

Investigation of the explosive hazard of mixtures containing hydrogen peroxide and different alcohols

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Received 25 November 2003; received in revised form 20 January 2004; accepted 20 January 2004

Abstract

The explosive properties of mixtures of aqueous hydrogen peroxide (H_2O_2) and different alcohols (R–OH) like 2-propanol (2-PropOH), 2-methyl-2-propanol (TBA), 2-methyl-2-butanol (TAA) and 2-methyl-2-pentanol (THA) were investigated. Among others, the potential hazard of such mixtures may be characterized by their ability to react by different mechanisms of an explosion in the condensed phase, e.g. the thermal explosion or the detonation. Accordingly, the mixtures were experimentally investigated either by heating them up under confinement in different autoclaves or by exposing them to a shock wave impact applying the steel tube test. The results are discussed and compared to literature data.

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Keywords: Mixtures of hydrogen peroxide and alcohols; Explosive properties; Steel tube test; TEVT; MCPVT

1. Introduction

In various chemical processes mixtures of H_2O_2 and organic compounds are present, e.g. for the production of H_2O_2 , for oxidation and bleaching processes or for the synthesis of organic peroxides [1,2]. Such mixtures are well known for their hazard potential [3,4]. There exists a range of concentrations where they have explosive properties. Possible explosion mechanism are thermal explosion, deflagration and detonation. The explosions can be initiated e.g. thermally, by shock wave impact, by ignition or by mechanical impact. Experts are quite aware of the fact, that the observed range of explosibility of different organic compounds mixed with H_2O_2 depends on the used experimental method as well as on the individual properties of the organic compounds and the concentration of H_2O_2 in the used mixtures [5–10].

Process design, like the determination of safe feed rates, safe initial concentrations and the operating temperature,

requires reliable knowledge of the thermal explosion and detonation behaviour of the reaction mixture. This article focuses on this basic information for alcohol/ H_2O_2 mixtures.

In the open literature, data for H_2O_2 /alcohol mixtures are mainly restricted to ethanol and 2-PropOH. Details of the explosivity of mixtures with alcohols of higher chain length, such as equal or greater than C_4 with a primary, secondary or tertiary structure are hardly known. To determine the explosive properties of such types of dangerous mixtures various methods are described. Frequently used test methods are the blasting cap test (shock sensitivity), the drop weight test (impact sensitivity), tests with spark ignition [5–7,10] and different small scale heating tests. Numerous standardized test methods are published in the UN Recommendations on the Transport of Dangerous Goods [11], which may be used not only for transport classification.

In this work, the thermal explosion range of mixtures of 2-PropOH, TBA, TAA and THA with aqueous H_2O_2 in various ratios were determined by heating them under confinement. In addition some investigations on mixtures of H_2O_2 with ethanol and 1-butanol were carried out. The influence of heating rate and sample mass were investigated only in a representative manner, using mixtures of H_2O_2 with

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TBA. Additionally, mixtures of H₂O₂ with 2-PropOH or TBA, respectively, were tested for their ability to propagate a detonation and the received results were compared with the results of the other tests.

2. Test procedure

The effect of heating under confinement was studied using the Mini Closed Pressure Vessel Test (MCPVT) [12–16] and the Thermal Explosion Vessel Test (TEVT) [17]. The TEVT was used in two modifications, version A, which is in compliance with [17]. The vessel was heated by a heating plate, while in version B the vessel was heated by a heating chamber. To investigate the ability of such mixtures to propagate a detonation the BAM 50/60 steel tube test (UN Test A.1) [11] in its cavitated version was used. This is a common method developed at BAM for testing organic peroxides and mixtures with H₂O₂, which can decompose by producing gas. For such systems it is highly recommended to investigate their ability to propagate a detonation using a cavitated version of a steel tube test [11,18].

A detailed description of the methods used is given in the literature, modifications will be explained in the following part. The essential parameters of methods relevant are listed in Table 1.

