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노말펜타데칸의 화재 및 폭발 특성치의 측정

하동명
세명대학교 보건안전공학과
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The Measurement of Fire and Explosion Properties of n-Pentadecane

Dong-Myeong Ha
Department of Occupational Health and Safety Engineering, Semyung University
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Abstract : For the safe handling of n-pentadecane, 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 explosion limits by using measured the lower and upper flash points for n-pentadecane were calculated. The lower flash points of n-pentadecane by using closed-cup tester were measured 118°C and 122°C. The lower flash points and fire point of n-pentadecane by using open cup tester were measured 126°C and 127°C, respectively. This study measured relationship between the AITs and the ignition delay times by using ASTM E659 apparatus for n-pentadecane. The experimental AIT of n-pentadecane was 195°C. The calculated lower and upper explosion limit by using measured lower 118°C and upper flash point 174°C for n-pentadecane were 0.54 Vol.% and 6.40 Vol.%.
Key Words : n-pentadecane, lower flash point, lower explosion limit, fire point, autoignition temperature(AIT)

1. Introduction

The fire and explosion properties necessary for safe storage, transport, process design and operation of handling 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. The flash point is one of the most important combustible characteristics that are used in risk assessments in the chemical plants. It is an important criterion for the fire hazard rating of these liquids. A liquid that exhibits a flash point value below ambient temperature, and can thus give rise to flammable mixtures under ambient conditions, is generally considered to be more hazardous than one reflecting a higher flash point. The fire point is the most temperature at which a vapor above a flammable liquid will continue to burn once ignited. Generally, the fire point is higher than the flash point. The fire point of a lubricant is the point at which vapors are released rapidly enough to support combustion[2].

The explosion limits are used to classify flammable liquids according to their relative flammability. Such a classification is important for the safe handling of flammable liquids which constitute the solvent mixtures. The explosion limit is divided into LEL and UEL[2].

The AIT is a phenomena of particular interest to the chemical and fire safety engineer concerned with safe operation, it involves the occurrence of combustion in the absence of an external ignition sources. The AIT describes the minimum temperature to which a substance must be heated, without the application of a flame or spark, which will cause that substance to ignite. 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 temperature of n-undecane, n-dodecane, n-tridecane and n-tetradecane through various combustion test methods were obtained[5-8].

In this study, we measured flash points, fire points and AIT for n-pentadecane. 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, fire investigation, resemble petroleums distinct etc..

†Corresponding Author: Dong-Myeong Ha, Tel : +82-43-649-1321, E-mail: hadm@semyung.ac.kr
Department of Occupational Health and Safety Engineering, Semyung University, 65, Semyung-ro, Jecheon 390-711, Korea

2. Combustion Hazard and Data Selection of n-Pentadecane

2.1. Data Selection of Combustion

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 typical handbooks are 「Fire Hazard Properties of Flammable Liquid, Gases, and Volatile Solids(NFPA)」[9], 「SFPE Handbook of Fire Protection Engineering(SFPE)」[10], 「The Sigma Aldrich Library of Regulatory and Safety Data」[11] and 「Ignition Handbook(SFPE)」[12].

2.2. Reaction and Combustible Characteristics of n-Pentadecane

The n-pentadecane 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-pentadecane 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 pentadecane, 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-pentadecane are heat, flame, spark and other ignition sources. The escape of n-pentadecane vapor can spread in a moment to ignite from ignition sources because the weight of n-pentadecane vapor is more than weight of air.

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

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

In our observation, the AIT and the explosion limits of n-pentadecane are not reported in the NFPA 325M, SFPE handbook, Ignition handbook and another articles in spite of the industrially important substance.

The flash point of n-pentadecane reported the only Sigma Aldrich as 132.2°C. Also, The Sigma Aldrich reported the LEL and the UEL of n-pentadecane as 0.45 Vol.% and 6.50 Vol.%, respectively.

4. Experimental Apparatus of Combustible Characteristics

4.1 Experimental Material

The n-pentadecane was purchased from Kanto(Japan), 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.[5,6].

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 (65 ml). The flash point(±0.1 K) 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

Table 1. 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°C/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°C/min.
ASTM D92 Cleveland open cup	6.4	3.4	80	The temperature of the specimen is increased at 5-6°C/min

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(70 ml) 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 1[7,8].

