CHEMICAL ENGINEERING TRANSACTIONS
VOL. 26, 2012
Guest Editors: Valerio Cozzani, Eddy De Rademaeker

ISBN 978-88-95608-17-4; **ISSN** 1974-9791

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1226009

Theoretical Evaluation of the Explosion Regimes of Hybrid Mixtures

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In a previous paper we showed that the theoretical evaluation of the thermo-kinetic parameters relevant to dust explosion (deflagration index; burning velocity and maximum pressure), may be performed by means of detailed simulations of the flame propagation of the volatiles produced during the pyrolysis/devolatilization step of the dust combustion.
We recently measured the deflagration index and the maximum pressure of hybrid mixtures (nicotinic acid and methane), identifying different explosion regimes as function of the dust and gas concentrations in air.
In this paper we present theoretical evaluation of the deflagration index, the burning velocity and maximum pressure for dust/gas-air mixtures at changing the concentration in order to identify the explosion regimes, experimentally found.

1. Introduction

Hybrid mixture explosions continue to occur in industrial processes that handle dust and flammable gases or vapors. Considerable research is therefore carried out throughout the world with the aim of both preventing the occurrence and mitigating the consequences of such events (Amyotte et al., 2009, 2010a, 2010b; Denkevits, 2007; Dufaud et al., 2008, 2009, 2010).
Bartknecht (1989) studied the explosibility of cellulose with adding methane, butane and propane. He found that a hybrid mixture constituted by non-explosible dust and non-explosible gas can turn into explosible one. In particular, when gas is added to a dust-air mixture, the maximum explosion pressure, P_{max} was found to have consistent increase, whereas a more dramatic effect was observed on the hybrid deflagration index, K_{St}.
Pilão et al. (2006) investigated the behaviour of the hybrid mixture of methane and cork. They observed that the presence of methane at concentration lower than LFL (1.98 and 3.5 vol%) affects both the explosion severity and the maximum explosion pressure for lower dust concentration (40 g/m^3), whereas both the parameters are slightly affected in the case of higher dust concentration (450 g/m^3).
Dufaud et al. (2008, 2009) studied the influence of mixing pharmaceutical dusts (excipients, vitamins, active ingredients) with solvents (ethanol, di-isopropyl ether, toluene) on maximum explosion pressure and maximum rate of pressure rise. They measured deflagration index values higher for dust-vapors air mixtures rather than for the pure fuels, thus concluding that there are more than simple additive effects on explosion severity.

Please cite this article as: Russo P., Di Benedetto A. and Sanchirico R., 2012, Theoretical evaluation of the explosion regimes of hybrid mixtures, Chemical Engineering Transactions, 26, 51-56 DOI: 10.3303/CET1226009

From the analysis of the literature, it appears the complexity of the hybrid explosion phenomenon. In fact, the violence of hybrid mixture explosions can be not predicted by simply overlapping the effects of the single (only dust and only gas) explosion. Moreover, there is not systematic study able to quantify the role of dust and gas in driving the explosion.

In this context, we make some efforts aiming at clarifying the synergetic effects of dust and gas in air during explosion. We previously analysed the explosion behaviour of hybrid mixtures and compared it with the explosion features of dust-air and vapour-air mixtures separately (Sanchirico et al., 2011). Explosion tests were performed on nicotinic acid-acetone-air mixtures in a standard 20 L Siwek bomb adapted to vapour-air mixture and in the same conditions (i.e., at same initial turbulence level) as explosion tests of dust-air mixtures. Results showed that the increase in explosion severity of hybrid mixtures has to be addressed to the role of level of turbulence prior to ignition. At a fixed value of the equivalence ratio, by substituting the flammable gas with the dust in a hybrid mixture the explosion severity decreases. Furthermore, the most severe condition was found corresponding to the explosion of the gas-air mixture at stoichiometric concentration.

