CHEMICAL ENGINEERING TRANSACTIONS
VOL. 53, 2016

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

Guest Editors: Valerio Cozzani, Eddy De Rademaeker, Davide Manca

ISBN 978-88-95608-44-0; **ISSN** 2283-9216

DOI: 10.3303/CET1653008

Autoignition Temperature of 1-Pentanol and its Binary Mixtures with Water

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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. In this work, the AITs of 1-pentanol and its binary mixtures with water are measured in compliance with the EN 14522:2005 and ASTM E659 method. The measured AITs are (288±1.5 °C, 298±1.5 °C), and for 1-pentanol and 1-pentanol+water mixtures, respectively. It is found that the AIT reported in DIPPR 2012 and HCH is in the reproducibility, and the difference is up to 10 °C. The ISCS, SFPE, Merck reports the AIT beyond the reproducibility in with differences of 32 °C, 152 °C and 22 °C. Measured AIT of 1-pentanol conducted with 12% of water will result in a value higher than the one without water by 10 °C.

1. Introduction

Aqueous solutions of alcohols are of considerable interest for a wide range of scientists and technologists. Aqueous solutions of alcohols are often employed in the extraction and manipulation of labile materials such as proteins (Franks and Desnoyers, 1989). 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. Autoignition, by its very nature, is dependent on the chemical and physical properties of the material and the method and apparatus employed for its determination. The autoignition temperature by a given method does not necessarily represent the minimum temperature at which a given material will self-ignite in air. 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.

Please cite this article as: Veres J., Skrinsky J., Travnickova J., Dalecka A., Sevcikova S., 2016, Auto-ignition temperature of 1-pentanol and its binary mixtures with water, Chemical Engineering Transactions, 53, 43-48 DOI: 10.3303/CET1653008

2. Experiment

2.1 Experimental device

Autoignition temperatures were measured from the AIT-12-l autoignition tester (SN: 321-OZM-13-01, OZM Research s.r.o., Czech Republic) see 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. 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. 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. 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.

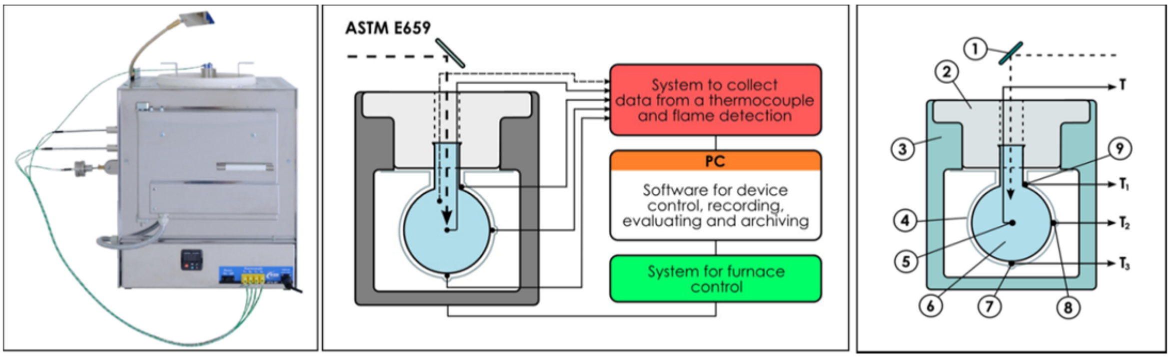

Figure 1: General diagram of the testing system adopted for the AIT tests

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).The temperature uniformity according to ASTM E659-78:2005 in Figure 2 were obtained with the furnace configuration shown in Figure 1.

