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노말헥사데칸의 화재 및 폭발 특성치의 측정

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The Measurement of Fire and Explosion Properties of n-Hexadecane

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Abstract : For the safe handling of n-hexadecane, the lower flash points and the upper flash point, fire point, AITs(auto-ignition temperatures) by ignition delay time were experimented. Also lower and upper **e**xplosion limits by using measured the lower and upper flash points for n-hexadecane were calculated. The lower flash points of n-hexadecane by using the Setaflash and the Pensky-Martens closed testers were measured 128 ℃ and 126 ℃, respectively. The lower flash points of the Tag and the Cleveland open cup testers were measured 136 ℃ and 132 ℃, respectively. The fire points of the Tag and the Cleveland open cup testers were measured 144 ℃. respectively. This study measured relationship between the AITs and the ignition delay times by using ASTM E659 apparatus for n-hexadecane. The experimental AIT of n-hexadecane was 200 ℃. The calculated lower and upper **e**xplosion limit by using measured lower 128 ℃ and upper flash point 180 ℃ for n-hexadecane were 0.42 Vol.% and 4.70 Vol.%.

Key Words : n-hexadecane, lower flash point, lower **e**xplosion limit, fire point, autoignition temperature(AIT)

1. Introduction

A working knowledge of the safe use, storage and disposal of the flammable liquids is probable as necessary to industrial fire and explosion safety. The fire and explosion properties necessary of flammable substances in chemical industries are lower explosion limits(LEL), upper explosion limits(UEL), flash point, fire point, AIT(auto ignition temperature), MIE(minimum ignition energy), MOC(minimum oxygen concentration) and heats of combustion etc.[1].

The flash point and the fire point are relevant to safety in chemical industries. The flash point is one of the most important combustible characteristics that are used in risk assessments in the chemical plants. The flash point is the lowest temperature at which the liquid will give off enough vapors to form an ignitable mixture. will momentarily flash across the surface of the liquid. The fire point is the most temperature at which a vapor above a flammable liquid will continue to burn once ignited. The fire point is a temperature, usually about 5 to 10 ℃ above the flash point. The fire point of a lubricant is the point at which vapors are released rapidly enough to support combustion[1].

The explosion limits are used to classify flammable liquids according to their relative flammability. The concentration of vapor and air mixture is generally given in percent by volume. The explosion limit is divided into LEL and UEL. The explosion limits may be used to specify operating, storage, and materials handling procedures for a material. They are particularly useful in specifying ventilation requirements for operations involving flammable liquids and gases[2].

The AIT is the temperature at which a material will autoignite when it contacts a surface at that temperature. The procedure consists of heating a glass flask and

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squirting small quantities of sample into it at various temperatures until the vapours autoignite. The AIT is dependent upon many factors, namely, ignition delay, ambient pressure, configuration, fuel/air stoichiometry, oxygen concentration, vessel size, flow condition, initial temperature, catalytic material, impurity etc.[3].

The flash point values of n-decane, n-undecane, n-tetradecane and n-hexadecane by using ASTM D92 (Cleveland Open Cup Tester) and ASTM D93 (Pensky-Martens Closed-cup Tester) were obtained[4]. Recently, the flash points and the autoignition temperatures of n-undecane, n-dodecane, n-tridecane, n-tetradecane and n-pentadecane through various combustion test methods were obtained[5-9].

In this study, we measured flash points, fire points and AIT for n-hexadecane. Predictive explosion limits based on measured flash point proposed as process safety data. These presented data and the prediction methods are typically used as MSDS update, petroleum tank fire extinguishment index, resemble petroleums distinct etc..

2. Combustion Hazard and Data Selection of n-Hexadecane

2.1 Physical Properties of n-Hexadecane

Several nations provide on MSDS for safety handling, transportation, storage and treatment of hazardous materials using the workplace. A lot of handbooks and articles appear to combustion characteristics of flammable substances. The physical Properties of n-hexadecane summerized in Table 1[10].