2.1. TEVT equipment and parameters

For both TEVT versions (versions A and B) the heating rate of 18 K/min was adjusted by calibrating the system with 5 g silicon oil as reference substance in a temperature range between 313 and 393 K. A 85 bar bursting disk was installed to protect the autoclave against dangerous overpressure. The TEVT was sealed by a FEP coated silicon O-ring. The glass sample holder had an outer diameter of 50 mm and a height of 20 mm. The temperature was recorded by two thermocouples, ones in the test substance and ones in the gas/vapour phase with 1 data point per second. The pressure was measured with 7500 data points per second.

The criteria for the evaluation is the pressure effect [17]. The pressure effect is the product of maximum pressure and maximum pressure rise. A result above 100 MPa²/s has to be evaluated as “violent”.

2.1.1. Version A (heating plate)

The power of the heating plate was about 2000 W. In order to achieve the required heating rate of 18 K/min a steering device has been installed.

2.1.2. Version B (heating chamber)

The heating chamber was double walled and heated by hot air which flowed through the chamber from the bottom.

2.2. MCPVT equipment and parameters

A standard heating rate of 2.4 K/min is proposed in the literature [12,13]. In addition, some measurements were carried out with heating rates of 4.8 and 9.6 K/min. The heating was constant over the whole temperature range. In deviation from [12] the autoclave was equipped with an aluminium seal (to avoid decomposition of H₂O₂ on the copper surface) and a 185 bar bursting disk. The pressure data capture rate was 10 000 data points per second. The temperature was recorded with 1 data point per second.

The criteria for the evaluation is the pressure rise in combination with the so called “event temperature” [14].

2.3. BAM 50/60 steel tube test (UN Test A.1, cavitated version)

In order to prevent the contact of the hydrogen peroxide with steel, the bottom of the tube was coated with Teflon and the inside was lined with a thin foil of polyethylene. The cavitation was achieved by passing a constant stream of gas bubbles of pure oxygen with a flow rate of about 28 l/min through the liquid. The bubbles were generated by a porous glass filter positioned centrally on the bottom. To consider the height of the glass filter and the distribution of the bubbles the tube was lengthened up to 600 mm. The tube was entrenched 550 mm deep in sand. In contrast to the tests concerning the thermal explosion range these test series have been carried out at room temperature.

The criteria for the evaluation is the type of fragmentation [11]. If the tube is fragmented completely than the substance is able to propagate a detonation (“yes”). “Partial” means that the tube is fragmented only at the initiator end and the fragmented length is greater than 1.5 times of the fragmentation length found with an inert material. Consequently, “no” means that the tube is fragmented only at the initiator end.

Table 1
Parameters of the discussed methods

Parameter	TEVT	MCPVT	SBC	BAM 50/60 (cavitated)	TNO 50/60 (not cavitated)
V _{vessel} (ml)	≈200	≈6	≈400	≈1170	≈980
V _{vessel} /V _{sample}	≈40:1	≈6:1	≈1.34:1	1:1	1:1
Heating rate (K/min)	18	2.4	30	–	–
Coating (%)	≈25	≈90	Not known	≈100	Not known
Sample mass (g)	≈5	≈1	–	–	–
Sample volume (ml)	–	–	≈300	≈1170	≈980
Detected explosion mechanism	Thermal explosion	Thermal explosion	Thermal explosion	Propagate a detonation	Propagate a detonation

