



Experimental Study on the Autoignition Characteristics of Water-Methanol-Diesel Mixtures

Jan SKRÍNSKÝ¹⁾, Ján VEREŠ²⁾, Silvie PETRÁNKOVÁ ŠEVČÍKOVÁ³⁾

¹⁾ VSB – Technical University of Ostrava, Energy Research Center, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic; email: jan.skrinsky@vsb.cz

²⁾ VSB – Technical University of Ostrava, Energy Research Center, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic; email: jan.veres@vsb.cz

³⁾ VSB – Technical University of Ostrava, Energy Research Center, 17. listopadu Str. 15, 708 33 Ostrava-Poruba, Czech Republic; email: silvie.sevcikova@vsb.cz

DOI: 10.29227/IM-2017-01-25

Abstract

The principal application of autoignition temperature (AIT) is to define the maximum acceptable surface temperature in a particular area. 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. Water/methanol injection (WMI) systems reduce air inlet temps and enhance combustion efficiency on turbo diesel applications. Simple mixtures exhibiting minimum autoignition behavior has been verified to be existed. However, the minimum autoignition behavior of multi-component mixture is not discussed in literature. The simple, binary and ternary solutions of n-heptane, acetone, methanol, diesel, methanol + water, methanol + diesel, methanol + water + diesel were selected as examples to investigate the minimum autoignition behavior of flammable liquids in this study.

Keywords: autoignition temperature, wastewater, n-heptane, acetone, methanol, diesel

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. Water/methanol injection systems reduce air inlet temps and enhance combustion efficiency on turbo Diesel applications, which allows an engine to deliver more power with less effort. Water/methanol injection also offers a host of benefits that promote engine longevity, including the reduction of carbon deposits left by a Diesel's exhaust gas recirculation (EGR) system. AEM's Water/Methanol Injection Systems for turbo Diesel trucks and SUVs utilize the most robust hardware combined with more advanced features than any other comparably priced water/methanol injection system. The performance advantages of using greater than 50% methanol concentrations are small, if they exist at all. However, the safety issues are very real and far outweigh any perceived benefit of running high concentrations of methanol. One of the key concerns with using alcohol fuels in diesel engines is their poor ignition quality. This work presents the ignition characteristics of methanol examined under simulated diesel engine conditions in a constant-volume 5-mL vessel. The ignition characteristics of acetone and normal n-heptane

measured under the same conditions are also included for reference.

Materials

All investigated chemicals are purchased from commercial companies with guaranteed mass fraction purity. The chemicals used are summarized in Table 1.

Test method

The prepared mixtures were stirred by a magnetic stirrer for 10 minutes before the autoignition test. The sample of the product to be tested, approximately (50 to 250) μL , was 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. When the mixture exhibited flames at the preset 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 autoignition temperature (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

Tab. 1 Physical properties of experimental materials

Tab. 1 Właściwości fizyczne materiałów użytych w eksperymentach

Component	Formula	Purity (mass %)	Water (mass %)	Company
n-heptan	C ₇ H ₁₆	>99.8	<0.1%	Merck
acetone	C ₃ H ₆ O	>99.9	<0.01%	Merck
methanol	CH ₃ OH	>99.8	<0.1%	Merck
diesel	hydrocarbons C9 - C20	-	-	MOL Česká republika, s.r.o.
water	H ₂ O	<0.1%	>99.998	Sigma Aldrich

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. The experimental precision of the ASTM E659 is defined in its document which includes: (1) repeatability duplicate results by the same operator should be considered suspect if their difference δAIT is more than $\delta\text{AIT}/\text{AIT} = 0.02$ where the temperature AIT is in degrees Celsius; (2) reproducibility the results submitted by each of two laboratories should be considered suspect if the two results as δAIT differ by more than $\delta\text{AIT}/\text{AIT} = 0.05$ where the temperature AIT is in degree Celsius. In this work, the reproducibility will be taken as the admissible error 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.

