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Reaction Calorimetry of Hydrogen Peroxide and Selected Alcohols

Reakčná kalorimetria peroxidu vodíka s vybranými alkoholmi

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Abstract

There are many industrial applications, where inorganic and highly reactive substances are being used. Hydrogen peroxide (H_2O_2) is an inorganic peroxide and is considered as hazardous substance, due to its strong oxidation properties. The aim of this paper is to determine the thermal reactivity of hydrogen peroxide / alcohol mixtures under isothermal conditions. The experiment was carried out using Sensitive Detector of Exothermic processes (SEDEX) – safety calorimeter. Tested mixtures consist of 15 ml of 30% hydrogen peroxide, heated and stabilized to three different temperatures (40 °C, 50 °C, 60 °C) and 1 ml of selected alcohol from homologous series methanol – pentan-1-ol. The most significant exothermic temperature changes (ΔT) occurred with the H_2O_2 / methanol mixture in all three series of measurements (0.90 °C, 0.74 °C, 0.69 °C). As the length of the carbon chain increases, the temperature decreases in the second and third series with the formation of exothermic reactions. The temperature differences before and after the reaction of butan-1-ol alcohol and pentan-1-ol in the third series are negligible.

Keywords: reaction calorimetry; thermal reactivity; hydrogen peroxide; alcohols

1 Introduction

Hydrogen peroxide H_2O_2 is an inorganic peroxide and is considered a hazardous substance under the Global Harmonized System of Classification and Labeling of Chemicals (GHS). It is classified as oxidising (category 2), corrosive (type G), irritant (eyes, skin) and causing acute toxicity. [1] The strong oxidizing properties of organic and inorganic peroxides are due to the relatively weak (–O – O–) bonds in their molecule [2]. Hydrogen peroxide is used for oxidation in organic and inorganic processes, in polymerization reactions [3] and

1 Úvod

Peroxid vodíka H_2O_2 patrí medzi anorganické peroxidy a podľa Globálneho harmonizačného systému klasifikácie a označovania chemikálií (GHS) sa považuje za nebezpečnú látku. Zaraďuje sa medzi oxidačné (kategória 2), korozívne (typ G), dráždivé (oči, koža) a spôsobujúce akútnu toxicitu. [1] Silné oxidačné vlastnosti organických a anorganických peroxidov sú spôsobené relatívne slabými (–O–O–) väzbami v ich molekule. [2] Peroxid vodíka sa využíva k oxidácii pri organických a anorganických in industrial waste treatment processes and the like [4]. Contact of H_2O_2 with various contaminants, leads to uncontrolled reactions. These reactions can occur when H_2O_2 is mixed with compounds such as iron, copper, sulfuric acid, propanone, sodium hydroxide etc. [5] Hydrogen peroxide is used in the production of methylethylketone peroxide (MEKPO), which caused many explosions and uncontrollable reactions leading to accidents. [6] The burning rate of liquid mixtures changes during a fire depending on their properties and the amount of heat transferred from the combustion zone to the surface of the liquid. The burning rate is not constant and in real fire conditions it varies depending on the temperature, the diameter of the vessel, the level in the vessel, the composition of the liquid, the wind speed and many other factors [7].

A safety calorimeter SEDEX (Sensitive Detector of Exothermic processes) was used for the experimental part (Fig. 1). The SEDEX safety calorimeter was developed for the purpose of fast and simple analysis of hazardous materials intended for the industrial sector. The calorimeter is used for the sensitive detection of exothermic reactions in substances and interacting mixtures under industrial conditions. The data obtained include, for example, a safe upper temperature limit, gas production and heat of reaction. From the obtained data it is possible to predict the behaviour of a given substance or mixture of substances at larger volumes and thus to prevent possible dangerous situations. [9]