2.2 Reaction and Combustible Characteristics of n-Hexadecane

The n-hexadecane is the third oils of fourth of hazardous materials in Hazardous Materials Safety Management Act. Also this material is working environment measurement and harmful material for adminstration in Industrial Safety and Occupational Act. The n-hexadecane is colorless liquid. It can not dissolve into water, and it can dissolve into ethanol, ether, acetone and chloroform. It is main raw material of n-hexadecane, others applications include: liquid mosquito-repellent incense, hydraulic oil of large-scale punch, paraffin chloride, anticorrosive paint. powder paint, and top-grade melt adhesive. The ignition sources of flee condition of n-hexadecane are heat, flame, spark and other ignition sources. The escape of n-hexadecane vapor can spread in a moment to ignite from ignition sources because the weight of n-hexadecane vapor is more than weight of air.

The fire extinguishing media of n-hexadecane use form, dry chemical or carbon dioxide (water may be ineffective). This material stores in the cool and dry places.

Table 1. Physical properties of n-hexadecane

Properties \ Component	n-Hexadecane
CAS number	544-76-3
Molecular formula	$C_{16}H_{34}$
Boiling point	286.8 ℃
Melting point	18.2 ℃
Critical temperature	449 ℃
Critical pressure	14 atm
Specipic gravity(Water=1)	0.7733 (25℃)
Vapor pressure	0.00143 ㎜Hg (25 ℃)
Solubility	0.0009 ㎎/L (25℃)

3. Anaylsis of Fire and Explosion Characteristics of n-Hexadecane

The LEL and the UEL of n-hexadecane reported only as 0.45 Vol.% and 6.50 Vol.% in the Ignition handbook in spite of the industrially important substance.

The several authoritative sources(SFPE and Igntion) reported the flash points of n-hexadecane as 126℃. The Lange and Flick reported as 135℃. And Montemayor et al. reported as 133.9 ℃(ASTM D93) and 138.8 ℃ (ASTM D92). According to prior articles, the flash points of n-hexadecane reported from 126℃ to 139℃. The flash points of n-hexadecane suggested by literatures are summarized in Table 2.

Table 2. The flash point of several reported data for n-hexadecane

Compound	Flash points [℃]					
	NFPA[11]	SFPE [12]	Ignition[13]	Lange[14]	Flick[15]	Montemayor[4]
n-Hexadecane	〉100	126	126	135	135	133.9(D93), 138.8(D92)

Table 3. The AIT of several reported data for n-hexadecane

Compound	AITs[℃]					
	NFPA[11)]	SFPE[12)]	Hilado[16)]	Zabetakis[17)]	Scott[18)]	Frank[19)]
n-Hexadecane	202	205	202	205	235	232

The several authoritative sources(SFPE and Igntion) reported the AIT of n-hexadecane as about 200 ℃. The Scott reported as 235℃. And Frank. reported as 232 ℃. According to prior articles, the AIT of n-hexadecane reported from 202℃ to 235℃. The AIT of n-hexadecane suggested by literatures are summarized in Table 3.

4. Experimental Apparatus of Combustible Characteristics

4.1 Experimental Material

The n-hexadecane was purchased from Alfa Aesar(UK, 99%), with a minimum purity of 99.0%. This chemical were used directly without any purification.

4.2 Experimental Apparatus

4.2.1 Flash Point Apparatus

Some of the parameters that affect flash points can be briefly considered tester configuration, ignition sources, temperature control, sample quantity, sample homogeneity, ambient pressure, operator bias etc.[5-9)].

In this study, the components for Pensky-Martens closed-cup, Setaflash closed-cup, Tag open cup and Cleveland open cup testers introduce briefly[5,6)]. These testers manufactured by Koehler Instrument Co..

The Pensky-Martens closed-cup tester(ASTM D93) consists of a test cup, cover and stove. The volume of the test cup is 100 ml and was made of brass. The flange is equipped with devices for locating the position of the test cup in the stove. The cover consists of cover proper, shutter, flame-exposure device, pilot flame and stirring device. Heat is supplied to the cup by means of the stove. The stove consists of an air bath and a top plate. The pure components is added by mass and the test cup is filled with the mixture (65ml). The flash point(±0.1K) is the lowest temperature at which application of the test flame causes the vapor above the mixture to ignite.

