A Study on Flammability of Bio Oil Combustible Vapour Mixtures

Mohanad El-Harbawi , Nurul Amirah Hanim Bt. Umar , Norizan Ali , and Yoshimitsu Uemura

Abstract—Study of fire and explosion is very important mainly in oil and gas industries due to several accidents which have been reported in the past and present. In this work, we have investigated the flammability of bio oil vapour mixtures. This mixture may contribute to fire during the storage and transportation process. Bio oil sample derived from Palm Kernell shell was analysed using Gas Chromatography Mass Spectrometry (GC-MS) to examine the composition of the sample. Mole fractions of 12 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 obtained from published literature. However, stoichiometric concentration method was used to calculate the flammability limits of some components which their flammability limit values are not available in the literature. The LFL and UFL values for the mixture 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 can be used to propose suitable inherently safer method to prevent the flammable mixture from occurring and to minimizing the loss of properties, business, and life due to fire accidents in bio oil productions.

Keywords—Gas chromatography, compositions, lower and upper flammability limits (LFL & UFL), flammability diagram.

I. INTRODUCTION

IN the developed and modern societies, energy sources play a significant role in human's life. People rely on the energy resources for homes, business and transportations. The world populations and global demand for energy supply are keeping increasing. In addition, the fossil fuel reserves (oil, coal, and gas) will be exhausted in less than another 30 years [1]. Therefore, recent development in bio oil production as a renewable energy source seems to be an ideal solution for global energy demands.

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Bio oil is mainly derived from biological carbon fixation or from biomass conversion. It can be produced from forest by-products such as wood, lumber, sawdust, and bark or from agricultural wastes such as bagasse, palm oil waste, peanut oil waste, coconut waste, canola oil waste, rice hush, and others. Bio oil is generally made up of different constituents: 20-25% water, 25-30% water insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars and 10-25% of other oxygenated compounds [2]. Milne et al. [3] summarized the composition of fast pyrolysis oils.

In general, bio oil is considered to be much safer than fossil fuels, due to its high flash point. The heating value of biooil is 40-45 % of that for fossil fuels [4]. Therefore, bio oil is much less flammable than other fossil fuels. However, bio oil is combustible but not flammable because of the low content of volatile components. Bio oil will combust if it is heated up to over 150 °C. Bio oil contains large assembly of organic compounds such as benzoic acid, acetic acid, formic acid, phenol, furfural, benzene, acetone, etc. According to Tian et al. [5], bio oil is a good potential source of light aromatics such as benzene, toluene and xylene. These components are similar to fossil fuel. Therefore it 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 fire. Prevention of unwanted fire accidents requires knowledge of flammability characteristics [6]. The first step in conducting flammability analysis has to involve characterizing the crucial flammability properties of chemicals that might potentially incur a fire/explosion in a plant. Fire triangle indicates that three elements necessary to ignite ordinary burning and fires are: fuel, oxygen and heat. Fire might end up in explosion, provided that certain parameters, i.e. the Lower Explosive Limit (LEL) and Upper Explosive Limit (UEL). 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 [7]. There are several available methods, databases and softwares that provide sufficient flammability information for various hydrocarbons and they can be found in different resources [6, 8-15].

Another important parameter to prevent fire is limiting oxygen concentration (LOC). 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 [15]. In essence, LOC varies with pressure and temperature and depends on the type of inert (non-flammable) gas present. A reaction cannot generate enough energy to heat the entire gas mixture required for the self-propagation of the flame if the oxygen concentration is below the LOC [7]. As such, the LOC is a useful parameter in terms of fire hazard prevention since explosions and fires can be prevented by reducing the oxygen concentration regardless of fuel concentration.

One of the well-known methods to examine the flammability of vapour mixtures is flammability diagram method. Flammability diagrams generally show the "area" of flammability in mixtures of fuel, oxygen and an inert gas. Flammability diagram method is described in details by several researches [7, 16-18].

The objective of this study is to estimate the flammability of bio oil vapour mixture. Findings from this study can be used to investigate the root cause of fire incidents caused by bio oil vapour mixtures.