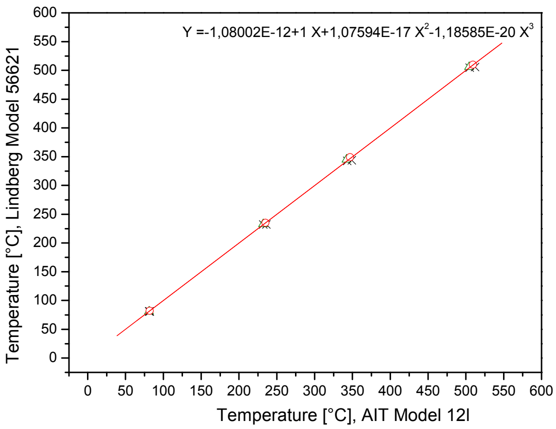

Figure 2: Temperature uniformity according to the Lindberg Model 56621

2.2 Chemicals used in the experiment

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: The purity of chemicals for the experiments

Chemical	Formula	Purity	Water	Company
Water (HPLC grade)	H_2O	≥ 99.9995%	≥ 99.9995%	Chemical Lab
1-pentanol	$C_5H_{12}O$	≥ 99.0%	< 0.5000%	Sigma-Aldrich

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 % for 1-pentanol and ≥ 99.9995% for water without further purification. The 1-pentanol (2.7 g) + water (97.3 g) mixture was prepared according to the limited, 12 vol.%, missibility of water in 1-pentanol.

3. Results and discussion

Guided by previous studies (Table 2), the AIT of 1-pentanol in its pure state has been investigated in the 284-310 °C region and extended to the 320 °C for water + 1-pentanol. 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 (Design Institute for Physical Property Research).

Table 2: Comparison of autoignition temperatures values adopted from the literature with experimentally derived data for 1-pentanol

Chemical	Present study[a]	ISCS	SFPE	HCH	Merck	DIPPR
1-Pentanol	288±1.5	320	440	300	310	300

a) experiments were carried out three times for each chemical

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 1-pentanol adopted from ISCS, SFPE, HCH and DIPPR (320 °C, 440 °C, and 300 °C, respectively) clearly appear to be quite different. The corresponding value provided by the chemical supplier of the 1-pentanol used herein, Sigma Aldrich, is 310 °C, which is quite similar to that value adopted by Merck. The experimentally derived autoignition temperature for 1-pentanol is lower as that found in various literature sources. Our experimental autoignition temperatures for the tested substance are close to the literature-derived values from HCH and DIPPR, except for the values 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.

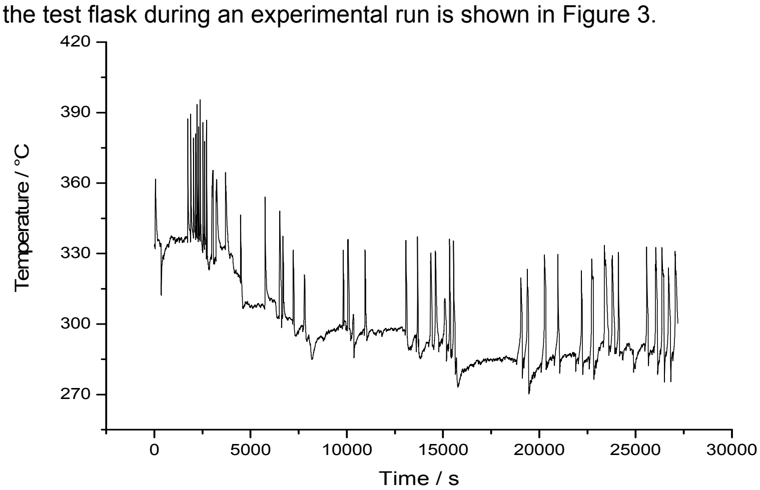

Figure 3: AIT owing to the 1-pentanol recorded at VEC, VSB-TU Ostrava

The occurrence of an autoignition was evidenced by the sudden appearance of a flame inside and outside of 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.

