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Explosibility and Fire Behavior of some Pyrethroids, Active Agents of Plant Protection Products

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Deflagration Index (Kst) parameter determines the speed of the pressure rise during the explosion of tested dust. The larger the Kst, the more severe the explosion. Kst value allows to assign tested compound to Dust Explosion Class, which is a benchmark of comparison for all dusts. Minimum explosible concentration (MEC) is one of the most important parameter for modern industry, allowing to determine the highest safe concentration of dust in workplace. Due to alarming results gain during our study upon flammability of pyrethroids we investigated explosive properties and Minimum Ignition Energy (MIE) of three most popular compounds. Lambda-cyhalothrine and deltamethrine exhibit week explosive properties (ST1) and MIE values of 1000 mJ and 300 mJ respectively. Beta-cyfluthrin classified to ST3 explosive class with Kst above 300 and MIE at 100 mJ. For all tested compounds we established MEC at 60 g/m^3. The paper shows also results of Maximum Pressure (Pmax) studies of tested pyrethroids.

1. Introduction

Dust explosions of organic compounds are a mayor threat for industry nowadays. Capacity and production velocity generates so many possibilities of incident occurrence that even current advanced technology of process control cannot prevent or even foresee all of theme. Explosion of phenol formaldehyde resin dust (*North Carolina; 1999*), polyethylene dust (*Massachusetts; 2003*), sugar dust (*Georgia; 2008*) (U.S. CSHIB, 2006, Fraser, 2015) are only some examples of modern day accidents. “Fire triangle” and “explosive pentagon” both includes presence of two crucial factors necessary to initiate fire or explosion: fuel and oxygen. What is sometimes forgotten is the fact that many organic compounds exhibit structural oxygen that can participates in the combustion process and even be a decomposition promoter. For example, sucrose ($C_{12}H_{22}O_{11}$) oxygen content is ~25% (% molar), it’s enough to transform all hydrogen into water or almost half of structural carbon into carbon dioxide. Organic peroxides thanks to unstable oxygen bonding shows very high detonation parameters that can even surpass some commonly known explosives.
Pyrethroids are the derivatives of chryzantemic (pyrethrin) acid, exhibiting highly neurotoxic effects on insects. They are being used as an active agent and constitute the majority of commercial insecticides. Although they didn’t supposed to interact on human body there are some papers describing poisoning accidents (Ray, Forshaw, 2000). They exhibit the presence of ether bonding placed between aromatic rings. Such low stable structure can under suitable conditions decompose creating large amounts of toxic gasses, smoke and large amounts of heat. Led by those circumstantial evidence we decided to investigate fire behavior and explosive parameters of main representatives of pyrethroids family.
In our latest studied we investigated the fire behavior and smoke generation during ability during thermal decomposition of three pyrethrin derivatives: lambda-cyhalothrin, deltamethrin and beta-cyfluthrin (Celinski and Domanski, being published). Studies were carried out according to ISO 5660-1 and ISO 5659-2 standards using a Fire Testing Technology Dual Cone Calorimeter and NBS Smoke Density Chamber (*FTT Limited, West Sussex*). To increase the accuracy of gain results, ten specimens of each pyrethroid were tested. Each sample was placed on an aluminum foil and exposed to an external heat flux of 25 kW·m^{-2}.

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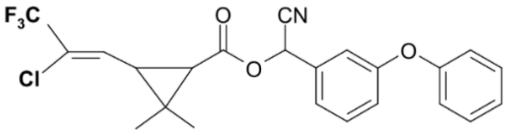
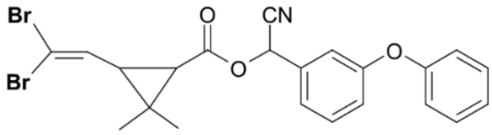
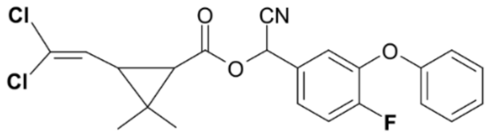


LAMBDA-CYHALOTRIN



DELTAMETHRIN



BETA-CYFLUTHRIN

Figure 1 Structures of pyrethrin's tested derivatives lambda-cyhalothrin, deltamethrin, beta-cyfluthrin.

Results of our research shown that two of studied compounds: lambda-cyhalothrin and beta-cyfluthrin exposed to low heat flux (25kW/m^2) exhibit relatively high value of Heat Release Rate (HRR) for such low sample mass weight (10g), surprisingly low time to ignition (It) and Fire Growth Rate (FIGRA) almost as high as polyethylene.

Table 1. Results of cone calorimeter study upon three pyrethroids:deltamethrin, beta-cyfluthrin, lambda-cyhalothrin..

