

Fire Hazard Posed by Sugar Alcohols

Maciej Celiński*, Monika Borucka

Central Institute for Labour Protection – National Research Institute, Warsaw, Poland
macel@ciop.pl

Sucrose is the most popular disaccharide used as a sweetener in food industry. Its annual global production ranks at 170 million metric tons. Such large quantity of produced organic compound in natural way poses a threat of the possibility of a major industrial accident. Chemical Safety Board in its report on fires and explosions of sugar dust stated that first reported combustion of sugar dust took place in 1925. Since then, despite all modern protection techniques, one can still observe accidents caused by this compound i.e. sugar dust explosion in: silo tower (Cantley, England, 2003), sugar mill (Baltimore, USA, 2007), silo tunnel (Georgia, USA, 2008).

Growing popularity of artificial sweeteners commonly used as a sucrose substitute causes a rapid increase in their production which is close to 2 million metric tons annual. Sugar alcohols dust qualifies as a potentially flammable or explosive due to their chemical structure. Short carbon chains combined with several hydroxy groups significantly increases molecular oxygen balance in those compounds which makes them good fuel even in low oxygen conditions. Therefore they pose a threat of a major industrial accident and should be examined for it.

The purpose of the following work was to determine and compare parameters describing the burning process of six sugar alcohols: d-sorbitol, d-mannitol, xylitol, maltitol, myo-inositol, meso-erythritol; with sucrose. The fire tests were conducted using cone calorimeter and smoke density chamber, in accordance with standards: ISO 5659 and ISO 5660. All data and conclusions will be presented during conference.

1. Introduction

Sugar alcohols are easily digestible carbohydrates, obtained by reduction (hydrogenation) of saccharides aldehyde groups: hydrogenated monosaccharides (sorbitol, mannitol –glucose derivatives); hydrogenated disaccharides (maltitol, isomalt, lactitol – lactose derivatives); mixtures of mono/di and oligosaccharides (Livesey, 2003; Shankar, 2013).

In nature sugar alcohols occurs in small amounts in fruits and vegetables. They are considered safe for health and used in pastry and as a additives in nutritional supplements (Wheeler and Pi-Sunyer, 2008; Fitch and Keim, 2012). Due to their low caloric value they are used as a sucrose replacement by people with diabetic problems. Sugar alcohols are also components of dental products and compounds of therapeutic importance (prebiotics, anti-carcinogenic and regulating the digestive system compounds) for example mannitol is being used in a treatment of diuretic for renal failure and intra-ocular hypertension (Grabitske and Slavin, 2008; EFSA, 2011).

Global annual production scale of sugar alcohols i.e. sorbitol, xylitol, mannitol, maltitol and isomalt is 1,6 million metric tons and increases rapidly. It is assumed that it will reach value of 2 million metric tons by the end of year 2022. Such large production scale of organic compounds, despite the current lack of incidents reports, poses a threat of a major industrial accident. Sugar alcohols dust qualifies as a potentially flammable or explosive due to their chemical structure. Short carbon chains combined with several hydroxy groups significantly increases molecular oxygen balance in those compounds which makes them good fuel even in low oxygen conditions. Based on those information we decided that there is an urgent need to conduct studies of compounds so widely used and processed in large quantities for their flammability and explosive properties.

In this study we focused on the recognition of parameters describing the combustion process of six sugar alcohols: d-sorbitol, d-mannitol, xylitol, maltitol, myo-inositol, meso-erythritol and compared them to the values obtained for sucrose.

2. Materials and methods

2.1. Materials

All compounds are commercially available products. The purity of tested compounds was 98-99%, except for Maltitol which purity was 95%.

2.2. Cone Calorimeter Test

The cone calorimeter is one of the most recognized fire testing apparatuses in the world. There are several parameters that can be investigated through it like: Heat Release Rate – HRR (kW/m^2), peak of Heat Release Rate – pHRR (kW/m^2) time to peak of Heat Release Rate – t-pHRR (s), Maximum Average Rate of Heat Emission – MARHE, Total Heat Release – THR (MJ/m^2), Ignition Time – TTI (s), Total Smoke Release – TSR (m^2). Fire safety characteristics requires the determination of the basic behavioral parameters under fire conditions. Parameters characterizing behavior of analyzed compounds in the presence of flame were studied according to standard ISO 5660-1. Three samples of equal mass for each compound, were covered with aluminum foil (100 mm x 100 mm x 25 mm) and treated with external Heat Flux (HF) at 35 kW/m^2 simulating the thermal exposure during the first phase of fire.