More recently, we focused on the identification of explosion regimes for a model hybrid mixture (Garcia-Agreda et al., 2011). The model gas/dust mixture was composed by methane and nicotinic acid whose single behaviour is well identified and quantified in the literature. Explosion experiments were performed in the 20 L Siwek bomb, but at ignition delay time of 0 ms (instead of 60 ms) and using a weak electric spark ignition source (instead of standard chemical igniters). In fact, the ignition delay time was chosen in order to avoid the effect of methane-dust unmixedness on the explosion features while the weak ignition source to prevent the overdriving the explosion behaviour due to chemical igniters. From the results, it was found that, the explosion behaviour of the methane-nicotinic acid mixture may be classified in five different zones (regimes) in the plane dust concentration vs. fuel concentration.

In this paper we present theoretical evaluation of the deflagration index, K_{St}, the burning velocity, S_l, and maximum pressure, P_{max}, for dust/gas-air mixtures at changing the concentration in order to identify the explosion regimes, experimentally found. In particular, we focused on the two regimes (gas and dual fuel driven explosion) where the highest severity of explosion was found.

2. Model

For organic dust such as nicotinic acid, it was observed that the dust explosion occurs through different steps: i) internal and external heating; ii) pyrolysis/devolatilization; iii) gas phase combustion. All of these steps are mutually dependent and are strongly affected by the particle size. Di Benedetto et al. (2010) studied the effect of particle size on the dust reactivity developing a model that takes into account all of the steps above mentioned. Varying the dust size, they identified different regimes depending on the values of the characteristic time of each step and several dimensionless numbers (Biot number, Bi; Damköhler number, Da; thermal Thiele number, Th). In particular, for small particle size (of the order of 10 μm for nicotinic acid) the pyrolysis/devolatilization is the step controlling the dust combustion.

In a previous paper (Di Benedetto and Russo, 2007) we showed that the theoretical evaluation of the thermo-kinetic parameters relevant to dust explosion (deflagration index K_{St}; burning velocity, S_l and maximum pressure, P_{max}), may be performed by means of detailed simulations of the flame propagation of the volatiles produced during the pyrolysis/devolatilization step of the dust combustion.

We calculated the deflagration index (K_{St}) by using the formula of Lewis von Elbe here reported:

$$K_{st} = \left(\frac{dP}{dt}\right)_{max} V^{1/3} \tag{1}$$

where the maximum pressure rise $(dP/dt)_{max}$ is calculated according to the formula proposed by Dahoe et al. (1996):

$$\left(\frac{dP}{dt}\right)_{max} = \frac{3(P_{max} - P_o)}{R_{vessel}}\left[1 - \left(\frac{P_o}{P}\right)^{\frac{1}{\gamma}} \frac{P_{max} - P}{P_{max} - P_o}\right]^{2/3} \left(\frac{P}{P_o}\right)^{\frac{1}{\gamma}} S_u \tag{2}$$

where: P_{max} is the maximum pressure reached in a closed vessel which has been calculated by using the equilibrium module of the CHEMKIN code; P_o is the initial pressure (1 bar); R_{vessel} is the radius of the reference spherical vessel (20 L), γ is the specific heat ratio and S_u is the burning velocity.
To take into account the effect of turbulence, S_u is assumed equal to turbulent burning velocity (S_t). S_t was calculated as function of the turbulence level (u'_{rms}) and of the laminar burning velocity by means of general formula:

$$S_t = S_l \left[1 + \beta \left(\frac{u'_{rms}}{S_l} \right)^{\alpha} \right] \tag{3}$$

