

## Autoignition Temperature of Alcohol/air mixtures

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The alcohol/air mixtures are successful in the practical use as gasoline and diesel fuel additives and this has motivated the full investigation of their combustion chemistry. The AIT for alcohol/air mixtures shows the large inconsistency due to various physical-chemical factors which effect its values as the chemical composition, concentration, volume and shape of the flask. The novelty of the article is the investigation of the effect of alcohol's isomeric structure on its combustion properties with no change in the fuel's physical-chemical properties. This paper describes a series of experiments performed to study the autoignition characteristics of propanol isomer (1-propanol and 2-propanol)–air binary mixtures. The experiments were conducted in two different experimental arrangements—a 500 ml spherical vessel and a 250 ml conical vessel—for different liquid equivalence ratios between 50  $\mu\text{l}$  and 300  $\mu\text{l}$ , and initial temperatures between 25 and 700  $^{\circ}\text{C}$ . We explored isomeric effect, and effects of the flask shape and volume on the measured AIT by using both the EN 14522:2005 and ASTM E659-78:2005 methods.

### 1. Introduction

AITs are together with flash-point, lower and upper explosion limits essential information to safely handle and operate flammable liquids. The interrelation of these safety parameters is depicted in Figure 1. The flash-point of a liquid is given in the Figure 1 as  $T_L$ . At that temperature, the vapour pressure at the liquid surface is at the lower flammable limit. The corresponding upper limit temperature is given as  $T_U$ . The principal application of AIT is to define the maximum acceptable surface temperature in a particular area.

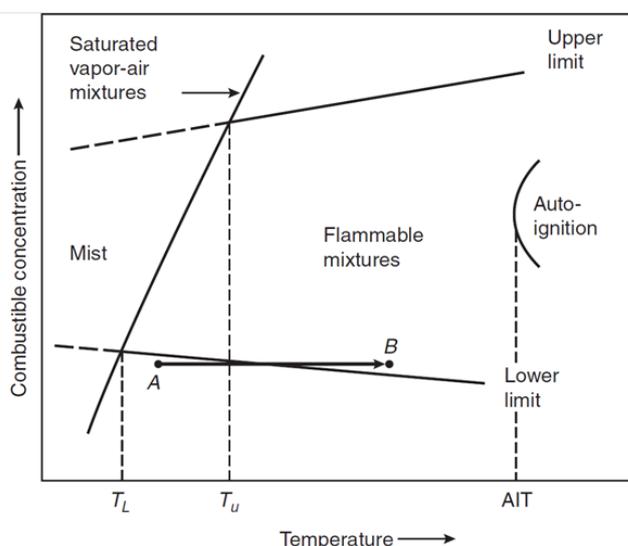


Figure 1: Effect of temperature on limits of flammability of a combustible vapour in air (SFPE, 2002)

AITs reported in different data compilations are very diverse as demonstrated in Table 1. The autoignition data for pure substances 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, DIPPR (Design Institute for Physical Property Research) or GESTIS (Gefahrstoff informations system).

Table 1: Comparison of AIT values adopted from the literature with experimentally derived data

Chemical	Present study <sup>a</sup>		Experiment <sup>b</sup>	ISCS	SFPE	HCH	Merck	DIPPR	GESTIS
	250 ml	500 ml	500 ml						
Methanol	462±9.2	434±8.7	433±8.7	464	385	464	455	464	440
1-Propanol	403±8.1	388±7.8	380±7.6	371	440	433	400	371	385
2-Propanol	440±8.8	427±8.5	-	456	-	-	425	455	425

<sup>a</sup>) experiments were carried out three times for each chemical; <sup>b</sup>) Chen et al., 2012

