Scientific paper

Evaluation of Burning Test Rate Method for Flammable Solids to Increase air-Cargo Safety

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Dedicated to the memory of the late Prof. Dr. Valentin Koloini

Abstract

This paper deals with a standard classification procedure for readily combustible solids and their assignment to the relevant packing groups according to international air-cargo legislation and regulations. The current International Air Transport Association and United Nations Orange Book regulations were used on chemically similar substances: hexamethylenetetramine and Dancook ignition briquettes, which are both assigned into the same Packing Group III. To critically evaluate the degree of hazard both chemicals present, a standard burning test rate as well as thermogravimetry, differential scanning calorimetry and evolved gas analysis measurements were performed. It was shown that relatively small changes in the chemical composition of the material may have essential influence on the package group determination. Taking into account all the facts collected in the experimental work, it was concluded that ignition briquettes will undergo spontaneous combustion if exposed to elevated temperatures and, from this point of view, represent higher risk than hexamethylenetetramine during air transportation. Therefore, ignition briquettes should be classified into Packing Group II.

Keywords: International Air Transport Association, United Nations Orange book, dangerous goods, burning test rate method, thermogravimetry, differential scanning calorimetry, evolved gas analysis, hexamethylenetetramine, ignition briquettes

1. Introduction

According to the the International Air Transport Association (IATA) dangerous goods regulations[1,2], hazards are categorized into nine classes. Regarding to the degree of hazard they present, dangerous goods are then assigned to the relevant packing group (PG) for air transportation: i.e. Packing Group I (high danger), Packing Group II (medium danger), and Packing Group III (low danger). Among the nine classes of hazards, Class 4 is of particular interest, since this class contains combustible solids. The class is divided into three divisions, each of which has very different properties. Subdivision 4.1 includes some commonly known products like red phosphorus, camphor, paraformaldehyde, and other any of those seem relatively harmless, but can be very dangerous unless properly packed, handled and transported. The substances and materials in this class are: i) solids possessing the properties of being easily ignited by external sources, such as sparks and hot surfaces, and of being readily combustible or being liable to cause or contribute to fire through friction, ii) self-reactive substances (solids or liquids), i.e. liable to undergo at normal or elevated temperatures a strong exothermic decomposition caused by excessively high transport temperatures or by contamination, and iii) desensitized explosives, which may explode if not diluted sufficiently. Some solids among Subdivision 4.1 substances can be highly flammable in transportation due to their physical and chemical properties and can cause numerous risks. The number of flammable solid substances in Class 4 is smaller than the number of liquid flammable substances. However, even though managing solid substances seems easier than managing liquids, the former can also cause fatal accidents when transported as air cargo[4]. Compared to flammable liquids, solids are less volatile due to lower partial pressure, while flammability and explosivity ranges are similar.

Classification procedures and testing conditions for readily combustible solids are described in IATA Dangerous Goods Regulations from the year 2003 and Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria.[1,2] Classification procedures for combustible solids include screening test, burning rate test and evaluation of whether a wetted zone stops propagation of the flame during the burning rate test (Figure 1). To categorize powdered, granular or pasty substances into classes and divisions and determine the appropriate packing group of the substance, the set standard procedure must be used.[1,2]

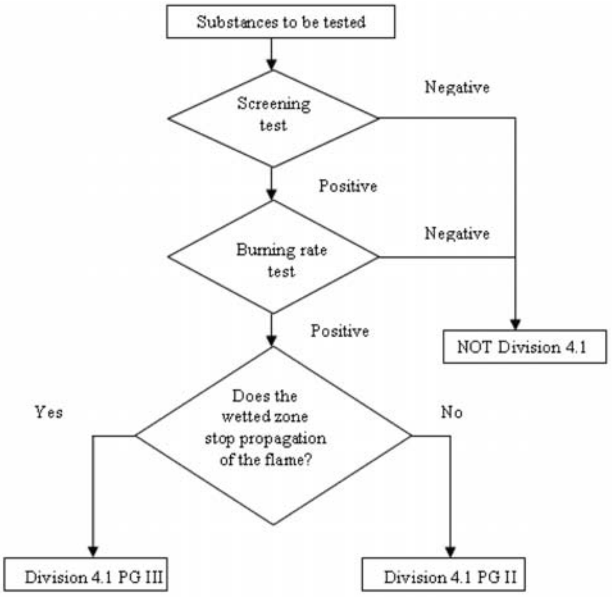

Figure 1. Classification procedure for readily combustible solids other than metal powders [1,2]