Parameter	lambda-cyhalothrin	beta-cyfluthrin	deltamethrin	N660 *
HRR (kW m^{-2})	86,7 ± 5,1	75,9 ± 5,1	41,4 ± 8,1	-
pHRR (kW m^{-2})	356,4 ± 33,1	340,1 ± 51,3	101,7 ± 16,2	710 ± 109
t-pHRR (s)	94,4 ± 7,8	90 ± 13,4	180,6 ± 21,8	177 ± 6
MAHRE (kW m^{-2})	92,9 ± 10,9	67,5 ± 8,5	14,9 ± 2,9	317 ± 47
FIGRA (kW m^{-2}s^{-1})	3,79 ± 0,41	3,87 ± 0,87	0,58 ± 0,14	4,0 ± 0,5
Ignition Time - It (s)	65,0 ± 8,0	75,4 ± 9,3	169 ± 21	58,3 ± 2,5

* ref. (Kruger et al., 2014)

This unusual observation convinced us that compounds from the pyrethroids family are much more dangerous than they were believed to be and that they not only can exhibit some serious explosive properties but also be vulnerable to ignition form low energy spark.

2. Experimental setup

20-L spherical apparatus

Deflagration index (Kst) and Maximum Explosion Pressure (Pmax) values are properties that can be measured in laboratory conditions to quantify the violence of a dust explosion. The explosion test is carried out according to standards PN EN 14034-1:2004 (determination of the maximum explosion pressure Pmax of dust clouds) and PN EN 14034-2:2006 (determination of the maximum rate of explosion pressure rise of dust clouds Kst). Explosibility tests were carried out in 20-L stainless steel spherical apparatus (*ANKO-LAB*) that can reproduce turbulences to simulate worst case process plant conditions. This primary device is used throughout the world to evaluate the explosibility of dusts. Main chamber is a near-spherical vessel with hinged top and coated by a water jacket for thermostatic control. Apparatus is equipped with two pressure detectors and thermocouple. Embedded in the base of chamber is the dust container in which tested dust is placed and covered with a dispersion nozzle.

Pressure inside testing chamber is evacuated to 0,53 bar absolute and after that automatic test sequence is initiated to pressurize the dust collector. Then the dust collector outlet is opened thanks to fast acting valve and material is pumped into the explosion chamber trough the dispersing nozzle by rapidly equalizing pressure difference. The rebound nozzle guaranties an equal dust distribution within the testing chamber. Dust is ignited by two 5 KJ chemical igniters (*SOBBE*) at the center of the sphere about 60 ms after dust dispersion. Explosion pressure is measured for a range of dust concentrations by two piezo-electric pressure transducers. Results are recorded and saved on local computer. From all tested series, the arithmetic mean of the maximum values (both maximum pressure and deflagration index was obtained.

Deflagration index K_{st} is essentially the maximum rate of pressure rise, generated by tested dust during the explosion in test chamber. (Frangos and De Nola, 2013) The Kst value is calculated from the cube law, see Eq(1) as an equivalent of pressure in a 1 m^3 sphere:

$$\boldsymbol{K_{ST}} = \left(\frac{\boldsymbol{dP}}{\boldsymbol{dt}}\right)_{\boldsymbol{max}} \times \boldsymbol{V}^{\boldsymbol{1}/\boldsymbol{3}} \qquad \text{Eq(1)}$$

where Kst – deflagration index (bar·m /s)

$(dP/dt)_{max}$ – maximum rate of pressure rise

V – volume of testing chamber

Although it has been proven that Kst value can vary significantly for different chamber volume, dust dispersion system and particle fragmentation (Eckhoff, 2003) it still remains an arbitrary measure of the explosion violence and provides a reasonable relative measurements for ranking the explosion capability from industrial dusts. Establishing of Kst & Pmax values in explosion testing is substantial to ratification protection design (explosion venting, explosion suppression and explosion containment).

Deflagration index is crucial parameter for qualification of dust to explosibility class (ST Class) established by OSHA according to the relative violence of their deflagrations. St Classes are presented in Table 3 with the examples of industrial dusts corresponding to each of the classes (U.S. OSHA, 2009, Traore, 2007, Ebadat, 2009).

Table 2: Dust Explosibility Classes ST

Explosibility class	Kst (bar·m/s)	Dust examples
ST 0	0	silica
ST 1	0-200	milk powder, sugar zinc
ST 2	200-300	cellulose, poly-methyl-acrylate
ST 3	300 <	Aluminium, magnesium

Although explosibility classes are just conventional values, they show with some approximation risk of possible explosion. It is also worth noticing that one of largest accidents involving dust explosion were caused by the combustion of low Kst compounds like sugar (*Imperial Sugar Company, Port Wentworth, Georgia, United States*) or wood flour (*Bosley, Cheshire, United Kingdom*).

