/N, C/H/O, C/H/O/N organic pure compounds in air at atmospheric pressure & room temperature (25°C). The equation derived in this study used 28 organic chemicals LFLs/UFLs for the derivation and validation. Comparisons between experimental data and estimated data show that the average absolute deviation is small enough and it can be ignored. Lower flammability limits estimation based on adiabatic temperature of the combustion reaction taking place and specific heat capacity, standard heat of formation, heat of reaction etc. For easier calculation of lower flammability limit, a program is written in "C" which makes simpler the estimation procedure of lower flammability limit. Further this method can be extended to estimate the lower flammability for chemicals containing C, H, N, O, S, Cl.

The flash point is an important indicator of the flammability of liquids and solids. Many methods of estimating the flash point of pure chemicals have been published. This work presents a method of estimating the flashpoint of general organic compounds based entirely on structural contributions and lower flammability limit using "C".

TABLE OF CONTENTS

Page No.

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURE

A	Slope of equation
B	Constant of equation
C_l	Mole fraction of the fuel gas in the fuel-inert blend
C_{in}	Mole fraction of inert gas in the fuel-inert blend
$C_{g,n}$	Greatest concentration of fuel in oxidant that are non-flammable
$C_{l,n}$	Least concentration of fuel in oxidant that are non-flammable
$C_{l,f}$	Greatest concentration of fuel in oxidant that are flammable
$C_{g,f}$	Least concentration of fuel in oxidant that are flammable
C_{pi}	Specific heat capacity of i^{th} component in the combustion reaction of product
$C_{p,prod}$	Heat capacity of combustion product mixture at constant pressure
$C_{p,\ fuel\text{-}air}$	Specific heat capacity of air –fuel mixture at constant pressure
ΔH_C^0	Standard Heat of combustion at 25^0C and 1 atm pressure
ΔH_C	Net heat of combustion (kcal/mole)
ΔH	Heat of combustion
H_i^0	Enthalpy of gas at reference temperature 298 K
$H_{fuel}\ (T_0)$	Enthalpy of air at the temperature T_0
$H_{air}\ (T_0)$	Enthalpy of fuel at the temperature T_0
$H_i\ (T_{ad})$	Enthalpy of i^{th} combustion product at the temperature T_{ad}
$H_{O2}\ (T_{ad})$	Enthalpy of oxygen at the temperature T_{ad}
n_i	Number of moles of i^{th} combustion products
$LFL_{T,P}$	Lower flammability limit at specific temperature and pressure
LFL_i	Lower flammability limit of i^{th} compound
LFL_l	Lower flammability limit of fuel in air
LFL_{fuel}	Lower flammability limit of fuel-inert gas mixtures
LEL	Lower explosive limit
M	Molecular weight of a vapour
P	Vapour pressure at its flash point(SI units)
Pmax	Maximum explosion overpressure
$(dP/dt)_{max}$	Rate of maximum explosion pressure rise
T	Temperature in °C

T_B	Boiling points (^0C)
T_F	Flash point (^0C)
$UFL_{T,P}$	Upper flammability limits at specific temperature and pressure
UFL_i	Upperer flammability limit of i^{th} compound
UFL_1	Upper flammability limit of fuel in air
UFL_{fuel}	Upper flammability limit of fuel-inert gas mixtures
UEL	Upper explosion limit
X_i	Mole fraction of i^{th} component
X	Halogens Atoms
T_{ad}	adiabatic flame temperature
ΔT	Temperature difference
T	Number of Silicon Atoms
U	Number of Halogens Atoms
V	Number of Sulphur Atoms
v/v %	Percentage volume by volume
W	Number of Nitrogen Atoms
X	Number of Carbon Atoms
Y	Number of Hydrogen Atoms
Z	Number of Oxygen Atoms

Greek Symbols:

β	number of moles of oxygen molecules in the combustion when the combustion takes place in stoichiometric conditions
γ	Slope of adiabatic flame temperature

CHAPTER: 1 INTRODUCTION

1.1. Introduction

The importance of safety, risk assessment and emergency planning for industrial incidents and the requirements of governmental agencies are the driving force in searching better and accurate technique for prediction of flammability limits. Flammability is an important factor in the development of safe practices for handling and storage of pure liquids or liquids mixtures. Flammability limits represent the concentrations of fuel in air that will just support flame propagation. The limits are better descriptors of a chemical's flammability and more useful for safe process design because they are applicable to solids, liquids and gases. Flammability limits data are reported generally reported at 298 K.

Traditional evaluations of explosion hazards rely on comparing the fuel concentration to the measured flammability limit. However, the flammability limit depends on the choice of ignition method and sample preparation. Consequently, different methods of measuring flammability have been devised such as the flash point test, spark ignition, temperature limit method, and concentration limit method. Each of these uses different ignition methods: an open pilot flame in the flash point test; a capacitive spark in the spark ignition test; an electrically heated fuse wire in the temperature limit test; and either a fuse wire or an electric arc in the concentration limit method. The most commonly used method of all, the flammability limit tube developed at the Bureau of Mines, has never been standardized. This method uses various ignition sources; one commonly employed is a quasi-continuous arc produced by a neon-sign transformer (20 kV, 30 mA) across a 0.00635 m gap. Our experience at Caltech is that results obtained with a 100 J spark igniters in a closed vessel are similar to those obtained with the Bureau Mines apparatus using a neon-sign transformer arc. They carried out experiments with stored energies of up to 8 J were used since this level is reasonable to achieve without creating the large amount of electrical noise that a 100 J spark produces.

Various ideas have been advanced to explain the phenomena of flammability and the relationship to tests developed in the process industries to determine flammability limits. It is important to note the distinction between the use of the term flammability limit by the safety community and by the combustion basic research community. Safety studies are concerned

with experimentally determining limiting concentrations, beyond which combustion cannot take place. The experimental determination of such limits is inextricably intertwined with the apparatus, including method of ignition, the test protocol, and the criteria for determining when ignition has occurred. Basically researchers prefer to think of limits in the abstract. Starting with Spalding, the generally accepted definition has become that the flammability limit is that state at which steady propagation of a one dimensional premixed flame fails to be possible. The theoretical determination of a limit defined in this fashion is likewise tied a specific configuration, a chemical kinetic model, diffusive and radiative transport models, and numerical solution methods. Recently there has been some progress towards connecting these two approaches to flammability.

From a theoretical point of view, limits arise because mechanisms such as chain terminating reaction steps, energy loss by radiation, and preferential diffusion eventually dominate the energy releasing chemical reactions and cause extinction at the flammability limit. The idea of heat losses creating a limiting condition was first advanced by Spalding but testing this notion quantitatively had to wait for the development of detailed reaction mechanisms and flame structure computation methods. Law and Egofopolous showed that turning points in one dimensional steady laminar flame computations with a simplified radiative loss model correlated reasonably well with known experimental limits for lean methane-air and rich hydrogen-air mixtures. More recent studies show that the situation is substantially more complex when the combined effects of strain and radiation are considered, particularly for mixtures with Lewis numbers less then unity. The doubly infinite and twin flame configurations considered in these studies is ideal for numerical simulation but quite far from the unsteady, multi-dimensional flame kernels in confined vessels that are utilized in most flammability tests.

Mixture at different temperature and pressures are used in industrial activities. The flammability limits can be used to determine the level of risk in different stages of process. Knowledge of flammable limits at elevated temperature and pressure is needed in order to ensure safe and economically acceptable operation of chemical processes. The flammability characteristics of chemical substances are very important for safety considerations in storage, processing, and handling. These characteristics which include the flash point, the auto ignition temperature, and the upper and lower flammability limits are some of the most

important safety specifications that must be considered in assessing the overall flammability hazard potential of a chemical substance, defined as the degree of susceptibility to ignition or release of energy under varying environmental conditions. Experimental values of these properties are always desirable, however, they are scars and expensive to obtain. When experimental values are not available and determining them by experimental means is not practical, a prediction method which is desirably convenient and fast must be used to estimate them.

Predictive theoretical methods are needed to estimate the flammability limits of mixture when there is lack of experimental data. The development of reliable predictive methods for estimating flammability limits would reduce significantly the amount of experimental data required for a complete flammability characterization. In addition, it is necessary to know the flammability limits under working conditions.

This work describes analytical method using "C" to calculate flammability limits of chemical compound and this result is compared with the data experimentally obtained. In this work, I also have taken the importance of temperature and its effect on flammability limits.

1.2. Objective:

- To develop an empirical equation to estimate LFL, UFL & Flash Point using standard heat of combustion, standard heat of formation & adiabatic temperature.
- To validate the derived equation with a set of available data from literature using "C".
- To investigate the effect of temperature on value of LFL & UFL.
- To investigate the effect of pressure on the value of LFL & UFL.
- To investigate the effect of LFL on flash point.

CHAPTER: 2 LITERATURE REVIEW

An exhaustive study has been done to explore the various types of mathematical model used for the estimation of flammability limits and flash point. The present literature review has been initiated to search for pertinent methodologies, theoretical and technical to develop the mathematical modelling for estimation of hazard point. The literature review is conducted to determine the current state of the theoretical and technical aspects of flammability limits and flash point.

The literature review covers the following topics:

1. Structural group contribution based flammability limits.
2. Study on flammability limits at high pressure.
3. Study on flammability limits based on characteristics.
4. Statistical analysis of flash point.

2.1. Structural group contribution based flammability limits

Mehdi Bagheri et.al.(2011) presents an important aspect of methodology that concerns quantitative structure property relation (QSPR) based studies. The main objective of this work is to provide simple techniques for the accurate prediction of the lower flammability limits through a robust QSPR approach. The obtained three parameter multivariate regression (MLR) and adaptive neuro-fuzzy inference system (ANFIS) modelling strategies resulted in encouraging statistics of R^2=0.906, *RMSE*=0.335 and R^2=0.930, *RMSE*=0.287 vol. %, respectively, using the entire DIPPR dataset. Using such a large dataset comprising of 1615 compounds from 82 diverse chemical material classes can highly benefit the study accuracy and comprehensiveness. Advantage of this model is that the model input variables can be easily calculated for non-specialist user.

Farhad Gharagheizi (2009) developed a quantitative structure property relationship (QSPR) to predict the upper flammability limit percent (UFLP) of pure compounds. The obtained model is five parameters multi linear equation. The parameters of the model are calculated only from chemical structure. The average absolute error and squared correlation

coefficient of the obtained model over all 865 pure compounds used to develop the model are 9.7%, and 0.92, respectively. In this step, the molecular structures of all 865 pure compounds were drawn into Hyperchem software and optimized using the MM+ molecular mechanics force field. Thereafter, using these optimized molecular structures; molecular descriptors were calculated by Dragon software. Dragon software can calculate 1664 molecular descriptors for every molecule. Of course, these molecular descriptors have been calculated for about 2,34,000 pure compounds using Dragon software and are accessible from Milano chemometrics and QSAR research group web site.