The aim of this work is to monitor the behaviour of hydrogen peroxide during isothermal heating, after application of a selected alcohol from the homologous series methanol – 1-pentanol. The experiment and its conditions were chosen on the basis of the industrial use of H_2O_2, for example in the production of disinfectants, in the oxidation of alcohols [8] and the conditions used in their storage and transport.

procesoch, pri polymerizačných reakciách [3] a pri priemyselných procesoch spracovávajúcich odpad a podobne [4]. Pri kontakte H_2O_2 s rôznymi kontaminantami dochádza k vzniku nekontrolovateľných reakcií. Tieto reakcie môžu nastať pri zmiešaní H_2O_2 so zlúčeniami ako železo, meď, kyselina sírová, propanón, hydroxid sodný a pod. [5] Peroxid vodíka sa využíva.pri výrobe metyletylketón peroxidu (MEKPO), čo viedlo k nekontrolovateľným reakciám vedúcich k haváriám. [6] Rýchlosť odhorievania kvapalných zmesí sa v priebehu požiaru mení v závislosti na ich vlastnostiach a množstve prestupujúceho tepla z pásma horenia na povrch kvapaliny. Rýchlosť horenia nie je konštantnou hodnotou a v reálnych podmienkach požiaru sa mení v závislosti na teplote, priemeru nádoby, výške hladiny v nádobe, zloženia kvapaliny, rýchlosti vetra a mnoho ďalších faktorov. [7]

Na experimentálnu časť bol využitý bezpečnostný kalorimeter SEDEX (Sensitive Detector of Exothermic processes) (Obr. 1). Bezpečnostný kalorimeter SEDEX bol vyvinutý za účelom rýchlej a jednoduchej analýzy nebezpečných materiálov určených pre priemyselný sektor. Kalorimeter slúži na citlivú detekciu exotermických reakcií v látkach a vzájomne reagujúcich zmesiach za priemyselných podmienok. Medzi získané údaje patria napríklad bezpečná horná teplotná hranica, produkcia plynov a produkcia tepla z reakcie. Zo získaných údajov možno predpovedať správanie sa danej látky alebo zmesi látok pri väčších objemoch a tým predísť možným nebezpečným situáciám. [9]

Cieľom tejto práce je sledovať správanie sa peroxidu vodíka pri izotermickom ohreve, po aplikovaní vybraného alkoholu s homologického radu metanol – 1-pentanol. Experiment a jeho podmienky boli zvolené na základe priemyselného využívania H_2O_2, napríklad pri výrobe dezinfekčných prostriedkov, pri oxidácii alkoholov [8] a podmienok používaných pri ich skladovaní a preprave.

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2 Material and Methods

Hydrogen peroxide with a concentration of 30 % and alcohols with a purity of 99.5 % from the supplier CentralChem s.r.o. were used. The properties of the used liquids can be found in Tab. 1.

2 Materiál a metódy

Na experiment sa použil peroxid vodíka s koncentráciou 30 % a alkoholy s čistotou 99,5 % od dodávateľa CentralChem s.r.o. Vlastnosti použitých kvapalín sa nachádzajú v Tab. 1.

Tab. 1 Physical and fire-technical properties of selected liquids [1, 10-14]

Tab. 1 Základné fyzikálne a požiarnotechnické parameter vybraných kvapalín [1, 10-14]

	T_v (°C)	T_t (°C)	T_{vz} (°C)	T_{svz} (°C)	*MV* (vol%)
Peroxid vodíka/ Hydrogen peroxide	150.2	-0.4	–	–	–
Metanol/ Methanol	64.7	-97.5	11	470	5.5 – 44
Etanol/ Ethanol	78.0	-114.1	13	425	3.5 – 15
1-Propanol	97.0	-97.6	15	405	
1-Butanol / Butan-1-ol	117.7	-89.8	35	343	1.4 – 11.2
1-Pentanol / Pentan-1-ol	138.0	-78.0	49	300	1.2 – 10