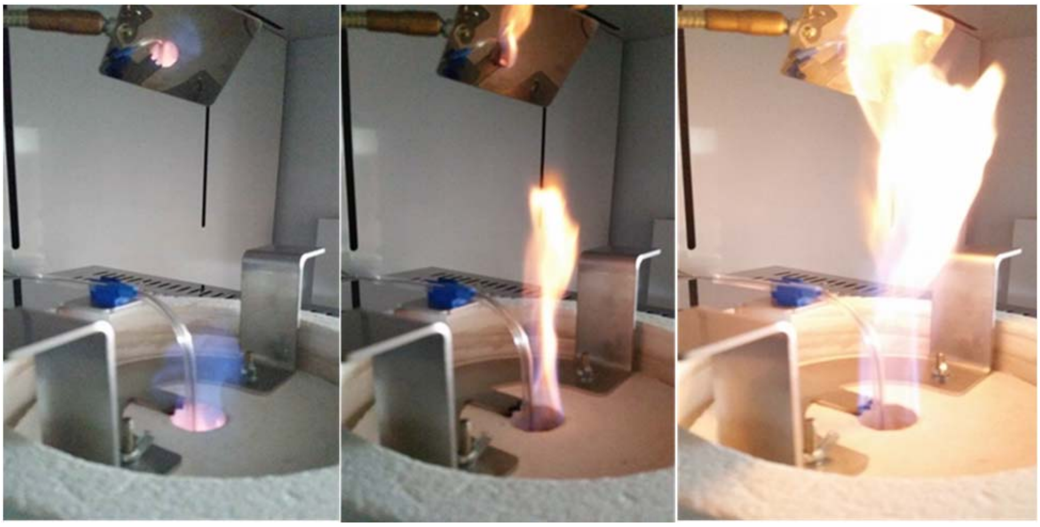

Figure 4: Development of the flames emitted above the top of the flask

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 5.

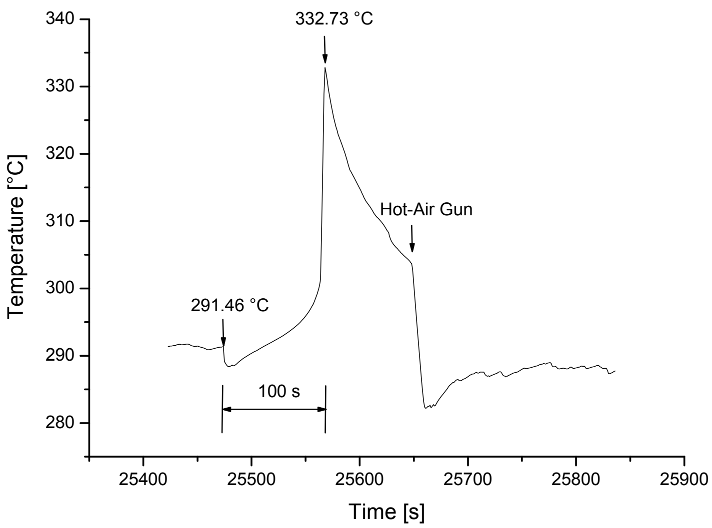

Figure 5: Time history of a typical autoignition experiment ($C_5H_{12}O$, 200 µl, 292 °C)

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 5. 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.

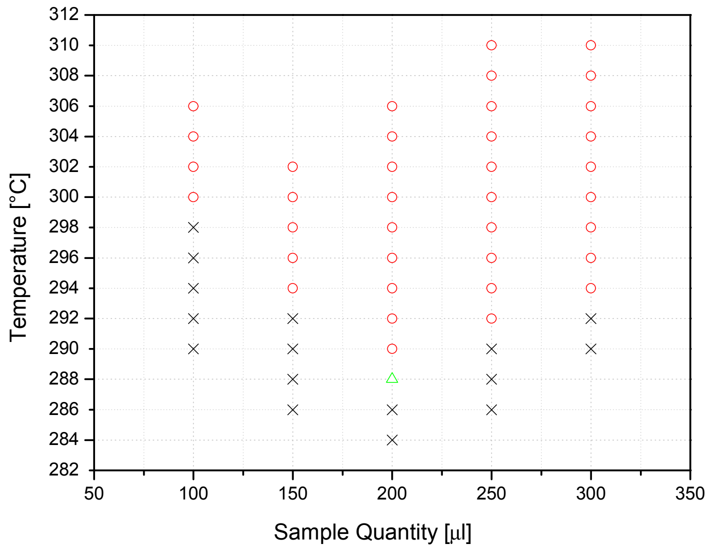

Figure 6: Ignition temperature at different sample volumes for 1-pentanol (circle: flammable case; cross: non-flammable case; triangle: the lowest flammable temperature)