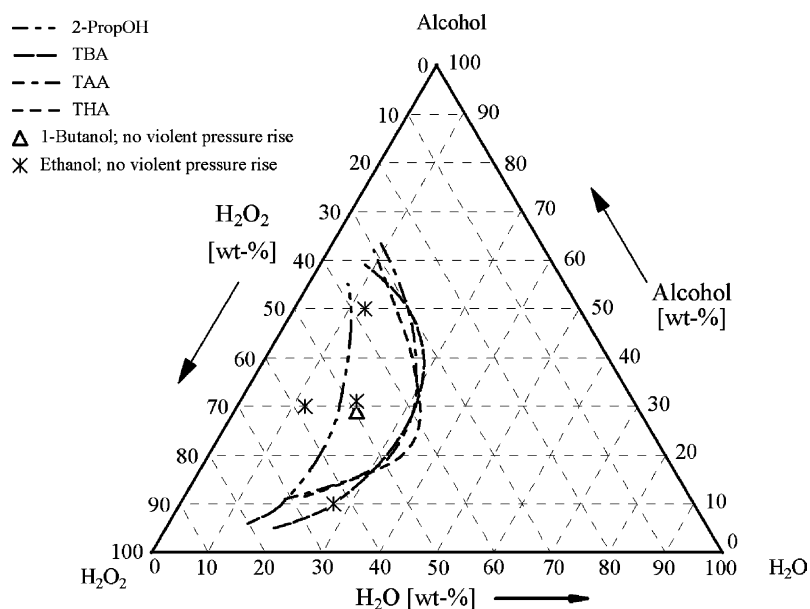


Fig. 1. Thermal explosion ranges of alcohol/H₂O₂ mixtures obtained in TEVT version B.

3. Results

The detected explosion ranges for the different alcohol/H₂O₂-mixtures characterized by violent pressure rise strongly depend on the used test method and the organic compound.

Figs. 1, 2 and 5 represent among other test results the concentration ranges where violent thermal explosion occurred, triggered by heating up the sample under confinement. The H₂O₂ concentrations in the aqueous stock solutions were varied between 85 and 50% (w/w) (H₂O₂ 85–50%). The amounts of R–OH were added in steps of 5% (w/w) to the aqueous H₂O₂ solutions. In the figures, the test points are

not given here but the borderlines, which separates very fast thermal explosions with violent pressure rise and decompositions with slow pressure rise. Violent pressure rise means that the bursting disk was ruptured. Slow pressure rise have been measured in a range of 0.001–0.1 MPa/s with a maximum pressure of about 0.6–1.0 MPa. This kind of result, without any transition range between ‘slow’ and ‘violent’ pressure rise was observed in most of thermal explosion tests (TEVT versions A and B, MCPVT). Only at one point (H₂O₂ 60% (w/w) aqueous solution with 50% (w/w) TBA) a transition from rupture of the bursting disk to a slower pressure rise was observed. Here, the bursting disk was not ruptured and the evaluation of this TEVT experiment showed

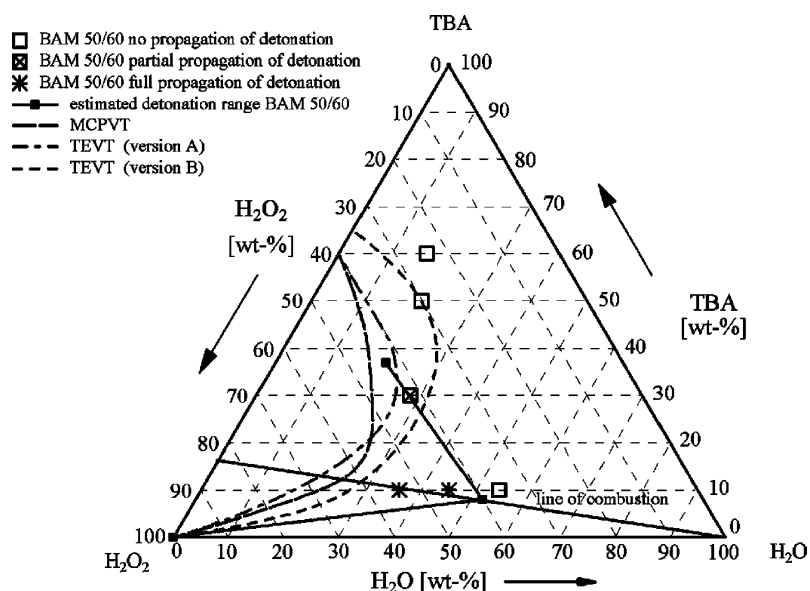


Fig. 2. Explosion ranges of TBA/H₂O₂ mixtures obtained with MCPVT, TEVT (versions A and B) and BAM 50/60 steel tube test, cavitated version.

a pressure effect of about $130 \text{ Mpa}^2/\text{s}$. According to the UN Recommendations [17] such a result should be classified as “violent”.