Although the existent classification procedure is clearly defined, determination of the appropriate packing group is sometimes still difficult. Specifically, the classification procedure for combustible solids does not take into account all their physical and chemical properties. For instance, sub-micrometer sized metal powders are an especially dangerous hazard with regards to ignition, because of the difficulty of extinguishing fire,[8] as carbon dioxide or water can even increase the hazard. In contrast, chemically the same substance may be assigned to the completely different packing group when the size of particles is increased. For example, about 20% of air traffic fatalities in the United States of America, and also worldwide generally, are attributed to fire in the cargo compartment which is often a consequence of an inappropriate hazards transportation.[5,22] Another problem, which at present is not reported in any safety codes in IATA Dangerous Goods Regulations, is the gas and smoke produced during burning of dangerous goods.[1] When combusted, the vapours and combustion products of flammable solids are in general poisonous and harmful to health.[5–13,20] Therefore, due to the possibility of expanding into the passenger compartment the danger may not originate only from the fire itself but also from toxic combustion products.[5–11,13,20–22] In particular, CO and CO_2 released during burning of dangerous goods are the key factors for passenger and crew survival.[10,11,20–22]

The aim of this paper is to evaluate the IATA regulations for hazards packing group assignments on two similar chemicals: hexamethylenetetramine and Dancook briquettes (powder preparation). Both chemicals contain the highly flammable substance hexamethylenetetramine and are as such, according to IATA, classified into Subdivision 4.1. Hexamethylenetetramine may be transported in air as a substance representing a low danger i.e. Packing Group III. Since similar hazards are classified into same IATA subdivisions and same package groups according to their chemical composition, one could expect that both products should be transported according to same general packing requirements. However, it is shown that relatively small changes in the chemical composition of hazards have an essential influence on the classification into package groups. These small changes in chemical composition may significantly influence the speed of flame propagation and maximum achieved temperature on the surface of a burning element.[4,5,14–18,21]

2. Experimental Procedure

The first testing substance used was hexamethylenetetramine (Merck, assay ≥ 99 %), an organic substance with an empiric formula of $C_6H_{12}N_4$. Hexamethylenetetramine (HMT) is a highly flammable substance with M = 140.19 g mol^{-1} and ρ = 1.33 g cm^{-3} at 20 °C. Chemical Abstracts Service (CAS) registry number is 100-97-0. The second investigated substance was commercial Dancook briquettes (IB); (Dancook – Kriswell A/S, powder preparation) with a CAS registry number 90583-16-7. They are produced according to Deutsches Institut für Normung (DIN) standard 66358-S. Both investigated substances are similar, commercially available, frequently used and transported.

Burning rate tests of both hazards were performed on powdered substances loosely filled into a mould according to the standard procedure described in the United Nations Orange Book.[2] A wetted zone in a loose powdered pile was prepared 40 mm beyond the marked 100 mm timing zone by wetting the whole cross-section of a pile with 5 mL of water. Each burning rate experiment was documented with a Sony video camera (DCR-TRV7E PAL). The shots were digitalised and subsequently used for the precise measurement of the combustion velocity. Carbon dioxide and carbon monoxide evolution during the combustion of 12.85 g of each substance was measured in a closed fume hut with the instrument Q-TRAK Plus, model 8553. Temperature profiles of burning powdered tracks were measured in a single dot using an optical pyrometer (Ircon, IPE 140 based on sample brightness). This pyrometer has a measuring range from 50 to 1200 °C and a very quick response time (1.5 ms). The accuracy of the optically measured temperature was ± 2.5 °C below 400 °C and ± 0.4% of a measured value (in °C) above 400 °C. Since the measured systems were all ceramic where exact mixtures' emissivities were unknown, the emissivity was set to 0.85 and was kept constant for all measurements. This value is close to the cited emissivities of some similar products in the measured temperature range. Temperature profiles of measured systems were taken from a distance of 10 cm, giving a spatial resolution of the temperature measurements (size of the measured spot on the sample surface) 0.3 mm.