2.2 Smoke Density Test

The smoke density characteristics in a closed room can be described by two main parameters: Optical Density of Smoke (Ds) and VOF4. Ds parameter determines visibility reduction and is the determinant of an amount of smoke produced during the first ten minutes of thermal degradation of tested material. VOF4 describes increasing rate of smoke density during the first four minutes, which are crucial during evacuation process. All parameters were measured using Smoke Density Chamber (FTT Limited, West Sussex) according to standard ISO 5659-2. Three samples of equal mass for each tested compound, were covered with aluminum foil (75 mm x 75 mm x 10 mm) and treated with external HF of 25 kW/m^2 .

3. Results

3.1. Cone calorimeter parameters

Average values of parameters characterizing the behavior of sugar alcohols under the influence of intense radiant heat gained during cone calorimeter measurements were summarized in Table 1.

Table 1. Calorimetric values of fire parameters for sugar alcohols and sucrose

Sample	TTI s	HRR kW/m^2	pHRR kW/m^2	t-pHRR s	THR MJ/m^2	TSR m^2/m^2
D-mannitol	108	183	362	155	31,7	72,9
D-sorbitol	104	170	344	155	31,3	72,9
xylitol	77	138	301	133	31,5	79,5
maltitol	88	237	580	148	29,8	98,7
meso-erythritol	72	185	371	138	32,1	63,1
myo-inositol	60	126	305	68	28,0	65,1
sucrose	70	161	614	93	22,4	61,5

Sucrose achieved the highest values of pHRR $\sim 600 \text{ kW/m}^2$, which is almost two times higher for values obtained for other sugar alcohols. It probably did not reach its full potential, due to the lack of steady burning phase, see figure 1. Sucrose reaches lowest THR value and the probable explanation of this behaviour is the chemical structure and chemical reactions in condensed phase. Combination of two cyclic ethers can explain reduction of molecule energy and therefore TTI. Also sucrose does undergo caramelization process and because cone calorimeter parameters are based on oxygen level in flaming phase, it is possible that decomposition of sucrose in the condensed phase is responsible for low THR. When heated above 140°C sucrose starts to decompose (caramelize) generating furans with very low flashpoint temperature (Fp) ($60-80^\circ\text{C}$) which can also be the cause of short TTI under higher HF (Fayle and Gerrard, 2012).

