Estimating the flammability of vapours above refinery waste water laden with hydrocarbons mixtures

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Abstract

In this study, the likelihood of fire hazards attributed to the vaporization of hydrocarbon components derived from refinery wastewater drainage systems was assessed. Liquid samples containing mixtures of hydrocarbon products and water were collected from a refinery drainage system and subjected to a distillation process to separate oil and water. The oil-liquid phase was analyzed using Gas Chromatography Mass Spectrometry (GC-MS) to examine the composition of the sample. Hydrocarbon compounds ranging from C_9 to C_{16} were detected. Mole fractions of 28 selected components in the liquid phase were obtained from the GC-FID data and used to calculate mole fractions of components in the gas phase via modified Raoult's law. Lower Flammability Limits (*LFL*s) and Upper Flammability Limits (*UFL*s) for individual components were calculated using a stoichiometric concentration method, while the *LFL* and *UFL* values for the mixture (LFL_{mix} and UFL_{mix}) were calculated using the Le Chatelier equation. The LFL_{mix} and UFL_{mix} values were used to construct a flammability diagram and subsequently used to determine the flammability of the mixture. The findings of this study may assist in minimizing fire hazards associated with presence of hydrocarbon vapours derived from refinery wastewater streams.

Keywords: Gas chromatography; compositions; Lower and Upper Flammability Limits; flammability diagram.

1. Introduction

Refineries are complex systems of numerous chemical process operations that refine crude oil into desired products such as Liquefied Petroleum Gas (LPG), petrochemical naphtha, motor gasoline, kerosene, diesel and other products. Petroleum refineries can consume high quantities of water for operational usage relative to other industrial and domestic users within a geographical region. Consequently, these refineries can generate large volumes of wastewaters containing various petroleum hydrocarbons, heavy metals, sulfur and ammonia at concentrations that typically require treatment (Al-Haddad et al., 2007) prior to final discharge. With respect to hydrocarbon components, highly flammable compounds such as benzene, toluene, ethylbenzene and xylenes may be present and they pose a significant threat of fire hazard. Over time, the mixture of water and hydrocarbon in drainage systems at certain conditions will naturally separate and form distinct liquid phases, based on density and polarity of the material (EPA, 1998). Hydrocarbon compounds from these drainage flows can vary widely in composition from day-to-day due to operational activities such as storage of waste liquids from drains, equipment cleaning and spills. Some of these compounds can evaporate and turn into vapour at ambient temperature and atmospheric pressure, thus creating potentially flammable mixtures in air. The presence of flammable mixtures exposes drainage systems to the possibility of fire and explosion.

The composition of hydrocarbon compounds can be determined and ignitable liquids can be identified (Newman et al, 1997) using comprehensive gas chromatography (GC) systems such as gas chromatography–isotope ratio mass spectrometry (GC–IRMS) and gas chromatography-mass spectrometry (GC-MS). GC analysis can determine the presence, type and concentrations of

contaminated hydrocarbons in wastewater (Senn and Johnson, 1987). However, GC analysis of sample compositions is not sufficient to predict the flammability of hydrocarbon mixtures. In this regard, a flammability diagram method can be suitably used for this purpose (Mashuga and Crowl, 1999). Flammability diagrams generally show the "area" of flammability in mixtures of fuel, oxygen and an inert gas. Mixtures of the three gases are usually depicted in a triangular diagram, also known as a Ternary plot. For more detailed information on the ignitability of mixtures and spark ignition, readers are directed to reviews by Mullins (1955), Lewis and von Elbe (1987), and Mullins and Penner (1959).

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 flammable limit (LFL), that is, the mixture is too lean for combustion. The mixture is also not combustible when its composition is too rich, that is, when it is above the upper flammable limit (UFL). As such, a mixture is flammable only when its composition is between LFL and UFL. These flammability limits can be measured experimentally, though they can still be determined without experimental data (Crowl and Louvar, 2002). There are several available methods, databases and software packages that provide sufficient flammability information for various hydrocarbons and they can be sourced from Coward and Jones (1952), Zabetakis (1965), Sax (1984), Kuchta (1985), Ohtani *et al*. (1994), Brooks and Crowl (2007a) and DIPPR (2010).

The limiting oxygen concentration (LOC) is defined as the minimum oxygen concentration in a mixture of fuel, air and inert gas that will propagate flame and is expressed in volume percent of oxygen (Zlochower and Green, 2009). In essence, LOC varies with pressure and temperature and depends on the type of inert (non-flammable) gas present. A reaction can not generate enough energy to heat the entire gas mixture required for the self-propagation of the

93 flame if the oxygen concentration is below the LOC (Crowl and Louvar, 2002). As such, the
94 LOC is a useful parameter in terms of fire hazard prevention since explosions and fires can be
95 prevented by reducing the oxygen concentration regardless of fuel concentration. This concept is
96 the basis for a common procedure called *inerting* used in safety engineering (Crowl and Louvar
97 2002; ASTM 2009). The LOC can be measured experimentally using a flammability apparatus
98 (British and European Standard, 2007; ASTM 2008a; ASTM 2008b) or it can be found from
99 different resources (NFPA 1994; CHEMSAFE, 2007). An example of experimental LFL and
100 LOC determination can be found from a study conducted by Brooks and Crowl (2007b), in
101 which they experimentally measured the LFL, LOC and the maximum safe solvent concentration
102 (MSSC) for ethanol and acetonitrile above aqueous solutions. If experimental and/or literature
103 data are not available, the LOC can be estimated using the stoichiometric combustion reaction
104 and the LFL. This procedure works relatively well for many different hydrocarbons (Siwek,
105 1996; Crowl and Louvar, 2002).
106 The objectives of this study were to estimate flammability limits and the LOC of the
107 hydrocarbon vapour mixture above refinery wastewater and subsequently determine the
108 flammability of the mixture. This was achieved by incorporating thermodynamics with process
109 safety concepts. Findings from this study can be used to investigate the root cause of fire
110 incidents in drainage systems due to the presence of flammable hydrocarbon vapour mixtures.
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2. Methodology