II.   METHODOLOGY

Evaluation of a material's flammability requires data from different laboratory tests combined with analysis and modelling to interpret the results properly. The methodology of this work is incorporate experimental and theoretical methods in order to examine a flammability of bio oil mixture.

A.   Bio Oil Sample (Liquid Phase)

In this study, the bio oil sample has been collected from biofuel centre at Universiti Teknologi PETRONAS, Malaysia. Bio oil used is this work was obtained from Palm Kernell Shell by fast pyrolysis process [19]. The process has been carried out in a fluidized bed fast pyrolysis unit under nitrogen gas flowrate of 1.35 m^3/h, with reactor temperature ranges from 400-600°C. Fast pyrolysis involves rapid heating of biomass and short vapour residence time. Heating rate is 300°C/min and the vapour residence time is below than 2 seconds.

The composition of the bio oil sample was analysed using both GC-MS (for identification) and GC-FID (Flame Ionisation Detection) (for quantitation). GC-MS was performed with Agilent7890A 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. Sample was injected into a HP5 fused silica (5% phenyl polysilphenylene-siloxane) capillary column BPX5 (30 m length; 0.25 mm i.d.; 0.25 μmfilm thickness) and the oven temperature was held at 35°C for 2 min. It was then increased to 250°C at 20°C/min and thereafter held for 20 minutes. The temperature of injection and detector port is 280°C.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 Shimadzu GC2014 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):

$$\psi_i = \frac{A_i}{A_T} \tag{1}$$

where,

ψ_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):

$$x_i = \frac{\psi_i / M_i}{\sum \psi_i / M_i} \tag{2}$$

where,

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

M_i is the molecular weight of component i.

B.   Vapour Phase

It was necessary to estimate the concentrations of components in the vapour phase, which has the major contribution to the flammability of the vapour mixture. Modified Raoult's law was used to estimate the amount of liquid vaporized at ambient temperature (Eq. 3).

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

where,

γ_i is the activity coefficient for component i,

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.

The activity coefficient for each component was calculated using COSMO-RS software. The fugacity coefficient, φ_i for each component in the mixture was determined using the Peng-Robinson method [20].

The total pressure for the mixture can be calculated from Eq. (4):

$$P_t = \sum \gamma_i\, x_i\, p_i^{sat} \tag{4}$$

The vapour pressures, p_i^{sat} of the components were calculated using Antoine equation [21]. Antoine equation constants were obtained from several sources [22, 23].

The flammability limits (LFL and UFL) for the components were obtained from different resources [14, 15]. However, flammability limits for some components (both

LFL and UFL) values that were not present in the published literature had been estimated using empirical equations proposed by Jones [24]. While, the *LFL* and *UFL* for mixtures (LFL_{mix} and UFL_{mix}) were calculated using the Le Chatelier equation [25]. LOC can be estimated using the stoichiometry of the combustion reaction and the *LFL* [7]. LOC for a vapour mixture can be calculated according to the model proposed by Zlochower and Green [15]. Figure 1 shows the methodology outline adopted in this study.
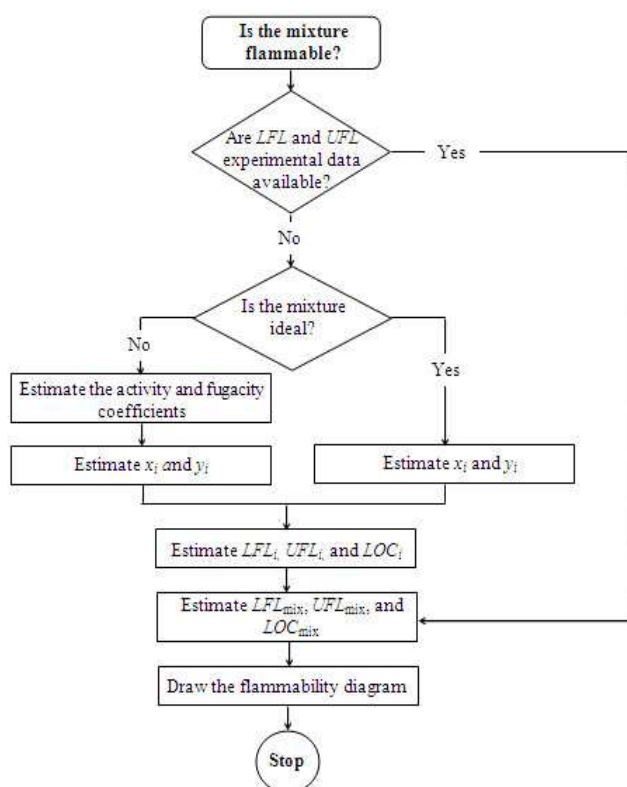