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 Lower Explosion Limit by Means of Measured Flash Point and Fire Point

The flash point is defined by the NFPA as the lowest temperature at which a flammable liquid gives off sufficient vapor to form an ignitable mixture with air near its surface or within a vessel. 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-pentadecane measured by Pensky-Martens closed-cup, Setaflash closed-cup, Tag open cup and Cleveland open cup testers. The fire point of n-pentadecane measured by using Tag open cup and Cleveland open cup testers.

The explosion limits of n-pentadecane 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[13) :

$$\log P^f = 7.02359 - \frac{1789.95}{(t+161.38)} \tag{1}$$

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 four testers for n-pentadecane in Table 2. The calculated LEL by flash point 118°C of Setaflash tester for n-pentadecane was about 0.54 Vol.%. And the calculated UEL by flash point 174°C of Setaflash tester for n-pentadecane was about 6.40 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-pentadecane are scarcely literaturesbut in the industrially important material. In order to review

Table 2. Comparison of calculated explosion limits by experimental flash points and fire point for n-pentadecane.

Testers	Experimental(°C)			Estimated(LEL) (Vol%)		
	Lower flash points	Upper flash points	Fire points	by Lower flash points	by Upper flash points	by Fire points
Pensky-Martens	122	-	-	0.67	-	-
Setaflash	118	174	-	0.54	6.40	-
Tag	126	-	133	0.84	-	1.15
Cleveland	127	-	134	0.86	-	1.21

Table 3. Comparison of lower flash points of several references for n-pentadecane

References / Compounds	NFPA[9]	SFPE[10]	Sigma Aldrich[11]	Affens[14]	Ha[5-8]	Monte mayor[3]
n-Hexane	-22°C	-22°C	-23.3°C	-	-	-
n-Hepatne	-4°C	-4°C	-1.1°C	-1°C	-	-
n-Octane	13°C	13°C	15.5°C	15°C	-	-
n-Nonane	31°C	31°C	32.8°C	33°C	-	-
n-Decane	46°C	44°C	46.1°C	48°C	-	52.8°C
n-Undecane	65°C(O.C.)	65°C(O.C.)	60°C	64°C(C.C.)	59(C.C.)	68.7°C
n-Dodecane	74°C	72°C	71.1°C	79°C	77°C～82°C	-
n-Tridecane	-	-	94°C	-	92°C	-
n-Tetradecane	100°C	-	-	-	104°C	109.3°C
n-Pentadecane	-	-	132.2	-	-	-

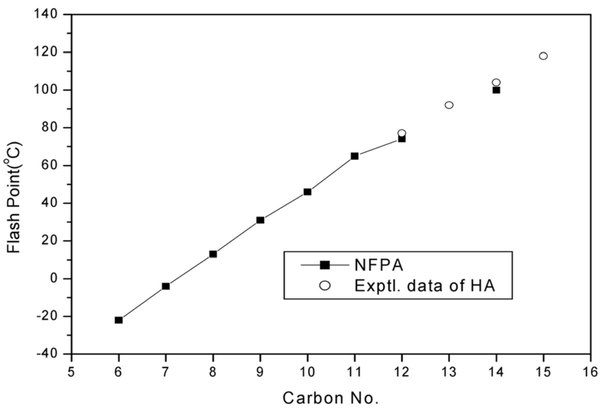

Fig. 1. A comparison between NFPA and Ha' flash points for n-alkanes.

validity of measured flash points for n-pentadecane, we compare with several sources(NFPA, SFPE, Sigma, Affens, Ha, and Montemayor) in Table 3.

Also, in order to investigate validity of flash points for n-pentadecane, we are plotted from n-hexane flash point to n-pentadecane flash point of NFPA literature and measured flash points from n-dodecane to n-pentadecane by Ha[5-8] in Fig. 1.

In plotting results, the flash point of n-pentadecane which proposed this study is similar trend the flash points of several established literatures and flash points by using Setaflash tester of Ha. Therefore, the measured flash points for n-pentadecane in this study has appropriated.