T_v – teplota varu / boiling point

T_t – teplota tuhnutia / melting point

T_{vz} – teplota vzplanutia / flash point

T_{svz} – teplota samovznietenia / autoignition temperature

MV – medze výbušnosti / flammability limits

The experiment consisted of three series of measurements. 15 ml of hydrogen peroxide, heated to three different temperatures (40 °C, 50 °C, 60 °C, heating rate 10 K min^{-1}), were used for the experiment. After stabilizing the temperature of the hydrogen peroxide sample and the oven temperature, alcohol (20 °C) was applied through a glass rod in a volume of 1 ml (Fig. 2). Five types of alcohols in the homologous series methanol – pentan-1-ol were used for the experiment.

Samotný experiment pozostával z troch sérií meraní. Na experiment sa použilo 15 ml peroxidu vodíka, zahriateho na tri rôzne teploty (40 °C, 50 °C, 60 °C, rýchlosť ohrevu 10 K min^{-1}) Po ustálení teploty vzorky peroxidu vodíka a teploty pece, sa aplikoval alkohol (20 °C) cez sklenenú tyčinku v objeme 1 ml (Obr. 2). Na experiment bolo použitých päť druhov alkoholov v homologickom rade metanol – 1-pentanol.

Fig. 1 Safety calorimeter SEDEX

Obr. 1 Bezpečnostný kalorimeter SEDEX

Fig. 2 Sample storage in a SEDEX safety calorimeter. 1 - Pt100 thermocouple, 2. glass rod for alcohol application, 3. thermocouple for sensing ambient temperature

Obr. 2 Uloženie vzorky v bezpečnostnom kalorimetri SEDEX. 1 - Termočlánok Pt100, 2. sklená tyčinka pre aplikáciu alkoholov, 3. termočlánok na snímanie teploty okolia

3 Results and discussion

For the first series of measurements, hydrogen peroxide was heated to 40 °C. Dependence graph of temperature on time of hydrogen peroxide and alcohols is shown in Fig. 3.

3 Výsledky a diskusia

Na prvú sériu meraní bol peroxid vodíka zahriaty na teplotu 40 °C. Graf závislosti teploty od času peroxidu vodíka a alkoholov je na Obr. 3.

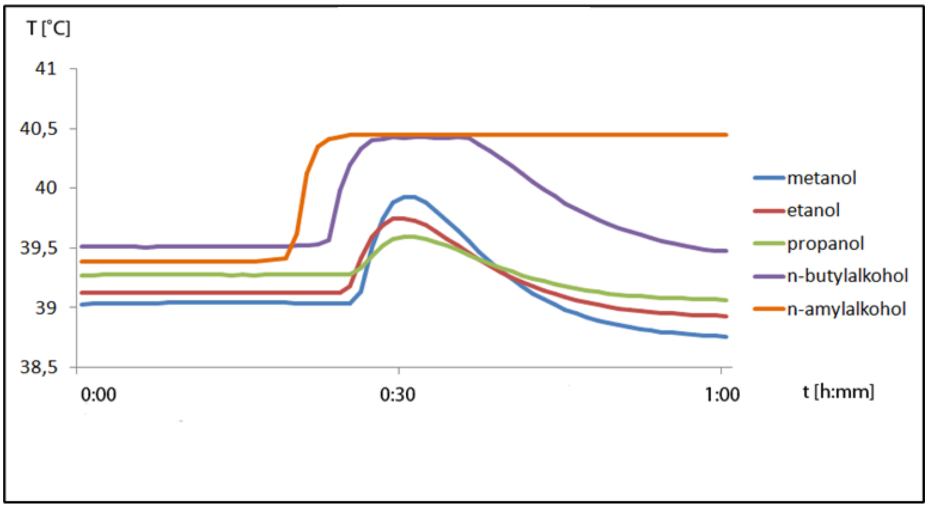

Fig. 3 Temperature on time dependence: Sample of hydrogen peroxide and alcohols during isothermal heating at ambient temperature 40 °C

Obr. 3 Graf závislosti teploty od času: Vzorka peroxidu vodíka a alkoholov počas izotermického ohrevu pri teplote okolia 40 °C

The second series of measurement was performed at a temperature of 50 °C. The graphical dependence of temperature on time is shown in Fig.4.