2.1.1 *Liquid Phase*

Liquid samples were collected from drainage lines in a refinery located in Malaysia. Residual water was removed from the samples using a simple distillation technique. The composition of the organic-phase liquid was analysed using both GC-MS (for identification) and GC-FID (Flame Ionisation Detection) (for quantitation). GC-MS was performed with a Shimadzu QP5050 GCMS using the following settings: Electron impact ionization, electron energy 70 eV and scan range 40 - 500 amu at 1 scan/s. The carrier gas (Helium 99.999%) flow rate was set to 1.5 ml/min with column inlet pressure 54.8 kPa and linear velocity 36.10 cm/sec. The end of the column was directly introduced into the ion source of a mass selective detector operated in an electron impact ionization mode. Samples were injected into a HP5 fused silica (5% phenyl polysilphenylene-siloxane) capillary column BPX5 (30 m length; 0.25 mm i.d.; 0.25 µm film thickness) and the oven temperature was held at 55^{o} C for 2 min. It was then increased to 300^{o}C at 5^{o}C/min and thereafter held for 40 minutes. The components of the liquid sample were identified by comparing their mass spectra with the NIST Mass Spectral Database. Pure samples of a selected number of compounds were analysed using the same GCMS conditions in order to verify the match from the database.

Quantitative analysis of the peaks was performed with a Shimadzu GC2010 with an FID using the same column and temperature parameters as for the GC-MS analysis.

The mass fraction of each component in the liquid phase can be determined from GC-FID data (Eq. 1):

$$\chi_i = \frac{A_i}{A_T} \quad (1)$$

where, χ_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.

The mass fraction is converted to mole fraction using Eq. (2):

$$x_i = \frac{\chi_i / M_i}{\sum \chi_i / M_i} \quad (2)$$

where, x_i is the mole fraction in liquid phase of component *i*, and M_i is the molecular weight of component *i*.

2.1.2 *Vapour Phase*

It was necessary to estimate the concentrations of components in the gas phase, which also contributed to the flammability of the mixture. Modified Raoult's law was used to estimate the amount of liquid vaporized at ambient temperature; Eq. (3) was used to calculate the mole fraction in the gas phase.

$$\gamma_i \, x_i \, P_i^{sat} = \varphi_i \, y_i \, P_t \quad (3)$$

where γ_i is the activity coefficient for component *i*, x_i is the mole fraction of in the 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*, y_i is the mole fraction of component *i* in the vapour phase, and P_t is the total pressure. Theoretically, the activity coefficient, γ_i , for an ideal solution is equal to 1. However, since the mixture is non-ideal (real), the activity coefficient was calculated using the

UNIversal Functional Activity Coefficient (UNIFAC) method. 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. 4) (Fredenslund et al., 1975):

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{4}$$

$\ln \gamma_i^C$ is given by Eq. (5):

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \,.\, \ln \frac{\theta_i}{\Phi_i} + l_i + \frac{\Phi_i}{x_i} \sum_{j=1}^{M} x_j . l_j \tag{5}$$

$$l_j \equiv \frac{z}{2}\left(r_j - q_j\right) - \left(r_j - 1\right) \tag{6}$$

Where z is the average number of nearest neighbours around a group in solution (constant value is used: $z = 10$). The segment fraction, Φ_i , and surface area fraction, θ_i, are defined, respectively by Eqs. (7) and (8):

$$\Phi_i = \frac{r_i x_i}{\sum_{j=1}^{M} r_j x_j} \tag{7}$$

$$\theta_i = \frac{q_i x_i}{\sum_{k=1}^{M} q_j x_j} \tag{8}$$

The molecular volume, r_j , is defined by the sum of its constituent group given by Eq. (9):

$$r_j = \sum_{k=1}^{N} v_k^j . R_k \tag{9}$$

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 the sum of the individual group areas in the molecules given by Eq. (10):

$$q_j = \sum_{k=1}^{N} v_k^j . Q_k \tag{10}$$

where Q_k is the group surface area.

R_k and Q_k are obtained from the van der Waals group volumes and surface areas.

$\ln \gamma_i^R$ was calculated from Eq. (11):

$$\ln \gamma_i^R = \sum_{k=1}^{N} v_k^i \left[ln\Gamma_k - ln\Gamma_k^i \right] \tag{11}$$

where Γ_k^i is the group residual activity coefficient of group k in a reference solution containing only molecules of type i. Γ_k is the group residual activity coefficient in the solution. The coefficients Γ_k^i and Γ_k are related to the composition and temperature according to Eq. (12):

$$\ln \Gamma_k = Q_k \left\{ 1 - ln\left(\sum_{m=1}^{N} \Theta_m . \psi_{mk} \right) - \sum_{m=1}^{N} \left[\frac{\Theta_m . \psi_{km}}{\sum_{n=1}^{N} \Theta_n . \psi_{nm}} \right] \right\} \tag{12}$$

In Eq. (12), the group interaction parameter, ψ_{mk} is defined by Eq. (13):

$$\psi_{mk} = e^{-\frac{a_{mk}}{T}}, \quad a_{mk} \neq a_{km} \tag{13}$$

where a_{mk} is the group interaction parameter between groups n and m. The surface contribution, Θ_m and the mole fraction of the group, X_m are defined by Eqs. (14) and (15), respectively:

$$\Theta_m \equiv \frac{Q_m . X_m}{\sum_{n=1}^{N} Q_n . X_n} \tag{14}$$

$$X_m \equiv \frac{\sum_{j=1}^{M} v_m^j . x_j}{\sum_{j=1}^{M} \sum_{n=1}^{N} v_n^j . x_j} \tag{15}$$

192 The fugacity coefficient, φ_i, for each component in the mixture was determined using the Peng-

193 Robinson method (Eq. (16) (Peng and Robinson, 1976):

194 $$ln\varphi_i = \frac{b_k}{b}(Z-1) - ln(Z-B) - \frac{A}{2\sqrt{2B}} \times \left(\frac{2\sum_i^N x_i a_{ik}}{a} - \frac{b_k}{b} \right) ln\left(\frac{Z+2.414B}{Z-2.414B} \right) \quad (16)$$

195 where φ_i is the fugacity coefficient, b is van der Waals co-volume defined by Eq. (17), Z is the

196 compressibility factor defined by Eq. (18), B is a constant defined by Eq. (19), A is a constant

197 defined by Eq. (20), x_i is the mole fraction, and a is the attraction parameter defined by Eq.

