CHEMICAL ENGINEERING TRANSACTIONS

VOL. 52, 2016

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Peng-Yen Liew, Jun-Yow Yong, Jiří Jaromír Klemeš, Hon Loong Lam

ISBN 978-88-95608-42-6; **ISSN** 2283-9216

DOI: 10.3303/CET1652212

Effect of Experimental Conditions on Measuring Autoignition Temperature of Met-OH and Et-OH Binary Mixtures

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The principal application of autoignition temperature (AIT) is to define the maximum acceptable surface temperature in a particular area, usually for electrical classification purpose. AIT is an important variable used to characterize the fire and explosion hazard of liquids and must be known for safe handling, storage, and transportation. The measurement of AIT is defined in test methods that are maintained by standardization bodies such as the Energy Institute in the UK, ASTM in the USA, CEN in Europe and ISO internationally. This paper describes measurement on AIT of Met-OH and Et-OH Binary Mixtures. We explored effects of flask material, ambient temperature, and ambient humidity on the measured AIT of ethanol using the EN 14522:2005 and ASTM E659-78:2005 methods. Results reveal that immiscibility in the two liquid phases could be ignored in the measuring of AIT. Potential application for the results concerns the assessment of fire and explosion hazards for chemical processes containing binary immiscible mixtures of Met-OH and Et-OH system.

1. Introduction

Autoignition temperature (AIT) is defined as the lowest temperature at which a substance will produce hot-flame ignition in air at atmospheric pressure without the aid of an external energy source such as a spark or flame. On the basis of the classical thermal theory of ignition, AIT was regarded as that temperature to which a combustible mixture must be raised so that the rate of heat evolved by the exothermic oxidation reactions of the system will just overcome the rate at which heat is lost to the surroundings. Obviously, the ability of a substance to spontaneously ignite is an important index of fire hazards for people who handle, transport, and store the flammable materials. The principal application of AIT is to define the maximum acceptable surface temperature in a particular area, usually for electrical classification purposes to prevent fire and explosion hazards. AIT is also frequently used to determine the possible consequence associated with leakage of flammable chemicals in hazard risk assessment methods. Although AITs are indispensable information to safely handle and operate flammable liquids, the AITs reported in different data compilations are very diverse. The difference between different data compilations might be up to more than hundreds Kelvins for many flammable liquids. Such diversity is attributed to many experimental factors. One of the factors that contribute to this diversity is that the method to determine the AIT of liquid chemicals is not unified yet. Most methods for measuring the AIT of liquid chemicals introduce the sample into the apparatus container which is preheated to a specific temperature, and autoignition is evidenced by the sudden appearance of a flame inside the container and by a sharp rise in the temperature of the gas mixture. However, the container shape and container size are different in each test method. When the AITs reported in different data compilations are inconsistent, it is generally hard for the users to determine which value is more feasible for their problems at hand because most of the data compilations do not report the test method of their AIT data. This paper describes the experimental measurements of AIT for methanol and ethanol. Methanol (Riaz et al. 2013) and ethanol (Phuangwongtrakul et al. 2016) can be an incredibly useful resource, whether you are using it as a chemical feedstock or for its many downstream applications (Liu et al. 2016). Both substances are flammable and corrosive, and is also toxic if ingested (Hussan et al. 2013). The industry is committed to proper safety and regulation to ensure appropriate care and measures are taken when working in the chemical industry or

Please cite this article as: Veres J., Skrinsky J., 2016, Effect of experimental conditions on measuring autoignition temperature of met-oh and et-oh binary mixtures, Chemical Engineering Transactions, 52, 1267-1272 DOI:10.3303/CET1652212

using methanol and ethanol. Knowing the risks associated with these substances and taking proper safety measures in its storage and transportation can ensure the well-being of workers (Gao et al. 2016).

2. Experiments

Measurements of the autoignition temperatures were obtained from the AIT-12-I autoignition tester (SN: 321-OZM-13-01, OZM Research s.r.o., Czech Republic), shown on Figure 1. The experimental set-up consists of an electrically heated crucible furnace capable of attaining a temperature of 600 °C or higher, commercial 500-mL borosilicate round-bottom short-necked boiling flask closely wrapped in reflective aluminium foil and fine chromel-alumel thermocouple (36 B and S gage) for measuring the gas temperature inside the flask. The apparatus involved control devices that program the instrument to heat the sample at a specific heating rate within a temperature close to the expected autoignition temperature. Autoignition temperatures of the pure liquid flammable substances were determined experimentally according to the EN 14522:2005 and ASTM E659-78:2005 standards with an accuracy of 1.5 °C. A small, metered sample of the product to be tested is inserted into a uniformly heated 500-mL glass flask containing air at a predetermined temperature. The contents of the flask are observed in a dark room for 10 min following insertion of the sample, or until autoignition occurs.