Druhá séria meraní bola vykonaná pri teplote 50 °C. Graf závislosti teploty od času vzorky peroxidu vodíka a alkoholov je na Obr. 4.

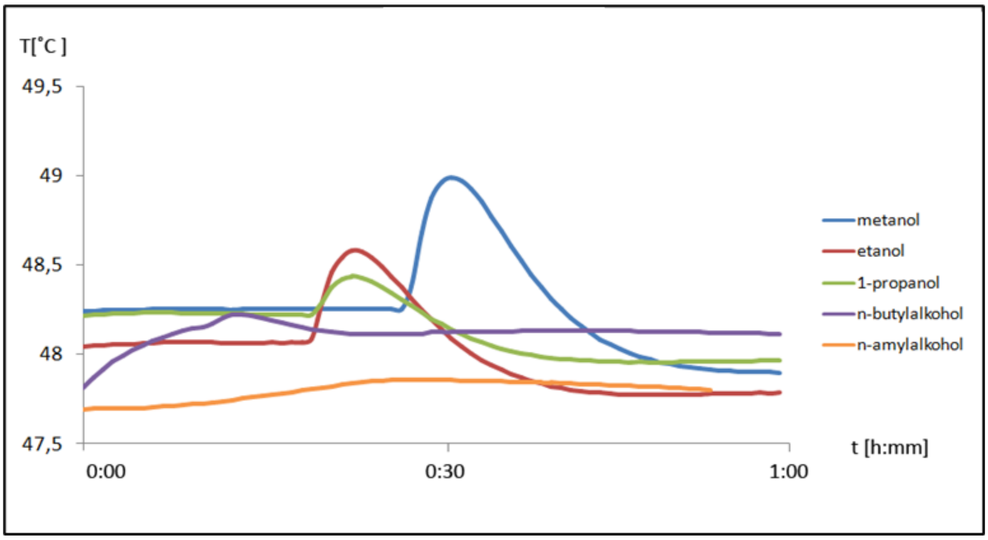

Fig. 4 Temperature on time dependence: Sample of hydrogen peroxide and alcohols during isothermal heating at ambient temperature 50 °C

Obr. 5 Graf závislosti teploty od času: Vzorka peroxidu vodíka a alkoholov počas izotermického ohrevu pri teplote okolia 50 °C

In the third series of measurements, the temperature was set on 60 ºC. The graphical dependence of temperature on time of a sample of hydrogen peroxide and alcohols is shown in Fig. 5.

Pri tretej série meraní sa nastavila teplota na 60 ºC. Graf závislosti teploty od času vzorky peroxidu vodíka a alkoholov je Obr. 5.