Experimental Apparatus

Autoignition temperature measurements were made on the AIT-12-L autoignition apparatus manufactured by the OZM, Research Company. The AIT-12-L instrument is designed to meet the test requirements described by the test method of ASTM E659-78 (2005).⁵ This apparatus consists of an ignition chamber of a commercial 500 mL borosilicate round-bottom, short-necked boiling flask wrapped with aluminum foil and an elec-

trical heated furnace with a cylindrical interior shape to maintain uniform temperature. Furnace temperatures were monitored at the bottom, side, and neck of the flask with three external thermocouples. A fine Chromel - Alumel thermocouple was used for measuring the gas temperature inside the flask. A furnace provides rapid response and 1°C stability throughout the operating range of 200 to 600°C. A 300 μL hypodermic syringe with a 5 cm needle was used to inject the sample into the flask. A mirror was mounted above the flask at approximately 60 degree angle to see into the flask without having to be directly over it.

Results and discussion

Figures 1 to 4 show the combustion plots of experiments for acetone, n-heptane, methanol, diesel, respectively. 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 Figures 1–4. In any plot, a circle is used to represent the flammable case, and a cross is used to represent the non-flammable case. Then, different sample quantities are employed until the amount giving the lowest temperature of autoignition is obtained. The autoignition temperature of a compound corresponds to this lowest temperature and is designated as a triangle in the plots.

Figures 1–4 shows experimental results for all the four test runs described further in Figures 5–8. Such experiments are carefully conducted in our laboratory flask according to the prescribed conditions listed in test method, and the results are summarized in Table 2. The results of pure chemicals have been used for more difficult investigation of their mixtures. A typical time history of the temperature inside the test flask during an experimental run is shown in Figures 5–8. In this figures 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

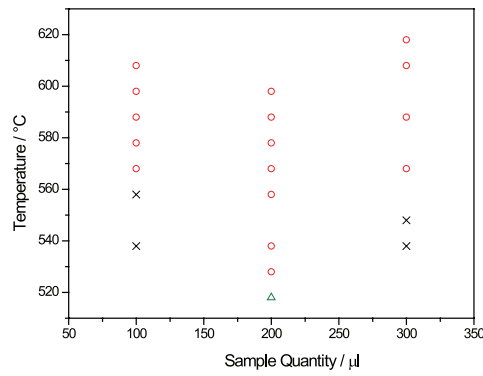


Fig. 1 Ignition temperature at different sample volumes for acetone
 Rys. 1 Temperatura zapłonu przy różnych objętościach acetonu

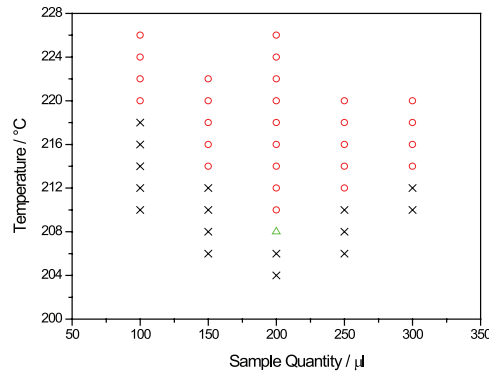


Fig. 2 Ignition temperature at different sample volumes for n-heptane
 Rys. 2 Temperatura zapłonu przy różnych objętościach n-heptanu

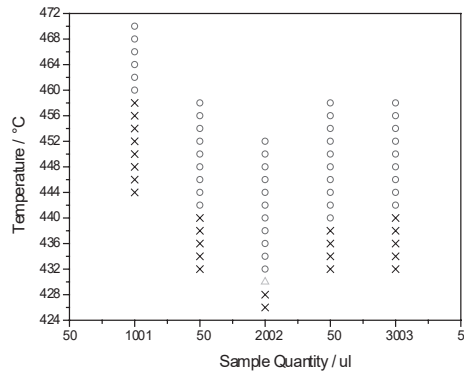


Fig. 3 Ignition temperature at different sample volumes for methanol
 Rys. 3 Temperatura zapłonu przy różnych objętościach metanolu