Fig. 1 Flowchart on the methodology used in this study

III. RESULTS AND DISCUSSIONS

The components of the sample were identified using GC-MS. The mass spectrometry analysis was conducted using Agilent 7890A mass selective detector. Figure 2 shows the retention time and peak abundance data for 42 components detected in the liquid phase via GC-MS analysis. This study has considered only the major peaks due to the difficulties of relying solely on mass spectral database matching for the identification of compounds that are very similar in molecular structure. These major peaks with matching percent> 95% are presented in Table 1. These major peaks constitute more than 85 % of the original sample components, which comprised 42 components. The validity of the 12 identified components by GC-MS was confirmed by pure injection test for each component. The results indicated that the GC-MS assignments are valid as described by Table I. The mass fraction of each component was estimated by dividing the GC-FID peak area of each component by the total peak areas (Eq. 1). The mass fraction then converted to mole fraction according to Eq. (2). Figure 3 shows the result distribution for the mole fraction for each component x_i in the liquid phase as calculated using compositional data determined by the GC-FID data. The mole fractions in the vapour phase have been estimated using the modified Raoult's law (Eq. 3). The activity and fugacity coefficients for all components in the vapour mixture are calculated and the values shown in Table 2. The average activity and fugacity coefficients for the vapour mixture were determined to be 1.32 and 0.88 respectively. Figure 4 shows the mole fraction for each component in the vapour phase, y_i based on combustible basis. The total mole fraction of the vapour mixture is 0.46 vol%, while the air content in the mixture is 99.54 vol%. Therefore, the percentages of N_2 and O_2 in the mixture are approximated to be 78.63 vol% and 20.90 vol%, respectively.

The LFL_{mix} and UFL_{mix} are determined to be 4.25vol% and 14.74vol%, respectively; while the LOC_{mix} value is 10.72vol%.

The flammability diagram (Fig. 5) generated according to the method described by Crowl and Louvar [7]. It can be clearly seen that the stoichiometric line did crosses the flammable zone. Therefore, it can be inferred that the vapour mixture is not flammable.

IV. CONCLUSION

In this study, experimental analysis was conducted using GC-MS to examine the composition of the bio oil sample. In addition, GC-FID was used to estimate the quantity of the components in the vapour phase. The results indicated that several components were presented in the bio oil sample. The flammability of the vapour mixture was predicted via theoretical work including thermodynamic fundamentals and flammability calculations. This study revealed that the vapour mixture of the bio oil sample which was studied is not flammable at ambient temperature and atmospheric pressure. Findings from this study afford a useful basis to assess the potential fire hazards associated with bio oil derive from agricultural waste.