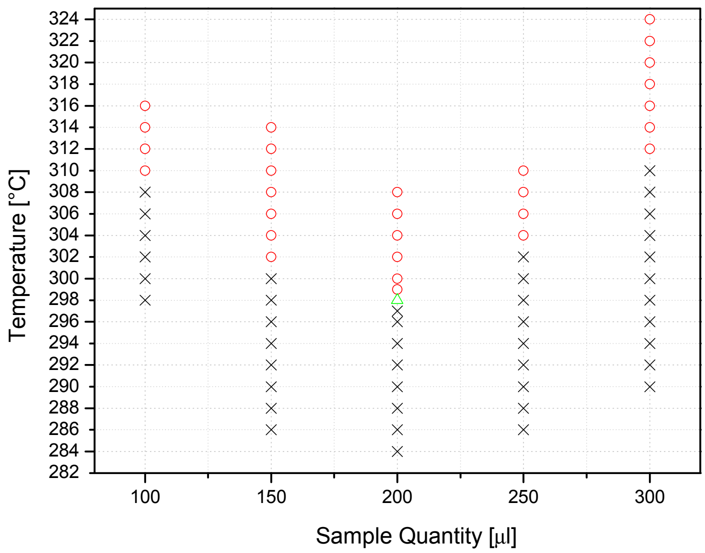

Figure 7: Ignition temperature at different sample volumes for 1-pentanol+water (circle: flammable case; cross: non-flammable case; triangle: the lowest flammable temperature)

The AIT values are plotted against the ambient temperature as shown in Figure 6-7. It is found 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 1-pentanol and 1-pentanol+water is found to be 288±1.5 °C and 298±1.5 °C, respectively. 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 behaviour. The experimental data of 1-pentanol was compared with 1-pentanol+water values. Significant 10 °C deviations were observed for the 12 vol.% 1-pentanol+water mixtures that implies the dependency. Figure 8 compares in detail the two individual AIT test results of 1-pentanol with and without water at the same experimental conditions.

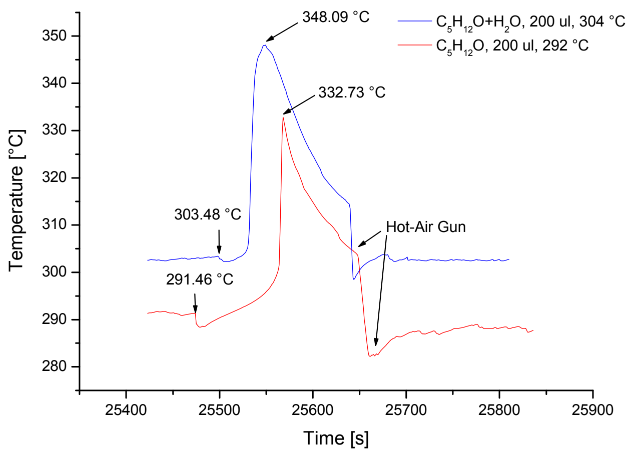

Figure 8: Comparison of two individual AIT test results of 1-pentanol with and without water at the same experimental conditions

4. Conclusions

In this work, the AITs of frequently used alcohols are measured in compliance with the EN 14522:2005 and ASTM E659-78:2005 standards. The AITs were measured for 1-pentanol and 1-pentanol/water mixture, respectively. The present work led to the accurate determination of autoignition temperatures of 1-pentanol and 1-pentanol/water mixture to be 288±1.5°C and 298±1.5°C. The autoignition temperature of 1-pentanol was experimentally obtained for the first time. 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. It is found that the AIT reported in SFPE is beyond the reproducibility in case of 1-pentanol, and the difference is up to 50 °C. The ISCS service reports the AIT beyond the reproducibility in 1-pentanol with differences of 34 °C and 32 °C, respectively. The DIPPR and HCH only report the AIT of 1-pentanol within the reproducibility. The Merck reports the AIT of investigated chemical out of the reproducibility with the difference of 22 °C. The AIT dependency of alcohols on water content described in detail on 1-pentanol+water mixture is not published in the literature while these mixtures are very widespread in process industry at given conditions.

Acknowledgments

This work would not have been possible without the financial support of Innovation for Efficiency and Environment - Growth, reg. no. LO1403 supported by National Programme for Sustainability and financed by the Ministry of Education, Youth and Sports.

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