Tareq A. Albahri(2003) developed a model based on the structural group contribution method for estimation of flammability characteristics of pure hydro carbon. This method is used to calculate the group contribution to estimate the flammability limits and arrive at the sets of groups that can best represent the auto-ignition temperature (AIT), the flash point, and the upper and lower flammability limits of about 500 different substances. The structural groups were based on Joback definition of group contributions and modified to account for the location of the structural groups in the molecule. According to him value of group contribution is helpful to estimate the flammability properties by knowing the molecular structure of the compound. This method is simple and used to predict the flash point and the AIT with average percentage errors of 1.8% and 4.2%, respectively. The upper and lower flammability limits are predicted with average deviations of 1.25 and 0.04 vol. %, respectively.

Tareq A. Albahri suggests that experimental values of lower flammability limits (LFL), upper flammability limit (UFL), auto ignition temperature (AIT), flash point temperature (FPT) are always desirable, however, they are scars and expensive to obtain. When experimental values are not available and determining them by experimental means is not practical, a prediction method which is desirably convenient and fast must be used to estimate them. Flammability limits are obtained by empirical equations. This paper is based on the structural group contribution (SGC) method to predict the FPT, AIT, UFL, and LFL of pure hydrocarbons with higher accuracy. Structural groups were derived from the Joback group contribution approach with some modification.

According to Tareq A. Albahri, flammability of chemical compound can be modeled by a simple SGC method using non-linear regression optimization models. Flammability

modelling is a difficult and complex process. First principles model of the flammability characteristics involves the kinetics and dynamics of combustion on the molecular level. The SGC method can be an effective alternative method to estimate the flammability limits. This model gives inherent relationships among structural groups and their contribution to the overall flammability property of the molecule such as group interactions, structural orientation, skew, hindrance, steric, resonance, inductive, and chiral effects that are usually unknown. Furthermore, the method is based on the molecule's structural data which is always known. Once a model is developed properly, SGCs offer predictions quickly and accurately on a personal computer using a spreadsheet. The SGC method can also be used for synthesizing molecules (i.e. choosing a molecule with a desired property). This can be done by invoking the inverse property of the model; what is the best combination of inputs that lead to certain outputs.

2.2. Study on flammability limits at high pressure

C.M. Piquerasa et.al.(2011) has calculated LFL at high pressure (where data are not available). Estimation of LFL is based on the value of adiabatic flame temperatures for the mixtures H_2 +O_2 in CO_2 and N_2, between 1.0 and 300 bar and 288–348K is presented. A group contribution equation of state has been effectively used to predict thermodynamic properties of the mixture such as residual enthalpy, heat capacity and others, as well as phase equilibrium data. These methods results a deviation lower than 10% at high pressures. CO_2 is used as diluents to increase the operational margin from 4.5 mol% H_2 at 1 bar up to ca. 7.0–9.0 mol% H_2 at 200 bar due to the increase in the heat capacity. At the same time use of nitrogen or air as diluents only increases the margin from 5.2 mol% H_2 at 1 bar up to ca. 6.0 mol% H_2 at 200 bar. LFL is based on certain generation rate of critical energy and a certain level of temperature in which the reactions occurring in the flame are stable. In this work critical reaction temperature is assumed to equal to adiabatic flame temperature as process is adiabatic. Goethals et al. studied the flammability limits of toluene–air mixtures at pressures up to 500 kPa and temperatures up to 250° C in a closed spherical vessel. They found that the flammability limits depend linearly upon temperature. In their studies, the mixture was considered flammable if a pressure rise of more than 2% was detected after ignition. Over the whole temperature range, the lower limits were close to each other. The upper limits, on the other hand, differ more. At increased pressures, the relative temperature dependence

increases. It is important to report the pressure criterion used in each flammability study because the lower flammability limit as measured by the pressure rise depends upon the pressure criterion used.

F. Van den Schoor et. Al. (2008) compared the results of three different numerical methods to calculate flammability limits namely (1) the calculation of planar flames with the inclusion of a (radiation) heat loss term in the energy conservation equation, and the application of (2) a limiting burning velocity and of (3) a limiting flame temperature. The result are compared with experimental data on the upper flammability limit (UFL) of methane/hydrogen/air mixtures with hydrogen fuel molar fractions of 20% and 40%, at initial pressures up to 10 bar and initial temperatures up to 200 ^{0}C. The application of a limiting burning velocity is found to predict the pressure dependence of the UFL well, while the application of a limiting flame temperature generally is found to slightly underestimate the temperature dependence of the UFL.

Liekhus et al. found the lower flammability limit of H_2 to be 5 and 6 at a 3.5 and 7% pressure rise criterion, respectively. The effect of larger variations in pressure is neither simple nor uniform but is specific for each flammable mixture. Increase of pressure above that of the atmosphere does not always widen the limits. On the contrary, the range of flammability of some mixtures is narrowed by increase of pressure, so that a mixture that can propagate flame at atmospheric pressure may not be able to do so at higher pressures. One chemical that exhibits this peculiar characteristic is ethylene. The lower limit of ethylene rises from 3.5% at normal pressure to 5% at 20 atm and then falls to 1.5% at 380 atm.

B. Vanderstraeten et.al. (1997) studied on the flammability limits of methane/air mixtures experimentally at pressures up to 5500 kPa and temperatures up to 200°C. Two different criteria based on the maximum explosion pressure are used to define the flammability limit, the tangent criterion and the min-max criterion. It is shown that the min-max criterion should be used to determine the upper flammability limit (UFL), because the tangent criterion underestimates the UFL at initial pressures higher than ambient. In the pressure-temperature range tested second order pressure dependences and linear temperature dependences of the UFL are found. The temperature dependence of the UFL is influenced by the initial pressure which is in contrast with previous findings.

2.3. Study on flammability limits based on characteristics:

Y. M. Chang et.al.(2008) investigates the mixing of toluene and methanol mixtures with five vapour mixing ratios (100/0, 75/25, 50/50, 25/75 and 0/100 vol. %) at initial conditions of 1 atm and 150°C. Flammability properties are determined to identify their potential for fire and explosion hazards. These safety related parameters includes the lower explosion limit (LEL), upper explosion limit (UEL), maximum explosion overpressure (Pmax) and rate of maximum explosion pressure rise $((dP/dt)_{max})$. These properties were measured by a 20L apparatus. Experimental results show that when methanol was increased, which could induce a higher range of flammability, afterwards the situation could be triggered to a dangerous level, such as fire or explosion.

In this Experiment 99.8 vol. % toluene and 99.8 vol. % methanol were supplied from Formosa Chemicals and Fiber Co. of Taiwan and Formosa Plastics Co. of Taiwan, respectively. Various toluene and methanol mixtures as 100/0, 75/25, 50/50, 25/75, 0/100 vol. %, measured for the experiment.

Initial pressure and temperature of 1 atm and 150°C, along with five setting samples and various oxygen concentrations were studied to evaluate the fire and explosion hazards under various required scenarios. Initial temperature, 150°C was chosen experimentally. We set the initial temperature as 150°C in order to exceed both the normal boiling point of toluene (119.6°C) and methanol (64.7°C) by a thermo oil bath, in order to ensure forming total flammable vapours so that flammability tests were carried out in a good mixing state in the vapour phase.

This paper also shows that flammability limits of toluene and methanol in 75/25, 50/50, 25/75 were between 100 vol. % toluene and methanol. The explosion range rises with increasing methanol proportion. Toluene acts as an inhibitor, reducing the flammability hazards of methanol only in this toluene/methanol mixture system.

R.L.Yun et.al. (2007) describes the fire and explosion characteristics of 3-methyl pyridine at 270^0 C with high oxygen concentration. A mixture of 3-methyl pyridine (3-picoline) and steam is used in the production of vitamin B3 in the gas phase. This study was done to investigate the effect of inert steam (H_2O) on the flammability characteristics of 3-

picoline in the manufacturing process. Four practical vapour mixing ratios of 3-picoline/steam mixtures, 5, 10, 30 and 100 vol. % 3-picoline, were taken for experiment. A series of flammability tests were performed for determining their fire and explosion characteristics. Fire tests H_2O: 3-picoline 5, 10, 30 and 100 vol. % was carried out in a 20-L-Apparatus under simulated conditions of 760 mmHg, 270^0 C, together with high oxygen concentrations (42 and 21 vol. %) used in the real process. The experimental results showed that the safety-related parameters and flammability hazard degrees were all able to be significantly reduced while substantial amount of steam was infused into the 3-picoline/steam system. While the steam proportion was up to 97 vol. %, 3-picoline/steam will be non-flammable. As a result, dosing steam to the process is one of the effective methods to prevent the relevant processes from incurring fire and explosion hazards.

Y. M. Chang et.al. (2006) presents the effects of binary solutions of benzene and methanol for their vapour flammability characteristics. Flammability behaviours are studied under different mixing ratios (100/0, 75/25, 50/50, 25/75 and 0/100 vol. %) samples and these sample are injected into a 20 liter spherical explosion vessel under various initial temperatures (100, 150 and 200°C). Experimental results shows that, the flammability diagram of mixtures can be completely illustrated and combined with specific safety related properties(i.e lower explosion limit (LEL), upper explosion limit (UEL), minimum oxygen concentration (MOC), maximum explosion overpressure (P_{max}), and gas or vapour deflagration index (Kg)). Experimentally it is verified that the UEL, P_{max} and Kg all increases with the temperature, pressure and oxygen concentration, whereas there was no significant variation on the part of LEL.

Samples of benzene and methanol are used for this paper were supplied from Formosa Chemicals and Fiber Corporation of Taiwan with 99.88 vol% benzene in purity and 99.99 vol. % methanol from Formosa Plastics Corporation of Taiwan and then stored at 4°C.

In this paper effect of pressure is also considered. For benzene:methanol (75:25 vol.%), the explosion parameters by raising initial pressure from 101 to 202 kPa under 150°C and 21 vol% oxygen concentration are shown in table given below. The P_{max}, (dP/dt)max and *Kg* values will increase rapidly with pressure increased.

Table 2.1 Fire and explosion characteristic

Initial pressure	101 kPa	202 kPa
P_{max}	3.20 bar	8.90 bar
$(dP/dt)_{max}$	258.00 bar s^{-1}	1523 bar s^{-1}
K_g	69.66 bar s^{-1}	411.21 bar s^{-1}
Explosion classes	St-1	St-3

Effect of oxygen concentrations is also taken in to the results. UEL is increases with increasing oxygen concentrations at the same initial pressure, and it is also increases with the amount of methanol. The flammability limits decreases with reducing the oxygen concentration with benzene and methanol. When oxygen concentration is below the MOC, an explosion is no longer possible.