In order to determine certain thermal properties both samples were submitted to TG and Differential Scanning Calorimetry (DSC) tests using Mettler TG-50 and Mettler DSC 20 standard cell TC 10A. Accuracy for Mettler DSC 20 standard cell TC 10A was ± 0.2 °C. Thermo-analytical tests were conducted in air and in an inert (N_2) atmosphere[3] at a flow rate of 100 mL min^{-1} and with a heating rate of 10 K min^{-1}. Thermogravimetry-Evolved Gas Analysis (TG-EGA) experiments were performed using 5 mg of sample and a NETZSCH STA 449 set-up with a microbalance having a sensitivity of ±0.1 µg coupled with AËOLOS 403C MS. All the experiments were carried out at a constant flow of air (50 mL/min). The amount of heat released during the samples' burning was determined with adiabatic bomb calorimeter C 4000 according to ISO standard 1928:1995(E).[19]

3. Results and Discussion

The preliminary flammability tests showed that the measurements of a burning front propagation are quite

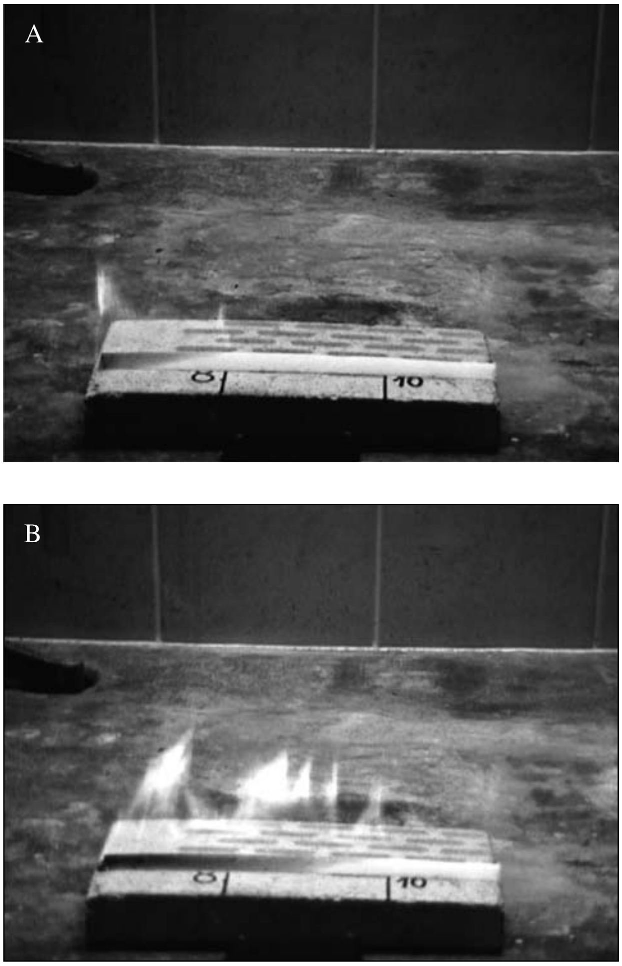

Figure 2. Combustion front propagation determination for hexamethylenetetramine: A) initial point, B) final point