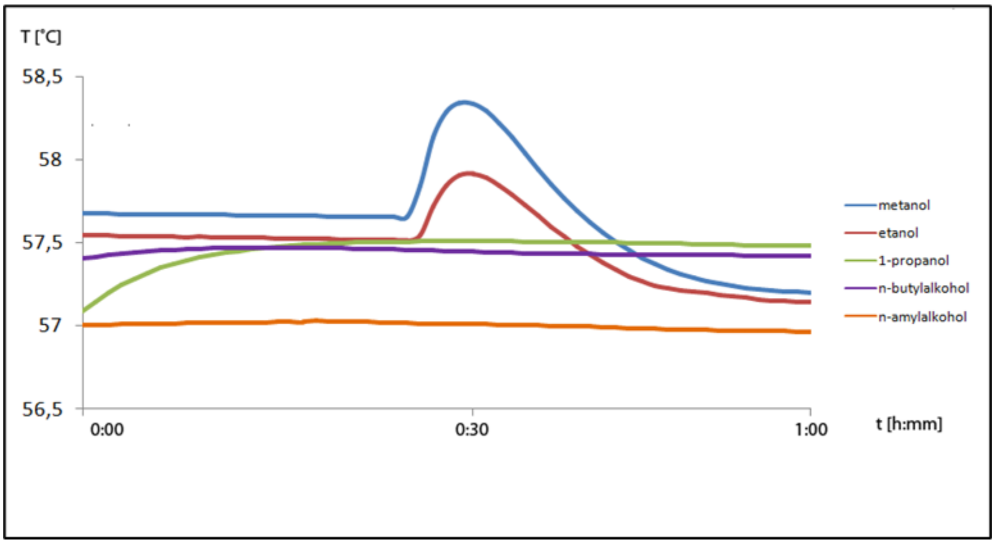

Fig. 6 Temperature on time dependence: Sample of hydrogen peroxide and alcohols during isothermal heating at ambient temperature 60 ºC

Obr. 5 Graf závislosti teploty od času: Vzorka peroxidu vodíka a alkoholov počas izotermického ohrevu pri teplote okolia 60 ºC

Tab. 2 lists the temperatures that occurred during the experiment. From the table it is possible to determine for which alcohols the most significant temperature differences occurred. At the same time, it is possible to compare at what temperature, to which the hydrogen peroxide sample was heated, the thermal change occurred. According to [4], a significant exotherm occurred when mixing hydrogen peroxide with ethanol, which corresponds to our results. Also, Sandri et al. [8] used hydrogen peroxide to oxidize higher alcohols at 50 ° C. In contrast to the work of Schreck et al. [5], who determined the potential danger of mixtures of hydrogen peroxide and selected isomers of propanol, butanol and pentanol, with uniform heating (up to 18 K / min), our work dealt with isothermal heating in conjunction with the mutual reactivity of the evaluated mixtures.

V Tab. 2 sa nachádzajú teploty ktoré nastali počas experimentu. Z tabuľky je možné určiť, u ktorých alkoholov nastali najvýraznejšie teplotné rozdiely. Zároveň, je možné porovnať pri akej teplote, na ktorú bola vzorka peroxidu vodíka zahriata, nastala tepelná zmena. Podľa [4], došlo pri zmiešaní peroxidu vodíka s etanolom k výraznej exotermickej reakcii, čo korešponduje s našimi výsledkami. Taktiež Sandri a kol. [8] využili peroxid vodíka na oxidáciu vyšších alkoholov pri 50 °C. Na rozdiel od práce Schrecka a kol. [5], ktorí stanovovali potenciálne nebezpečenstvo zmesí peroxidu vodíka a vybraných izomérov propanolu, butanolu a pentanolu, pri rovnomernom ohreve (do 18 K/min), sa naša práca zaoberala izotermickým ohrevom v súčinnosti so vzájomnou reaktivitou posudzovaných zmesí.

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Tab. 2 Measured temperatures during isothermal heating of hydrogen peroxide at ambient temperatures of 40 °C, 50 °C and 60 °C

Tab. 2 Namerané teploty počas izotermického ohrevu peroxidu vodíka pri teplote okolia 40 °C, 50 °C a 60 °C