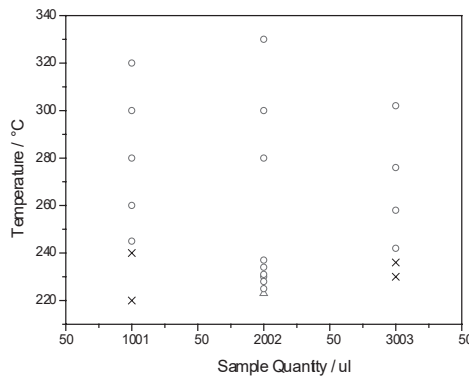


Fig. 4 Ignition temperature at different sample volumes for diesel
 Rys. 4 Temperatura zapłonu przy różnych objętościach oleju napędowego

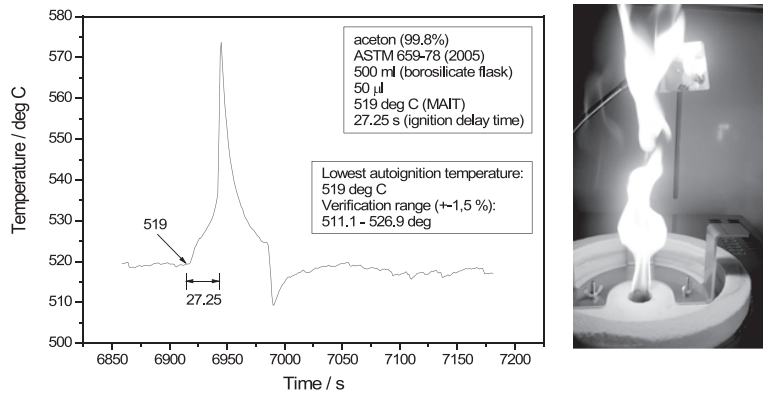


Fig. 5 Minimum autoignition temperature at 50 μ l sample volume for acetone
Rys. 5 Minimalna temperatura samozapłonu przy objętości próbki 50 μ l dla acetonu

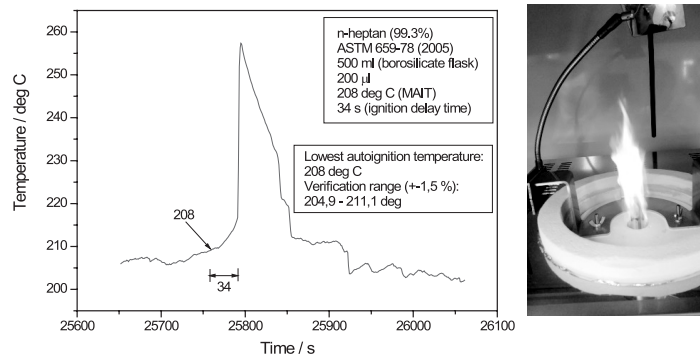


Fig. 6 Minimum autoignition temperature at 200 μ l sample volume for n-heptane
Rys. 6 Minimalna temperatura samozapłonu przy objętości próbki 200 μ l dla n-heptanu

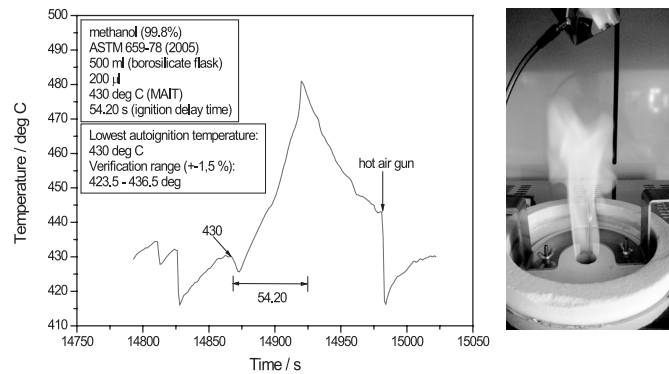


Fig. 7 Minimum autoignition temperature at 200 μ l sample volume for methanol
Rys. 7 Minimalna temperatura samozapłonu przy objętości próbki 200 μ l dla metanolu