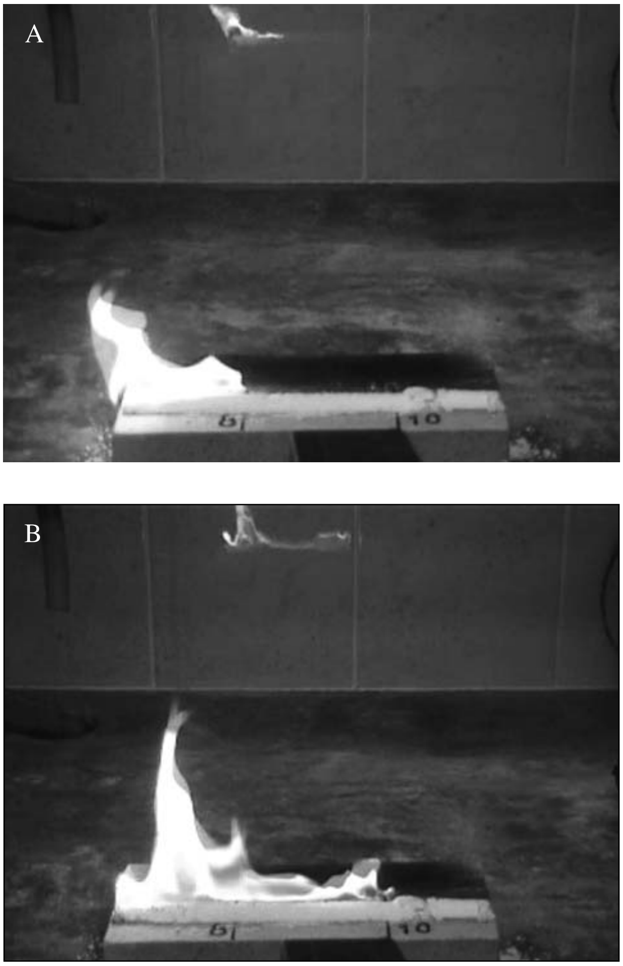

Figure 3. Combustion front propagation determination for Dancook briquettes: A) initial point, B) final point

subjective and sometimes difficult to determine. For this reason, a digital camera was used to define the exact combustion time and flame propagation (Figs. 2 and 3). The combustion front propagation velocity was obtained by dividing the distance of 100 mm with the time of the spread of flame [1,2] (Tables 1).

One criterion for the packing group allocation of flammable solids is the propagation of a burning front. According to the IATA criteria for package classification, all flammable solids in IATA Subdivision 4.1 in which flame propagation does not exceed 2.2 mm s^{-1} and the wetted zone stops the flame propagation for at least four minutes may be assigned to Package Group (PG) III. Since the average rate of combustion for hexamethylenetetramine was determined to be 2.08 mm s^{-1} and the wetted zone stopped the flame propagation in all experiments, the package group (PG) III for hexamethylenetetramine was confirmed. In contrast, Dancook briquettes burned five times faster ($\bar{v}$ = 10.57 mm s^{-1}) compared to the IATA reference rate of combustion. Furthermore, we noticed that the wet zone (damp area) did not stop the combustion propagation. Thus, although both tested substances have very similar chemical compositions, according to the conducted experiments, the Dancook briquettes should be classified into Packing Group (PG) II.

Table 1. Average rate of combustion for hexamethylenetetramine – HMT

Sample HMT	$t_i - t_f$/s	*v/mm s^{-1}*	
1	*45*	*2.22*	
2	*37*	*2.70*	
3	*50*	*2.00*	
4	*49*	*2.04*	
5	*47*	*2.13*	
6	*60*	*1.67*	
7	*55*	*1.82*	
	$\bar{t}$/s	$\bar{v}$/mm.s^{-1}	*PG*
	49	2.08±0.3	III

t_i initial time measured at start point of timing zone
t_f final time measured at the end point of timing zone

Table 2. Average rate of combustion for ignition Dancook briquettes – IB

Sample IB	t_i - t_f/s	*v/mm s^{-1}*	
1	9	11.11	
2	9	11.11	
3	8	12.50	
4	11	9.09	
5	10	10.00	
6	9	11.11	
7	11	9.09	
	$\bar{t}$/s	$\bar{v}$/mm.s^{-1}	PG
	10	10.57±1.1	II

t_i initial time measured at start point of timing zone
t_f final time measured at the end point of timing zone