TABLE I
VERIFICATION OF GC-MS PEAK ASSIGNMENTS

No.	R_T (min) GC-MS	R_T (min) GC-FID	Compound	Formula	Database match %	Verified by standard	Bp °C	M_i	Area (Abundance)
1	2.81	3.674	Acetic acid	$C_2H_4O_2$	91	/	117.1	60.0	1988878
2	5.084	5.923	Furfural	$C_5H_4O_2$	96	/	161.8	96.0	637948
3	6.678	7.492	Phenol	C_6H_6O	96	/	181.8	94.0	7933644
4	7.375	7.697	2-Methylphenol	C_7H_8O	98	×	191.0	108.1	138239
5	7.623	7.944	2-Methoxyphenol	$C_7H_8O_2$	97	×	205.0	124.1	298143
6	7.872	8.309	2,4-Dimethylphenol	$C_8H_{10}O$	95	×	210.9	122.1	205042
7	8.46	8.47	2-Methoxy-4-methylphenol	$C_8H_{10}O_2$	96	×	220.0	138.1	275754
8	9.103	9.354	4-Ethyl-2-methoxyphenol	$C_9H_{12}O_2$	96	×	246.5	152.1	1125923
9	9.865	9.857	4-Methoxybenzoic acid	$C_8H_8O_3$	96	×	278.3	152.0	149649
10	10.092	10.634	Vanillin	$C_8H_8O_3$	95	×	282.6	152.0	137216
11	10.967	10.917	Dodecanoic acid	$C_{12}H_{24}O_2$	97	×	296.1	200.2	89741
12	12.944	13.141	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	95	×	332.1	270.3	79705