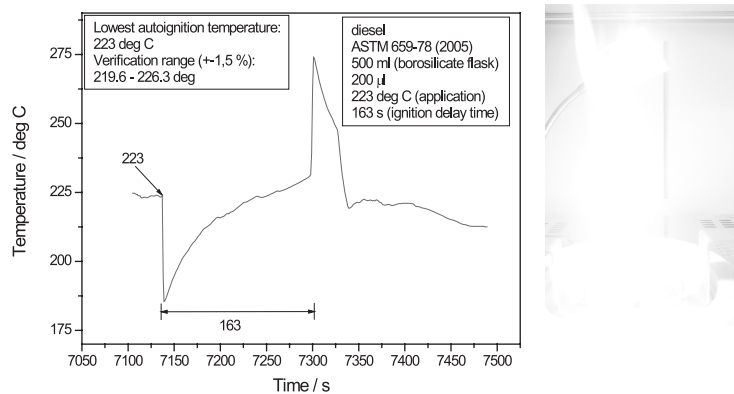


Fig. 8 Minimum autoignition temperature at 200 μ l sample volume for diesel
Rys. 8 Minimalna temperatura samozapłonu przy objętości próbki 200 μ l dla oleju napędowego

Tab. 2 Comparison of AIT values adopted from the literature with experimentally derived data

Tab. 2 Porównanie wartości AIT ze źródeł literaturowych oraz zmierzonych podczas badań

Component	Present study	Experimental data	ISCS	SFPE	HCH	Merck	DIPPR	GESTIS
n-heptane	208±1.0	221	220.0	215.0	223.0	215.0	204.0	220.4
acetone	519±1.5	535	465.0	465.0	538.0	465.0	465.2	527.5
methanol	430±1.5	433	464.0	385.0	464.0	455.0	463.9	440.0
diesel	218±1.0	210	269.5	225.0	-	-	-	225.0
methanol+water	460±1.5	-	-	-	-	-	-	-
methanol+diesel	423±1.5	-	-	-	-	-	-	-
methanol+water+diesel	513±1.5	-	-	-	-	-	-	-

the figure is caused by cooling due to vaporization of the sample (in Figure 7 denoted as hot air gun). 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. This behavior could be possibly explained as follows. The AIT is regarded as the 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 overbalance the rate at which heat is lost to the surroundings. However, in the ASTM E659 method, a flask with opening to the ambient environment is used as the ignition container; thus, besides the heat loss to the electrically heated furnace, the heat loss to the ambient environment should also be considered. In the aspect of heat loss, there are three mechanisms that heat could release to the electrical heated furnace and ambient environment: conduction, convection, and radiation. However, only the former two mechanisms are important to a combustion process at low temperature, which is the case of autoignition. The liquid inter-laboratory test samples (acetone and n-heptane) in Figures 5–6 were chosen because they are the verification substances in the recent edition of EN 14522:2005, Annex 1, Table A.1.

As seen from Figures 5–8, there is a specific amount of sample quantity at which this minimum ignition temperature of a chemical occurs. If the quantity added is higher or less than this specific amount, it needs higher temperature to ignite the chemical. This specific sample amount that results in the autoignition temperature is listed in the second column in Figures 5–8 for all investigated chemicals. The ignition delay time is defined to be the time lapse between application of heat to a material and its ignition. Obviously it is an important characteristic of flammable liquids for assessing fire safety hazards. Figures 5–8 also lists the ignition delay time at the experimental condition that AIT occurs for all investigated pure chemicals. The ignition delay times are found to be of 39.2 s, 110.0 s, and 132.0 s for methanol + water, methanol + diesel, methanol +

water + diesel, respectively. The ignition delay times are longer than one minute for all explored mixtures in contrast with pure chemicals, except for diesel and methanol + water mixture.

The autoignition data for a pure substance have been 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, the DIPPR (Design Institute for Physical Property Research) or GESTIS (Institute for Occupational Safety and Health of the German Social Accident Insurance). Table 2 compares the experimentally-derived data in this study with experimentally derived data for the minimum autoignition temperature for the studied pure chemicals and the values adopted from the literature.