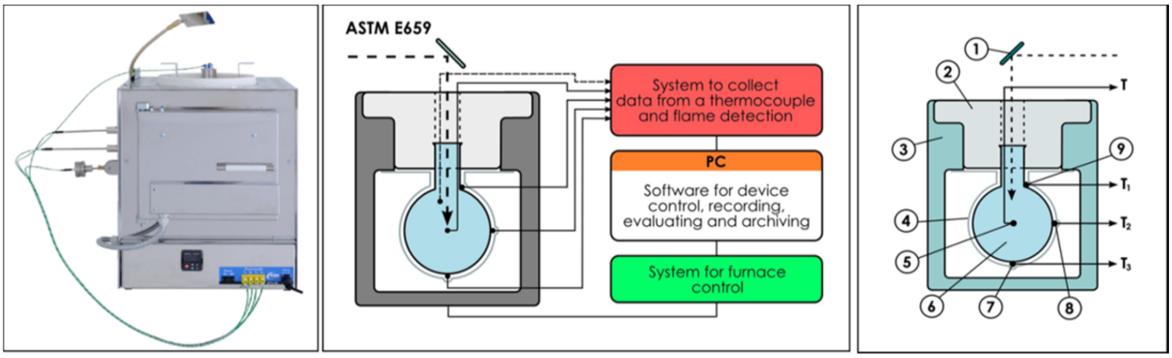

Figure 1: General diagram of the testing system adopted for the AIT tests

Figure 1 describes the individual parts of apparatus: 1) mirror mounted above the flask so that the observer may see into the flask without having to be directly over it; 2) insulated cover; 3) electrically heated crucible furnace; 4) aluminium, to promote temperature uniformity; 5) test temperature Chromel-Alumel thermocouple T, 6) borosilicate round-bottom, short-necked boiling flask; 7) external thermocouple T3 (bottom); 8) external thermocouple T2 (middle); 9) external thermocouple T1 (top). Autoignition is evidenced by the sudden appearance of a flame inside the flask and by a sharp rise in the temperature of the gas mixture. The lowest internal flask temperature (T) at which hot-flame ignition occurs for a series of prescribed sample volumes is taken to be the hot-flame AIT of the chemical in air at atmospheric pressure. Ignition delay times (ignition time lags) are measured in order to determine the ignition delay-ignition temperature relationship. The experimental procedure was repeated three times for each measurement. The experimental error given by the manufacturer for a temperature interval up to 600 °C was 1.5 °C. The autoignition analyser measured the autoignition temperature of the pure organic solutions methanol and ethanol. All investigated chemicals are purchased from commercial companies with guaranteed mass fraction purity. The physical properties of experimental materials used are summarized in Table 1.

Table 1: Physical properties of experimental materials

Chemical	Formula	Purity	Water	Company
Methanol	CH_4O	≥ 99.8 %	< 0.05 %	Merck
Ethanol	C_2H_8O	≥ 99.0 %	< 0.10 %	Merck

The details of chemical information for the compounds used in this investigation includes: the chemical formula, the mass fraction purity, the water content, and the supplier company. The guaranteed mass fraction purities of all chemicals used in the present study are more than 99.0 %.

3. Results and discussions

3.1 Effect of volume

Numerous investigators have noted that the larger the test vessel the lower is the autoignition temperature. Thus, caution is indicated in applying the temperatures derived by this method to practical situations. The determination of the vessel volume effect involves repeating these rocedures in three or more test volumes, such as 250, 500, 1,000 and 5,000 mL, of the same geometry. A plot of autoignition temperature versus logarithm of the vessel volume can be helpful in estimating the AITs at other volumes. At the present study we have investigated the AIT at the tested volume 500 mL. The effect of volume on AIT is presented in Figure 2.