Minor II – Modified Hartman's Tube

The minimum ignition energy (MIE) is considered to be the lowest electrical energy stored in a device capacitor which is sufficient to effectively ignite of dust-air mixture under specific test conditions.

Minor II apparatus is a modified Hartmann tube explosion vessel with a volume of 1.2. Dust is dispersed from the "mushroom-shaped" dispersion system attached to the base, around which the sample is loosely scattered. Measurements were carried out according to PN-EN. 13821:2004. Potentially explosive atmospheres – Explosion prevention and protection – Determination of minimum ignition energy of dust/air mixtures.

Dust at different concentrations was loaded into the dispersion cup. The tube was covered from above by a busting vent. After the start of the test, blast of compressed, synthetic air dispersed the dust into the glass cylinder. Air-dust mixture was then ignited by an electrical spark generated between two electrodes with energy according to Eq(2) (Eckhoff, 2005, Huéscar et al., 2013, Eckhoff, 2002):

$$E = 0{,}5C \cdot U^2 \qquad \text{Eq(2)}$$

where: E – spark energy [mJ]

C – total capacitance of the discharge circuit [F]

U – voltage of the capacitor [V]

Measurements were made for dust concentration range: 500÷3000 g/m^3. Applied energy range was 1-1000 mJ and ignition delay with respect to the creation of a dust cloud:100-120 ms.

3. Results

Before the beginning of the study sieve analysis of all three pyrethroids was conducted. Over 90% of tested dust particles were from the range of 125-500 µm. The fraction was collected and used to determine all explosive and combustive properties. Broad range of compounds concentration was tested to establish highest generated explosion pressure (Pmax) and Minimum Explosible Concentration (MEC). Presented dust concentration is the dust mass used in the experiment divided by the volume of testing chamber, 20 liters for 20-L sphere and 1,2 liter for MINOR II apparatus. Test results were compiled and presented as a graph in figure 2.

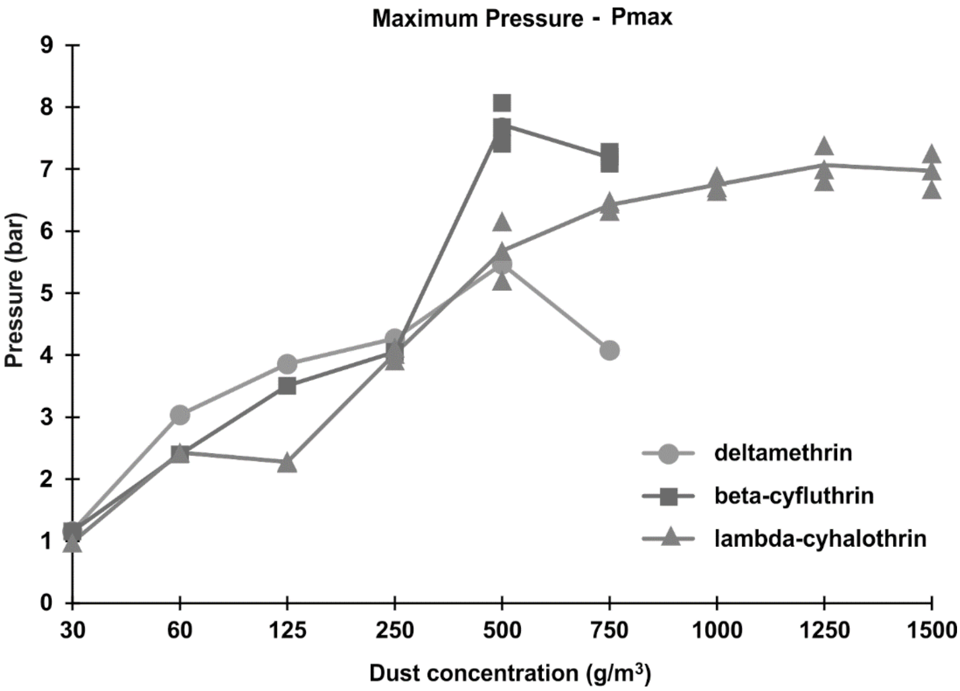


Figure 2 Measurement results of explosive properties in a) 20-L spherical chamber b) MINOR II apparatus

Deltamethrin and beta-cyfluthrin exhibit maximum explosion pressure at 500 g/m^3 while lambda-cyhalothrin gain Pmax at 1250 g/m^3. Possible explanation of this phenomenon lies in Kst value. Lambda-cyhalothrin maximum Kst for 1250 g/m^3 is ~170 (bar·m/s) and for 500g/m^3 is ~105 (bar·m/s), while for deltamethrin and beta-cyfluthrin Kst for 500 g/m^3 values are 156 (bar·m/s) and 323 (bar·m/s) respectively. Low Kst means slow combustion spread, which indicates that lambda-cyhalothrin can effectively combust only in dense dust-air mixture.