Laurence G. Britton et.al.(2005) study the ignitability, flammability, and explosibility of fuel and air mixtures. In this paper and in the E27 standards, the terms "flammability" and "explosibility" are used interchangeably. These terms are used to refer to the ability of a gas mixture or dust cloud to propagate a deflagration after it has been initiated by a sufficiently strong ignition source. Historically, the term "flammability" has been used more often for gases, and "explosibility" more often for dusts.

ASTM E27 Standard Test Method E 502 for "Selection and Use of ASTM Standards for the Determination of Flash Point of Chemicals by Closed Cup Methods" gives advice for the use of flash point methods developed by other ASTM committees. Despite being one of the earlier standards of the E27 Committee, E 502 is still widely used. This test method is used for the determination of the flash point of liquid and solid chemical compounds flashing from below -10 to 370° C (16–700° F). E 502 method uses the procedures and apparatus in ASTM Test Methods D56, D93, D3278, D3828, and D3941. It provides additional explanatory notes and procedure modifications not contained in the individual methods. E 502 method also permits determination of flash point for solids and highly viscous liquids.

ASTM standard test method E 1232 determines the "Temperature Limit of Flammability of Chemical compounds". The temperature limit of flammability test measures the minimum temperature at which liquid or solid chemicals evolve sufficient vapours to

form a flammable mixture with air under equilibrium conditions. This test is designed to remedy limitations inherent in flash-point tests, and yields a result closely approaching the minimum temperature of flammable vapor formation for equilibrium situations. This test method is highly helpful for chemical processing industry, such as in process vessels, storage tanks, and similar equipment. This test also allows the use of oxidant/diluents mixtures other than air.

A.A. Shimy(1970) pointed out that flammability limits are function of constituting atoms for fuels. He gave some empirical equations to estimate the lower flammability limit and upper flammability limit separately for various chemicals at atmospheric pressure and room temperature. In Shimy's equations, the lower flammability limit is only dependent on the numbers of carbon atoms, while the upper flammability limit is associated with the numbers of carbon atoms, hydrogen atoms in radicals, and hydrogen atoms not in radicals.

Table 2.2 Shimy's Equations for flammability limits estimation at standard conditions

	LFL	**UFL**
Paraffinic Hydrocarbons and Olefins	$\frac{6}{nC^{a}}+0.2$	$\frac{60}{nH^{b}}+\frac{nC}{20}+2.2$
Iso-Hydrocarbons	$\frac{6}{nC}+0.1$	$\frac{60}{nH}+2.3$
Benzene Series	$\frac{8}{nC}$	$\frac{86}{2nH_r^{c}+nH^{d}}$
Alcohols	$\frac{6}{nC}-0.7$	$\frac{80-2nH}{2nC}+3$

[a] nC is the number of carbon atoms

[b] nH is the number of hydrogen atoms

[c] nHr is the number of hydrogen atoms in radicals

[d] nH' is the number of hydrogen atoms not in radicals

2.4. Statistical analysis of flash point

Sung Young Kim and Bomsock Lee (2010) predicted a model based on the partial least squares of the multivariate statistical analysis methods was developed for the flash point (FP) of binary liquid mixtures. Estimation of the FP of flammable substances is important for safety measures in industrial processes. Since experimental FP data of liquid mixtures are scarce in the literature, there have been many researches to estimate the FP of liquid mixtures using physicochemical laws. In this study, the partial least squares (PLS) method using experimental data were used as a prediction model of the FP of binary liquid mixtures. The FPs predicted from the PLS method were also compared to results from the existing calculating methods using physicochemical laws such as Raoult's law and the Van Laar equation.

This paper suggested a PLS method for the prediction of the FP of binary liquid mixtures based on reported experimental data and pure component properties such as the Antoine constants related to the vapour pressure, the mole fraction and LFL(or LEL). Establishing the prediction model by regression of the training set, unknown experimental FPs of n-propanol and n-propionic can be predicted using the PLS method. The PLS method is not only easier to use to predict the FP than other calculating methods, but it also demonstrates better prediction results than other calculating methods involving physicochemical approaches such as Raoult's law, and the Van Laar equation.

For the prediction of the FP of binary liquid mixtures, the experimental FP data is necessary. However, experimental FP data of binary liquid mixtures is scarce. It is possible that the FP of binary liquid mixtures composed of pure components not in the training set can be predicted. However, prediction results are unsatisfactory at times.

Horng-Jang Liaw & Yi-Yu Chiu (2006) developed a mathematical model for predicting the flash point of miscible mixtures. This model is reducible and adequate for some specified systems. Except for multiple aqueous-organic solutions, the predictive capability of the reduced form for other miscible mixtures, including binary aqueous-organic solutions and flammables only analogues, has been verified previously. The model was validated using the ternary aqueous-organic solutions, water + methanol + ethanol/iso-propanol. The results of the study confirm that the model predicts the flash points of these solutions by utilizing the flash points of the individual components. Further, if the binary interaction parameters for a

ternary aqueous organic solution are not accessible, a model based upon the binary interaction parameters of the binary solutions may provide a very acceptable means of predicting the flash point for such a ternary solution through comparison of the predicted and experimental data.

The model for a ternary aqueous organic solution was used to predict the flash point of water + methanol + ethanol/iso-propanol systems. The results thus obtained were compared with the corresponding experimentally derived data. This study also compared the predictive capability of our proposed model with Garland and Malcolm's statistical analogue. The aqueous solutions of methanol, ethanol and iso-propanol are all non-ideal, and the activity coefficients corresponding to the flammable components for such solutions are all greater than unity. By contrast, the binary solution of methanol + ethanol behaves almost like an ideal solution. The liquid phase activity coefficients for the flammable components of these ternary aqueous organic solutions were estimated using the Wilson, NRTL and UNIQUAC equations. These estimated activity coefficients were subsequently used in this proposed model to predict the corresponding flash points for the ternary aqueous organic solutions. The parameters required for this model include the Antoine coefficients for the flammable components and the binary interaction parameters of the Wilson, NRTL or UNIQUAC equations. In addition, it is necessary to input the flash points of the solution components into this model to predict the mixture flash point. The Antoine coefficients were sourced from the literature. The binary interaction parameters of the Wilson, NRTL and UNIQUAC equations for these two mixtures were also derived from the same literature.

Brian Hanley (1988) reported that flash point is one of the major physical properties used to determine the fire and explosion hazards of a liquid. Flash points are used by virtually all governmental entities worldwide to define "flammable" and "combustible" materials for shipping and safety regulations. A model is described here for the calculation of closed cup flash points for multi component, single liquid phase, mixtures. The model is based upon rigorous vapour/liquid equilibrium calculations supplemented with information about the lower flammable limits (LFL) and heats of combustion ΔH_C for the mixture's constituent components. The closed cup flash points predicted with this model are typically within $\pm 5^0$C of the experimentally reported values. Such a model is useful as a means of verifying experimental data and as a tool for screening product formulations prior to experimental flash

point determination. The model should considerably enhance the safety evaluation portion of the product development cycle, thus leading to shortened product time-to-market cycles. While flash points calculated with this model are in excellent agreement with experiment, experimental determination is still encouraged for critical safety applications.

Hanley said prediction of closed cup flash points is, in theory, straightforward. One calculates the composition of the head space gas as a function of temperature from vapour/liquid equilibrium data or models for the solution. In addition, one must be able to calculate the composition dependence of the lower flammable limit. Unfortunately, the thermodynamics of multi component mixtures is oftentimes unknown. In addition, prediction of the LFL with composition has apparently not been attempted.

Atsushi Fujii and Edward R. Hermann (1982) investigated a correlation between flash points and vapour pressures at 25 ^{0}C for pure organic compounds. It was found that classification of organic compounds according to their chemical structural characteristics (functional groups) was necessary for the correlation study. Under this classification, linearity seems to be the most appropriate correlation to explain the relationship between the inverse of flash points (K) and the logarithm of vapour pressures (mm Hg) at 25 ^{0}C for pure organic compounds. A test study to evaluate the validity of a regression line as an estimation of an unknown flash point from a known vapour pressure was carried out with a data set containing 31 alkanes and aromatics; 55% of the flash points were predicted within ± 5 ^{0}C and 89% were within ± 10 ^{0}C. Within limits of ± 5 to 10 ^{0}C the procedure is useful but should be improved.

Limits of flammability are essentially independent of the ignition source strength. They give a measure of the ability of a flame to propagate away from the ignition source. In practice, the flammability limits of a particular system of gases are affected by the temperature, pressure, direction of flame propagation, gravitational field strength, and surroundings. When a source of ignition is introduced into a flammable mixture, flame tends to travel away from the source in all directions. The flame propagation could be upward, downward, or horizontal. The limits of flammability will depend on the direction of flame propagation under consideration. For safety in industrial operations it is generally wisest to consider the limits of upward propagation since these limits are wider than those for horizontal or downward propagation of flame.

Lower flammability limit depends on the temperature and chemical compound. So its estimation is done into two parts:

- Estimation of LFL at reference temperature.
- Effect of initial temperature on the LFL.

3.1. Modelling of LFL at reference temperature (298 K)

General combustion reaction is proceeding according to following reaction:

$$C_xH_yO_zN_wS_vX_uSi_t + \beta\ O_2 = xCO_2 + (y-u)/2\ H_2O + v\ SO_2 + t\ SiO_2 + u\ HX + w/2\ N_2$$

There is a relationship between LFL, enthalpy, stoichiometric coefficient of combustion reaction, oxygen and adiabatic temperature. This relationship is given below:

$$LFL(T_0)H_{fuel}(T_0) + (100 - LFL(T_0))H_{air}(T_0) = LFL(T_0)\sum_{products} n_i H_i(T_{ad}) + (100 - LFL(T_0))H_{air}(T_{ad}) - LFL(T_0)\beta H_{O_2}(T_{ad})$$

(Eq. 3.1)

Above equation can be rearrange as

$$LFL(T_0) = \frac{100[H_{air}(T_{ad}) - H_{air}(T_0)]}{[H_{fuel}(T_0) - \sum_{product} n_i H_i(T_{ad}) + \beta H_{O_2}(T_{ad}) + H_{air}(T_{ad}) - H_{air}(T_0)]} \quad \text{(Eq. 3.2)}$$

Or $$LFL(T_0) = \frac{100}{[1 + \frac{H_{fuel}(T_0) - \sum_{product} n_i H_i(T_{ad}) + \beta H_{O_2}(T_{ad})}{[H_{air}(T_{ad}) - H_{air}(T_0)]}]} \quad \text{(Eq.3.3)}$$

Assuming T_0 =298 K and $H_{air}(298)$=0;

The above equation can be written as

$$LFL(298) = \frac{100}{[1 + \frac{H_{fuel}(T_0) - \sum_{product} n_i H_i(T_{ad}) + \beta H_{O_2}(T_{ad})}{H_{air}(T_{ad})}]} \quad \text{(Eq.3.4)}$$

Or $$LFL(298) = \frac{100}{1+\gamma} \quad \text{(Eq.3.5)}$$

$$\gamma = \frac{H_{fuel}(T_0) - \sum_{product} n_i H_i(T_{ad}) + \beta H_{O_2}(T_{ad})}{H_{air}(T_{ad})} \quad \text{(Eq.3.6)}$$

Step 1: Adiabatic flame temperature: Adiabatic temperature is maximum temperature achieved by combustion of a compound when they are taken in stoichiometric ratio. Since the condition is adiabatic hence, there is no loss of energy to the surrounding.