where S_l is the laminar burning velocity, while α and β are parameters dependent on the formula used for the evaluation of the turbulence burning velocity. As previously shown, different equations can be adopted to calculate the turbulent burning velocity (Garcia-Agreda et al., 2010). Here, the Generalized Reduced Gradient algorithm (used by Excel's Solver) was used to find the α and β parameters that give the best fit between the K_{St} values calculated by means of Eq.1-3 and the K_{St} measured from experiments. The α and β values obtained were 0.64 and 0.6 for methane and 0.78 and 0.53 for hybrid mixture, respectively.
The value of u'_{rms} (20 m/s) was assumed equal to the value measured by Dahoe et al. (2001).
The laminar burning velocity of the hybrid mixture was here calculated from the composition of the mixture given by the methane and the pyrolysis products generated from the dust pyrolysis/devolatilization step. In particular, the composition of pyrolysis products from nicotinic acid was assumed to be equal to the thermodynamic distribution in inert atmosphere of the volatiles of nicotinic acid calculated by using the CEA code (Gordon et al., 1994). The CEA code allows the calculation of the equilibrium conditions by minimizing Helmholtz energy at constant temperature and volume; or by minimization of Gibbs free energy, for the chemical equilibrium at constant temperature and pressure. In this regard, we found that in the range of temperatures between 700 °C and 1800 °C the pyrolysis products content ranges from 25 up to 26 wt%, and the composition at the temperature of 1800 °C was that reported in Table 1.

Table 1: Composition (wt%) of pyrolysis products of nicotinic acid at 1800 °C in inert atmosphere

CO	H_2	N_2	C
15.2	23.5	0.9	60.4

The calculation of S_l was carried out by means of simulations of the one-dimensional, planar, adiabatic, steady, unstretched, laminar flame propagation. The Sandia PREMIX module of the CHEMKIN package was used by implementing the detailed reaction scheme GRI-Mech 3.0 (Bowman et al., 1999). Since in the pyrolysis products of nicotinic acid solid carbon is present, the mechanism was implemented considering also the oxidation reaction of this chemical specie.

3. Results

For the quantification of the severity of explosion of hybrid mixtures in terms of maximum pressure and deflagration index, experiments were performed varying the methane concentration in the range 1.0–10 vol% and the nicotinic acid in the range 30–250 g/m^3 (Gracia-Agreda et al., 2011). All the explosion data of the CH_4-nicotinic acid-air mixtures were reported in the form of a map, where methane content (vol%/LFL) and dust concentration (C/MEC) are respectively the x- and y-axes (Figure 1). The LFL of methane was measured equal to 6 vol% and the MEC of nicotinic acid was 125 g/m^3.
In the figure, the measured data of the deflagration index are represented by the filled circles whose diameter increases proportionally to the value of K_{St}, while white circles refer to experiments where explosion does not occur. In the same figure, the Le Chatelier's line and Bartknecht curve are also shown. These curves delimit the explosive vs. the non-explosive region. In particular, the Le Chatelier' law, originally developed for homogeneous mixtures by considering constant flame temperature for a given class of fuels (Glassman, 1996), is given by the following equation:

$$LFL_{hybrid} = \frac{1}{\frac{y_{CH4}}{LFL_{CH4}} + \frac{y_{dust}}{LFL_{dust}}} \quad (4)$$

The Bartknecht curve was derived for hybrid mixture of methane and PVC, as follows (Bartknecht, 1989):

$$MEC_{hybrid} = MEC\left(\frac{y_{CH4}}{LFL} - 1\right)^2 \quad (5)$$

MEC of hybrid mixture decreases with increasing the gas concentration by a second order equation. Finally, the stoichiometric line (red curve) is also plotted. The equation of this line is the following:

$$\frac{C}{MEC} = 4.8 - 3.03\frac{y_{CH4}}{LFL} \quad (6)$$

From figure 1 it appears that all the white circle symbols lay below Le Chatelier's line, while the solid circles lay all above, which means that Le Chatelier's line well separates the explosive from the non-explosive region. In fact, it was found that the adiabatic pressure (and then temperature) of methane and nicotinic acid, calculated by CEA code, are comparable and then their mixture verify Le Chatelier's criterion for flammability.

Moreover, the explosion behaviour of the methane-nicotinic acid mixture may be classified in five different zones (regimes) in the plane dust concentration vs. fuel concentration. The no-explosion zone lays below Le Chatelier's curve. Above this line the synergic explosion behaviour zone is present; this zone is limited by Le Chatelier's curve and the LFL (for gas) and MEC (for dust) lines. The dust (or gas) driven explosion zone is the region in which the dust (or gas) concentration is higher than the MEC (or LFL) and the methane (or dust) concentration is lower than the LFL (or MEC). Finally, the dual-fuel explosion zone is above both LFL and MEC concentrations. In this zone both methane and nicotinic acid contribute to the explosion. Finally from the figure it appears that the maximum values of the deflagration index lay close to the stoichiometric line.