Kst value of beta-cyfluthrin is astonishing, especially in comparison with dried aluminum dust with similar particle size which Kst value is 102 (bar·m/s) and Pmax is about 7,2 bar (Traore, 2007).

Lowest concentration of tested compounds that was still able to combust during 20-L spherical chamber test was 60 g/m^3. Below this concentration we noted only pressure rise gained from used chemical igniters.

MIE studies shows that tested pyrethroids are also vulnerable to low energies of electrical spark. Beta-cyfluthrin exhibit combustion from 100 mJ electrical spark in very broad range of concentration, see figure 3. It’s much lower than aluminum dust with particle size about 125µm (Dufaud et al., 2011). This was very disturbing yet very attractive revelation. We did not noticed ignition at any tested concentration for 30 mJ energy although some local sparkles were observed at 2000 and 2500 g/m^3.

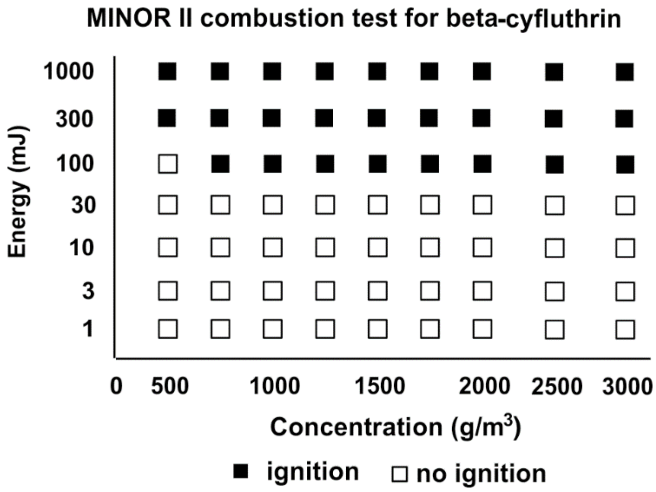


Figure 3 MINOR II results of MIE for beta-cyfluthrin

High MIE value for lambda-cyhalothrin - 1000 mJ, seem to stand in contradiction to results gained from cone calorimeter which suggested that this compound is the least stable of all tested. It is possible that -CF_3 group is responsible for higher resistance to low energies of electrical spark due to it stabilizing effect (Balashov et al. 2005) and low melting point that grants higher vapor density in elevated temperatures which allows lambda-cyhalothrin to combust much faster than other two pyrethroids.
Most surprising results were observed for deltamethrin, this almost non-flammable compound with the highest melting and boiling temperature showed higher vulnerability then lambda-cyhalothrin. Combustion from 300 mJ electrical spark energy is a result we weren't prepare to achieve based on cone calorimeter tests we gathered before. On the other hand explosive parameters shows that deltamethrin combust with higher pressure at low concentrations then other two pyrethroids. All resuts are presented in table 3.

Table 3. 20-L spherical chamber and MINOR II results

Parameter	lambda-cyhalothrin	beta-cyfluthrin	deltamethrin
Pmax (bar)	7,06	**7,72**	5,47
Kst (bar·m/s)	170	**323**	156
MIE (mJ)	1000	**100**	300

4. Conclusions

Based on the lately developed research on the subject of flammability of three pyrethroids with different terminal substitutents of ethylene group: lambda-cyhalothrin, deltamethrin and beta-cyfluthrin we decided to investigate explosive parameters (Pmax, Kst, MEC) and minimum ignition energy (MIE). As it turned out lambda-cyhalothrin, most flammable of all previously tested compound, showed highest MIE value and rather low explosive properties. On the other hand deltamethrin exhibited lowest explosive parameters but surprisingly is more vulnerable to electrical spark then lambda-cyhalothrin. Beta-cyfluthrin exhibited highest Kst value, that classified this compound as a ST 3 class dust with very strong explosive properties, also obtained MIE value was even lower then aluminium powder with similar particle size. All tested dusts exhibit MEC at concentration value of 60 g/m^3. Those results clearly shows the importance of testing of organic dusts that are widely used in the industry to prevent possible occurrence of major industrial accidents and ensure safety of workers, firefighters, medical services and other people.

Acknowledgments

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