In the Fig. 1, the trend of flash point of n-undecane is beside the point from the flash points of NFPA literature because flash point of n-undecane measured the open cup(O.C.) tester.

5.3. Investigation of Autoignition Temperature of n-pentadecane

It is understood that autoignition means the ignition of combustible matter in air subjected to uniform heat. The temperature of the surrounding atmosphere(storage temperature) which initiates autoignition after self-heating of the product is called the AIT. The AIT describes the minimum temperature to which a substance must be heated, without the application of a flame or spark, which will cause that substance to ignite.

We have searched the several handbooks and references in order to investigate validity the measured AIT for n-pentadecane. But the AIT for n-pentadecane are not reported in the several handbooks and references. Therefore, we proposed experimental data which obtained in this study.

In this study, the initial temperature of autoignition for n-pentadecane set up to 170 based on the AIT of hydrocarbon compounds, however n-pentadecane do not ignited in this temperature. When temperature of autoignition set up to 200°C, a rise 30°C. The n-pentadecane ignited in 87.32 second. We are found AIT 195°C to turn down 5°C based on 200°C. The ignition delay time of AIT 195°C is ignited 199.90 second. And the ignition delay time of the ignition temperature 270°C to turn down 5~10°C based on the AIT 195°C is ignited 1.28 second.

Table 4. Comparison of experimental and calculated ignition delay time by the AIT for n-pentadecane

No.	T[K]	$\tau_{exp.}$[s]	$\ln\tau_{exp.}$	$\tau_{est.}$.(Eq. 2)
1	468	199.90	5.29782	153.61
2	473	87.32	4.46958	105.93
3	483	49.50	3.90197	51.55
4	493	25.50	3.23868	25.83
5	503	12.67	2.53924	13.31
6	513	6.57	1.88251	7.03
7	523	3.83	1.34286	3.81
8	533	2.17	0.77473	2.11
9	543	1.28	0.24686	1.20
A.A.D.	-	-	-	7.62

The relationship between the ignition temperature and the ignition delay time for n-pentadecane are summarized in Table 4.

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.

$$\ln\tau = -30.13 + 16463.38\left(\frac{1}{T}\right) \tag{3}$$

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

$$\log\tau = -13.09 + 7149.97\left(\frac{1}{T}\right) \tag{4}$$

The comparison of experimental and calculated ignition delay time by the AIT for n-pentadecane are illustrated Table 4 and Fig. 2.

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

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

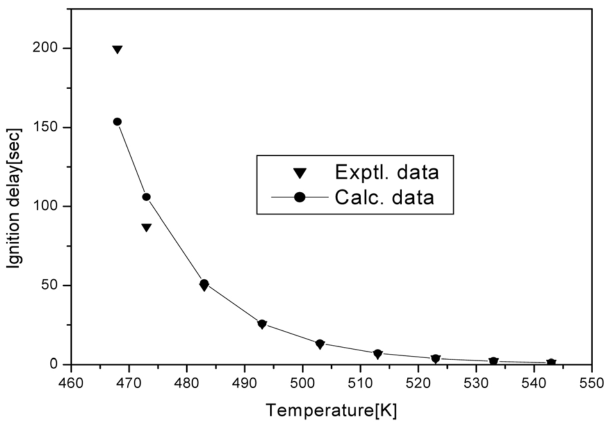

Fig. 2. A comparison between the experimental and calculated delay times for n-pentadecane.

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 7.62 second and the coefficient of determination(r^2) is 0.93.

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[12]. The activation energy can calculate by using Semenov equation[15]. Semenov related several variables by the equation

$$\log\tau = \frac{52.55E}{T} + B \tag{6}$$

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 136.06 kJ/mol.

6. Conclusions

For the safe handling of n-pentadecane, 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-pentadecane by using closed-cup tester were experimented 118°C and 122°C. The lower flash points and fire point of n-pentadecane by using open cup tester were measured 133°C and 134°C. The upper flash points of n-pentadecane by using open cup tester was measured 174°C. The calculated lower and upper explosion limit by using measured lower 118°C and upper flash point 174°C for n-pentadecane were 0.54 Vol.% and 6.40 Vol.%. The experimental AIT of n-pentadecane was 195°C. The activation energy value for n-pentadecane was 136.06 kJ/mol.

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