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A Study on the Correlation Between Lower Flammable Limit and Stoichiometric Ratio of Xylene

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Abstract: Xylene is used as a solvent in various industrial fields and is a flammable substance its Lower Flammability Limit (LFL) and stoichiometric ratio are crucial factors for safety in relation to fire which is a major risk. Although, many related studies on the LFL and stoichiometric ratio of xylene have been conducted to date, the results from these studies are inconsistent. Consequently, data from previous studies are confusing to industries that use xylene in various processes. This study aimed to investigate the exact correlation between the LFL and the stoichiometric ratio of xylene. To determine this correlation, flash points were measured using a tag closed cup apparatus (ASTM D56-15) and a new and improved formula was derived for the relationship between the LFL and the stoichiometric ratio of xylene through the measured flash points. This study provides important basic safety data for industrial fields that use xylene a flammable substance.

Key words: Flashpoint, complete combustion equation, stoichiometric ratio, tag closed cup tester, vapor pressure, Korea

INTRODUCTION

Xylene is a derivative of benzene in which two hydrogen atoms of the benzene ring are substituted with two methyl groups that can exist as a mixture of three isomers (Meng *et al*., 2016). It is used as a solvent in the productions of chemicals, tires, agricultural sprays, adhesives and roads and particularly for manufacturing various rubber products (USEP., 1994; Lawrence, 1993; Manuel and Dierkes, 1997). Xylene has three isomers, namely, o-xylene, m-xylene and p-xylene which differ depending on the location of the methyl groups as shown in Fig. 1 (Stellman, 1998).

Physical properties such as boiling point, melting point, vapor pressure, Flash Point (FP) and auto-ignition temperature and various combustion properties, vary according to the type of isomer as summarized in Table 1 (Anonymous, 2008).

As shown in Table 1, xylene with a maximum FP of 32°C, is a flammable liquid and has been classified as such by the National Fire Protection Association (NFPA) (Anonymous, 2003). Common hazards of xylene include fire and explosion. Therefore, to minimize these hazards, knowledge of FPs and Lower Flammable Limits (LFLs) is important (Crowl and Louvar, 1990; In, 2015). Many methods have been used to predict the FPs of pure compounds and mixtures (Carareto *et al*., 2012; Hristova, 2013; Liaw *et al*., 2011; Liaw and Tsai, 2013, 2014). The information provided by research in these areas will help in preventing fires and explosions.

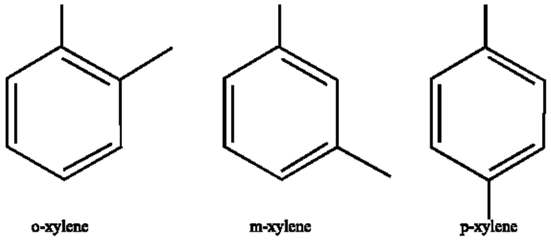

Fig. 1: Molecular structures of the xylene isomers

An accurate LFL must be calculated in order to establish appropriate measures for fire and explosion prevention. Therefore, accident prevention equipment such as explosion proof equipment can only be expected to be effective when accurate LFL information is available. Hence, the present study aimed to investigate, through experiments, the correlation between LFL and the stoichiometric ratio of xylene with a wide variety of other applications.

Literature review: Many different formulas have been developed for expressing the correlation between LFL and the stoichiometric coefficient, C_{st}. The most commonly used formula, reported by Jones (1948) is given in Eq. 1:

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Table 1: Characters of xylene isomers