In the Figure 2 the results relevant to the theoretical evaluation of the deflagration index were reported in the methane/nicotinic acid concentration map. We focused on the two regimes (gas and dual fuel driven explosion) where the highest severity of explosion was found. From comparison between experimental and theoretical results it appears that model well predicts the deflagration index in both regimes. It was calculated an average error between K_{St} from model and from experiments of the order of 15 %. Furthermore, these results confirm the relevant role of the explosion diagram regime for hybrid mixtures which can be theoretically evaluated.

4. Conclusions

The theoretical evaluation of the deflagration index K_{St} for a model hybrid mixture (methane-nicotinic acid) at changing the gas and dust concentration is here reported. The model, previously developed for evaluate the explosion parameters (deflagration index, burning velocity and maximum pressure) of dust, was here modified in order to take into account the presence of gas in the hybrid mixture.

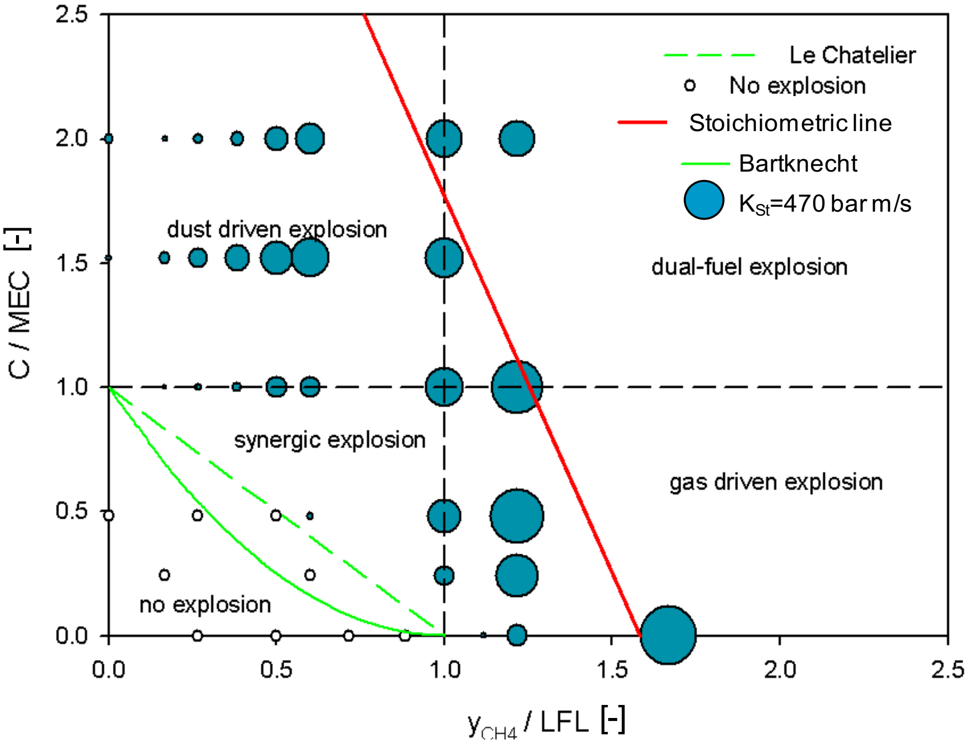

Figure 1. Experimental results of explosion regimes in the plane methane/nicotinic acid concentration (Garcia-Agreda et al., 2011).