CO and CO$_2$ release during burning is another very important parameter when estimating the risk of transporting dangerous goods. Experimental testing revealed that under similar burning conditions hexamethylenetetramine in comparison to ignition briquettes releases more CO and CO$_2$ (Figure 4). The maximum reached concentration of CO$_2$ for hexamethylenetetramine was approx. 1337 ± 41 ppm (dotted black line) while the maximum concentration of CO$_2$ for ignition briquettes was only approx. 700 ± 22 ppm (full black line). Similarly, the maximum reached concentrations of CO for hexamethylenetetramine and ignition briquettes were 3.6 ± 0.1 ppm (doted grey line) and 2.5 ± 0.1 ppm (full grey line), respectively. Such information may be interpreted to mean that hexamethylenetetramine in general is more harmful to health in the case of fire. However, to confirm such a statement a more complete image of released volatile product must be presented. Both substances may, with respect to their chemical composition, also release some other toxic volatiles i.e. nitrogen oxides (NO$_x$), formaldehyde, ammonia, and hydrogen cyanide which present high risk for human health.[7–11]

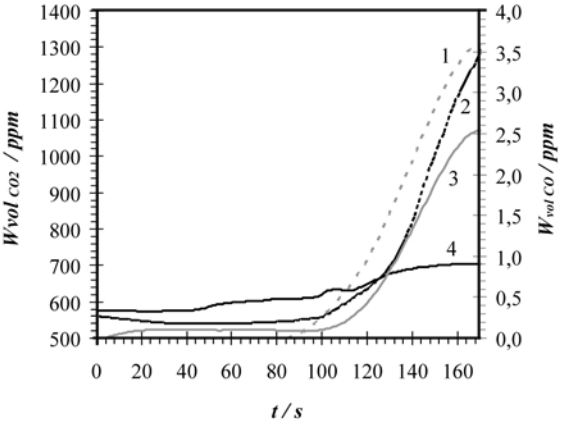

Figure 4. Average CO and CO$_2$ concentrations increase in a fume hut during burning of hexamethylenetetramine – HMT and ignition briquettes – IB; 1: HMT: CO-concentration, 2: HMT: CO$_2$-concentration, 3: IB: CO-concentration, 4: IB: CO$_2$-concentration

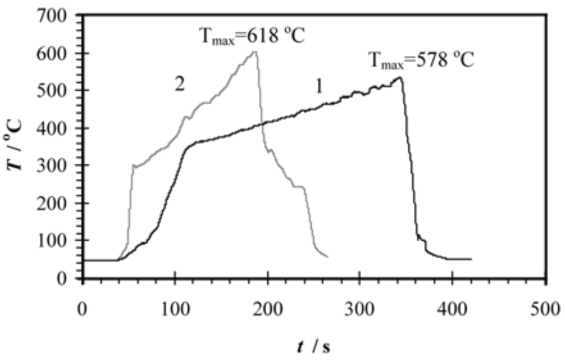

Figure 5. Measured temperature profiles for hexamethylenetetramine – HMT and ignition briquettes – IB; 1: HMT, 2: IB

When temperature profiles of both substances are compared some very distinctive differences are observed (Figure 5). Specifically, ignition briquettes burn much faster in comparison to hexamethylenetetramine. Additionally, maximum burning temperature (T_{max}) and temperature increase at the early stages of burning is greater in the case of ignition briquettes. Maximum heating rates ($\partial T/\partial t$) achieved during the combustion reactions of both samples were calculated as 44.14 °C s^{-1} for ignition briquettes and 12.29 °C s^{-1} for hexamethylenetetramine, respectively. When these values were divided by the measured wave velocity values ($\bar{v}$)*, the maximum thermal gradient* $(\partial T/\partial x)_{\max}$ in the flame propagating coordinate was calculated 4.18 °C mm^{-1} for ignition briquettes and 5.91 °C mm^{-1} for hexamethylenetetramine. Relatively high values of $\partial T/\partial t$ and $(\partial T/\partial x)_{\max}$ are an indication of another hazard both substances signify. When ignited, the temperature (especially in the case of ignition briquettes) will rise very quickly, bursting into flames and also igniting neighbouring substances in a cargo compartment, thereby making it more difficult to extinguish fire.