Fig. 1 shows results of the TEVT version B for mixtures of H_2O_2 with different alcohols. 2-PropOH, a secondary alcohol, leads to the smallest explosion range. The explosion ranges of the tertiary alcohols (TBA, TAA, THA) are similar to each other and substantially larger than the observed range for 2-PropOH. 2-PropOH and the tertiary alcohols differ in their structure and the inductivity to the OH-bond. The tertiary alcohols differ in their chain length. Shape and position of the explosion ranges will be influenced by the portion of atoms in the alcohol molecules, which are still oxidizable. It seems, that under the used test conditions the influence of the chain length is comparatively small to the influence of inductivity.

Investigations with 1-butanol confirm this predication (see Fig. 1). In the middle of the concentration range for mixtures of TBA with aqueous H_2O_2 where violent thermal explosions occurred, mixtures with the same concentration of 1-butanol showed no violent thermal explosions under the same test conditions.

The shape of the explosion range obtained from thermal explosion tests was more different than expected (see Fig. 2). All authors [5–7,9,10] have published the point of intersection (POI) of upper and lower explosion limits on or nearby the stoichiometric line of combustion of H_2O_2 and R-OH. Heemskerk and Scholtes [8] showed this for their thermal explosion investigation with the so-called small scale cook-off autoclave (SBC). Using the TEVT, we found the POI for the violent thermal explosions at about 32% (w/w) H_2O_2 , 40% (w/w) TBA and 28% (w/w) water (TEVT version B) and at about 42% (w/w) H_2O_2 , 35% (w/w) TBA and 22% (w/w) water (TEVT version A). That is a difference to the concentration of stoichiometric combustion partially up to about 30% (w/w) alcohol and also to the shape of the detonation range.

4. Comparison of the results

In order to obtain the basic process design data for mixtures of H_2O_2 containing TBA, such mixtures were investigated with different test methods. Fig. 2 shows the results for the TEVT version A and B, the MCPVT and BAM 50/60 steel tube test in its cavitated version.

The explosion ranges for a thermal explosion vary from test method to test method. Using the TEVT version B the largest explosion range was detected. With the MCPVT the smallest explosion range was found. The contours of the explosion ranges for TEVT and MCPVT differ also.

The different results of the TEVT version A and B can be explained by a different heat transfer into the autoclave (see test description). The consequence are different temperature profiles from the bottom to the top of the autoclave. A strong temperature gradient in version A causes a separation of the mixture compounds. During the experiment a condensed reflux from the top cools the autoclave. Remains of the mixture were found under the sample glass holder after the experiment. These effects were strongly reduced when the TEVT version B was used.

Fig. 3 shows temperature versus time plots for both TEVT versions with the same concentrations of H_2O_2 and TAA. The difference in temperature courses is discernible, especially in the gas/vapour phase. The temperature in the gas/vapour phase was measured about 4 cm above the measurement point of the sample temperature. The sample temperature observed in TEVT version A shows a striking change in temperature progress at about 115°C . Above the boiling point (bp) of this mixture (bp TAA = 102.2°C [19]; bp $\text{H}_2\text{O}_2(60\%) = 119^\circ\text{C}$ [1]) the temperature rise of the sample in TEVT version A is strongly reduced, and did not reach the temperature where the violent reaction starts. The bursting disk did not rupture, in contrast to the result from TEVT version B.