198 (21):

199 $$b = \sum_i^N x_i b_i \quad (17)$$

200 $$Z = \frac{P\nu}{RT} \quad (18)$$

201 $$B = \frac{bP}{RT} \quad (19)$$

202 $$A = \frac{aP}{R^2T^2} \quad (20)$$

203 $$a = \sum_i^N \sum_j^N x_i x_j a_{ij} \quad (21)$$

204 where P is the pressure defined by Eq. (22), T is the temperature, v is the molar volume, R is the

205 universal gas constant, a_{ij} is defined by Eq. (23), and i, j, k are component identifications.

206 $$P = \frac{RT}{\nu - b} - \frac{a(T)}{\nu^2 + 2b\nu - b^2} \quad (22)$$

207 $$a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2} \quad (23)$$

where, δ_{ij} is an empirically determined binary interaction coefficient for components *i* and *j*.

Applying Eq. (24) at the critical point, we obtain:

$$a(T_c) = 0.45724 \frac{(RT_c)^2}{P_c} \tag{24}$$

$$b(T_c) = 0.07780 \frac{RT_c}{P_c} \tag{25}$$

$$Z_c = 0.307$$

At temperatures other than the critical:

$$a(T) = a(T_c).a(T_r, \omega) \tag{26}$$

$$b(T) = b(T_c) \tag{27}$$

where $a(T_r, \omega)$ is a dimensionless function of reduced temperature and acentric factor, ω and equals unity at the critical temperature.

The total pressure for the mixture can be calculated from Eq. (28):

$$P_t = \sum \gamma_i x_i p_i^{sat} \tag{28}$$

The vapour pressures of the components were calculated using the classic (Eq. 29) and extended Antoine equations (Eq. 30):

$$\log_{10} P^{sat} = A - \frac{B}{C + T} \tag{29}$$

$$\log_{10} P^{sat} = A - \frac{B}{T} + C \log_{10} T + DT + ET^2 \tag{30}$$

where

P^{sat} is the vapour pressure (mmHg) while *A*, *B*, *C*, and *D* are the component-specific constants. These constants were obtained from several sources (Wichterle and Linek, 1971; Yaws, 1992; Dykyj et al., 1999; Yaws et al., 2009; www.chemspider.com).

2.2.1 *LFL and UFL*

For some situations, it may be necessary to estimate the flammability limits without experimental studies. Jones (1938) found that for many hydrocarbon vapours, the *LFL* and *UFL* were functions of the stoichiometric concentration of fuel (C_{st}) (Eq. 31 and Eq. 32):

$$LFL = 0.55C_{st} \tag{31}$$

$$LFL = 3.5C_{st} \tag{33}$$

The stoichiometric concentration, C_{st} for organic compounds was determined using the general combustion reaction (Eq. 33).

$$C_m H_x O_y + zO_2 \rightarrow mCO_2 + \left(\frac{x}{2}\right) H_2O \tag{33}$$

where z is equivalent moles O_2/moles fuel which can be determined from Eq. (34):

$$z = m + \frac{x}{4} - \frac{y}{2} \tag{34}$$

The stoichiometric concentration, C_{st} can be determined as a function of z by Eq. (35):

$$C_{st} = [\text{moles fuel}/ (\text{moles fuel} + \text{moles air})] \times 100 = \frac{100}{[1 + (z/0.21)]} \tag{35}$$

Substituting Eq. (34) into Eq. (35) and applying Eq. (31) and Eq. (32) yield Eqs. (36) and (37):

$$LFL\,(vol\ \%) = \frac{0.55(100)}{4.76m + 1.19x - 2.38y + 1} \tag{36}$$

$$UFL\,(vol\%) = \frac{3.50(100)}{4.76m + 1.19x - 2.38y + 1} \tag{37}$$

where *LFL* and *UFL* are the lower and upper flammable limits, respectively.

The *LFL* and *UFL* for mixtures (LFL_{mix} and UFL_{mix}) were calculated using the Le Chatelier equation (Eqs. 38 and 39) (Le Chatelier, 1891):

$$LFL_{mix}\,(vol\%) = \frac{1}{\sum\left(y_i/LFL_i\right)} \tag{38}$$

$$UFL_{mix}\,(vol\%) = \frac{1}{\sum\left(y_i/UFL_i\right)} \tag{39}$$

where LFL_i and UFL_i are the lower and upper flammable limits, respectively, for component *i* in fuel and air while *n* represents the number of combustible species.

2.2.2 *Limiting Oxygen Concentration (LOC)*

LOC can be estimated using the stoichiometry of the combustion reaction and the *LFL* (Crowl and Louvar, 2002). Eq. (40) can also be used to estimate LOC for a vapour mixture (Zlochower and Green, 2009):

$$LOC_{mix} = \sum y_i\, R_i \,/ \sum y_i \,/\, L_i^* = \sum y_i\, R_i \,/ \sum y_i\, R_i \,/ LOC_i \tag{40}$$

$$L_i^* = LOC_i \,/ R_i \tag{41}$$

where LOC_{mix} is the limiting oxygen concentration for the vapour mixture (vol%), 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 (vol%). Figure 1 shows the methodology outline adopted in this study.