The total amount of heat released during the samples' burning, as determined with calorimetry, was 29.6 kJ g^{-1} and 43.9 kJ g^{-1} for hexamethylenetetramine and ignition briquettes, respectively.

In order to obtain a more detailed picture about hexamethylenetetramine and ignition briquette, burning both samples were subjected to TG and DSC tests (Figs. 6 and 7). According to the obtained results, some significant discrepancies may be expected when both samples are heat treated. More specifically, hexamethylenetetramine exhibited two endothermic effects without exothermic effects during heating in air or N_2 up to 400 °C. Peak temperatures of both effects ~265 °C and ~298 °C may be ascribed to hexamethylenetetramine melting and sublimation, respectively. This means that under heat load without direct ignition hexamethylenetetramine will sublimate into the cargo compartment rather than undergo spontaneous ignition. Hexamethylenetetramine sublimation is also indicated by the TG curves taken in air or N_2 (Figs. 6 and 7), which revealed only one region of mass loss with a peak temperature of 296 °C. In this region, the sample, lost 99.8 % of its original mass regardless of the atmosphere in which measurements were conducted.

In contrast, ignition briquettes under heat load in air exhibited an exothermic effect just below 300 °C which was ascribed to the substance oxidation (Figure 6). To corroborate that this exothermic effect with peak temperature 291 °C is in fact related to the substance combustion with air, DSC measurements were also conducted in N_2 inert atmosphere (Figure 7). According to Figure 7 thermal treatment of ignition briquettes in an inert atmosphere did not result in any exothermic effect. Instead, the whole DSC response was reduced to one broad endothermic effect in a range between 205–275 °C. Mass losses that accompanied heat effects also indicate that combustion of ignition briquettes is more complex than combustion of pure hexamethylenetetramine since in the case of ignition briquettes mass is changed throughout several consecutive steps. The total mass loss during the heat treatment of ignition briquettes in N_2 or air atmosphere was measured 84.8 % and 98.2 %, respectively. The sample residue after the heat treatment in N_2 atmosphere was black powder, while air atmosphere burned the ignition briquettes almost completely.

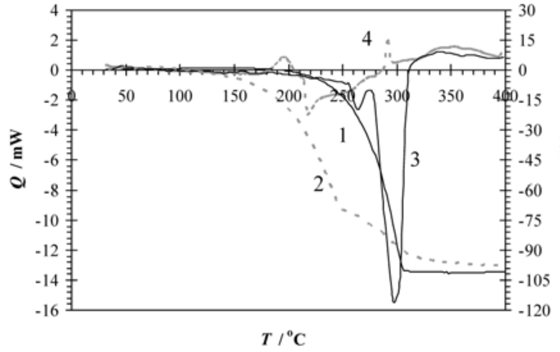

Figure 6. DSC and TG curves of hexamethylenetetramine and ignition briquettes taken in air; 1. TG HMT, 2. TG IB, 3. DSC HMT, 4. DSC IB

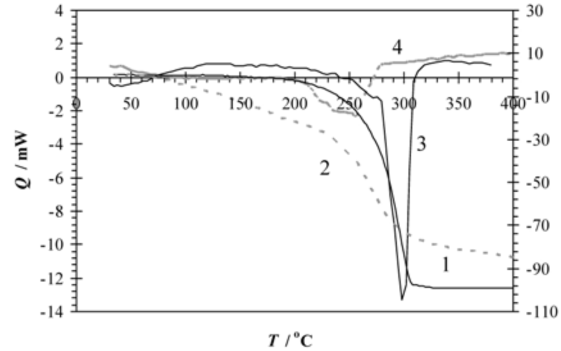

Figure 7. DSC and TG curves of hexamethylenetetramine and ignition briquettes taken in N_2; 1. TG HMT, 2. TG IB, 3. DSC HMT, 4. DSC IB

Volatile products release during heat treatment of both substances (hexamethylenetetramine or ignition briquettes) in synthetic air was monitored using TG-EGA analysis (Figs. 8 and 9). According to these results, the mass spectrometry (MS) response detected during the hexamethylenetetramine analysis was rather complex with m/e (atom mass unit) fragmental peaks at 15, 42, 85, 92, and 140. However, all m/e peaks may be attributed merely to the hexamethylenetetramine sublimation. As represented in Figure 8, the evolution of the main and most significant m/e fragmental signal at 42 (and all other m/e peaks) strictly followed the substance sublimation that is indicated by the TG curve.