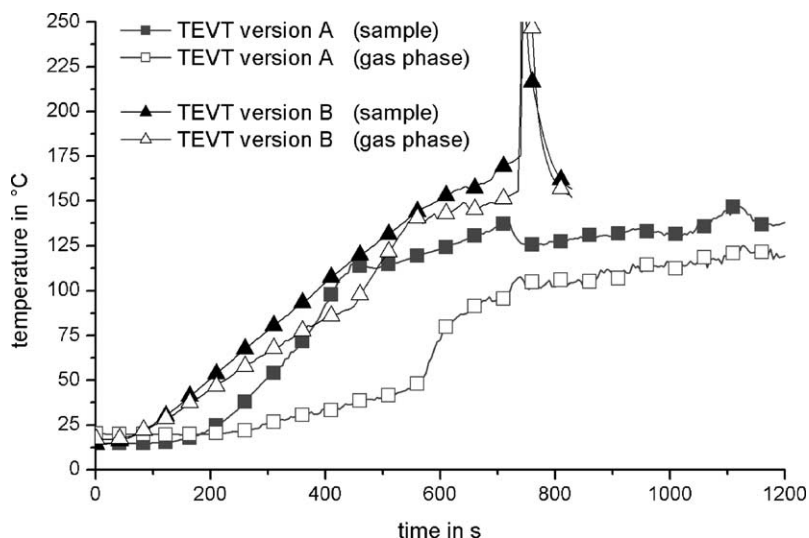


Fig. 3. Effect of different kinds of heat transfer by using TEVT versions A and B (aqueous H_2O_2 60% in mixture 60 wt.% H_2O_2 to 40 wt.% TAA).

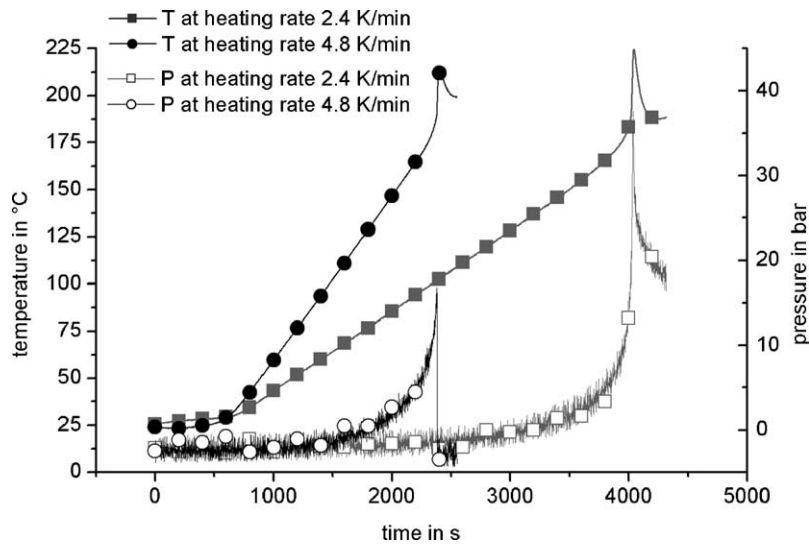


Fig. 4. Temperature and pressure courses effected by different heating rate in MCPVT (aqueous H₂O₂ 80% in mixture 50 wt.% H₂O₂ to 50 wt.% TBA).

The MCPVT is a screening method for testing the effect of heating up substances under confinement with special emphasis on the observation of the resulting pressure build-up. It is well known, that the heating rate affects the results in this thermal test, as described among others by Hasegawa and Tamura [20] for different self-reactive substances. In order to investigate this influence on the mixtures considered in this study a mixture of aqueous H₂O₂ 80% (w/w) and 50% (w/w) TBA were heated up with varying rates up to 9.6 K/min.

Fig. 4 shows temperature and pressure profiles for two different heating rates (2.4 and 4.8 K/min). The test with the standard heating rate of 2.4 K/min reached a higher maximum temperature, but the bursting disk was not destroyed.