Table 1 compares the experimentally derived data in this study with those for the autoignition temperature for the studied chemicals and the values adopted from literature as the ISCS, the SFPE handbook, HCH, the Merck index, DIPPR and Gestis. In Table 1, for example the values of the AIT for 1-propanol adopted from ISCS, SFPE, HCH, DIPPR and Gestis (371 °C, 440 °C, 433 °C, 371 °C and 385 °C) clearly appear to be quite different. The corresponding value provided by the chemical supplier of the 1-propanol used herein, Merck, is 400 °C, which is quite similar to the value measured in present study. The most conservative values are found in Chen et al., 2012. It seems that the values reported for 1-propanol by SPFE and HCH with a greater difference from other sources, is similar to that obtained for 2-propanol. The difference between different data compilations appears to be up to 60 °C for 1-propanol while the experimental error given by the standards is 2 % that is in the order of 10 °C. 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. The effect of chamber size on the observed autoignition temperature was previously studied in ERC by means of test units of the following volumes: 0.008, 0.035, 0.2, 12, and 15 dm<sup>3</sup> depicted in Figure 2. From the results presented in Figure 2 it is evident that the autoignition temperature of the liquid is decreasing with the increasing volume of the test flask.

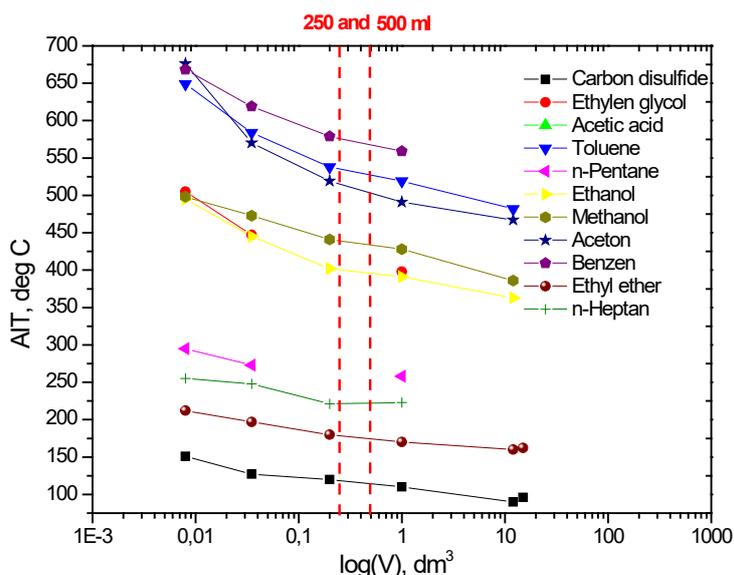


Figure 2: Autoignition temperature of selected substances

## 2. Experiment

### 2.1 Methods used for experimental measurement of AITs

The sample, approximately (50 to 300)  $\mu\text{l}$ , was inserted into a uniformly heated 250 or 500-ml glass flask containing air at a predetermined temperature. The contents of the flask have been 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 (ASTM E659, 2015). When the mixture exhibited flames at the pre-set temperature, the next sample was tested at a lower temperature. These procedures were repeated until the lowest temperature at which the mixture exhibited flame was obtained. The quantity of added sample was then systematically varied to determine the lowest temperature at which the hot flame ignition occurs, and the lowest internal flask temperature at which hot-flame ignition occurred was taken to be the AIT of the chemical in air at atmospheric pressure. Hot-gun air was used to purge the product gases after a test was completed and before the next test. To avoid interference from the ambient temperature, 10 min elapsed time is considered to allow time for ambient temperature of thermal equilibrium between trials. During the experiment, the ambient temperature is controlled to be about 20 °C. 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 autoignition temperature (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. In this work, the reproducibility will be taken as the admissible error of 2 % to compare experimental results with those reported in other data compilations. Because all existing methods of measuring AIT detect the sudden appearance of a flame inside the ignition container by visual inspection, the accuracy for measuring AIT is greatly limited by human capabilities. For example, it has been pointed out that in some cases autoignition actually begins with a nonluminous or barely luminous reaction, which is difficult to detect by visual inspection. Beside the problem of human capability, some researches also revealed that the measurement of AIT was notorious sensitive to vessel cleanliness, injection rate and uniformity of sample dispersion.