The general equation for combustion is assumed as follows:

$$C_xH_yO_zN_wS_vX_uSi_t + \beta\ O_2 = xCO_2 + (y-u)/2\ H_2O + v\ SO_2 + t\ SiO_2 + u\ HX + w/2\ N_2 \quad \text{(Eq.3.7)}$$

Where, X= Halogens Atoms and

β is obtained by comparing the coefficient of both side of the combustion reaction, hence β is given as

$$\beta = x+(y-u)/4+v+t-z/2 \qquad \text{(Eq.3.8)}$$

Heat of combustion of organic compound per unit kg of air can be expressed according to the following equation:

$$\Delta Hc(MJ/kg\,air) = \frac{(\text{heat of reaction per mole of organic compound} \times 0.21)}{(\text{number of moles of } O2 \times 28.95)} \qquad \text{(Eq.3.9)}$$

Molecular weight of air = 28.95 gm/mol

Mole fraction of oxygen = 0.21

Heat of combustion of several organic compounds based on the above equation (3.9) by developing an algorithm in "C" is given below:

Table 3.1 Heat of combustion of n-alkanes

Compound	Formula	ΔH_c(kJ/mol of compound)	ΔH_c(MJ/kg of air)
Methane	$CH_{4(g)}$	-890.3	3.229
Ethane	$CH_3CH_{3(g)}$	-1559.7	3.233
Propane	$CH_3CH_2CH_{3(g)}$	-2219.2	3.220
Butane	$CH_3(CH_2)_2CH_{3(g)}$	-2876.5	3.200
Pentane	$CH_3(CH_2)_3CH_{3(l)}$	-3509.1	3.182
Hexane	$CH_3(CH_2)_4CH_{3(l)}$	-4163.0	3.179
Heptane	$CH_3(CH_2)_5CH_{3(l)}$	-4816.0	3.176
Octane	$CH_3(CH_2)_6CH_{3(l)}$	-5470.2	3.174
Nonane	$CH_3(CH_2)_7CH_{3(l)}$	-6124.6	3.173
Decane	$CH_3(CH_2)_8CH_{3(l)}$	-6777.9	3.172
Undecane	$CH_3(CH_2)_9CH_{3(l)}$	-7430.9	3.171
Dodecane	$CH_3(CH_2)_{12}CH_{3(l)}$	-8086.5	3.171

Table 3.2 Heat of combustion of branched alkanes

Compound	Formula	ΔH_c(kJ/mol of compound)	ΔH_c(MJ/kg of air)
2-methyl propane	$(CH_3)_2CHCH_{3(g)}$	-2868.5	3.201
2-Methylbutane	$(CH_3)_2CHCH_2CH_{3(l)}$	-3503.4	3.177
2-Methylpentane	$(CH_3)_2CH(CH_2)_3CH_{3(l)}$	-4157.0	3.174
2-Methylhexane	$(CH_3)_2CH(CH_2)_4CH_{3(l)}$	-4811.4	3.173
2-Methylheptane	$(CH_3)_2CH(CH_2)_5CH_{3(l)}$	-5465.2	3.172
2,2-Dimethylpropane	$C(CH_3)_{4(g)}$	-3492.5	3.167

Table 3.3 Heat of combustion of cyclo alkanes

Compound	Formula	ΔH_c(kJ/mol of compound)	ΔH_c(MJ/kg of air)
Cyclopropane	$(CH_2)_{3(g)}$	-2091.4	3.371
Cyclobutane	$(CH_2)_{4(g)}$	-2720.9	3.289
Cyclopentane	$(CH_2)_{5(l)}$	-3289.4	3.181
Cyclohexane	$(CH_2)_{6(l)}$	-3919.5	3.159
Cycloheptane	$(CH_2)_{7(l)}$	-4598.4	3.177
Cyclooctane	$(CH_2)_{8(l)}$	-5266.7	3.184
Cyclononane	$(CH_2)_{9(l)}$	-5932.5	3.188

Table 3.4 Heat of combustion of alkenes

Compound	Formula	ΔH_c(kJ/mol of compound)	ΔH_c(MJ/kg of air)
Ethene	$CH_2=CH_{2(g)}$	-1410.8	3.411
Propene	$CH_2=CHCH_{3(g)}$	-2058.1	3.317
But-1-ene	$CH_2=CHCH_2CH_{3(g)}$	-2716.8	3.284
trans-But-2-ene	$CH_3CH=CHCH_{3(g)}$	-2705.0	3.270
cis-But-2-ene	$CH_3CH=CHCH_{3(g)}$	-2709.4	3.276
Hex-1-ene	$CH_2=CH(CH_2)_3CH_{3(l)}$	-4003.4	3.227
Buta-1,2-diene	$CH_2=C=CHCH_{3(g)}$	-2593.7	3.421
Buta-1,3-diene	$CH_2=C=CHCH_{3(g)}$	-2541.3	3.351
Cyclohexene	$CH_2(CH_2)_3CH=CH_{2(l)}$	-3751.9	3.111
Phenylethene (styrene)	$C_6H_5CH=CH_{2(l)}$	-4395.0	3.188

Table 3.5 Heat of combustion of alkynes

Compound	Formula	ΔH_c(kJ/mol of compound)	ΔH_c(kJ/kg of air)
Ethyne	$CHCH_{(g)}$	-1300.8	3.772
Propyne	$CH_3CHCH_{(g)}$	-1938.7	3.516
1-Butyne	$CH_3CH_2CCH_{(g)}$	-2596.6	3.424
2-Butyne	$CH_3CCCH_{3(l)}$	-2576.8	3.398

Table 3.6 Heat of combustion of Arenes

Compound	Formula	ΔH_c(kJ/mol of compound)	ΔH_c(kJ/kg of air)
Benzene	$C_6H_{6(l)}$	-3267.4	3.160
Napthalene	$C_{10}H_{8(s)}$	-5155.9	3.117
Methylbenzene	$C_6H_5CH_{3(l)}$	-3909.8	3.151
Ethylbenzene	$C_6H_5CH_2CH_{3(l)}$	-4563.9	3.153
Propylbenzene	$C_6H_5(CH_2)_2CH_{3(l)}$	-5218.0	3.154
1,2-Dimethylbenzene	$C_6H_5(CH_3)_{2(l)}$	-4552.6	3.072
1,3-Dimethylbenzene	$C_6H_5(CH_3)_{2(l)}$	-4551.6	3.071
1,4-Dimethylbenzene	$C_6H_5(CH_3)_{2(l)}$	-4552.6	3.072
Ethenylbenzene (vinyl)	$C_6H_5CH{=}CH_{2(l)}$	-4395.0	3.188

Since heat of combustion of a organic compound per unit mole of oxygen (or per kg of air) is nearly constant. Its value is approximately 3 MJ/kg air. This result is found analylitically by calculating the above said value for different compound. The above result has assumed the air composition as 79 % nitrogen and 21 % oxygen by volume. The combustion takes place at 298 K and 1 atm.

From the above table it is clear heat of combustion is only depend on moles of oxygen (air) consumed.

Hence, $\Delta H_c = 3.0$ MJ/kg Air (Eq.3.10)

This result can be used to find out the heat of combustion of any organic compound.

Let heat of combustion is ΔH and adiabatic flame temperature is ΔT. Also specific heat capacities is represented by C_{pi}, then heat balance equation can be written as

$$\Delta H = \sum n_i C_{pi} . \Delta T \qquad \text{(Eq.3.11)}$$

Hence, $$\Delta T = \frac{\Delta H}{\sum_{product} n_i C_{pi}}$$

Hence from above equation adiabatic flame temperature can be calculated.

Step: 2 Effect of temperature on enthalpy

$dH = C_p dT$

Integrating the above equation between T_{ad} and 298 K, we get the following result as given below:

$$H_i(T_{ad}) = H_i^0 + C_{p,i} (T_{ad} - 298K) \qquad \text{(Eq.3.12)}$$

Here $C_{p,i}$ is assumed to approximately constant.

3.2. Effect of initial temperature on LFL

Let heat capacity is approximately constant with temperature. Then equation (3.1) may be written as

$$LFL(T).(-\Delta H_C^0) + \overline{C}_{P,fuel-air}(T - 298) = \overline{C}_{P,Prod}(T_{ad}(T) - 298) \qquad \text{(Eq.3.13)}$$

Comparing above equation at two different temperature say T_1 & T_2 , we get the following two sets of equations:

$$LFL(T_1).(-\Delta H_C^0) + \overline{C}_{P,fuel-air}(T_1 - 298) = \overline{C}_{P,Prod}(T_{ad}(T_1) - 298) \qquad \text{(Eq.3.14)}$$

$$LFL(T_2).(-\Delta H_C^0) + \overline{C}_{P,fuel-air}(T_2 - 298) = \overline{C}_{P,Prod}(T_{ad}(T_2) - 298) \quad \text{(Eq.3.15)}$$

Solving the above sets of equations for the LFL (T_2), we get the following results

$$LFL(T_2) = LFL(T_1) + \frac{\overline{C}_{p,fuel-air}(T_1 - T_2) - \overline{C}_{p,prod}(T_{ad}(T_1) - T_{ad}(T_2))}{(-\Delta H_C^0)} \quad \text{(Eq.3.16)}$$

According to Rowley, adiabatic flame temperature decreases linearly with initial test temperature. This relation may be written as

$$T_{ad} = \gamma.T + b \quad \text{(Eq.3.17)}$$

3.3. Upper flammability limits

According to Affens, UFL and LFL are related as per given relation:

$$\frac{1}{UFL(T_0)} = 0.0993\left(\frac{1}{LFL(T_0)}\right) + 0.0472 \quad \text{(Eq.3.18)}$$

Where, LFL and UFL are calculated at 298 K.

Zebatakis has given a relation to for temperature dependency of UFL, which is given below:

$$UFL(T) = UFL(25^0C)[1 + 7.21\times10^{-4}(T - 25)] \quad \text{(Eq.3.19)}$$

From above two equations UFL can be calculated at any temperature. Equation 3.18 is used to calculate the UFL at 298 K and equation 3.19 is used to calculate the UFL at required temperature.