3. Results and Discussion

3.1 *Compositions*

The components were identified using a combination of the retention time, comparison of mass spectrum derived from GC-MS analysis of the hydrocarbon mixture to a mass spectral library, and comparison to known standards. Figure 2 shows the retention time and peak abundance data for 77 components detected in the liquid phase via GC-MS analysis. Considering the difficulties of relying solely on mass spectral database matching for the identification of compounds that are very similar in molecular structure, it was felt prudent to take the following precautions in deciding which of the 77 individual compounds observed in the gas chromatogram should be used in calculations. Firstly, using pure compounds that were readily available it was ascertained that peaks 3, 14, 41, 52, 75, and 77 were simple straight chain hydrocarbons (Table S1 - electronic Supplementary material) and that the compound ID from the NIST database matched with the compounds injected. These results confirmed that the output from the mass spectral comparison was valid, particularly for compounds with higher than 95% match. Subsequently, all compounds with a minimum 95% database match were considered to have been correctly identified. As a check on this assumption it was noted that the database identification of peaks 28, 42, 50, and 63 were for simple straight chain alkanes and produced a homologous series with the positively identified compounds. Additionally, it was noted that the difference in retention times between these compounds, running from nonane to hexadecane, were consistent providing further evidence that these were compounds of a homologous hydrocarbon series. There are 28 compounds (Table S1- also contains the properties relevant for

this study) that meet the above criteria and their order of elution based on their boiling points, (i.e. those with higher boiling points elute later) is also consistent with expected results. These selected 28 compounds cover all the major identified peaks (including numbers 42, 50, 63) and account for a 56% of the total area in the chromatogram (as determined from GC-FID data).

The identification of individual components shows that the liquid sample contains a large number of hydrocarbon components ranging from C_9 to C_{16}. The predominant hydrocarbon groups are alkane and alkene with a relatively minor presence of arenes. The peak numbers 14, 28, 41, 52, 65, and 75 are assigned to decane, undecane, dodecane, tridecane, tetradecane, and pentadecane, respectively, and these six components constitute more than 43% of the total chromatogram area,. The mass fraction of each component was estimated by dividing the GC-FID peak area of each component by the total peak area. The mass fraction was then converted to mole fraction according to Eq. (2) and the resulting distribution for the mole fraction for each component x_i in the liquid phase is shown in Figure 3.

3.2 *Mole Fraction in Vapour Phase*

The activity and fugacity coefficients for all components in the vapour mixture are calculated and the values shown in Table S1. The average activity and fugacity coefficients for the vapour mixture were determined to be 1.02 and 0.88 respectively. Figure 4 shows the mole fraction for each component in the vapour phase, y_i based on combustible basis. Interestingly, the values of y_i for most components are small; possibly due to the low volatility of the heavy hydrocarbon components detected in the liquid phase. The low volatilities of the components were due to the low vapour pressure, which range from 5×10^{-3} mmHg to 6.74 mmHg. The total

mole fraction of the vapour mixture is 0.12 vol %, while the air content in the mixture is 99.88 vol%. Therefore, the percentages of N_2 and O_2 in the mixture are approximated to be 79 vol% and 21 vol%, respectively.

3.3 *LFL*, *UFL*, and *LOC*

The calculated *LFL* and *UFL* as well as *LOC* values are listed in Table S1. The calculated *LFL* and *UFL* values are in agreement with those obtained from other databases and open literatures (Figures 5a and 5b). It should be noted that not all *LFL* and *UFL* values could be found in other database and published literatures and some of these values were not indicated in Table S1. The LFL_{mix} and UFL_{mix} are determined to be 0.72 vol% and 4.60 vol%, respectively while the LOC_{mix} value is 11.40 vol%.

3.4 *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, (1) fuel (hydrocarbon vapour mixture), (2) inert material, and (3) oxygen. In order to plot the flammability diagram, concentrations of the fuel, oxygen, and inert material (in volume or mole %) are required. The air line is plotted by taking the compositions of air from Table S1 (78.91 % nitrogen and 20.98 % oxygen). The intersection of the stoichiometric line with the oxygen axis is given by $100\left(z/1+z\right)$ (Crowl and Louvar, 2002). The LOC_{mix} line can be drawn by locating the LOC_{mix} value (11.40%) 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 6 represents the triangular flammability diagram for the hydrocarbon mixture. It can be clearly seen that the stoichiometric line crosses the flammable zone. Therefore, it can be inferred that the vapour mixture is flammable.

4. Conclusions

In this study, theoretical work including thermodynamic fundamentals and flammability calculations were applied to estimate the flammability limits of hydrocarbon vapours derived from refinery wastewater. Detailed inspection of the customised flammability diagram showed that the vapour mixture derived from the wastewater was flammable and may pose a potential fire hazard. As such, it is always prudent for refinery workers to exercise caution when handling wastewater laden with hydrocarbon residuals. Findings from this study afford a useful basis for safety officers and engineers from other refineries to assess the potential fire hazards associated with hydrocarbon vapours derived from wastewater streams.

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Figure Captions

Fig.1. Flowchart on the methodology used in this study.

Fig. 2. GC analysis for the liquid sample.

Fig. 3. Percentages of hydrocarbon mole fractions in the liquid phase.

Fig. 4. Percentages of hydrocarbon mole fractions in the vapour phase.

Fig. 5a&b. Comparison between calculated and literature values of *LFL and UFL.*

Fig. 6. Triangular flammability diagram of the hydrocarbon mixture.