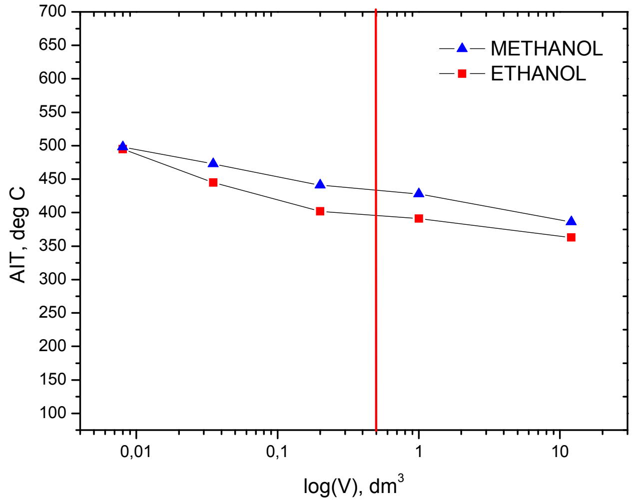

Figure 2: Autoignition temperature owing to the MeOH and EtOH with denoted AIT (red line) recorded at VEC, VSB-TU Ostrava

3.2 Effect of concentration

The autoignition data for a pure substance were obtained from various sources, such as ISCS (International Safety Chemical Cards), the SFPE (Society of Fire Protection Engineers) handbook, HCH (Hazardous Chemicals Handbook), the Merck index or DIPPR (2016).

Table 2: Comparison of autoignition temperatures values adopted from the literature with experimentally derived data for methanol and ethanol

Chemical	Present study[a]	Experimental data[c]	ISCS	SFPE	HCH	Merck	DIPPR
Methanol	430 ± 1.5	433.1 ± 8.7	464	385	464	455	464
Ethanol	376 ± 1.5	368.8 ± 7.4	363	365	423	425	403

[a)] experiments were carried out three times for each chemical; [b)] EN 14522:2007; [c)] Chen et al., 2012

Table 2. compares the experimentally derived data in this study with those for the autoignition temperature for the studied chemicals and the values adopted from the literature ISCS, the SFPE handbook, HCH, the Merck index and DIPPR. In Table 2., for example the values of the AIT for methanol adopted from ISCS, SFPE, HCH and DIPPR (363 °C, 365 °C, 423 °C and 403 °C, respectively) clearly appear to be quite different. The corresponding value provided by the chemical supplier of the ethanol used herein, Merck, is 425 °C, which is quite similar to that value adopted by HCH. The experimentally derived autoignition temperature for methanol and ethanol is the same as that found in various literature sources EN 14522:2007 and Chen et al., 2012, although there appeared some slight deviation between our experimentally derived data and the analogous value reported for methanol and ethanol in the literature. Our experimental autoignition temperatures for the tested methanol and ethanol substances are close to the literature-derived values ISCS and SPFE, except for the ethanol mentioned above with a greater difference from other sources (Table 2.). A typical time history of the temperature inside the test flask during an experimental run is shown in Figure 3.

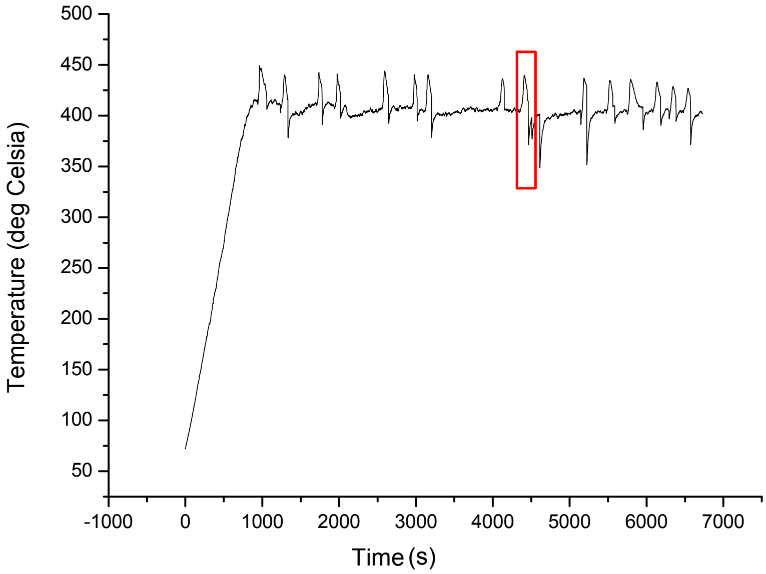

Figure 3: Autoignition temperature owing to the MeOH/EtOH (50:50 vol.%) recorded at VEC, VSB-TU Ostrava with denoted minimum autoignition temperature (rectangle)

The occurrence of an autoignition was evidenced by the sudden appearance of a flame inside the flask and by a sharp rise in the temperature of the gas mixture. When the mixture exhibited flames (Figure 4) at the preset temperature, the next sample of the same quantity is tested at a lower temperature.