Substances	Boiling point (°C)	Melting point (°C)	Vapor pressure (kPa) at 20°C	FP (°C)	Auto-ignition temperature (°C)	Explosive limit, vol. (%) in air (°C)
o-xylene	144	-25	0.7	32	463	0.9~6.7
m-xylene	139	-48	0.8	27	527	1.1~7.0
p-xylene	138	13	0.9	27	528	1.1~7.0

$$LFL = 0.55C_{st} \quad (1)$$

Furthermore, if the half stoichiometric rule for predicting the LFL of hydrocarbons composed of C, H, O and non-hydrocarbon compounds applies, then the correlation coefficient (α) of 0.5 is smaller than the existing value as shown in Eq. 2 (Jones, 1998):

$$LFL = 0.5C_{st} \quad (2)$$

For substances containing C, H and O, Hilado proposed Eq. 3 for the LFL (Casal, 2017):

$$LFL = 0.537C_{st} \quad (3)$$

Moreover, a recent study on xylene isomers by Ha *et al.* expresses the correlation between LFL and C_{st} as follows (Ha and Lee, 2009):

$$LFL = 0.59C_{st} \quad (4)$$

If these formulas are combined, then the correlation between LFL and C_{st} is as follows:

$$LFL = 0.50\sim 0.59C_{st} \quad (5)$$

where, C_{st} is the ideal ratio between fuel and air and is calculated by:

$$C_{st} = \frac{\text{Moles of fuel}}{\text{Moles of fuel} + \text{Moles of air}} \times 100 \quad (6)$$

As discussed before, in the case of xylene, the three isomers have different characteristics such as boiling points, melting points, vapor pressures, FPs, auto-ignition temperatures and range of flammabilities. However, the complete combustion equation, shown in Eq. 7, cannot distinguish between these isomers because the equation depends only on the number of elements in the molecule, not on its chemical structure:

$$2C_8H_{10}+21O_2 \rightarrow 16CO_2+10H_2 \quad (7)$$

Using Eq. 7 for the complete combustion of xylene, C_{st} can be calculated according to Eq. 8:

Table 2: Correlation coefficient (α) and calculated $LFL^{cal.}$ using literature formulas

Variables	Jones	Half stoichiometric rule	Hilado	Ha
Correlation coefficient (α)	0.550	0.50	0.537	0.590
$LFL^{cal.}$	1.078	0.98	1.053	1.157

$LFL^{cal.}$: Calculated Lower Flammable Limit; α: Correlation coefficient of stoichiometric coefficients with the lower flammable limit

$$C_{st} = \frac{2}{2+21\times\frac{100}{21}} \times 100 = 1.96078 \quad (8)$$

Through the application of Eq. 1~4, LFL values can be obtained and are listed in Table 2. However, both the International Chemical Safety Cards ICSC and NFPA (Anonymous, 1994) list the LFL of o-xylene to be 0.9% and that of m-xylene and p-xylene as 1.1%. There are obvious differences between the $LFL^{cal.}$ values and the ICSC and NFPA data. Clearly, the establishment of a new experimental equation for xylene is required because there are significant differences between the existing equations. In this research, a Tag closed cup tester, designed to accurately measure the FPs of petroleum products with FPs of 93°C or below was used (Anonymous, 2010, 2016). The measured FPs were used to correlate LFL with C_{st} and derive a formula that is exclusive to xylene.

In addition, although FPs are divided into upper and lower FPs, FPs generally refer to lower FPs. Likewise, the FPs in this research are based on the lower flammable limits and the term "flash point" refers to the lower FP.

MATERIALS AND METHODS

Materials: The xylene samples used in this research were used as obtained from the manufacturers, without any further refinement processes. The sample details are listed in Table 3 while the purchased materials are shown in Fig. 2.

Sample preparation: Sample measurements involved single component systems containing the pure xylene isomer, binary blends containing 1:1 mixtures of o-xylene and m-xylene, o-xylene and p-xylene and m-xylene and p-xylene and ternary blends containing a 1:1:1 mixture of o-xylene, m-xylene and p-xylene.