The Setaflash closed-cup tester(ASTM D3278) consists of a sample cup, time controller, test flame device, thermometer and temperature controller. The Setaflash closed cup tester is operated according to the standard test method.

The Tag open cup tester(ASTM D1310) consists of a sample cup, water bath, test flame device, level gauge, electrical heater, overflow path, thermometer and temperature controller. The pure components is added by mass and the sample cup(70ml) was filled with the mixture. A test flame is passed at a uniform rate across the sample cup at specific interval, 0.5 K until a flash occurs.

The Cleveland open cup tester(ASTM D92) consists of test flame applicator, brass test cup, thermometer support, heating plate and electric heater. Applicator is precisely aligned per specifications and pivots for the test flame application at specified temperature intervals. Hinged thermometer support raises to facilitate placement and removal of test cup.

Some of the parameters of the standard flash point test methods are summarized in Table 4[7,8)].

Table 4. Comparison of several flash point test methods

Test methods	Test vessel diameter(cm)	Test vessel depth(cm)	Test vessel volume(ml)	Heating methods
ASTM D93 Pensky-Martens closed-cup	5.085	5.6	100	For ordinary liquids, the temperature of the specimen is increased at 5-6℃/min
ASTM D3278 Setaflash closed-cup	5.0	1.0	2 or 4	Sample cup is electrically heated or chilled and sample temperature is kept constant
ASTM D1310 Tag open cup	5.3	5.0	70	The temperature of the specimen is increased at 1±0.25℃/min.
ASTM D92 Cleveland open cup	6.4	3.4	80	The temperature of the specimen is increased at 5-6℃/min

4.2.2 Autoignition Temperature Apparatus(ASTM E659)

This test method covers the determination of hot flame and cool flame autoignition temperatures of a liquid chemical in air at atmospheric pressure in a uniformly heated vessel. AIT tests are conducted according to ASTM E659(Standard Test Method for Auto-ignition Temperature of Liquid Chemicals). This tester consists of furnace, temperature controller, thermocouple, test flask, hypodermic syringe, mirror, and air gun.

The test procedure employs a 500 ml flask that is uniformly heated in a special purpose furnace. A fine thermocouple in the flask is used to monitor temperature changes that occur upon injection of a small quantity (0.1ml) of fuel into the flask. The test temperature is progressively lowered until ignition does not occur within 10 minutes at any fuel concentration[7,8].

5. Results and Investigations

5.1 Prediction of Explosion Limits by Means of Measured Flash Point and Fire Point

The open cup(O.C.) flash points are generally somewhat higher than the closed-cup(C.C.) flash points for same materials.

Special precautions should be taken when the product has a low flash point. Materials that have a low flash point are a greater fire hazard than materials having a high flash point. From the definition of flash point, the flash point of a flammable liquid is defined as that temperature at which the vapor pressure of the specified liquid is such as to produce a concentration of vapor in the air that corresponds to the lower flammable limit.

In this study, the flash point of n-hexadecane measured by Pensky-Martens closed-cup, Setaflash closed-cup, Tag open cup and Cleveland(Manual and Auto) open cup testers. The fire point of n-hexadecane measured by using Tag open cup and Cleveland open cup testers.

The explosion limits of n-hexadecane predicted by using the measured flash points and fire points. An equation for the saturated vapor pressure, P^f, is needed to estimate the explosion limits. One of the most common correlation is the Antoine equation[20) :

$$\log P^f = 7.02870 - \frac{1830.510}{(t+154.45)} \tag{1}$$

where, P^f is saturated vapor pressure(mmHg), t is flash point temperature(℃).

In this study, it is summarized estimated explosion limits values by equation (1) with experimental flash points and fire point by using five testers for n-hexadecane in Table 5. The calculated LEL by the lower flash point 128 ℃ of Setaflash tester for n-hexadecane was about 0.42 Vol.%. And the calculated UEL by the upper flash point 180 ℃ of Setaflash tester for n-hexadecane was about 4.70 Vol.%. The proposed LEL can use efficiently in the fire and explosion protection equipment.

5.2 Propriety Investigation of Measured Flash Point

The flash points of n-hexadecane are scarcely literatures but in the industrially important material. In order to review validity of measured flash points for n-hexadecane, we compared with several sources(NFPA, SFPE, Sigma, Affens, Ha, and Montemayor) in Table 6.