Ignition briquette thermal decomposition, in contrast, may not be qualified simply to the substance sublimation.

More specifically, in addition to the already-mentioned m/e fragmental peaks that are characteristic for hexamethylenetetramine sublimation, MS responses at m/e 18, 28, 30, 44 and 128 were detected and ascribed to H_2O, CO, NO, CO_2 and naphthalene evolution. While naphthalene evolution was noticed only during the first stage of mass loss (with TG peak temperature ~200 °C), hexamethylenetetramine was also detected in the second interval of mass loss (TG peak temperature ~290 °C). This fact confirms that during both stages of mass changes some material was lost due to sublimation: however, H_2O, CO, NO and CO_2 evolution indicated that substance combustion was triggered with ignition briquette thermal treatment.

Regarding all the facts collected with the conducted TG, DSC and EGA analyses, one may conclude that ignition briquettes will undergo spontaneous combustion if exposed to elevated temperatures and, from this point of view, represent a higher risk during air transportation.

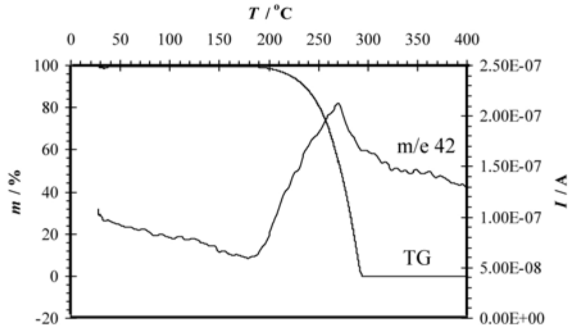

Figure 8. TG-EGA test of hexamethylenetetramine taken in air

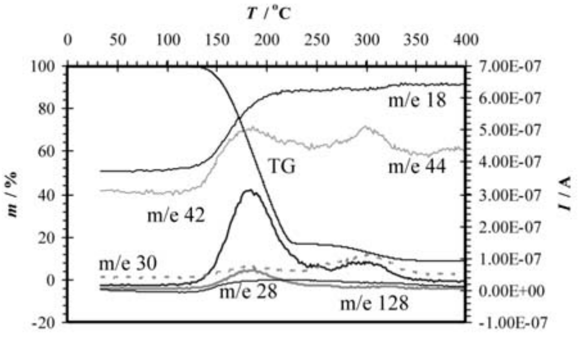

Figure 9. TG-EGA test of ignition briquettes taken in air

4. Conclusions

The main purpose of this paper was a critical evaluation of the standard classification procedure for readily combustible solids and their assignment to the relevant packing group when transported as air cargo. Although chemically similar hazards like hexamethylenetetramine and Dancook ignition briquettes are assigned to the same package groups, it was shown that relatively small changes in the chemical composition of the hazards may have an essential influence of the package group determination. According to the obtained results, ignition briquettes will undergo spontaneous combustion, which is accompanied by some evolution of toxic gases, when exposed to temperatures above ~150 °C while pure hexamethylenetetramine sublimates under similar conditions. Furthermore, in the case of fire in an airplane cargo compartment, ignition briquettes will burst into flames much easier with a rapid heat rise and will reach higher combustion temperature than hexamethylenetetramine. Therefore, IB should be classified into Packing Group II. Unfortunately, the current IATA test method does not require measurements and evaluation of all the necessary physical characteristics of hazards when assigning the packing group. However, with respect to the conducted work, such methodology may in some cases lead to inappropriate decisions regarding the packing group determination and should be further improved.