The thermal explosion at 4.8 K/min is very fast and violent (bursting of the disk). A heating rate of 4.8 K/min expands the range of thermal explosion with violent pressure rise considerably.

Among other things Figs. 2 and 5 show results of BAM 50/60 steel tube tests, cavitated version. The connecting line between the tested concentration points was drawn as recommended in the literature [5–10]. That means, the upper and lower detonation limit meet at the stoichiometric line of complete combustion and are placed between the results “propagation of a detonation” and “no propagation of a detonation”.

In contrast to the results of the thermal explosion tests, the detonation range of mixtures of H₂O₂ with 2-PropOH (POI: H₂O₂ = 31% (w/w), 2-PropOH = 7% (w/w), H₂O = 62%

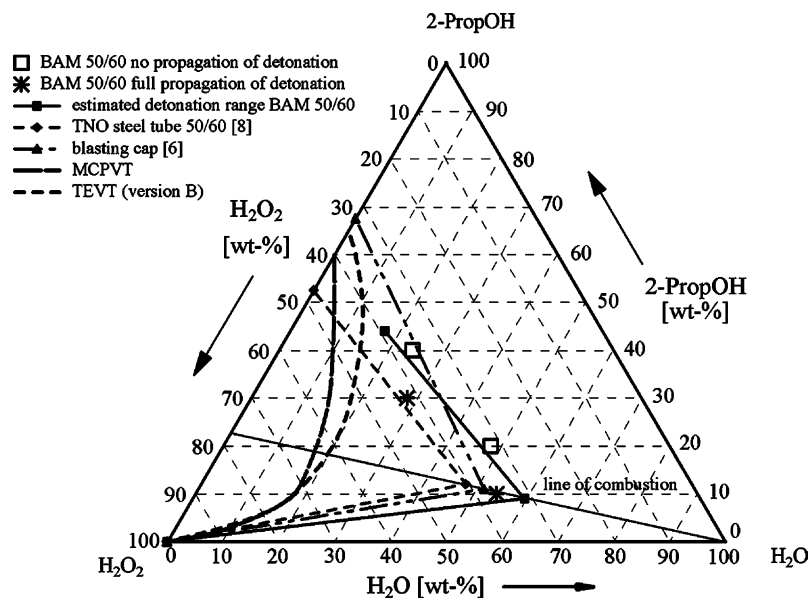


Fig. 5. Investigated explosion range of 2-PropOH/H₂O₂ mixtures and comparison to data from literature.

(w/w)) is larger than the detonation range for mixtures with TBA (POI: $\text{H}_2\text{O}_2 = 40\%$ (w/w), TBA = 8% (w/w), $\text{H}_2\text{O} = 52\%$ (w/w)). The most violent fragmentation of the steel tubes we found was at concentrations nearby the stoichiometric line of complete combustion. The results of thermal explosion tests and the BAM 50/60 steel tube test (cavitated version) differ significantly, what principally has to be expected. The variation of the shapes of explosion ranges and also the difference of concentrations at the points of intersection of upper and lower explosion limits were higher than expected.

5. Discussion

Obviously there is a strong dependence of the explosive properties of the investigated mixtures on the chemical structure of the alcohols, especially on the inductive effect on the OH-bond. Thermal explosion test results for 2-PropOH differ from results for tertiary alcohols like TBA, TAA and THA. Similar results for primary and secondary alcohols were described in experimental studies by Brieschke [21]. The thermal explosion behaviour investigated in the TEVT versions A and B for alcohols like ethanol and 2-PropOH gave comparable results to those for 2-PropOH presented in this paper.

Fig. 1 shows also some test concentrations for mixtures of H_2O_2 with 1-butanol and ethanol tested in TEVT version B. They react very slowly, while comparable mixtures of H_2O_2 and TBA show violent reactions (bursting of the disk). The thermal explosion range with violent pressure rise is essentially smaller for 1-butanol than for TBA and TAA.