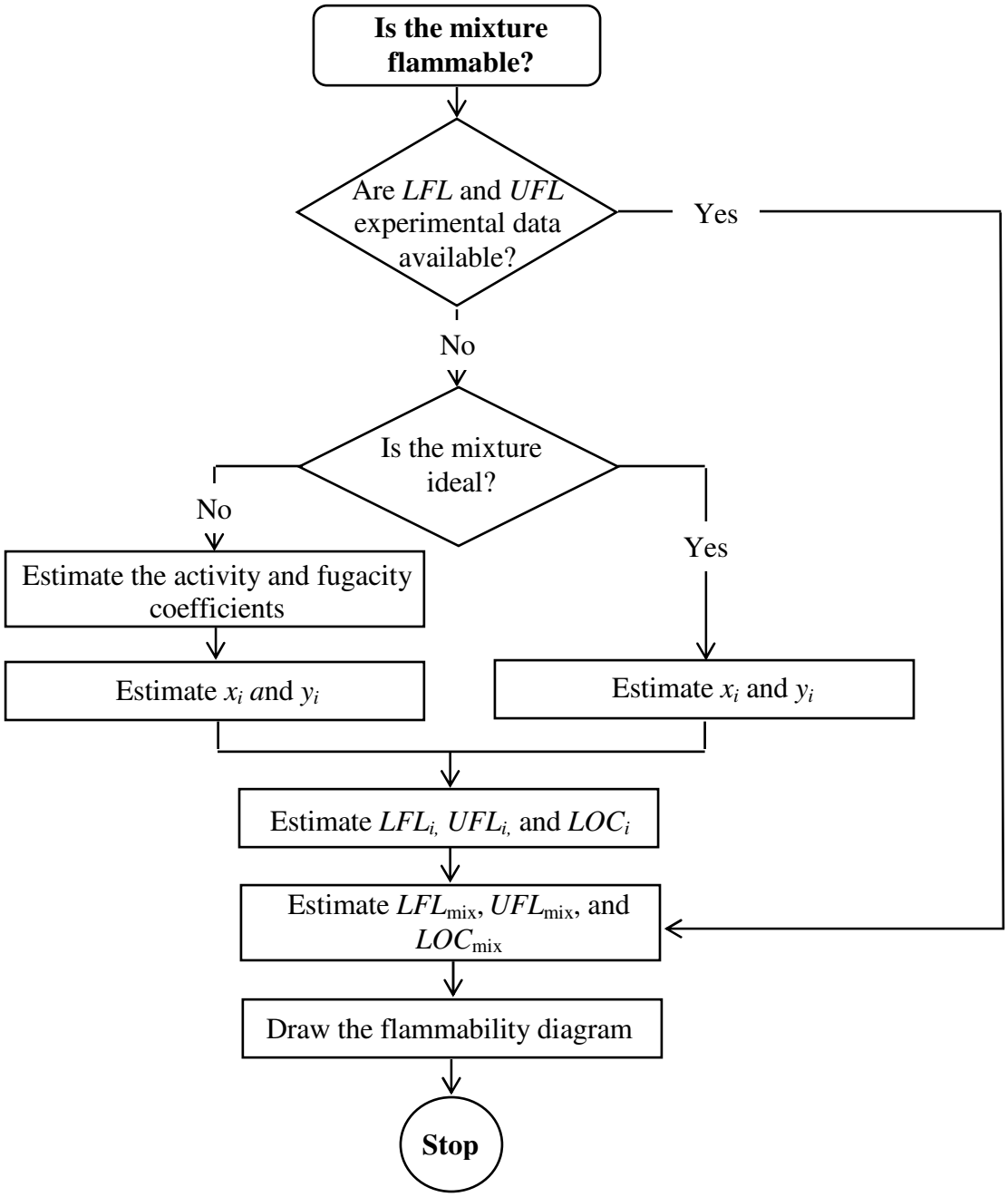


Fig. 1: Flowchart on the methodology used in this study.