5. References

1. IATA Dangerous Goods Regulations, International Air Transport Association, Montreal, **2003**, 44, 87–91.
2. Recommendations on the Transport of Dangerous Goods – Manual of Tests and Criteria, United Nations, New York and Geneva, **2003**, 4, 351–356.
3. Brown M. E., Handbook of thermal analyses and calorimetry, Elsevier Science, **1998**, *1*, 147–178.
4. Burke R., Hazardous Materials Chemistry for Emergency Responders, CRC, **2002**, *2,* 228–242.
5. Wichman I.S., Prog. Ener. Combust. Sci. **2003**, *29,* 247–299.
6. D. Blake, J. Suo-Anttila, Fire Saf. J. **2008**, *43,* 576–582.
7. Fenimore, C. P., Combust. Flame **1972**, *19,* 289–296.
8. Bowman, C. T., Fossil Fuel Combustion – A source Book, John Wiley, New York, **1991**.
9. F. Lestaria, A.R. Greenb, G. Chattopadhyayc, A. J. Hayesa, Fire Saf. J. **2006**, *41,* 605–615.
10. Meyers, R. A. M., and Thom, In Hyperbaric Medicine Practice, (E. P. Kindwall, Ed.), Best Publishing, Flagstaff, **1995**, 343–372.
11. Hartzell G. E., Toxicology, **1996**, *115,* 7–23.
12. Chervin S., Bodman G. T., J. Hazard. Mater., **2004**, *115,* 107–110.
13. Bigda R., Mianowski A., J. Therm. Anal. Calorim., **2006**, *84,* 453–465.
14. Lyon R. E., Walters R. N., J. Anal. Appl. Pyrol., **2004**, *71,* 27–46.
15. Fernandez-Pello A. C., Combust. Sci. Tech., **1983**, *32,* 1–31.
16. Fernandez-Pello A. C., Combust. Sci. Tech., **1984**, *39,* 119–134**.**
17. R. E. Lyona, J. G. Quintiere, Combust. Flame, **2007**, *151,* 551–559.
18. Babrauskas V., Peacock R.D., Fire Saf. J., **1992**, *18,* 255–272.

19. SIST ISO standard 1928, **1995**.
20. Blomqvist P., Doctoral Thesis, Lund University, **2005**. Utiskul Y., Doctoral Thesis, University of Maryland, **2007.**
22. Smith R. L., *Risk Analysis for the Fire Safety of Airline Passengers*, http://www.fire.nist.gov/bfrlpubs/fire94/art141.html, (accessed: June 1994)

Povzetek

Izdelali smo kritično evaluacijo standardne testne metode za razvrščanje trdnih vnetljivih snovi v pakirne razrede glede na predpise pri prevozu nevarnih snovi v zračnem prometu. Uporabili smo heksametiltetramin in vžigne brikete proizvajalca Dancook, ker sta kemijsko podobni snovi. Obe snovi sta po kriterijih Združenja letalskih prevoznikov (IATA) in Oranžne knjige Organizacije združenih narodov razvrščeni v isti pakirni razred III. Kritična evaluacija stopnje nevarnosti za obe snovi je bila izdelana na podlagi standardne testne metode za razvrščanje trdnih vnetljivih snovi ter termoanalitskih metod: termogravimetrija (TG), diferencialna dinamična kalorimetrija (DSC) in analiza razkrojnih plinskih produktov (EGA). V članku je prikazano, da imajo relativno majhne spremembe v kemijski strukturi snovi bistven vpliv na razvrščanje v ustrezne pakirne razrede. Na podlagi vseh dejstev, ki izhajajo iz eksperimentalnega dela, lahko zaključimo, da je proces gorenja pri vžignih briketih spontan, če so izpostavljeni dovolj visoki temperaturi. Zaradi tega dejstva predstavljajo vžigni briketi med prevozom v zračnem prometu višjo stopnjo tveganja kot heksametiltetramin. Vžigni briketi bi morali biti razvrščeni v pakirni razred II.