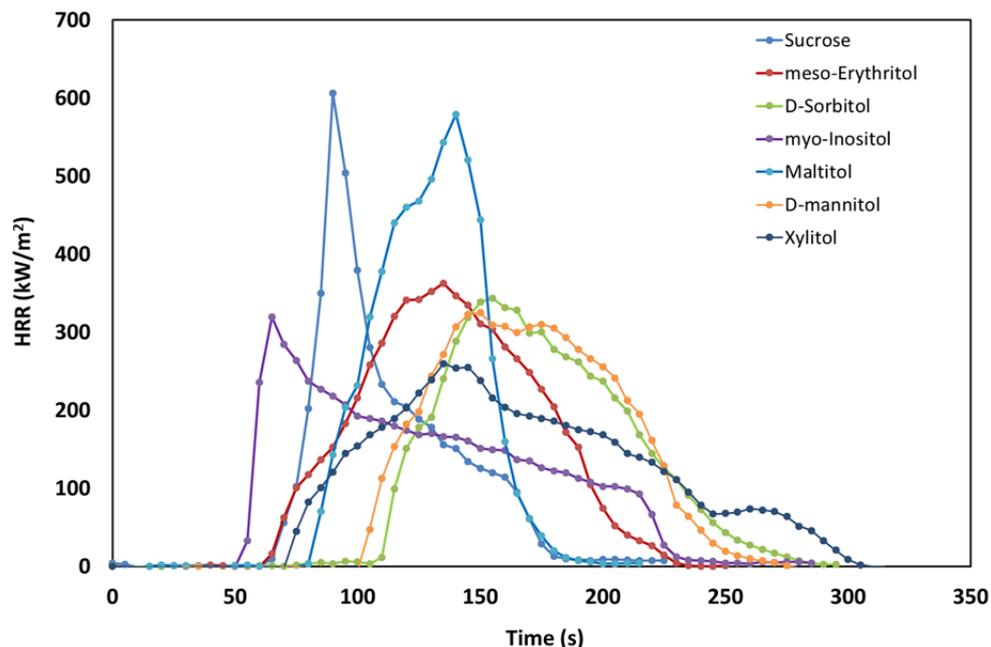


Figure 1: Comparison of HRR development during burning stage for tested compounds ($HF = 35 \text{ kW/m}^2$).

As a result of analysis of maltitol's HRR, it can be concluded that the initial increase of the HRR is being followed by a slow growth up to the maximum value. The first stage is the ignition of flammable pyrolysis products while the second stage is limited by the rate of decomposition and the emission of combustible products into the combustion zone. Due to high molecular weight and contribution of functional groups, maltitol shows the highest HRR, THR and TSR values. Maltitol, does not caramelize, therefore it generates large amount of soot as a result of incomplete combustion. Myo-inositol is characterized by very short TTI. It also shows low HRR, and its flaming phase is statistically longer than for the rest of the tested compounds. Such behaviour is characteristic for compounds with the ability to generate a swollen char on the surface of the sample, see figure 2.



Figure 2: Swollen char layer formed on the surface of myo-inositol sample.

Reason for the char formation is the presence of cyclohexane ring. Dehydration of hydroxyl groups leads to the formation of double bonds and aromatic structures like benzene or naphthalene, foundation of char. Swelling process forms thick carbonized barrier limiting access of oxygen and heat to the main material and slows the release of flammable pyrolysis products. Confirmation of char production is the presence of high

level of CO gas, see figure 3. Only two of tested compounds generated layered char structure: sucrose and myo-inositol. Sucrose char was thin and very unstable, yet its impact can be seen in figure 3a (after the flameout CO production increased rapidly which is most probably an impact of char layer that promoted slow pyrolysis process and incomplete combustion near the surface of the sample –smoldering effect). Production rate CO and CO₂ of compounds other than sucrose and myo-inositol decreases after the flameout due to the lack of organic material, see figure 3a and 3b.