Fig. 2: Photos of the xylene samples used: a) O-xylene; b) m-xylene and c) p-xylene

Fig. 3: Photos of the tag closed cup tester: a) Whole apparatus; b) Control panel and c) Gauge

Table 3: Xylene samples used in this study

Substances	o-xylene	m-xylene	p-xylene
Country of manufacture	South Korea	South Korea	Japan
Manufacturer	SAM CHUN	SAM CHUN	Junsei
Purity	98%	99%	98.5%

Table 4: Measured FP values for each xylene sample

Component system	Chemical composition	Mixing ratio	Average FP (Average of 5 measurements) (°C)
1	o-xylene	1	33.0
	m-xylene	1	26.0
	p-xylene	1	24.0
2	o-xylene +m-xylene	1:1	29.6
	o-xylene +p-xylene	1:1	28.4
	m-xylene +p-xylene	1:1	25.0
3	o-xylene +m-xylene +p-xylene	1:1:1	27.7

Apparatus: The experimental tag closed cup apparatus satisfied the ASTM standards and is shown in Fig. 3 (Anonymous, 2010).

Method of measurement: According to the test equipment manufacture'rs manual, when following the ASTM D56-15 protocol if the expected FP of the sample is below 60°C, 50±0.5 mL of the sample was added to the test cup, sealed and the sample heated at a rate of 1°C/(60±6)sec in temperature increments of 0.5°C (Anonymous, 2016). The flame generated at every ignition interval contacted the test cup which automatically measured the minimum temperature required to ignite the vapor generated by the heated sample.

The test was repeated five times for each sample to ensure FP measurement accuracy and this research considered the mean of five temperatures to be the measured FP of the substance. The measured temperatures are listed in Table 4. Errors quoted represent the differences between the average of five experiments and the literature values.

RESULTS AND DISCUSSION

Comparison of flash points: The FP temperatures of xylene show slight variances between those reported by ICSC, NFPA, Lange and Sigma as shown in Table 5 (John,1998; Lenga and Votoupal, 1993).

The FP values obtained from our experiments are very similar to those reported in the literature, approximately 32°C for o-xylene, 25~27°C for m-xylene and 27°C for p-xylene. Moreover, measurements on the mixtures of xylene isomers show that the FP changes in a consistent fashion with the mixing ratio and is dependent on the molar ratio of each substance. Also, based on the literature FPs of the mixtures, the FP of each heterogeneous mixture can be predicted by taking into account the dependence of FPs of each component on the molar composition. If the predicted values are compared with the experimental values, a graph of FP as a function of molar composition can be constructed as shown in Fig. 4 for the binary mixtures of xylenes.

Determination of the correlation between C_{st} and LFL from the measured FPs

Calculation of vapor pressure: The Antoine equation was used for the calculation of the vapor pressure. The National Institute of Standards and Technology (NIST) Chemistry WebBook expresses the Antoine Eq. 9 as follows:

$$\log_{10} p = A - \left(\frac{B}{T+C}\right) \qquad (9)$$

Where:

P = Vapor Pressure (bar)
A, B and C = Constants (the Antoine coefficients)
T = Temperature (K)

Moreover, the Antoine equation coefficients differ with temperature and the substances and are shown in Table 6 for the xylenes (Willingham *et al*., 1945; Pitzer and Scott, 1943; Osborn and Douslin, 1974; Ambrose *et al*., 1967).

As shown in Table 6, the Antoine coefficients are applied differently depending on the temperature the Antoine coefficients used in this research are based on the measured FPs which are 33°C (306.15 K) for o-xylene, 26°C (299.15 K) for m-xylenem and 24°C for p-xylene.

Furthermore, for mixtures of xylene, the FP depends on the mixing ratio of each substance. Accordingly, Dalton's law of partial pressure was applied when the vapor pressure is calculated for each heterogeneous mixture.

Table 5: Literature flash point temperatures of xylene

Chemical composition	ICSC (°C)	NFPA (°C)	Lange (°C)	Sigma (°C)
o-xylene	32	32	32	32.2
m-xylene	27	27	25	25
p-xylene	27	27	27	27
o-xylene +m-xylene	None	None	None	None
o-xylene +p-xylene	None	None	None	None
m-xylene +p-xylene	None	None	None	None
o-Xylene +m-xylene +p-xylene	None	None	None	None