The difference in the results between the thermal explosion test methods shown in Fig. 2 is significant, but can be explained. Test parameters, like the heating rate and the ratio of sample volume to vessel volume have an influence on the test results especially if during the experiment a combustible gas/vapour atmosphere is produced in the autoclave. The MCPVT with the recommended parameters heating rate 2.4 K/min and 1 g sample mass shows the smallest concentration range of violent thermal explosion. That is in agreement with the results for TBA in Fig. 2 and 2-PropOH in Fig. 5. MCPVT results should therefore be regarded with care and only used when knowing the test parameters. The dependence of the test results from the chosen test parameters can also be found in the investigation by Heemskerk with SBC [8]. By using a heating rate of about 30 K/min some mixtures of 2-PropOH and aqueous H_2O_2 undergo a transition from a thermal explosion to a detonation. The detected detonation range was identical in shape and concentration to results of steel tube test (not cavitated).

No investigation was possible with respect to the ability of formation of alkyhydroperoxides during the heating phase with the thermal explosion tests and its possible consequences.

The results of the BAM 50/60 steel tube test, cavitated version, for mixtures containing 2-PropOH are comparable with results presented in literature, but the sensitivity of the cavitated version of the test is higher (see Fig. 5). The BAM steel tube test in its cavitated version and the blasting cap test [6] detect the largest detonation range. In the BAM steel tube test aqueous H_2O_2 40% (w/w) and 60% (w/w) in mixture with 2-PropOH was used for the investigation.

Monger et al. [6] used H_2O_2 concentrations of 50% (w/w) and higher. They reported 'positive' results for mixtures of 2-PropOH with aqueous solution H_2O_2 from 65% (w/w) up to 90% (w/w), and extrapolated for mixtures with lower aqueous H_2O_2 concentrations. They defined a positive result if it was comparable in noise and destruction to an experiment with aqueous H_2O_2 90% (w/w).

The results of Heemskerk et al. [8] with a different steel tube test (non cavitated) show a smaller range for propagating a detonation in comparison with other detonation tests.

The chain length of the alcohols also influence the detonation range. We found an increasing detonation range with a decreasing chain length for mixtures of aqueous H_2O_2 with 2-PropOH and TBA. Results for TAA, detected with the same method [22] and literature data for Ethanol and 1-PropOH/ 2-PropOH [7,10] showed the same tendency.

6. Conclusion

The assessment of the test results for aqueous H_2O_2 in mixture with different alcohols is not easy, because different methods characterize different stress situations. The thermal explosion tests are able to detect violent reactions by heating under confinement. The thermal explosion tests used for the described investigations were carried out with heating rates up to 18 K/min. Under these test conditions, we found, additional to the detonation range determined by steel tube tests, mixtures of H_2O_2 and TBA which have a very dangerous potential. For process evaluation, this additionally range of violent thermal explosion has to be considered. The points of intersection for the upper and lower explosion limits differ from those of the steel tube tests.

That is why it is recommended to carry out a suitable thermal explosion test like the TEVT (version B) in addition to a detonation test (e.g. the BAM 50/60 steel tube test, cavitated version) to determine the range of dangerous concentrations (possibility of a detonation or a very fast and violent thermal explosion) for mixtures of H_2O_2 and different alcohols.

Steel tube tests disclose the ability of such mixtures to propagate a detonation. The BAM 50/60 steel tube test in its cavitated version seems to be the most sensitive detonation test. The shape of the detonation range corresponds to the energy content of the samples for the reaction path of combustion the organic compound (point of intersection for upper and lower explosion limit at the stoichiometric line of combustion) [22].

Finally it should be pointed out, that a detonation causes more destructive effects than the other types of explosions. Substances and mixtures with a higher energy content and a given detonability can undergo a transition from a thermal runaway via a deflagration to a detonation. Therefore, it is a matter of safety to use the information obtained from different tests for the determination of explosive properties of energetic substances and mixtures for a safe handling.