Effect of pressure on flammability limits:

Dependency on pressure can be described by the equation given by G. A. Melhem which is given below:

$$LFL = 4.90\text{-}0.71 \log P \quad \text{(Eq.3.20)}$$

$$UFL = 14.1 + 20.4 \log P \quad \text{(Eq.3.21)}$$

Where, LFL & UFL are lower & upper flammability in volume %.

P = Initial system pressure in atm.

3.4. Analytical method to calculate flash point

Predictive theoretical methods are needed to estimate the flash point of mixtures when experimental data are unavailable. Flash point determinations for mixtures generally are based on the Le Chatelier equation together with a vapour–liquid equilibrium model calculation of the vapour composition when liquids are involved. Most existing predictive methods are applicable only for atmospheric conditions, which do not necessarily represent the conditions encountered in industry. Generally, mixtures are not ideal in either the vapour or the liquid phases and the pressures may not be atmospheric. One example is the storage and transmission of chemicals at a variety of temperatures and pressures.

The development of reliable predictive methods for estimating flash points would reduce significantly the amount of experimental data required for a complete flammability characterization. In addition, it is necessary to know the flammability characteristics under the working conditions, i.e., at process temperature and pressure, to evaluate the hazards involved in a process and to ensure safe and optimal operation of processes. This study addresses the need for a comprehensive mathematical model for estimating mixture flash point.

- For n-alkanes from methane through dodecane, Affens expressed the flash points (T_F ^{0}C) in terms of lower flammable limits (LFL% V/V at 25 ^{0}C) using

the following equation:

$$(T_F + 277.3)^2 = 77291(1/LFL) - 3365 \qquad \text{(Eq.3.22)}$$

- For pure hydrocarbons, closed cup flash points (T_F ^{0}C) were also expressed as a function of boiling points (T_B ^{0}C):

$$T_F = a.\ T_B - b \qquad \text{(Eq.3.23)}$$

Table 3.7 Numerical values of the coefficients a and b

a	b	Reference
0.73	72.6	AFMFI, 1940
0.68	71.7	Butler, 1956
0.69	73.7	Affens, 1966

Average value: a=0.70, b=72.7

CHAPTER 4: RESULTS AND DISCUSSION

The flammability limits of a combustible mixture are those limiting compositions that will just support flame propagation when stimulated by an external ignition source. Identifying these limits is of great interest to the chemical industry and safety engineers, and compilations of flammability limits have been published by the Bureau of Mines. Although there is no widely accepted theoretical method of predicting flammability limits, there are a number of empirical rules and simple models, the classical results are summarized in Lewis and Von Elbe and updated in the series of reports by Hertzberg. The fuel type, mixture properties and mass diffusion of the deficient reactant are all factors in defining the limiting composition. Mixtures that are either too rich or too lean are not flammable. Lower or lean flammability limits are known in the literature as LFL, upper or rich flammability limits are known as UFL.

4.1. Lower flammability limit of methane

4.1.1. Adiabatic flame temperature of methane

Theoretically complete combustion reaction in 100% O_2 is given as below:

$$CH_4 + 2O_2 = CO_2 + 2\ H_2O \qquad \text{(Eq.4.1)}$$

Let us take air contains 21% O_2 & 79% N_2 by volume.

1 mole O_2 = (79/21) mole N_2

=3.7619 mole N_2

In air the above reaction (4.1) will take place as given below:

$$CH_4 + 2O_2 + (158/21)\ N_2 = CO_2 + 2\ H_2O + (158/21)\ N_2 \qquad \text{(Eq.4.2)}$$

Since nitrogen will act as inert reactant. Hence it will remain unchanged at the end of reaction.

Moles of O_2 taking part in the reaction = 2

Hence heat of reaction $\Delta H_c = 413.76 \times 2$ kJ

$= 827.52$ kJ

Applying energy balance for the above equation in adiabatic condition

$\Delta H_c = \sum n_i C_{p,i} \Delta T$

Hence, we can write as

827.52 kJ/mol $= \sum n_i C_{p,i} \Delta T$

$827.52 \times 10^3 = (1 \times 54.3 + 2 \times 41.2 + 7.52 \times 32.7) \times \Delta T$

Hence,

$\Delta T = 2161.87$

$T_{ad} = T_{ref} + \Delta T;$

$T_{ad} = 25 + 2161.87$

Adiabatic flame temperature is $= 2186.87\ ^0C = 2459.87$ K

Table 4.1 Specific heat capacity data

Chemical Compound	**Specific heat capacity at constant pressure(C_p)**
CO_2	54.3 J/mol
H_2O	41.2 J/mol
N_2	32.7 J/mol

4.1.2. Enthalpy of methane

Ideal gas of heat of formation of methane,

$$H_{CH_4}(T_0) = -74.87 kJ/mol$$

Ideal gas of heat of formation of oxygen, $H_{O_2}(T_0) = 0$

Applying equation (3.10) to calculate enthalpy of oxygen at adiabatic temperature,

$$H_{O_2}(T_{ad}) = H_{O_2}(T_0) + C_{p,O_2}(T_{ad} - T_0)$$

$$= 0 + C_{p,O_2}(T_{ad} - 298)$$

$$= 34.9 \times (2459.87 - 298)$$

$$= 75449.263 \text{ J/mol}$$

Specific heat capacity of mixture is given by

$$C_{p,mixture} = \sum x_i \, C_{p,i} \qquad \text{(Eq.4.3)}$$

Hence for air (21% O_2 & 79% N_2 by volume), specific heat capacity is given as

$$C_{p,air} = 0.21 \times 34.9 + 0.79 \times 32.7$$

$$= 33.162 \text{ J/mol-K}$$

Ideal gas of heat of formation of air, $H_{air}(T_0) = 0$

Applying equation (3.10) to calculate enthalpy of air at adiabatic temperature,

$$H_{air}(T_{ad}) = H_{air}(T_0) + C_{p,air}(T_{ad} - T_0)$$

$$= 0 + 33.162 \text{ (2459.87-298)}$$

$$= 71691.9 \text{ J/mol}$$

Standard enthalpy of CO_2, H_2O & N_2 is given below

$$H_{CO_2}(T_0) = -393.52 kJ/mol$$

$$H_{H_2O}(T_0) = -241.818 kJ/mol$$

$$H_{N_2}(T_0) = 0$$

Using equation 3.10, we get the following result

$$H_{CO_2}(T_{ad}) = 510909.54 J/mol$$

$$H_{H_2O}(T_0) = 330887 J/mol$$

$$H_{N_2}(T_0) = 70693.149 J/mol$$

Using equation 3.6 to calculate the value of γ, we get the following results

$$\gamma = \frac{74.87-(1\times510.9+2\times330.9+7.52\times70.7)+2\times75.45}{71.69}$$

$$\gamma = -21.62$$

Making value of γ to positive, i.e

$$\gamma = 21.62$$

Hence value of LFL at reference temperature (298 K) is

$$LFL = \frac{100}{1 + 21.62}$$

$$=4.420$$

This is very close to experimental value of LFL 5.00.

4.2. LFL for methyl isocynate (MIC)

4.2.1. Adiabatic flame temperature of MIC

Combustion reaction for methyl isocynate can be expressed as given below:

$$CH_3NCO + 2.25\ O_2 + 8.46\ N_2 = 2\ CO_2 + 1.5\ H_2O + 0.5\ N_2 \qquad \text{(Eq.4.4)}$$

$$H_{fuel}(T_0) = 92\ \text{kJ/mol}$$

Heat of reaction can be evaluated as

$$\Delta H = 413.76 \times 2.25$$

$$= 930.96\ \text{kJ/mol}$$

Applying energy balance (equation 5.4) for the above equation in adiabatic condition

$$\Delta H_c = \sum n_i\ C_{p,i}\ \Delta T$$

Hence, we can write as

$$930.96\ \text{kJ/mol} = \sum n_i\ C_{p,i}\ \Delta T$$

Hence, $\Delta T = 2008.4$

$T_{ad} = 2306.4\ K$

4.2.2. Enthalpy of methyl isocynate

$$H_{O_2}(T_{ad}) = 29.3468 \times 2008.4$$

$$= 58.94\ \text{kJ/mol}$$

$$H_{air}(T_{ad}) = 58.23\ \text{kJ/mol}$$

$$H_{CO_2}(T_{ad}) = 468.32\ \text{kJ/mol}$$

$$H_{H_2O}(T_{ad}) = 309.27 \text{ kJ/mol}$$

$$H_{N_2}(T_{ad}) = 58.50 \text{ kJ/mol}$$

Using equation 3.6 to calculate the value of γ, we get the following results

$$\gamma = -20.7$$

Taking positive value, $\gamma = 20.7$

Hence, LFL = (100/21.7) = 4.6

Similarly we can obtain for the lower flammability limits for other compound. Some of the chemical compounds LFL are calculated based on the above method. LFL values thus obtained are listed in table given below. These listed values are obtained by developing an algorithm in "C" which gives an effective solution to the empirical equations.

Table 4.2 Lower flammability limits for some organic compounds are listed below based on the analytical modelling calculation:

Compound	LFL (v/v %)	Reference value of LFL (v/v %)
CH_4	4.77	5.0
C_2H_6	2.79	3.0
C_3H_8	1.98	2.1
C_4H_{10}	1.54	1.6
C_5H_{12}	1.26	1.4
C_6H_{14}	1.06	1.2
C_7H_{16}	0.92	1.1
CH_3NCO	3.76	3.4
C_3H_6O	2.39	2.5
C_2H_2	4.57	2.5
Aniline	1.34	1.3
Phenol	1.42	1.8
Styrene	1.05	1.1
Toluene	1.16	1.2
1-Butene	1.65	1.6
Propylene oxide	2.27	2.3
Xylene	0.98	1.1
Dioxane	1.82	2.0
Cyclohexane	1.13	1.3
Acrolein	2.56	2.8
Acrylonitrile	2.88	3.0
Carbon Monoxide	12.48	12.5
Ethyl alcohol	2.83	3.3
Benzene	1.40	1.3
Trimethylamine	1.82	2.0
Methyl alcohol	5.30	6.0
Ethyl alcohol	3.01	3.3
Cumene	0.86	0.9