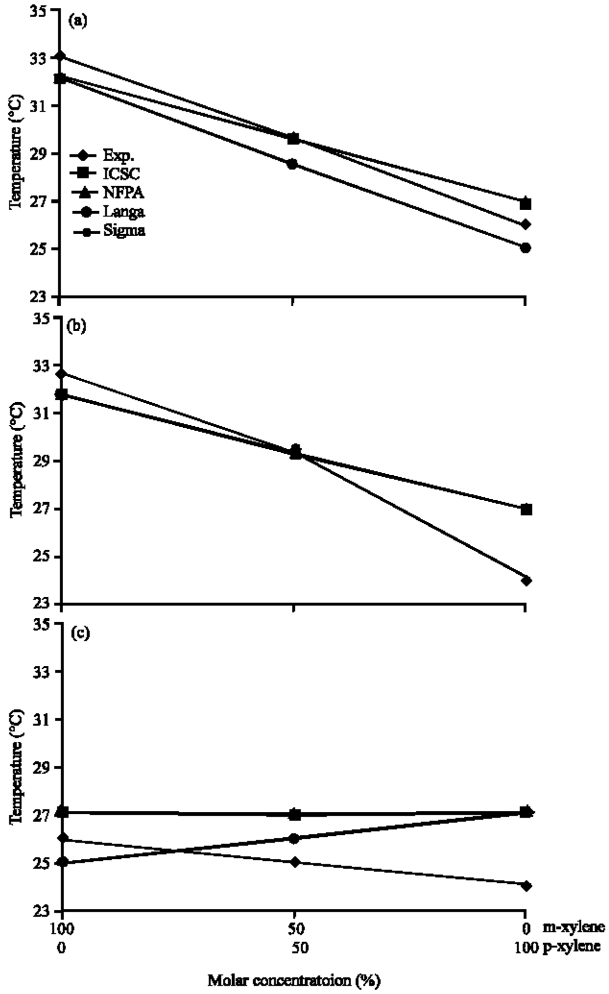

Fig. 4: Binary mixture flash points as functions of molar compositions: a) Flash point according to the concentration of binary mixtures of o-xylene and m-xylene; b) Flash point according to the concentration of binary mixtures of o-xylene and p-xylene and c) Flash point according to the concentration of binary mixtures of m-xylene and p-xylene

Table 6: Antoine constants for xylene isomers

Substances	Temperature (K)	Coefficients A	B	C
o-xylene	336.61~418.52	4.12928	1487.244	-59.076
	273~323	4.93755	1901.373	-26.268
m-xylene	332.4~413.19	4.13607	1463.218	-57.991
	273~333	5.09199	1996.545	-14.772
p-xylene	286.43~452.38	4.14553	1474.403	-55.377
	420.00~600.00	4.50944	1788.910	-13.902
	331.44~412.44	4.11138	1450.688	-58.160
	298~333	4.44889	1644.214	-40.229

Table 7: Calculated partial Pressures P and P_f for each sample in bar and mmHg, respectively

Chemical composition	Bar	mmHg
o-xylene	0.013934	10.451199000
m-xylene	0.011783	8.837785000
p-xylene	1.100319	8.362426000
o-xylene+m-xylene	0.012858	9.644492777
o-xylene+p-xylene	0.012541	9.406813073
m-xylene+p-xylene	0.011466	8.600105916
o-xylene+m-xylene+p-xylene	0.012289	9.217137255

P: Vapor pressure at flash point (bar), P_f: Vapor pressure at flash point (mmHg)

By calculating each value separately and summing proportionately, the calculated values are shown in Table 7.

LFL calculations: According to ASTM, the relationship between P_f and LFL, based on the FPs from closed cup tests, follows Eq. 10 given as (Anonymous, 2017):

$$\text{LFL} = \frac{P_f}{P_o} \times 100 \tag{10}$$

Where:

P_f = Vapor Pressure in mmHg

P_o = Standard atmospheric Pressure (760 mmHg)

Table 8 compares the LFL values calculated using Eq. 10 and the literature corresponding literature values.

Calculation of the correlation between LFL and C_{st} Assumption: For LFL^{cal}, only o-xylene showed a 0.4% error while both m-xylene and p-xylene showed close correspondences between the data over the five experiments.