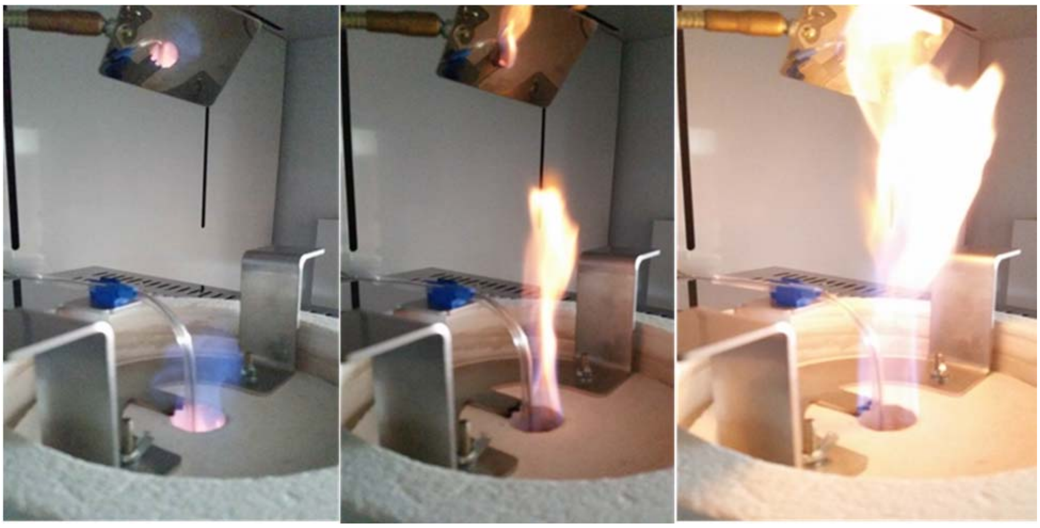

Figure 4: Development of the flames emitted above the top of the flask

These procedures were repeated until the lowest temperature at which the sample of a given quantity exhibited flame was obtained. Such a series of tests was represented by those points on the same vertical line shown in any of the plots in Figure 3.

In Figure 5 exact magnitudes of the temperature are not intended to be necessarily significant as the recorder is set to be of different scaling factors in different temperature ranges. The initial dip on the curve shown in the figure is caused by cooling due to vaporization of the sample. When the mixture exhibited flames at the preset temperature, the next sample of the same quantity is tested at a lower temperature.

These procedures were repeated until the lowest temperature at which the sample of a given quantity exhibited flame was obtained. Such a series of tests was represented by those points on the same vertical line shown in any of the plots in Figure 3. In any plot, a circle is used to represent the flammable case, and an x is used to represent the nonflammable case. Then, different sample quantities are employed until the amount giving the lowest temperature of autoignition is obtained.

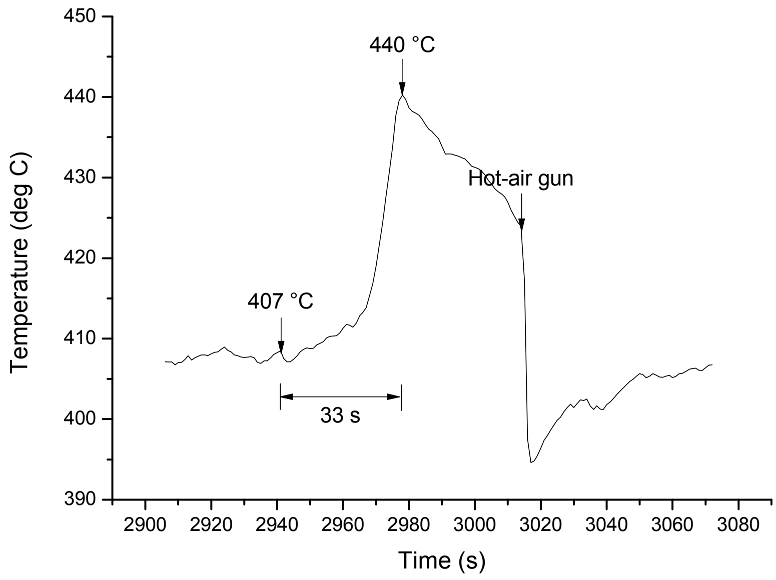

Figure 5: Time history of minimum autoignition experiment for MeOH/EtOH (50:50 vol.%)