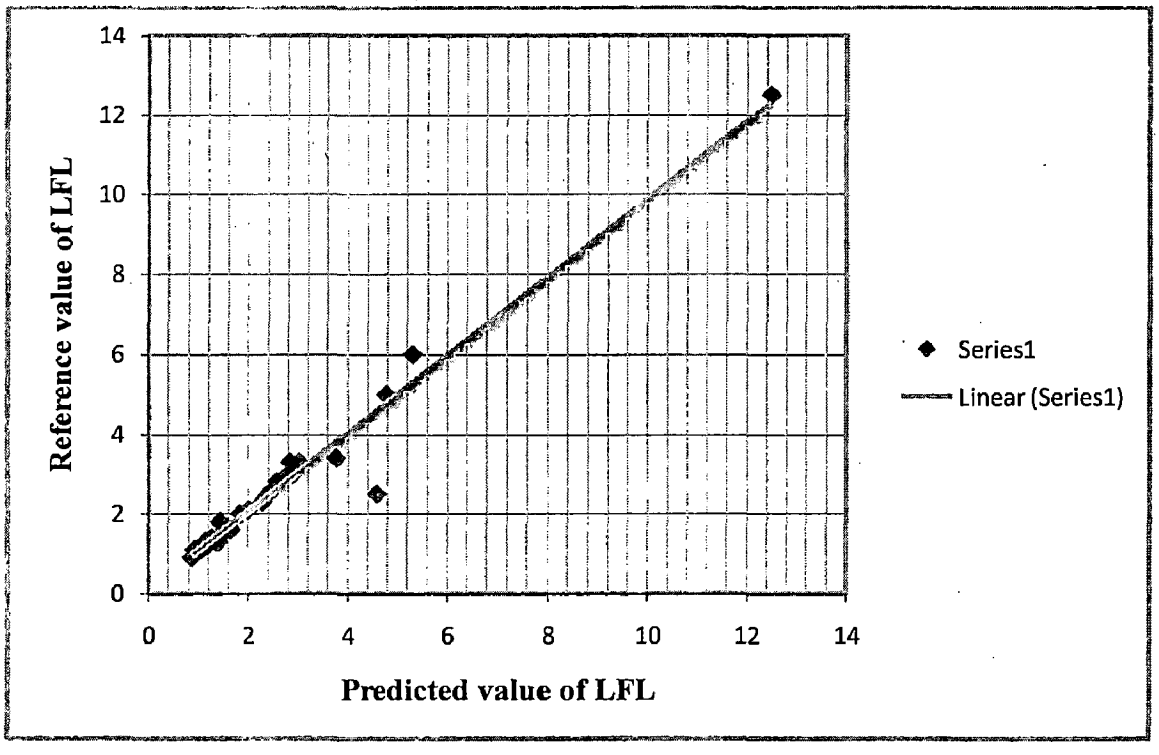

Figure 4.1 Comparison of Predicted LFL with Reference LFL for general organic compound.

Above results shows that predicted value of LFL is very close to the reference value of LFL. This graph also suggests that there is very little deviation of LFL value from the desired value.

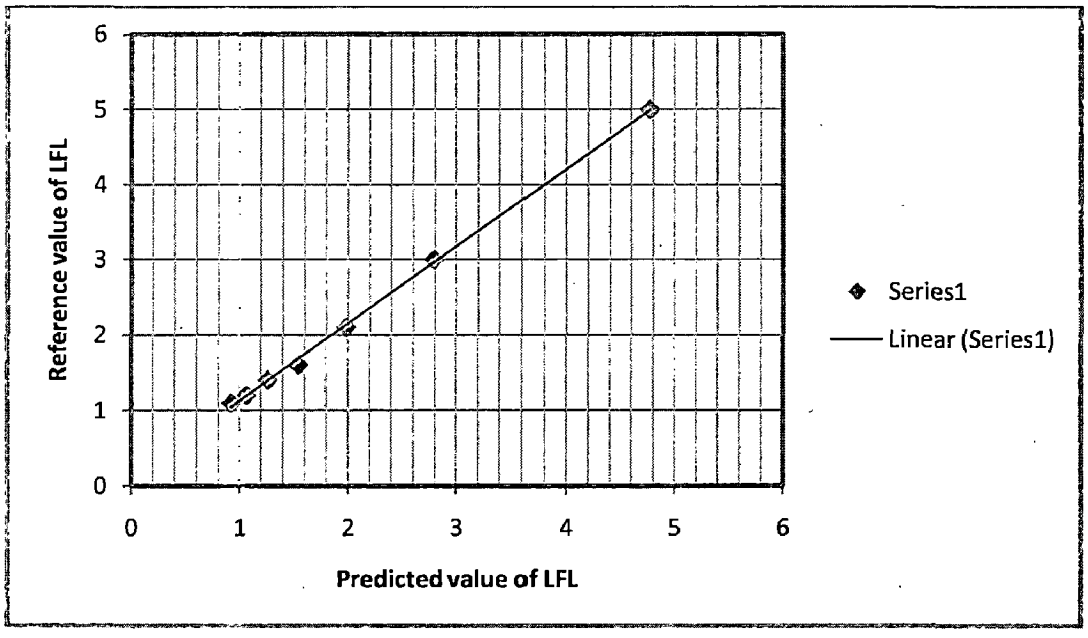

Figure 4.2 Comparison of Predicted LFL with Reference LFL for n-alkane

It is clear from the above graph that predicted value of LFL for n-alkane is very close to the reference value of LFL. There is very small deviation from the standard value of LFL.

Table 4.3 Upper flammability limits for some organic compounds are listed below based on the analytical modelling calculation:

Compound	UFL (v/v %)	Reference value of UFL (v/v %)
CH_4	11.48	14.67
C_2H_6	12.05	12.5
C_3H_8	10.25	9.5
C_4H_{10}	8.94	8.4
C_5H_{12}	7.93	7.8
C_6H_{14}	7.08	7.5
C_7H_{16}	6.43	6.7
CH_3NCO	13.55	26.4
C_3H_6O	11.25	13.0
C_2H_2	14.47	100
Aniline	8.23	11.0
Phenol	8.52	8.6
Styrene	7.05	7.0
Toluene	7.52	7.1
1-Butene	9.30	10.0
Propylene oxide	10.98	36.0
Xylene	6.72	6.6
Dioxane	9.81	22.0
Cyclohexane	7.39	8.0
Acrolein	11.61	31.0
Acrylonitrile	12.22	17.0
Carbon Monoxide	18.07	74.0
Ethyl alcohol	12.13	19.0
Benzene	8.45	7.9
Trimethylamine	9.81	12.0
Methyl alcohol	15.13	36.0
Ethyl alcohol	12.45	19.0
Cumene	6.14	6.5

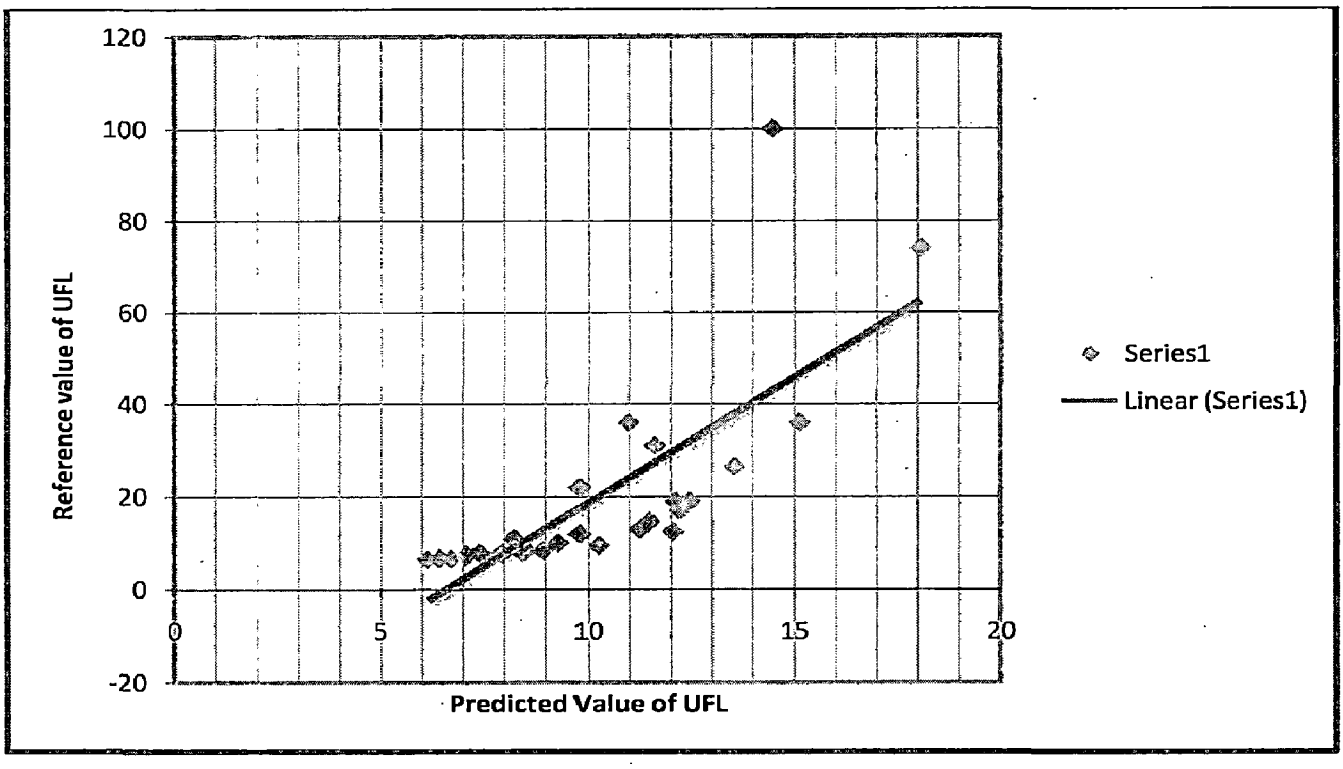

Figure 4.3 Comparison of Predicted UFL with Reference UFL for general organic compound.

Above graph shows that reference value of UFL and predicted value of follow a straight line and does not passes through origin. There is large deviation from of UFL values from the desired value of UFL.