The value of the autoignition temperature for e.g. for methanol adopted from (Dinenno et al., 1995) and (Gestis, 2016) (385.0 and 440.0°C, respectively) clearly appear to be quite different. The corresponding value provided by the chemical supplier of the methanol used herein, Merck, is 455°C, which appears to be quite similar to that value adopted by (DIPPR 2016; Carson et al., 2002; ISCS, 2016). The experimentally derived value of the MAIT for diesel is similar as the value adopted from various literature sources (Dinenno et al., 1995) and (ISCS, 2016), although there did appear to exist some slight deviation between our experimentally derived data and the analogous value reported for n-heptane and acetone in the literature. Our experimental MAIT for those four substances are close to the literature-derived values (Gestis, 2016), except for the methanol and diesel mentioned above with a greater difference from other sources (Table 2). There are currently not published studies on methanol + water, methanol + diesel, methanol + water + diesel mixtures.

Conclusion

In this work, the AITs of four frequently used pure chemicals are measured in compliance with

the ASTM E659 test method. The measured AITs are (208.0±1.0)°C, (519.0±1.5)°C, (430.0±1.5)°C, (218.0±1.0)°C, for n-heptane, acetone, methanol, diesel, respectively, and (460.0±1.5)°C, (423.0±1.5)°C and (513±1.5)°C for methanol + water (90:10), methanol + diesel (50:50), methanol + water + diesel (45:5:50) mixtures, respectively. It is found that the differences in measured AIT and the one reported are beyond the reproducibility in n-heptane, acetone and

methanol. The mixtures AITs have been measured for the first time.

Acknowledgements

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.

Literatura – References

1. CARSON, Phillip, et al. Hazardous Chemicals Handbook. 2nd edition. Oxford: Elsevier, 2002, ISBN: 978-0-7506-4888-2.
2. DINENNO, Philip, et al. SFPE Handbook of Fire Protection Engineering. 2nd edition. Boston: Society of Fire Protection Engineers 1995.
3. DIPPR Project 801 - Full Version. Design Institute for Physical Property Research/AICHe. Design Institute for Physical Properties, Sponsored by AICHe.
4. FRANKS, Felix et al. Water Science Reviews 1. 1st edition. Cambridge: Cambridge University Press, 1989, ISBN: 9780521099028.
5. International Labour Organization, International Safety Chemical Cards database [online]. [cit. 2016-05-11]. Available on WWW: <<http://www.ilo.org/dyn/icsc/showcard.home>>.
6. The GESTIS Substance Database contains information for the safe handling of hazardous substances and other chemical substances at work. Available on WWW: <gestis-en.itrust.de/>.
7. The Merck Index. 14th edition. Whitehouse Station, New Jersey: Merck & Co., Inc., 2007, ISBN: 978-0-911910-00-1.
8. SKŘÍNSKÝ, Jan et al. Flashpoint prediction for binary mixtures of alcohols with water in order to improve their safety. In Chemical Engineering and Technology 38, 2015, p. 727-733.

Badanie eksperymentalne charakterystyki samozapłonu mieszanek wodno-metanolo-olejowych

Głównym zastosowaniem wartości temperatury autozapłonu (AIT) jest określenie maksymalnej akceptowalnej temperatury powierzchni. AIT jest ważną zmienną stosowaną w celu opisanego zagrożenia pożarowego i wybuchowego cieczy i musi być znana w celu zapewnienia bezpieczeństwa, określenia warunków przechowywania oraz transportu. Systemy zapłonu woda/metanol (WMI) redukują temperaturę powietrza na wlocie i zwiększają efektywność spalania w silnikach diesla. Stwierdzono, że proste mieszanki wykazują minimalny poziom samozapłonu. Jednakże minimalny poziom temperatury samozapłonu mieszanki wieloskładnikowej nie został dotąd przedstawiony literaturze. Proste, dwu i trójskładnikowe roztwory inheptanu, acetonu, metanolu, oleju napędowego, metanolu z wodą, metanolu z olejem napędowym, metanolu z wodą oraz olejem napędowym zostały wybrane jako przykłady do zbadania minimalnej temperatury samozapłonu.

Słowa kluczowe: temperatura autozapłonu, woda odpadowa, n-heptan, aceton, metanol, olej napędowy