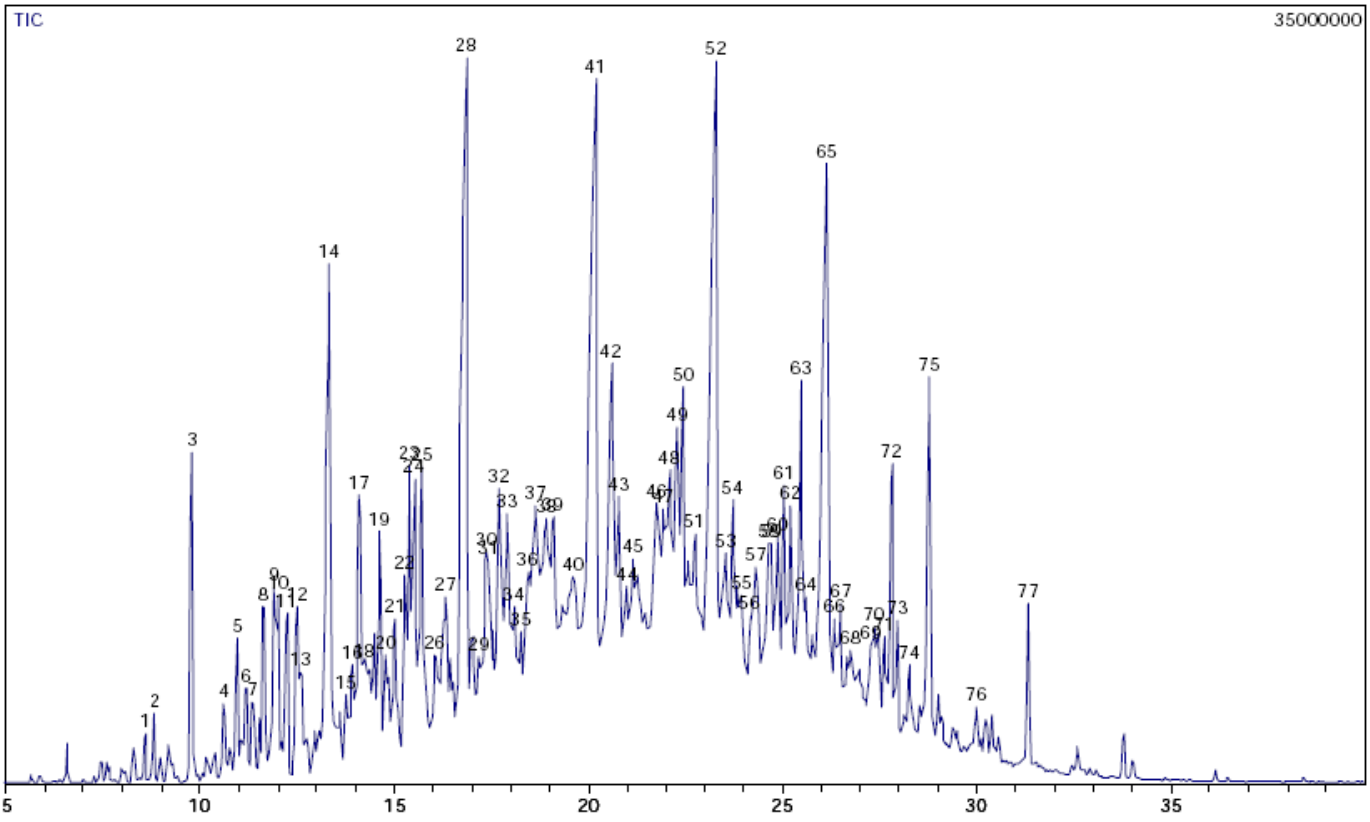


Fig. 2. GC-MS analysis for the liquid sample.

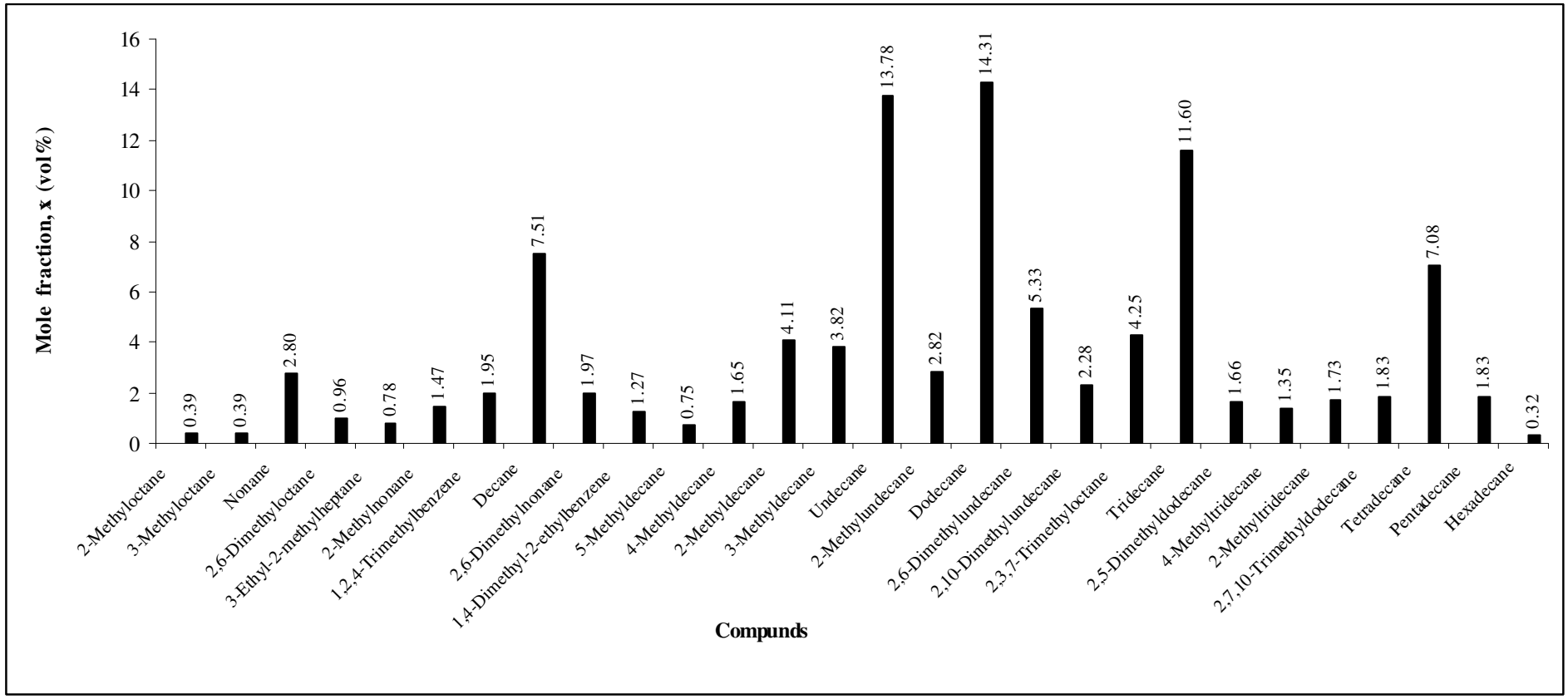


Fig. 3. Mole fractions of the selected 28 hydrocarbon components in the liquid phase.