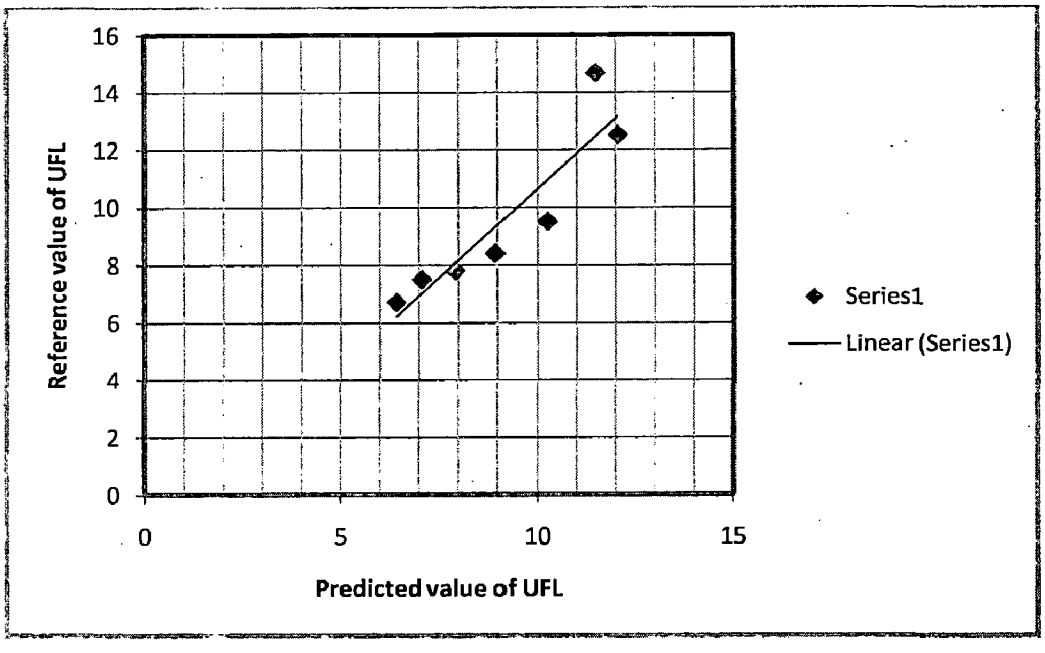

Figure 4.4 Comparison of Predicted UFL with Reference UFL for n-alkane

This graph shows that predicted value of UFL is consistent with the reference value of UFL. When they are plotted on x-y diagram, they fall on a straight line. There is a small deviation from the reference value for n-alkane.

Table 4.4 Relation of LFL with Flash point calculation for n-Alkane

Chemical Compound (n-alkane)	LFL (v/v %)	Flash Point (T ^{0}C)	Flash Point (T ^{0}F)
CH_4	4.77	-163.993	-263.187
C_2H_6	2.79	-121.294	-186.329
C_3H_8	1.98	-88.4327	-127.179
C_4H_{10}	1.54	-60.9116	-77.6408
C_5H_{12}	1.26	-36.5157	-33.7283
C_6H_{14}	1.06	-13.5747	7.565553
C_7H_{16}	0.92	6.684078	44.03134

From the above result a graph can be plotted between flash point and LFL (v/v %) which is given below. From this graph we obtained a polynomial of order 3. So we can say that n-alkane follow a similar relationship with LFL.

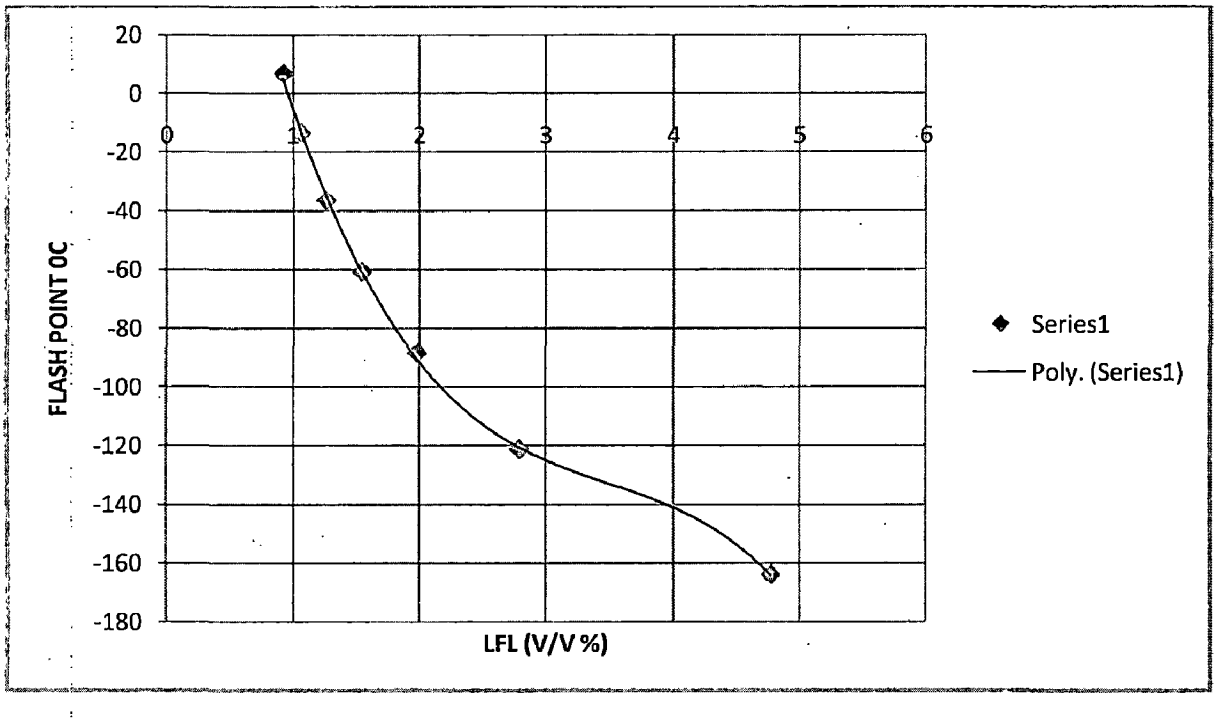

Figure 4.5 Relations between Flash Point and LFL for n-Alkane.

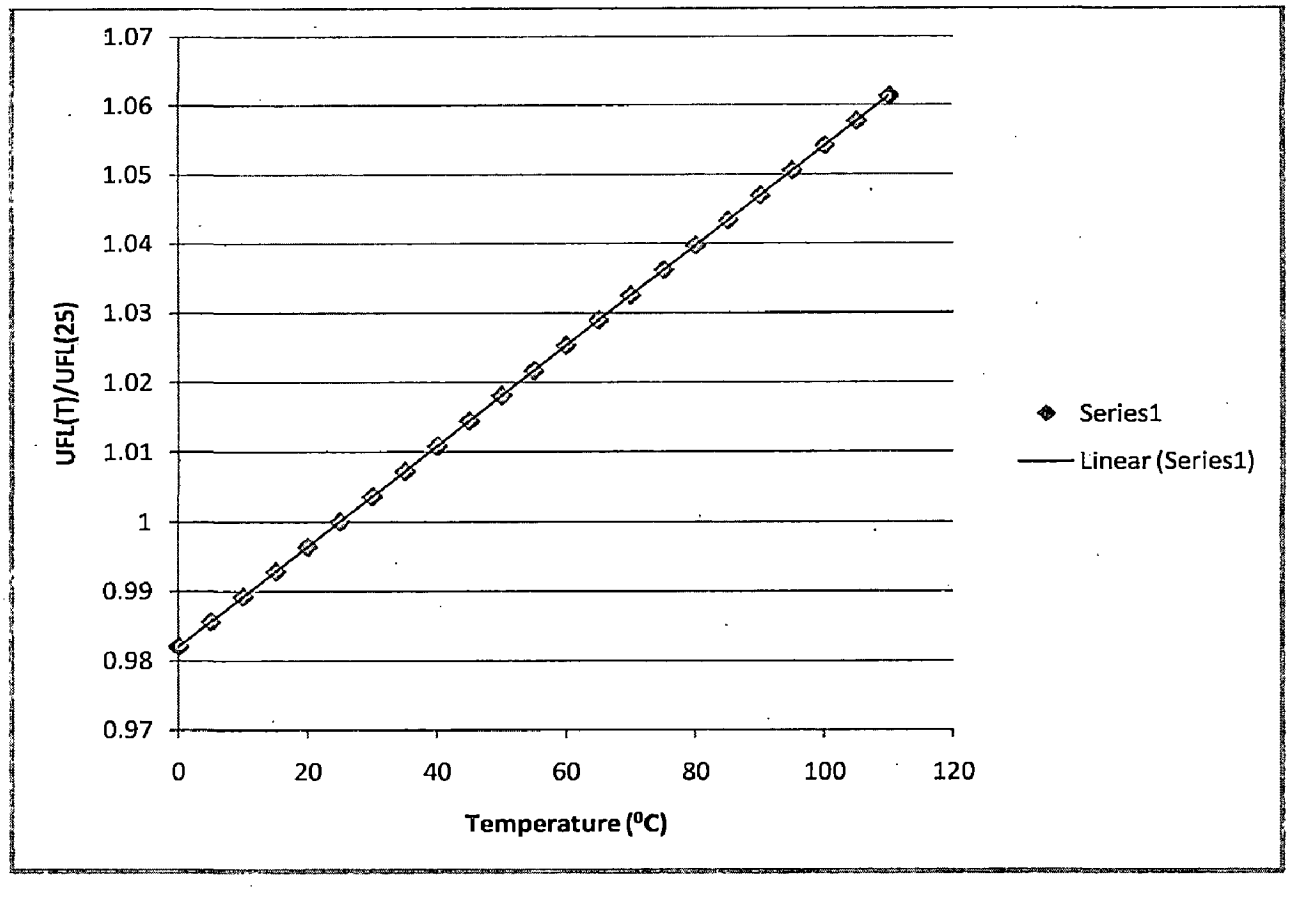

Figure 4.6 Relation between UFL and temperature.

Above graph shows a relation between UFL and temperature. The variation of UFL & temperature is a linear profile.

Similarly LFL is also linearly dependent on temperature.

With the help of equation 3.20, value of LFL & UFL can be found at different pressure & also they are plotted with the help of MS-Exel which is given below:

Table 4.5 Relation between Pressure and LFL

P(atm)	LFL(v/v)	P(atm)	LFL(v/v)
0.1	5.61	3.5	4.513712
0.3	5.271244	3.7	4.496577
0.5	5.113731	3.9	4.480344
0.7	5.00998	4.1	4.464923
0.9	4.932488	5	4.403731
1.1	4.870611	10	4.19
1.3	4.8191	15	4.064975
1.5	4.774975	20	3.976269
1.7	4.736381	40	3.762537
1.9	4.702085	80	3.548806
2.1	4.671224	120	3.423781
2.3	4.643173	160	3.335075
2.5	4.617463	200	3.266269
2.7	4.593732	400	3.052537
2.9	4.571697	600	2.927513
3.1	4.551133	800	2.838806
3.3	4.531855	1000	2.77

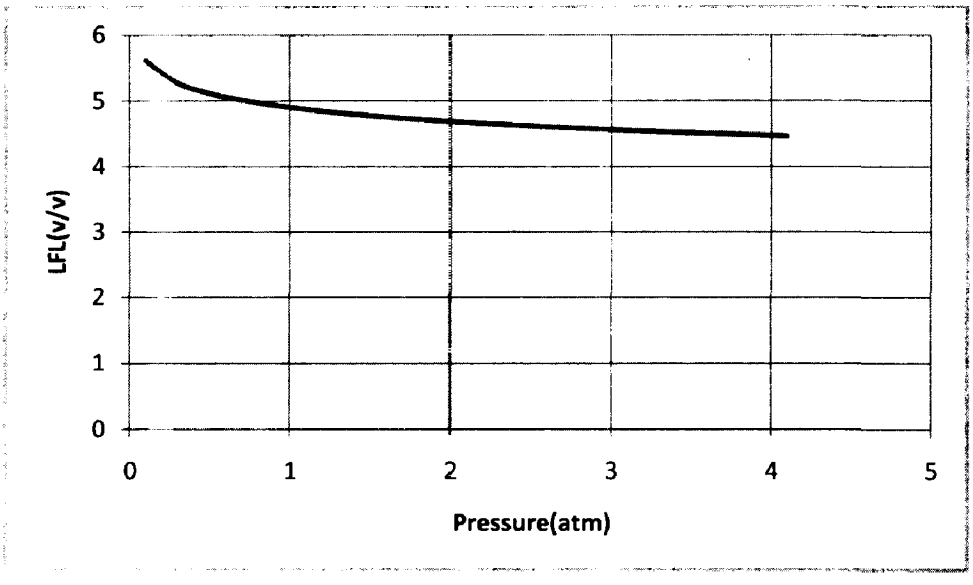

Figure 4.7 Relation between Pressure and LFL at low pressure.