Also, in order to investigate validity of flash points for n-hexadecane, we are plotted for the flash points from n-hexane to n-tetradecane of NFPA literature and measured flash points from n-undecane to n-hexadecane by Ha literature[5-9) in Figure 1.

In plotting results, the lower flash point of n-hexadecane which measured this study was similar trend the flash points

Table 5. Comparison of calculated explosion limits by experimental flash points and fire point for n-hexadecane

Testers	Experimental (℃)			Estimated(LEL) (Vol%)		
	Lower flash points	Upper flash points	Fire points	by Lower flash points	by Upper flash points	by Fire points
Pensky-Martens	126	-	-	0.41	-	-
Setaflash	128	180	-	0.42	4.7	-
Tag	136	-	144	0.70	-	1.03
Cleveland(Manual)	132	-	144	0.57	-	1.03
Cleveland(Auto)	136	-	-	0.70	-	-

Table 6. Comparison of lower flash points of several references for n-hexadecane

Compounds \ References	NFPA[11]	SFPE[12]	Sigma[21]	Affens[22]	Ha[5-9]	Montemayor[4]
n-Hexane	-22℃	-22℃	-23.3℃	-	-	-
n-Hepatne	-4℃	-4℃	-1.1℃	-1℃	-	-
n-Octane	13℃	13℃	15.5℃	15℃	-	-
n-Nonane	31℃	31℃	32.8℃	33℃	-	-
n-Decane	46℃	44℃	46.1℃	48℃	-	52.8℃
n-Undecane	65℃(O.C.)	65℃(O.C.)	60℃	64℃(C.C.)	59(C.C.)	68.7℃
n-Dodecane	74℃	72℃	71.1℃	79℃	77℃~82℃	-
n-Tridecane	-	-	94℃	-	92℃	-
n-Tetradecane	100℃	-	-	-	104℃	109.3℃
n-Pentadecane	-	-	132.2℃	-	118℃	-
n-Hexadecane	〉100℃	126℃	-	-	128℃	134℃

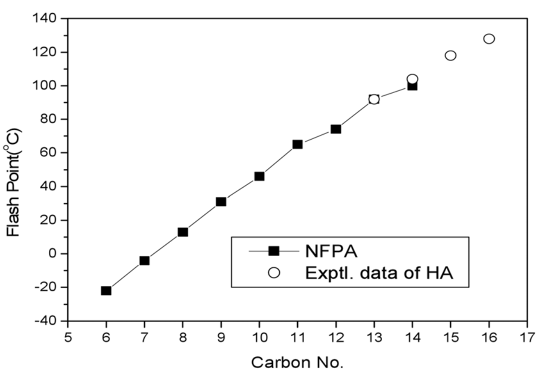

Fig. 1. A comparison between NFPA and experimental lower flash points for n-alkanes.

of several established literatures and flash points by using Setaflash tester of Ha literature[5,6,7,8]. Therefore, the measured flash points for n-hexadecane in this study has appropriated.

5.3 Investigation of Autoignition Temperature of n-Hexadecane

The autoignition temperature(AIT) of a substance is the lowest temperature at which the material will spontaneously ignite in the absence of an external ignition source, such as a spark or flame. The autoignition temperature may be used to specify operating, storage, and materials handling procedures for a material.

The several references reported the AIT of n-hexadecane as about 200 ℃. According to prior articles, the AIT of n-hexadecane reported from 202℃ to 235℃.

We have searched the several handbooks and references in order to investigate validity the measured AIT for n-hexadecane. Therefore, we proposed experimental data which obtained in this study.

In this study, the initial temperature of autoignition for n-hexadecane set up to 160℃ based on the AIT of hydrocarbon compounds, however n-hexadecane do not ignited in this temperature. When temperature of autoignition set up to 190 ℃, n-hexadecane do not ignited in this temperature. When temperature of autoignition set up to 220 ℃, a rise 30℃. The n-hexadecane ignited in 27.01 second. We are found AIT 200 ℃ to turn down 5 ℃ based on 200 ℃. The ignition delay time of AIT 200 ℃ is ignited 93.35 second. And the ignition delay time of the ignition temperature 280 ℃ to increase 5 ~10℃ based on the AIT 200 ℃ is ignited 1.37 second.