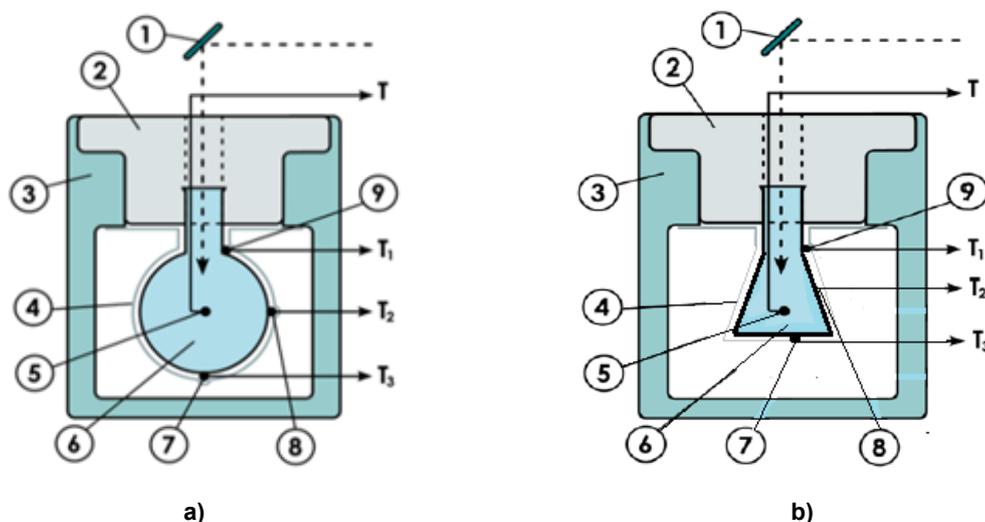


Figure 3: AIT apparatus with a) 500 ml round bottom and b) 250 ml conical flask.

Figure 3 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 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. The autoignition analyser measured the autoignition temperature of the pure organic solutions methanol, and propanol isomer (1-propanol and 2-propanol)-air binary mixtures was produced by OZM Research, s.r.o.

## 2.2 Materials tested

The flammable liquids selected for these tests are listed in Table 2.

Table 2: List of alcohols selected for the tests

Chemical	Formula	Purity	Water	Company
Methanol	CH <sub>4</sub> O	≥ 99.8%	< 0.05%	Merck
1-Propanol	C <sub>3</sub> H <sub>8</sub> O	≥ 99.9%	< 0.05%	Penta
2-Propanol	C <sub>3</sub> H <sub>8</sub> O	≥ 99.9%	< 0.05%	Penta

All investigated chemicals are purchased from commercial companies with guaranteed mass fraction purity. 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

Figure 4 below illustrates the temperature-time record of experimentally determined AIT (selected) for 1-propanol.