Acknowledgements

We thank Mr. Ing. J. Wanjek, Mr. R. Jungnickel and Mrs. T. Tschinkel for their help in the experimental part of the work. We are thankful to Mrs. Dr. U. Rockland for helpful discussions.

References

- [1] W. Weigert (Ed.), Wasserstoffperoxid und seine Derivate, Hüthig Verlag, Heidelberg, 1978.
- [2] G. Goor, W. Kunkel, in: Ullmann's Encyclopaedia of Industrial Chemistry, Vol. A13, VCH, Weinheim, 1989, pp. 443–463.
- [3] P.G. Urben (Ed.), Bretherick's Handbook of Reactive Chemical Hazardous, 6th edition, Butterworth-Heinemann, Oxford, 1999, pp. 1624–1643.
- [4] B.G. Chemie (Ed.), Unfallverhütungsvorschrift Organische Peroxide. BGV B4, Jedermann-Verlag, Heidelberg, 2000.
- [5] E.S. Shanley, J.R. Perrin, *Jet Propulsion* 28 (1958) 385.
- [6] J.M. Monger, H. Sello, D.C. Lehwalder, *J. Chem. Eng. Data* 6 (1961) 23.
- [7] E.S. Shanley, F.P. Greenspan, *Ind. Eng. Chem.* 39 (1947) 12.
- [8] A.H. Heemskerck, J.H.G. Scholtes, *Loss Prevention Safety Promotion Process Ind.* 1 (1995) 411.
- [9] J. Mackenzie, *Plant/Operations Progress* 10 (1991) 3.
- [10] Shell Chemical Company (Ed.), Concentrated hydrogen peroxide, Summary of Research Data on Safety Limitations, Vol. 59, Bulletin, SC, New York, 1961, p. 44.
- [11] UN (Ed.), Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 3rd revised edition, United Nations Publication, New York/Geneva, 1999.
- [12] Adolf Kühner AG, Mini-autoclave instruction manual. Basle, Switzerland.
- [13] K. Hasegawa, M. Tamura, Paper Presented at the Meeting of OECD–IGUS Energetic and Oxidising Substances Working Group, Japan, 1996.
- [14] M.W. Whitmore, G.P. Baker, *J. Loss Prevention Process Ind.* 14 (2001) 223.
- [15] K.D. Wehrstedt, A. Knorr, P. Schuurman, *J. Loss Prevention Process Ind.* 16 (2003) 523.
- [16] A. Schreck, T. Gmeinwieser, A. Knorr, K.D. Wehrstedt, J. Steinbach, in: Dechema (Ed.), *Achema 2000 Proc. Safety Technologie Frankfurt a. M., Deutschland 2000*.
- [17] UN (Ed.), Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 2nd edition, United Nations Publication, New York/Geneva, 1990.
- [18] P.A. Wandrey, K.D. Wehrstedt, in: Dechema (Ed.), *Praxis der Sicherheitstechnik*, Vol. 4, Dechema e.V., Frankfurt/Maine, 1997, pp. 133–145.
- [19] R.H. Perry, D.W. Green, *Perry's Chemical Engineers' Handbook*, 7th edition, McGraw-Hill, New York, 1998.
- [20] K. Hasegawa, M. Tamura, Paper presented at the Adhoc-meeting of OECD–IGUS Energetic and Oxidising Substances Working group, Tsukuba, Japan, 2000.
- [21] J. Brieschke, Vergleich zweier Versionen des Thermal Explosion Vessel Test (TEVT) anhand ausgewählter Wasserstoffperoxid/Alkohol-Gemische, Studienarbeit, Technische Universität Berlin, 2001.
- [22] A. Schreck, Systematische sicherheitstechnische Untersuchung zur Synthesereaktion von ausgewählten Alkylperoxiden, Dissertation TU-Berlin, 2003.