TABLE II
FLAMMABILITY LIMITS OF THE VAPOUR MIXTURE CALCULATION

| No.	Compound	Area (Abundance)	Mass Fraction, x_i	Mole Fraction x_i (vol%)	LFL (vol.%)	UFL (vol.%)	P^{sat} (mmHg)	Activity Y_i	Fugacity $Ø_i$	$x_i*P^{sat}*Y_i$	$Pt*Ø_i$	y_i(vol%)	y_i(%)	y_i/LFL_i	y_i/UFL_i	z	LOC_i (vol%)	z/(1+z)	$\sum y_i*z$	$\sum(y_i*z)/LOC_i$
1	Acetic acid	1988878	0.152	23.41	5.4	16.0	13.87	0.92	0.950	300.323	721.92	4.2E-01	9.0E-01	1.7E-01	5.6E-02	2	10.80	66.67	1.79	0.17
2	Furfural	637948	0.049	4.69	2.1	19.3	2.23	0.17	0.934	1.783	709.92	2.5E-03	5.4E-03	2.6E-03	2.8E-04	5	10.50	83.33	3E-02	3E-03
3	Phenol	7933644	0.607	59.61	1.5	8.6	0.61	0.86	0.930	31.310	706.72	4.4E-02	9.5E-02	6.4E-02	1.1E-02	7	10.50	87.50	0.67	6E-02
4	2-Methylphenol	138239	0.011	0.90	1.4	7.6	0.38	0.95	0.909	0.326	690.61	4.7E-04	1.0E-03	7.3E-04	1.3E-04	8.5	11.90	89.47	9E-03	7E-04
5	2-Methoxyphenol	298143	0.023	1.70	1.3	9.6	0.18	1.16	0.900	0.351	683.85	5.1E-04	1.1E-03	8.5E-04	1.2E-04	8	10.40	88.89	9E-03	9E-04
6	2,4-Dimethylphenol	205042	0.016	1.19	1.1	6.4	0.13	1.10	0.892	0.168	677.92	2.5E-04	5.3E-04	4.9E-04	8.4E-05	10	11.00	90.91	5E-03	5E-04
7	2-Methoxy-4-methylphenol	275754	0.021	1.41	1.2	7.6	0.08	1.75	0.889	0.193	675.26	2.9E-04	6.1E-04	5.2E-04	8.1E-05	9.5	11.30	90.48	6E-03	5E-04
8	4-Ethyl-2-methoxyphenol	1125923	0.086	5.23	1.0	6.6	0.02	1.60	0.880	0.142	668.50	2.1E-04	4.6E-04	4.4E-04	7.0E-05	11	11.33	91.67	5E-03	4E-04
9	4-Methoxybenzoic acid	149649	0.011	0.70	1.3	8.4	2.0E-3	1.01	0.878	0.168	666.98	2.1E-06	4.5E-06	3.4E-06	5.4E-07	8.5	11.27	89.47	4E-05	3E-06
10	Vanillin	137216	0.011	0.64	1.2	8.8	2.0E-3	0.30	0.823	4E-04	625.10	6.2E-07	1.3E-06	1.1E-06	1.5E-07	8.5	10.20	89.47	1E-05	1E-06
11	Dodecanoic acid	89741	0.007	0.32	0.6	5.1	1.0E-3	2.74	0.788	9E-04	598.88	1.4E-06	3.1E-06	5.2E-06	6.1E-07	17	10.20	94.44	5E-05	5E-06
12	Hexadecanoic acid, methyl ester	79705	0.006	0.21	0.03	3.2	1.5E-4	3.27	0.755	1E-04	573.80	1.8E-07	3.8E-07	1.3E-05	1.2E-07	24.5	0.74	96.08	9E-06	1E-05
Total		13059882	1	100			17.51	15.83	10.53	334.599	7999.46	0.46	1	0.24	0.07		120.14	1058.38	2.52	0.24
Average								1.32	0.88								10.01	88.20		
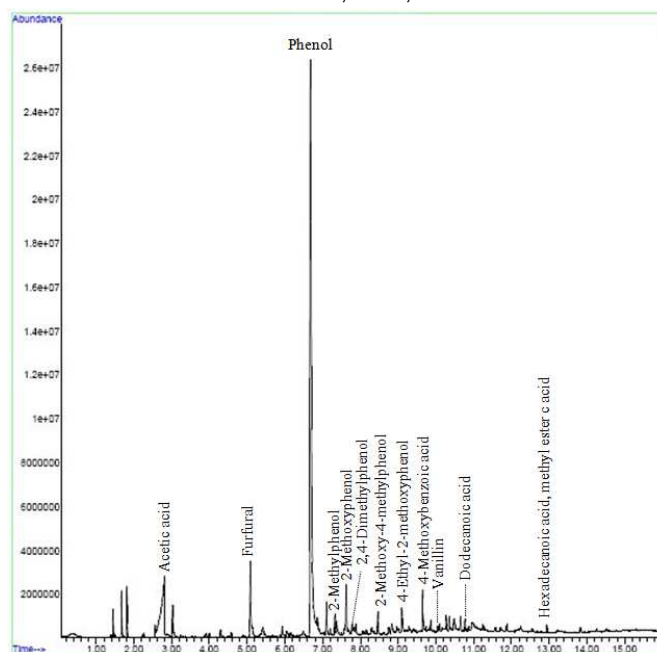
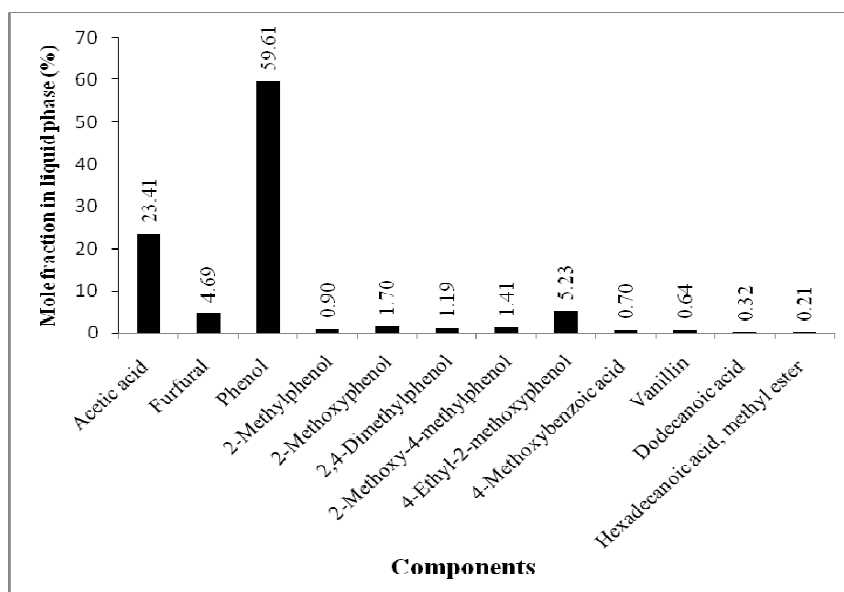Fig. 2 GC-MS analysis for the bio oil sample