The AIT values are plotted against the ambient temperature as shown in Figure 6. It is found from Figure 6 that there is a quadratic relation between the reported AIT and the ambient temperature (see the first crosses after circles). According to this quadratic relation, the ambient temperature at which the lowest AIT of MeOH/EtOH mixture is found to be 407 ± 1.5. The reason why such a quadratic relation between the AIT and ambient temperature holds for alcohols is still not clear to us. Therefore, the further studies are planned to understand such phenomena to make sure this behavior is experimentally repeatable. We have conducted other experiments with alcohols to be confident about this behavior.

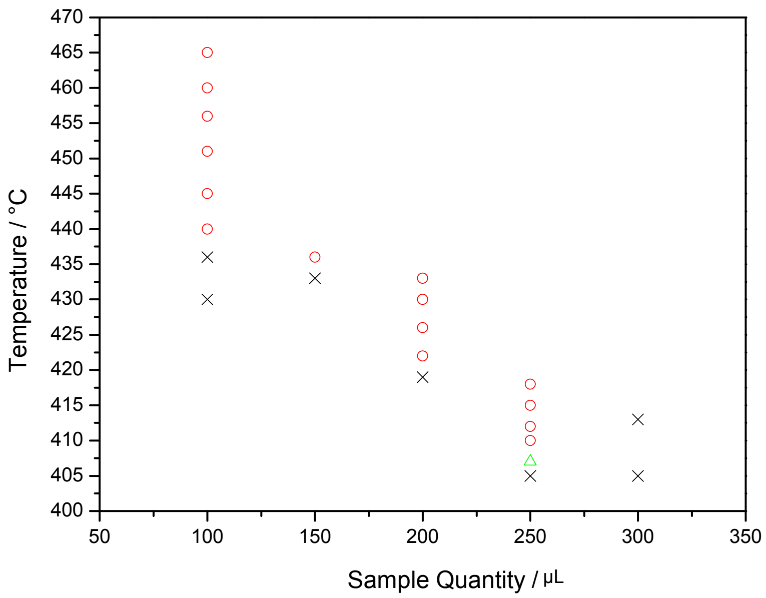

Figure 6: Ignition temperature at different sample volumes for MeOH/EtOH (50:50 vol.%): circle - flammable case; cross - non-flammable case; triangle - the lowest flammable temperature

4. Conclusions

In this work, the AITs of frequently used alcohol are measured in compliance with the ASTM E659-78:2005 standard. The AITs were measured for methanol and ethanol, respectively. The present work led to the accurate determination autoignition temperatures of methanol and 1-penthanol to be 430 ± 1.5 and 376 ± 1.5 °C. However, although AITs are indispensable information for safely handling flammable liquids the reported AITs of flammable liquids in different data compilations are very much diverse. This could be because of different experimental conditions on measuring autoignition temperature It is found that the AIT reported in ISCS is beyond the reproducibility in cases of methanol and ethanol, and the difference is up to 30 °C and 10 °C. The SFPE service reports the AIT beyond the reproducibility in methanol and ethanol with differences of 45 °C and 11 °C, respectively. The DIPPR reported the AIT of methanol and ethanol with differences similar to HCH and ISCS and 27 °C, respectively. The HCH reports the AIT of both investigated chemicals out of the reproducibility for the ethanol with the difference of 46 °C and for the methanol with the difference of 34 °C that is similar to Merck with differences 50 °C and 34 °C, respectively. We reported the autoignition temperature 407 ± 1.5 °C owing to the MeOH/EtOH (50:50 vol.%) for the first time. The corresponding ignition delay is 33 s for 250 μL sample volume.

Acknowledgments

This work was prepared within the project „Innovation for Efficiency and Environment - Growth“, identification code LO1403 with the financial support from the Ministry of Education, Youth and Sports in the framework of the National Sustainability Programme I.

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