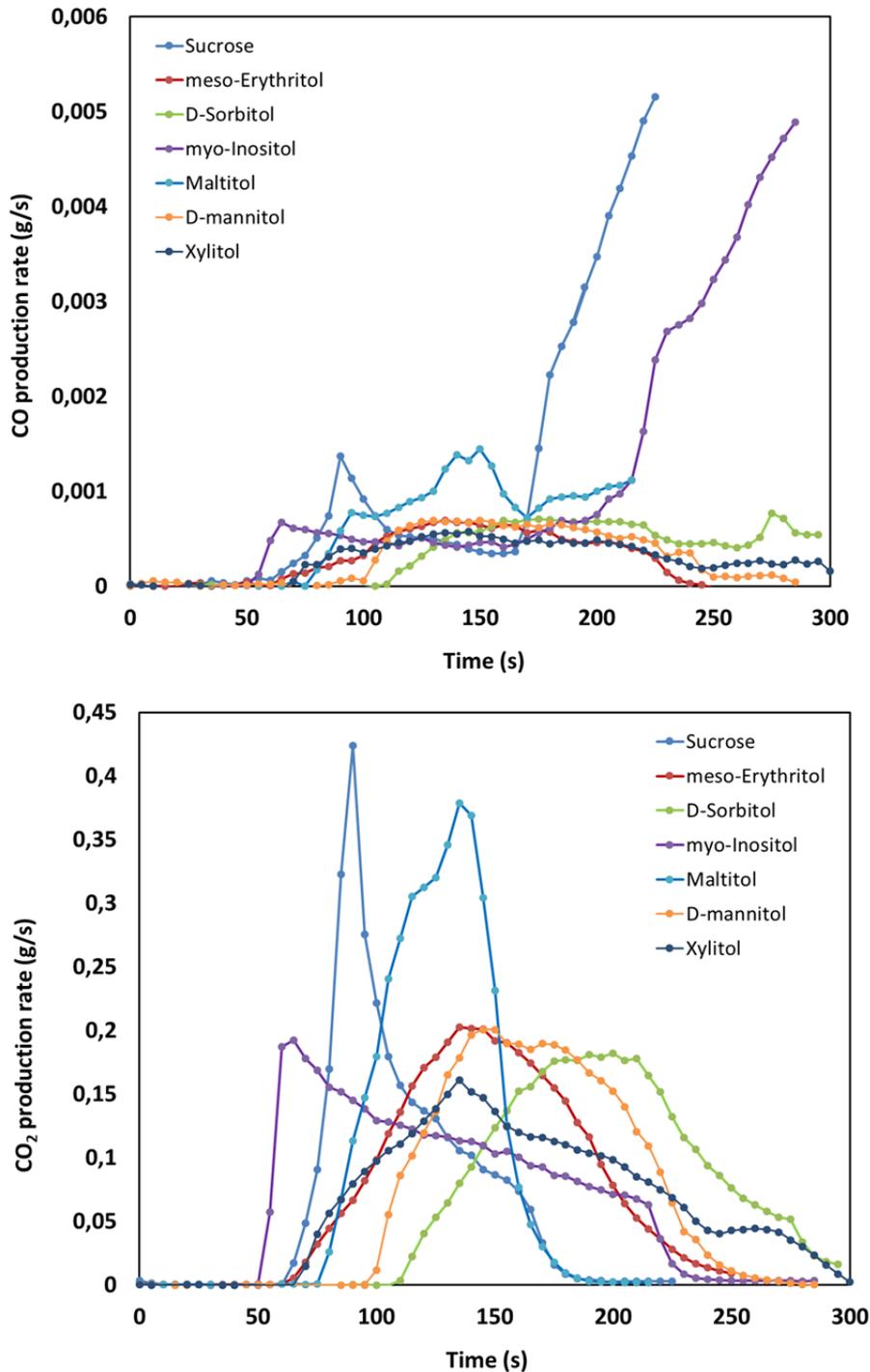


Figure 3: a) (top) CO production and b) (bottom) CO₂ production during Cone Calorimeter Test for sugar alcohols.

D-mannitol and d-sorbitol, shows high thermal stability. Those compounds are characterized by long TTI, low HRR and stable burning process. Similar characteristic of these to compounds are a result of their chemical structure. Both alcohols are isomers, and differ only in spatial orientation of hydroxyl group at second carbon atom. Even such subtle structural difference shows an impact on their behaviour under fire conditions. D-sorbitol is characterized by higher thermal stability (longer TTI) than D-maltitol although other parameters are practically the same. Erythritol is relatively stable to heat ($F_p = 209^{\circ}$) and does not undergo Maillard reaction. This means that erythritol rather vaporize than decompose under low temperatures and its F_p is much higher than F_p of sucrose's decomposition products, like furfuryl alcohol (77°C) (de Cock P., 2012; Zeitsch, 2000). This translates into a longer TTI and a relatively low HRR parameter value. Xylitol is most similar to the meso-erythritol based on the chemical structure. Additional carbon atom and hydroxyl group show some impact on HRR value and smoke production especially during smoke density tests.

3.2. Smoke Density Test

The results gained during smoke density test indicates that the meso-erythritol, compound with the shortest TTI during cone calorimeter test, was the only compound that did not ignite, see table 2. This behaviour can be explained by the low mass of its four-hydroxyl butanoic chain and probable evaporation before reaching its ignition temperature.