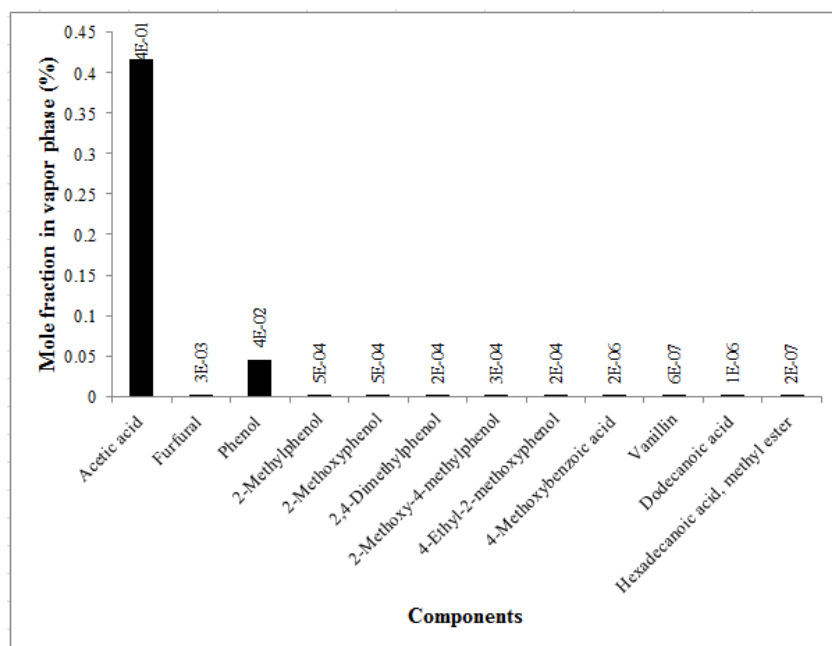Fig. 3 Mole fraction of the selected 12 components in liquid phase

Fig. 4 Mole fraction of the selected 12 components in vapour phase
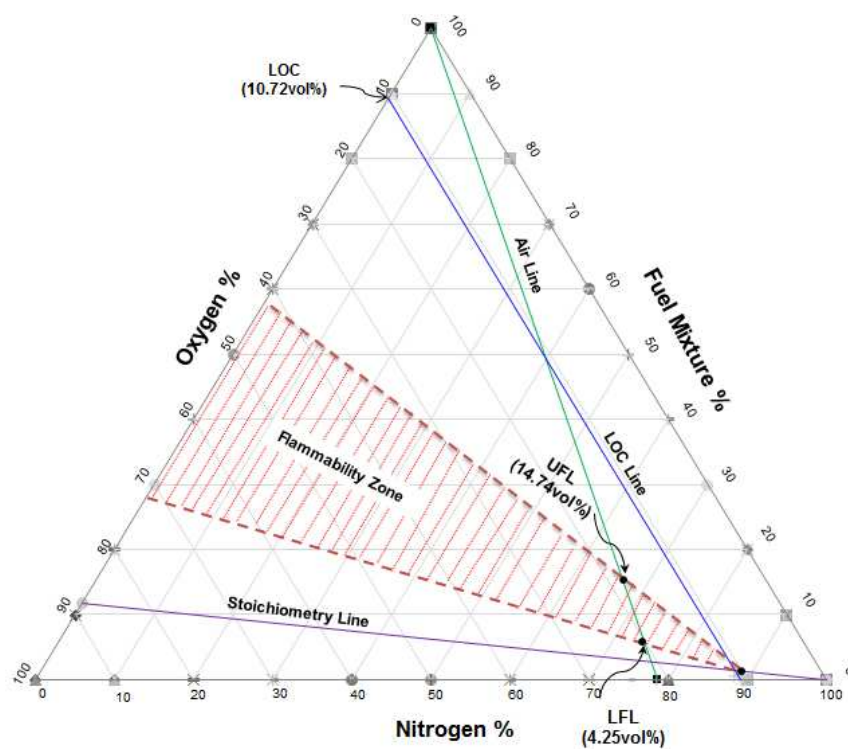

Fig. 5 Triangular flammability diagram of the bio oil mixture

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