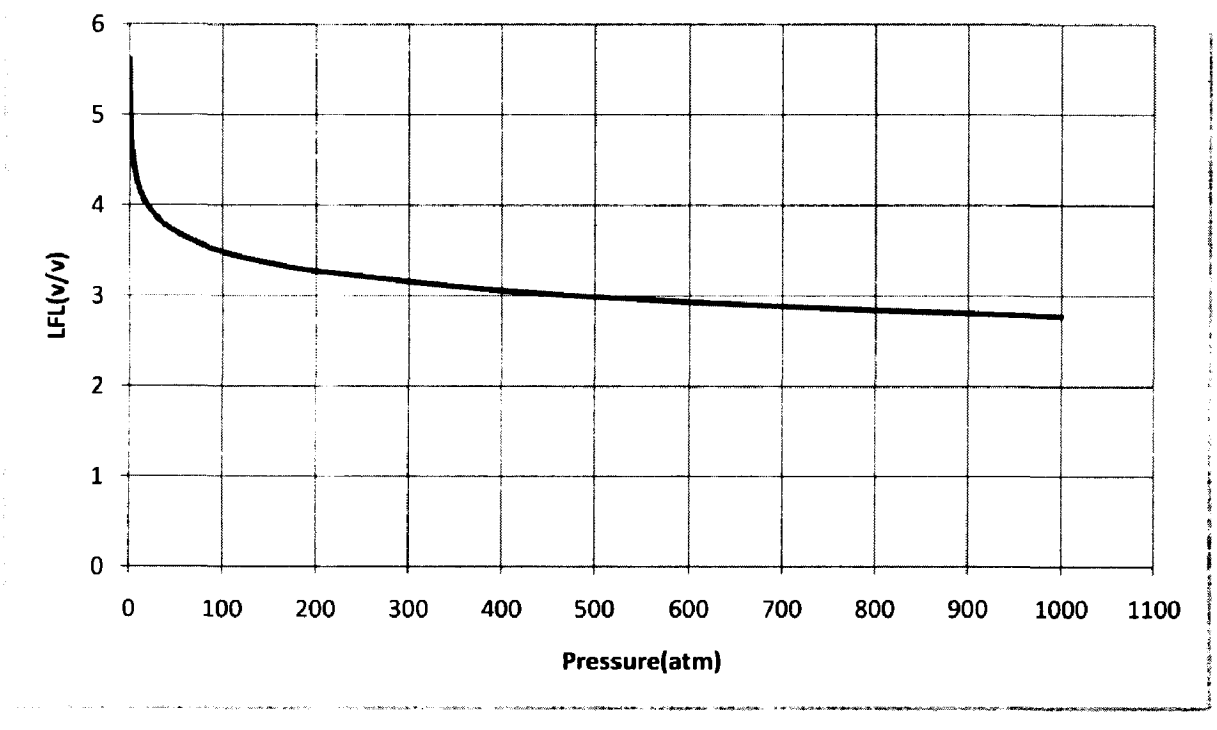

Figure 4.8 Relation between Pressure and LFL at high pressure.

Above graph shows that LFL at high pressure is nearly constant.

Table 4.6 Relation between Pressure and UFL

P(atm)	UFL(v/v)	P(atm)	UFL(v/v)
0.1	-6.3	3.5	25.19899
0.3	3.433274	3.7	25.69132
0.5	7.958988	3.9	26.15772
0.7	10.94	4.1	26.60
0.9	13.16655	5	28.35899
1.1	14.94441	10	34.5
1.3	16.42444	15	38.09226
1.5	17.69226	20	40.64101
1.7	18.80116	40	46.78202
1.9	19.78657	80	52.92304
2.1	20.67327	120	56.5153
2.3	21.47925	160	59.06405
2.5	22.21798	200	61.04101
2.7	22.89982	400	67.18202
2.9	23.53292	600	70.77429
3.1	24.12378	800	73.32304
3.3	24.67768	1000	75.3

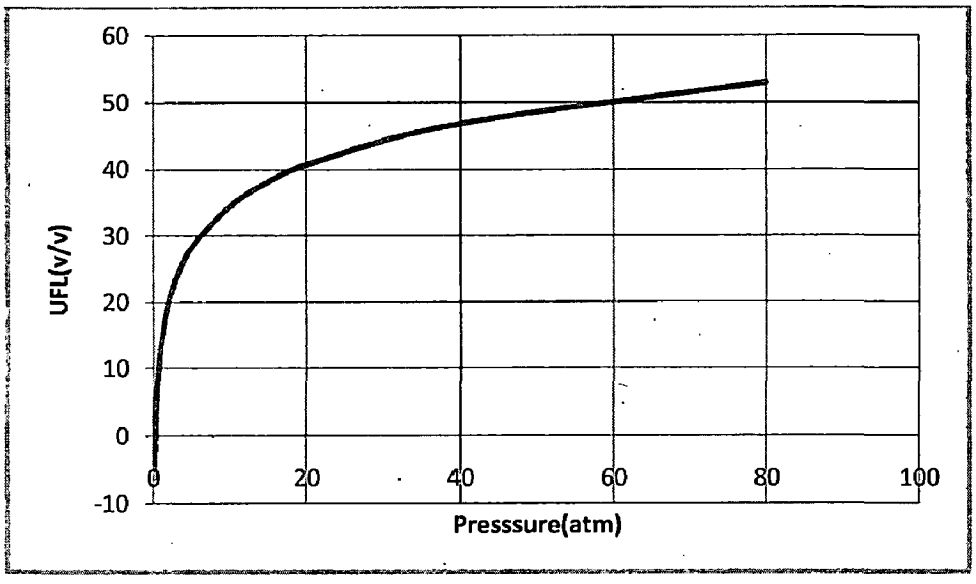

Figure 4.9 Relation between Pressure and UFL at low pressure.

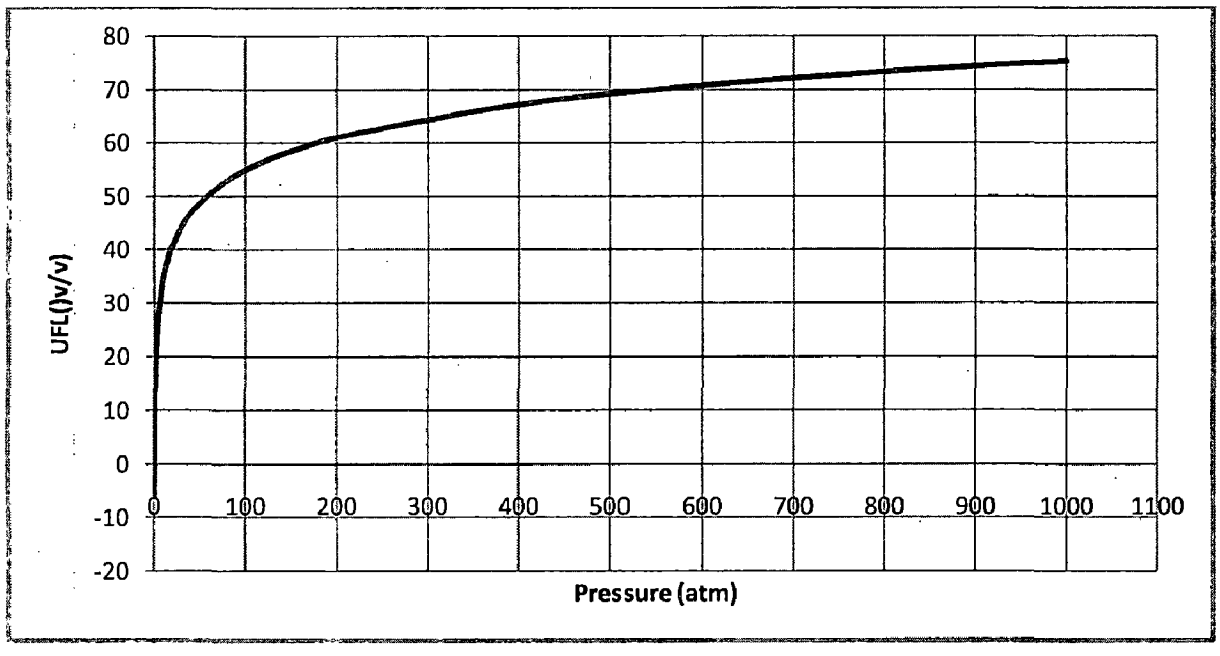

Figure 4.10 Relation between Pressure and UFL at high pressure.

Above graph shows that UFL at high pressure is depend on pressure & increasing.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

The critically reviewed set of data is used to develop predictive correlations for the flammability limits and flash point, so that values may be accurately predicted for chemicals with no experimental data. This method for estimating flammability limits is specially developed for organic compound. In this work flammability limits is calculated based on the number of atoms of the chemical compound, i.e this methods depends upon the standard enthalpy of formation and number of carbon atoms, number of hydrogen atoms, number of oxygen atoms, specific heat capacity etc.

Generally estimation of flash points or flammability limits is based on Le Chatelier's principle and this method is not applicable at elevated temperature and pressure. Some methods requires flash point of all component for the calculation of mixture flash point. This results an error, because list flash point data does not provides reference conditions of temperature and pressure. This method is valid for the condition for which it is developed.

By comparing the predicted value of LFL (or UFL) with the reference value (experimental value) of LFL (or UFL), it is found that there is a small deviation from the desired value. This method is helpful in calculating the flammability limits and flash point effectively.

It is also found that LFL and flash point have polynomial relation relationship with each other for n-Alkane organic compound. This relation is very successfully described by the help of plotted graph. This method is helpful in determining the value of Flash point.

It is to be recommended that more research is performed with other fuels to confirm the general validity of the pressure and temperature dependence of the UFL found in this study.

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