Also, since, the error for the o-xylene value is not very large, it was regarded to be a measurement error. Consequently, the values of LFL^{cal} obtained from this research were assumed to be accurate.

Calculation: The calculated C_{st} of xylene from Eq. 7 and 8 is approximately 1.96078% and the respective LFLs of the xylene isomers are shown in Table 6. However, because the complete combustion equation does not differ for the

Table 8: Comparison of LFL values (%)

Chemical composition	$LFL^{exp.}$	ICSC (NFPA)
o-xylene	1.3752	0.9
m-xylene	1.1629	1.1
p-xylene	1.1003	1.1
o-xylene+m-xylene	1.2690	-
o-xylene+p-xylene	1.2377	-
m-xylene+p-xylene	1.1316	-
o-xylene+m-xylene+p-xylene	1.2128	

Table 9: Errors in LFL (%)

Chemical composition	$LFL^{exp.}$	$LFL^{cal.}$	Error (Absolute value)
o-xylene	1.3752	1.2137	0.1614
m-xylene	1.1629	1.2137	0.0509
p-xylene	1.1003	1.2137	0.1134
o-xylene+m-xylene	1.2690	1.2137	0.0553
o-xylene+p-xylene	1.2377	1.2137	0.0240
m-xylene+p-xylene	1.1316	1.2137	0.0821
o-xylene+m-xylene+p-xylene	1.2128	1.2137	0.0009

LFL^{Exp} Spilled LFL determined by Experiment; $LFL^{cal.}$ calculated LFL

Table 10: Comparison of errors with experimental values from previous research and this research

Variables	Experiment	Half rule	Hilado	Jones	Ha.	This study
α	-	0.5000	0.5370	0.5500	0.5900	0.6190
LFL error	1.2128	0.9804	1.0529	1.0784	1.1569	1.2137
Absolute value	0	0.2324	0.1598	0.1344	0.0559	0.0009

xylene isomers, the correlation for xylene was calculated using the LFL of a 1:1:1 mixture of o-xylene, m-xylene and p-xylene. Previous literature and research has shown that the correlation follows LFL = $\alpha \times C_{st}$. The calculated C_{st} of xylene was approximately 1.96078% and the calculated LFL from the measurements was 1.212781218%. Therefore, the value of α is approximately 0.619. Hence, the relationship between LFL and C_{st} for xylene isomers was determined to follow Eq. 11:

$$LFL = 0.619 \times C_{st} \tag{11}$$

Error evaluation of the correlation formula between LFL and C_{st} Eq. 11. The calculations for each xylene isomer using Eq. 11 were compared with the experimental values in order to evaluate the errors; the results are listed in Table 9.

The results of this evaluation showed that the maximum error came from pure o-xylene in which the LFL showed a 0.16% difference between the calculated and experimental values. However, this error is not significant and is considered to be negligible. In addition, the error in this study was found to be 0.0009% (Table 10).

CONCLUSION

The following conclusions can be drawn from the FP measurements of xylene isomers provided by this research and previous literature data. Various correlation coefficient (α) between LFL and C_{st} namely 0.5, 0.537, 0.55 and 0.59 have been reported previously. This study has verified that these variations produce errors when calculating Fps. Measurements of FPs using the Tag closed cup tester showed that the FP is proportional to the ratio of the xylene isomers being mixed and that this was proportional to the molar ratio or volume fraction. The correlation between the stoichiometric ratio and LFL was determined by measuring the FPs of xylene isomers and by using the complete combustion equation. The equation for the ternary mixture containing all three xylene isomers was found to be LFL = $0.619C_{st}$.

Correlation coefficients in previous research were in the range 0.5~0.59 and are only slightly different from the coefficient obtained in this study. In addition, investigations of errors using correlations from previous research, reveal minimum and maximum errors of 0.0559% and 0.2324%, respectively, when compared with experimental values. In contrast, the error in this study was only 0.0009% which is considerably smaller than hose from previous research.

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