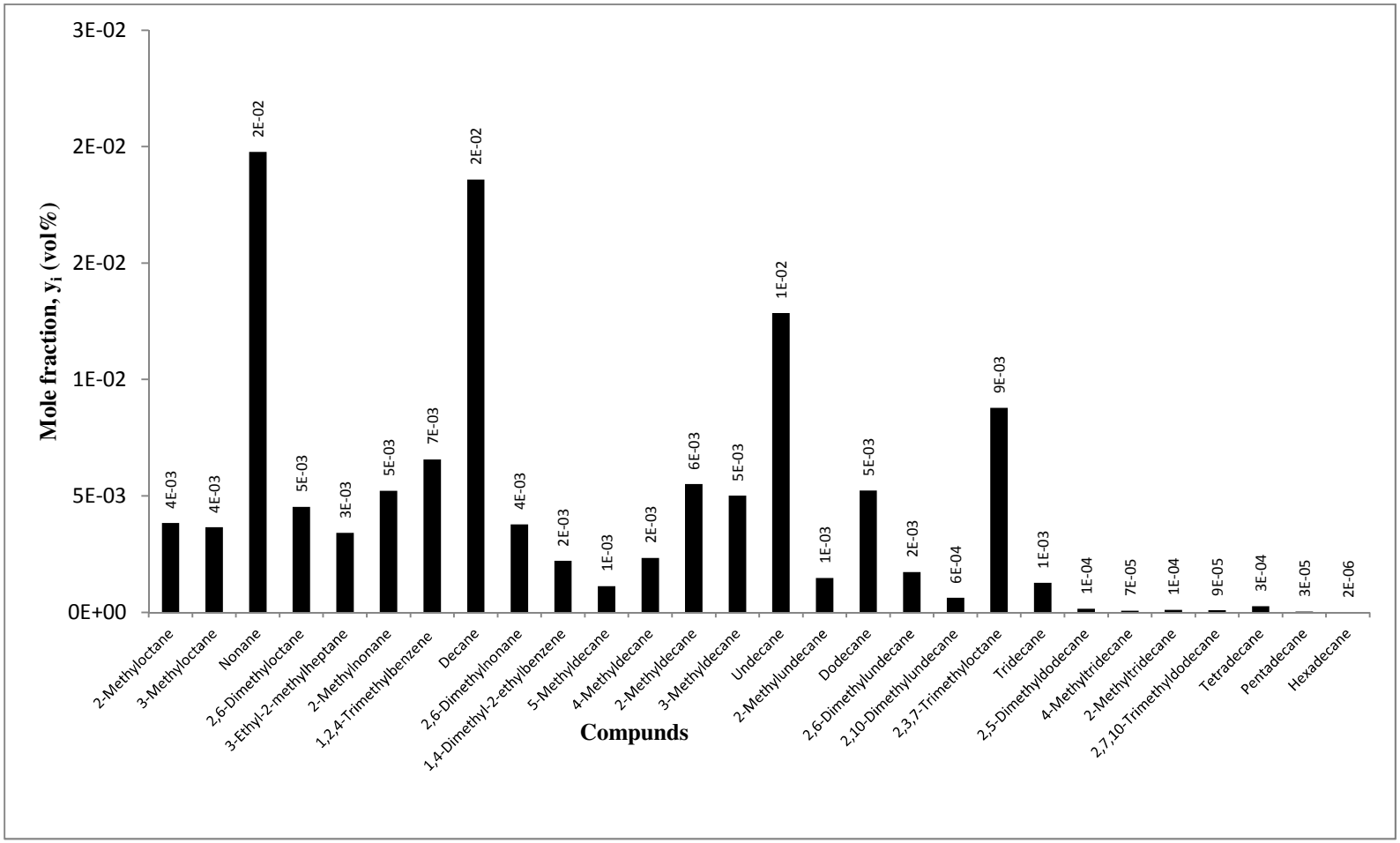
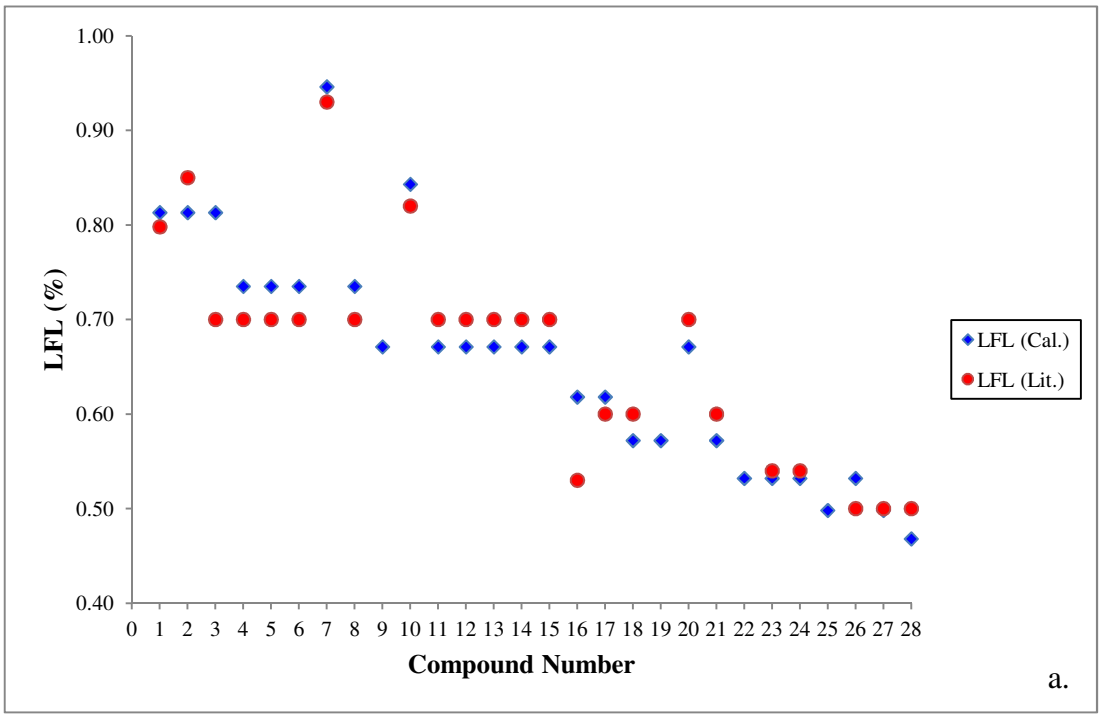
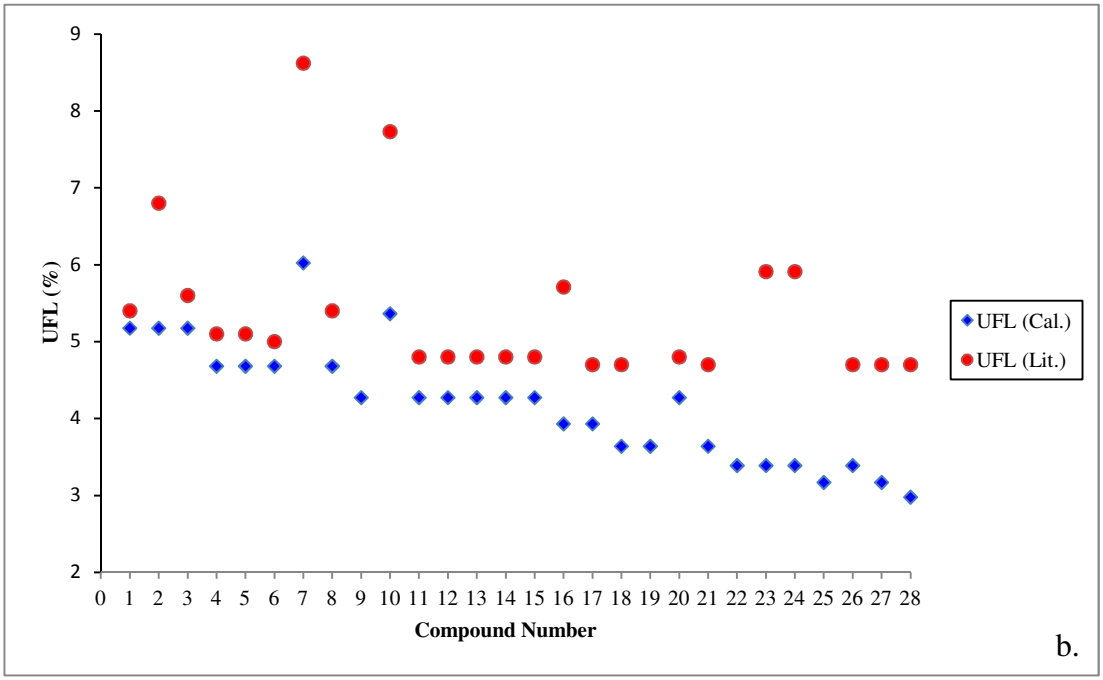