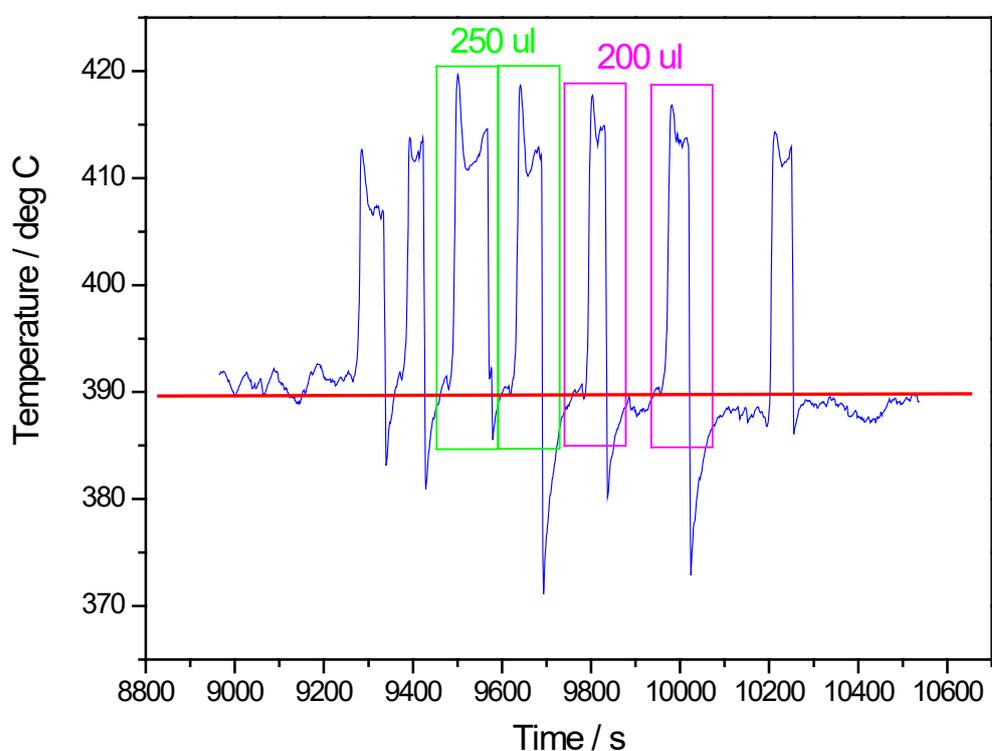


Figure 4: Minimum autoignition temperature at 200  $\mu$ l and 250  $\mu$ l sample's volume for 1-propanol

Figure 4 shows the typical combustion plot records. In this Figure, the x-axis is the time when the sample is added into the combustion container, and the y-axis is the preheated temperature of the combustion container. The red line denotes derived AIT. In Figure 4, AITs of 1-propanol are measured with 500 ml flask in compliance with the ASTM E659-78:2015 method. In case of both 200  $\mu$ l sample introduced generates a hot flame in several seconds, these cases are taken as a flammable one. In case of both 250  $\mu$ l samples do not generates a hot flame and these cases are taken as a non-flammable one.

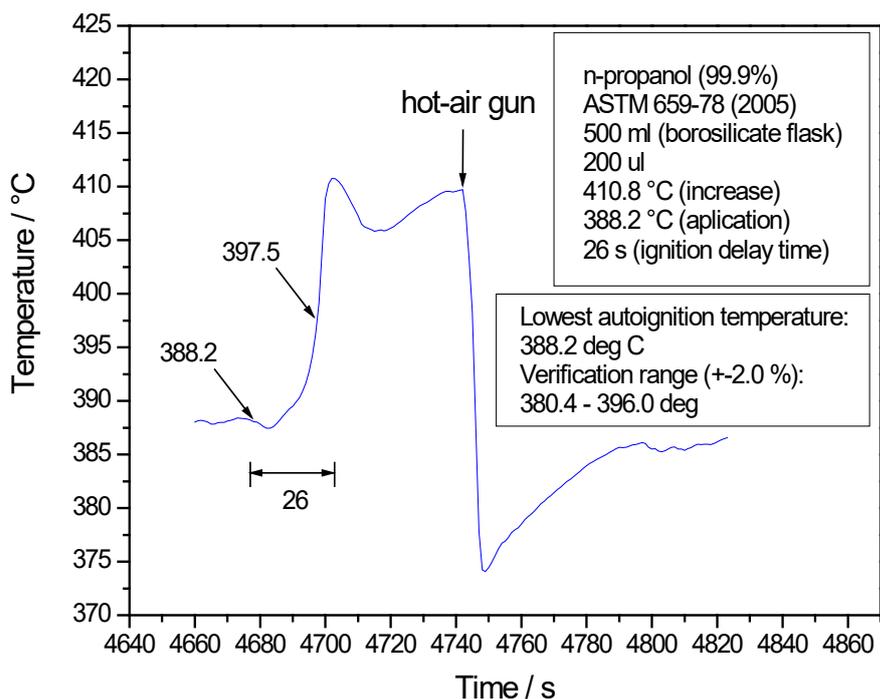


Figure 4: Minimum autoignition temperature at 200  $\mu$ l sample volume for 1-propanol