The relationship between the ignition temperature and the ignition delay time for n-hexadecane are summarized in Table 7.

In the case of most combustible materials. the relationship between the ignition temperature and the ignition delay time may be approximated within finite limits by the equation

$$\ln\tau = A + B\left(\frac{1}{T}\right) \tag{2}$$

where τ is the ignition delay time, T is the ignition temperature[K], and A and B are constant.

The coefficients of optimized equation by regression analysis is following.

$$\ln\tau = -24.51 + 13718.13\left(\frac{1}{T}\right) \tag{3}$$

The equation (3) are presented in equation (4) by the relationship between logτ and $\left(\frac{1}{T}\right)$.

$$\log\tau = -10.64 + 5957.72\left(\frac{1}{T}\right) \quad (4)$$

The comparison of experimental and calculated ignition delay time by the AIT for n-hexadecane are illustrated Table 7 and Figure 2.

It is another index, replacing average absolute deviations(A.A.D.) in situation when an accurate quantitative comparison between the reported value and the estimated value are attempted. The average absolute deviations(A.A.D.)[5,6] is :

$$A.A.D. = \sum \frac{|\tau_{est.} - \tau_{\exp.}|}{N} \quad (5)$$

where the A.A.D. is a measure of agreement between the experimental data and the calculated values.

The predicted ignition delay times by Equation (3) are in agreement with the experimental ignition delay times, and A.A.D. is 1.02 second and the coefficient of determination(r^2) is 0.99.

In the high temperature regime, the effective activation energy is 50 to 90 kJ/mol, while in the low temperature region values 140 to 190 kJ/mol[13]. The activation energy can calculate by using Semenov equation[23]. Semenov related several variables by the equation

$$\log\tau = \frac{52.55E}{T} + B \quad (6)$$

where τ is ignition delay(s), E is activation energy (kJ/mol) and B is constant.

The calculated activation energy by the relationship between equation (4) and equation (6) is 113.37 kJ/mol.

Table 7. Comparison of experimental and calculated ignition delay time by the AIT for n-hexadecane

No.	T[K]	$\tau_{exp.}$[s]	$\ln\tau_{exp.}$	$\tau_{est.}$.(Eq. 2)
1	473.15	93.35	4.5364	88.63
2	493.15	27.12	3.3003	27.35
3	513.15	8.40	2.2182	9.25
4	533.15	3.25	1.1787	3.39
5	543.15	2.27	0.8198	2.11
6	553.15	1.37	0.3148	1.34
A.A.D.	-	-	-	1.02

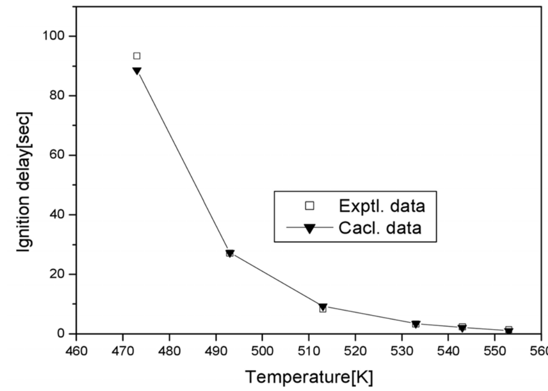

Fig. 2. A comparison between the experimental and calculated delay times for n-hexadecane.

6. Conclusions

For the safe handling of n-hexadecane, the lower flash points, the upper flash point, fire point and AITs(autoignition temperatures) by ignition delay time were experimented. And predictive explosion limits based on measured flash point proposed as process safety data.

The lower flash points of n-hexadecane by using closed-cup tester were experimented 126 ℃ and 128 ℃. The lower flash points and fire point of n-hexadecane by using open cup tester were measured 132 ℃and 136 ℃. The upper flash points of n-hexadecane by using open cup tester was measured 180℃. The calculated lower and upper explosion limit by using measured lower 128℃and upper flash point 180 ℃ for n-hexadecane were 0.42 Vol.% and 4.70 Vol.%. The experimental AIT of n-hexadecane was 200 ℃. The activation energy value for n-hexadecane was 113.37 kJ/mol.