Fig. 4. Mole fractions of the selected 28 hydrocarbon components in the vapour phase.





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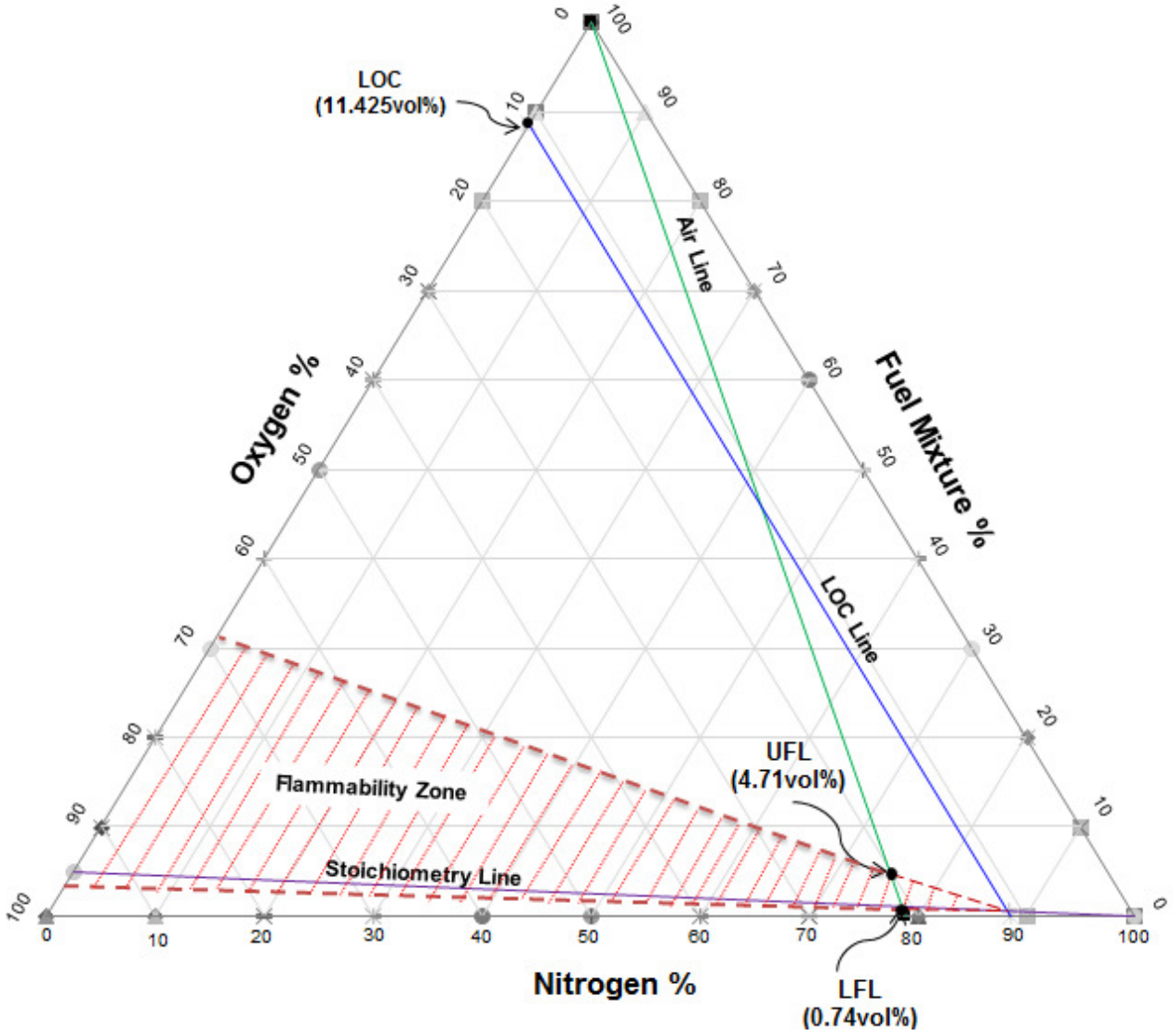

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