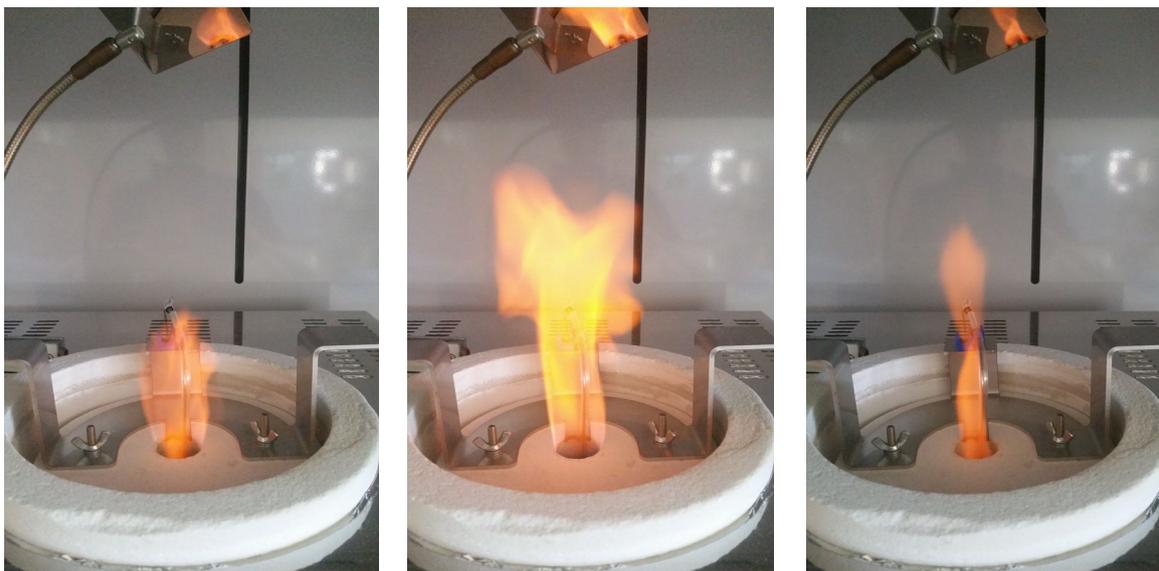


Figure 5: Development of the flames emitted above the top of the flask

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. In Figure 4 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. Then, different sample quantities are employed until the amount giving the lowest temperature of autoignition is obtained.

#### 4. Conclusions

In this work, the AITs of frequently used alcohol are measured in compliance with the ASTM E659-78:2015 and EN 14522:2005 standards. The AITs were measured for propanol isomer (1-propanol and 2-propanol)–air binary mixtures, respectively. The present work led to the accurate determination of autoignition temperatures of 1-propanol and 2-propanol to be  $440\pm 8.8$  °C and  $427\pm 8.5$  °C. It is found that the AIT reported in SPFE and HCH are beyond the reproducibility in cases of 1-propanol, and the difference is up to 35 °C and 45 °C. The AIT reported in SPFE and HCH are beyond the reproducibility in cases of 2-propanol. The SPFE and HCH reported the AIT of 1-propanol with differences similar to present study, Merck and GESTIS for 2-propanol, respectively. We reported the autoignition temperature  $440\pm 8.8$  °C and  $427\pm 8.5$  °C owing to the 2-propanol-air mixture for the first time. The corresponding ignition delay is 28 s for 250  $\mu$ l sample volume. The experiments were conducted in two different experimental arrangements - one was a 500 ml spherical vessel and the other a 250 ml conical vessel - for different liquid equivalence ratios between 50  $\mu$ l and 300  $\mu$ l, and initial temperatures between 25 and 700 °C. We explored that the effects of the flask shape and volume on the measured AIT by using both the EN 14522:2005 and ASTM E659-78:2015 methods is 15 °C in case of 1-propanol and 13 °C in case of 2-propanol at given experimental conditions. The structure isomeric effect - arrangements of OH atoms in propanol molecules introduced the difference of 37 °C and 39 °C for 1-propanol and 2-propanol –air binary mixtures. Based on the knowledge of these characteristics, it is possible to evaluate the influence of the carbon chain structure and blending ratio on the fundamental combustion characteristics – flash-point and lower flammable limit and upper flammable limit of these alcohol mixtures and compare them with the values from small-scale experiments.

#### Acknowledgments

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