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References

1) F.P. Lees, “Loss Prevention in the Process Industries”, Vol. 2, 2nd ed., Butterworth-Heinemann, 1996.
2) T.H. Ladwig, “Industrial Fire Prevention and Protection”, Van Nostrand Reinhold, 1991.
3) A.E. Cote and J.L. Linville, “Fire Protection Handbook”, 18th ed., NFPA, 2002.

4) R.E. Montemayor, J.E. Rogerson, J.C. Colbert and S.B. Schiller, “Reference Verification Fluids for Flash point Determination”, J. of Testing and Evaluation, Vol. 27, No. 6, pp. 423-427, 1999.
5) D.M. Ha, “The Investigation of Combustible Hazard by Measurement of Flash Point and Auto-ignition Temperature of n-Dodecane”, J. of the Korean Institute of Fire Sci. & Eng., Vol. 25, No. 2, pp. 120-125, 2011.
6) D.M. Ha, “The Investigation of Compatibility of Combustible Characteristics for n-Tridecane“, J. of the Korean Society of Safety, Vol. 27, No. 3, pp. 83-88, 2012.
7) D.M. Ha, “The Evaluation of Hazard by Measurement of Combustible Characteristics of n-Tetradecane”, J. of the Korean Society of Safety, Vol. 27, No. 5, pp. 70-76, 2012.
8) D.M. Ha, “The Measurement of Combustible Characteristics of n-Undecane”, J. of the Korean Institute of Fire Sci. & Eng., Vol. 27, No. 2, pp. 11-17, 2013.
9) D.M. Ha, “The Measurement of Fire and Explosion Properties of n-Pentadecane”, J. of the Korean Society of Safety, Vol. 28, No. 4, pp. 53-57, 2013.
10) R.H. Perry and D.W. Green, “Perry's Chemical Engineers' Handbook”, 7th ed., McGraw-Hill, 1997.
11) NFPA, “Fire Hazard Properties of Flammable Liquid, Gases, and Volatile Solids”, FPA 325M, NFPA, 1991.
12) SFPE, “SFPE Handbook of Fire Protection Engineering”, 2nd ed., SFPE, 1995.
13) V. Babrauskas, “Ignition Handbook”, Fire Science Publishers, SFPE, 2003
14) J.A. Dean, “Lange's handbook of Chemistry”, 14th ed. McGraw-Hill, 1992.
15) E.W. Flick, “Industrial Solvent Handbook”, 3rd. ed., Noyes, Data Corp., Park Ridge, N.J., 1985.
16) C.J. Hilado and S.W. Clark, “Autoignition Temperature of Organic Chemicals”, Chemical Engineering, Vol. 4, pp.75-80, 1972.
17) G.M. Zabetakis, “Flammability Characteristics of Combustible Gases and Vapors”, US Bureau of Mines, Bulletin, 1965.
18) G.S. Scott, G.W. Jones and F.E. Scott, “Determination of Ignition Temperature of Combustible Liquids and Gases”, Analytical Chemistry, Vol. 20, No.3, pp. 238-241, 1948.
19) C.E. Frank and A.U. Blackham, “Investigation of Hydrocarbon Ignition”, Technical Note, NACA, 1952.
20) J. Gmehing, U. Onken and W. Arlt, “Vapor-Liquid Equilibrium Data Collection”, DECHEMA, 1980.
21) R.E Lenga and K.L. Votoupal, “The Sigma Aldrich Library of Regulatory and Safety Data, Volume Ⅰ～Ⅲ”, Sigma Chemical Company and Aldrich Chemical Company Inc., 1993.
22) W.A. Affens and G.W. McLaren, “Flammability Properties of Hydrocarbon Solutions in Air”, J. of Chemical and Engineering Data, Vol. 17, No. 4, pp.482-488, 1972.
23) N.N. Semenov, “Some Problems in Chemical Kinetics and Reactivity”, Vol. 2, Princeton University Press, Princeton, N.J., 1959.