Table 2. Summary of smoke density chamber parameters for tested compounds

Sample	Ds (TMDS) - (s)	VOF4	TTI' s
D-mannitol	497 (418)	51,6	410
D-sorbitol	391 (395)	48,3	395
xylitol	673 (433)	109	452
maltitol	281 (256)	148	251
meso-erythritol	890	238	-
myo-inositol	147 (530) / 507	- / 204	131 / -
sucrose	175 (202)	-	143

Longest TTI' was observed for xylitol, followed by two isomers: d-mannitol and d-sorbitol, maltitol and finally sucrose. Myo-inositol, due char generating ability, did not ignite during the first test, resulting in a VOF4 value of 204. Yet, generated char is not always dense enough to protect the sample from external heat, especially in case of compound with such a short TTI like myo-inositol, which ended in very short TTI' during second test. Sucrose TTI' was too short to determine even VOF4. Ds obtained after ignition cannot be a comparative criterion for tested substances since the presence of a flame interferes with the readings of the light analyzer, making it impossible to determine the actual degree of smoke inside the chamber. Lowest VOF4 parameter was obtained for D-sorbitol with a self-ignition temperature of 420°C (Roth, 2015). This compound ignited 6,5 minutes after the test initiation, allowing the estimation of VOF4 on the level of 48,3. In turn, the highest value was obtained for meso-erythritol.

4. Conclusion

Fire parameters of sugar alcohols were investigated with the use of cone calorimeter under a heat flux of 35 kW/m^2 . Correlation analysis between the HF and the characteristic parameters was properly described. Based on gained results in can be concluded that sucrose is the most flammable of all tested sugar alcohols. Nonetheless four of tested sugar alcohols show higher average HRR and THR value. Maltitol's characterizes with similar pHRR but shows longer TTI. Myo-inositol shows shortest TTI and the initial raise of HRR is very steep. If not for charring properties, this compound could show rather high combustion parameters. Data obtained from the smoke density test indicate that the time to ignite sucrose is the shortest of tested substances. Myo-inositol was the only compound that did not ignite. The lowest values of the VOF4 parameter were obtained by the two isomers D-mannitol and D-sorbitol, which in combination with a relatively long TTI makes these compounds one of the safest sweeteners from the group of poly-alcohol. In conclusion, from a fire safety standpoint, under specific conditions, sugar alcohols can create a potentially hazardous situation similar to those for sucrose leading to serious industrial failures.

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References

- Boileau J., Fauquignon C., Hueber B., Meyer H.H., 2005, Explosives, Ullmann's Encyclopedia of Industrial Chemistry, Weinheim Wiley-VCH.
- de Cock P., 2012, Erythritol. Chapter In: O'Brien-Nabors L. (Ed.) Alternative sweeteners, 4th edn. CRC Press, Boca Raton, 249 – 262.
- EFSA, 2011, Scientific opinion on the substantiation of health claims related to the sugar replacers xylitol, D-tagatose, xylitol, sorbitol, mannitol, maltitol, lactitol, isomalt, erythritol, D-tagatose, isomaltulose, sucralose and polydextrose and maintenance of tooth mineralization by decreasing tooth demineralization, EFSA Journal 9, 2076.
- Fayle S.E., Gerrard J.A., 2002, The Maillard Reaction, Cambridge, Royal Society of Chemistry, 124, 40, 12054-12054.
- Fitch C., Keim K.S., 2012, Position of the Academy of Nutrition and Dietetics: use of nutritive and nonnutritive sweeteners, Journal of the Academy of Nutrition and Dietetics, 112, 739–758.
- Grabitske H.A., Slavin J.L., 2008, Perspectives in practice low-digestible carbohydrates in practice, Journal of the American Dietetic Association, 108,1677–1681.
- Livesey G., 2003, Health potential of polyols as sugar replacers, with emphasis on low-glycaemic properties. Nutrition Research Reviews, 16, 163–191.
- Roth C., 2015, D-sorbit, Material Safety Data Sheet.
- Shankar P., Ahuja S., Sriram K., 2013, Non-nutritive sweeteners: review and update, Nutrition, 29,1293–1299.
- Sheskey P.J.(Ed.), 2012, Handbook of Pharmaceutical Excipients, 7th edition, Pharmaceutical Press, London.
- Wheeler M.L., Pi-Sunyer X., 2008, Carbohydrate issues. Type and amount. Journal of the American Dietetic Association, 108,34–39.
- Zeitsch K.J., 2000, The chemistry and technology of furfural and its many by-products, Sugar Series, 13, 240.