Vzorka zahriata na teplotu 40 ºC / Sample heated to 40 ºC					
Zmes / Mixture	**T [°C]**	**T_{max}[ºC]**	**T_{min} [ºC]**	**ΔT_1 [ºC]**	**ΔT_2 [ºC]**
$H_2O_2 + CH_3OH$	39.03	39.93	38.75	0.9	0.28
$H_2O_2 + C_2H_5OH$	39.13	39.75	38.92	0.62	0.21
$H_2O_2 + C_3H_7OH$	39.28	39.60	39.07	0.32	0.21
$H_2O_2 + C_4H_9OH$	39.51	40.43	39.44	0.92	0.07
$H_2O_2 + C_5H_{11}OH$	39.38	40.45	-	1.07	-
Vzorka zahriata na teplotu 50ºC / Sample heated to 50 ºC					
$H_2O_2 + CH_3OH$	48.25	48.99	47.90	0.74	0.35
$H_2O_2 + C_2H_5OH$	48.01	48.58	47.77	0.57	0.24
$H_2O_2 + C_3H_7OH$	48.23	48.44	47.96	0.21	0.27
$H_2O_2 + C_4H_9OH$	47.92	48.22	48.11	0.30	-0.19
$H_2O_2 + C_5H_{11}OH$	47.63	47.86	47.80	0.23	-0.17
Vzorka zahriata na teplotu 60ºC / Sample heated to 60 ºC					
$H_2O_2 + CH_3OH$	57.66	58.35	57.23	0.69	0.43
$H_2O_2 + C_2H_5OH$	57.54	57.92	57.13	0.38	0.41
$H_2O_2 + C_3H_7OH$	57.38	57.51	57.08	0.13	0.20
$H_2O_2 + C_4H_9OH$	57.42	57.47	56.98	0.03	0.44
$H_2O_2 + C_5H_{11}OH$	57.02	57.03	56.74	0.01	0.28

T – teplota okolia / ambient temperature

T_{max} – maximálna teplota, v dôsledku vzniku exotermickej reakcie / maximum temperature, due to the formation of an exothermic reaction
T_{min} – minimálna teplota, v dôsledku ochladenia a odparenia vzorky / minimum temperature, due to cooling and evaporation of the sample
ΔT_1 – rozdiel teplôt T_{max} a T / temperature difference Tmax and T
ΔT_2 – rozdiel teplôt T a T_{min} / difference of temperatures T and Tmin
Priemerné hodnoty z troch opakovaní / average values from three repetitions

4 Conclusion

The article was focused on monitoring the mutual reactivity of hydrogen peroxide and selected types of alcohols from the homologous series methanol - pentanol during isothermal conditions. The mentioned methodology and results are applicable especially in the field of storage, transport and handling of hazardous substances. The SEDEX safety calorimeter (Sensitive Detector of Exothermic Processes) was used to allow sensitive detection of exothermic reactions. Temperature versus time dependence was used to monitor the course of the mixture reactions. Five types of alcohols were used: methanol, ethanol, 1-propanol, butan-1-ol and pentan-1-ol. The problem could

4 Záver

Článok bol zameraný na sledovanie vzájomnej reaktivity peroxidu vodíka a vybraných druhov alkoholov z homologického radu metanol – pentanol v izotermických podmienkach. Uvedená metodika a výsledky sú aplikovateľné predovšetkým v oblasti skladovania, prepravy a manipulácie s nebezpečnými látkami. Bezpečnostný kalorimeter SEDEX (Sensitive Detector of Exothermic processes) bol použitý z dôvodu umožnenia citlivo detegovať vznik exotermických reakcií. Na sledovanie priebehu reakcií peroxidu vodíka s alkoholmi, boli použité závislosti teploty od času. Bolo použitých päť druhov alkoholov: metanol, occur with insufficient heat dissipation, but such a configuration is unlikely to occur. The drop in temperatures was due to cooling. Based on the obtained results, the exothermic reactions generated under the given experimental conditions do not pose a risk of fire, because the temperature difference between the sample before and after the reaction was minimal. The problem could occur with insufficient heat dissipation, but such a configuration is unlikely to occur.

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etanol, 1-propanol, 1-butanol a 1-pentanol. Na základe získaných výsledkov meraní vzniknuté exotermické reakcie pri daných podmienkach experimentu nepredstavujú riziko vzniku požiaru. Rozdiel teplôt vzorky pred a po reakcii bol minimálny. Problém by mohol nastať pri nedostatočnom odvode tepla, ale vznik takejto konfigurácie je nepravdepodobný.

Poďakovanie

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