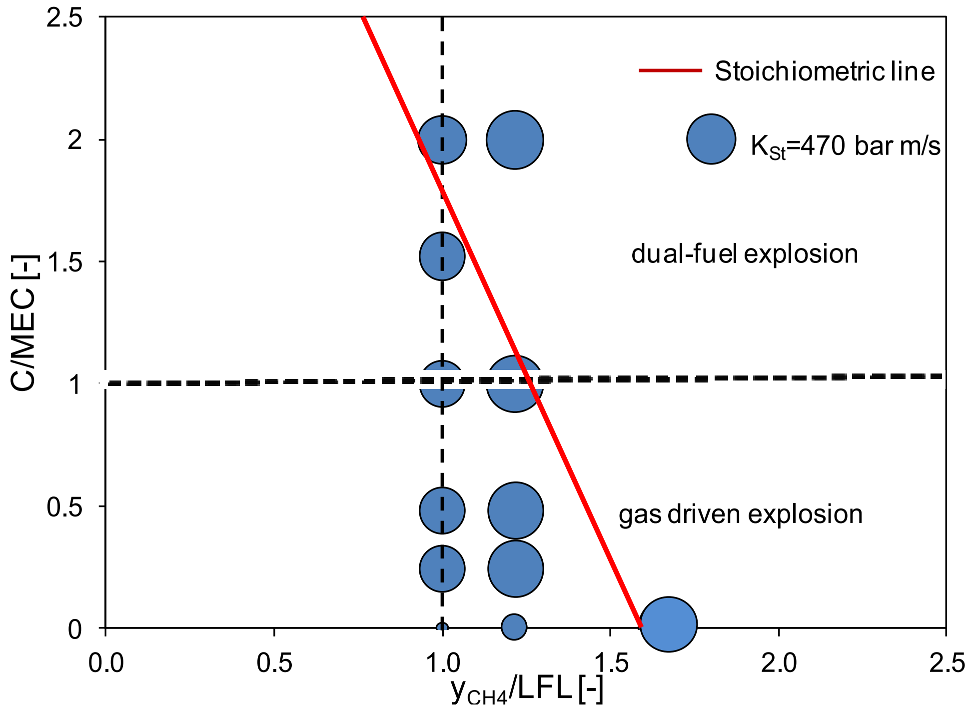

Figure 2. Theoretical results of explosion regimes in the plane methane/nicotinic acid concentration.

We have shown the availability of the pyrolysis/devolatilization data calculated from equilibrium conditions for the evaluation of dust volatiles in the model, when the composition of dust pyrolysis products is not experimentally available. In particular, the model was implemented in order to take into account also the presence of solid carbon in the pyrolysis products.
In the two regimes, gas and dual fuel driven explosion, where the highest severity of explosion was experimentally found, the model well predict the deflagration index of the hybrid mixture.
Future works will explore the ability of the model to describe the other regimes.

References

Amyotte P., Lindsay M., Domaratzki R., Marchand N., Di Benedetto A., Russo P., 2009, Prevention and mitigation of polyethylene and hydrocarbon/polyethylene explosions, Paper 7D, In: Proceedings of 43rd Annual Loss Prevention Symposium (AIChE 2009 Spring National Meeting), Tampa, FL, United States, April 26-30 2009, 541-556.

Amyotte P., Abuswer M., Di Benedetto A., Russo P., 2010a , Determination of hybrid mixture explosion severity, In G. Suter, E. De Rademaeker (Eds.), Proceedings of the 13th International Symposium on Loss prevention and Safety Promotion in the process Industries, Brugge, Be June 6-9 2010, Vol. 2, pp. 149-156.

Amyotte P., Lindsay M., Domaratzki R., Marchand N., Di Benedetto A., Russo P., 2010b, Prevention and mitigation of dust and hybrid mixture explosions, Process Safety Progress, 29(1), 17-21.

Bartknecht W., 1989, Explosions: Course, prevention, protection. Springer, Berlin, Germany.

Bowman C.T., Frenklach M., Gardiner W.C., Smith G.P., 1999, <www.me.berkeley.edu/gri mech/> Accessed 20.11.2011.

Dahoe A.E., Zevenbergen J.F., Lemkowitz S.M., Scarlett B., 1996, Dust esplosion in spherical vessels: the role of flame thickness in the validity of ‘cube-root law’, Journal of Loss Prevention in Process Industries, 9, 33-44.

Dahoe A.E., Cant R.S., Scarlett B., 2001, On the Decay of Turbulence in the 20-Liter Explosion Sphere, Flow Turbulence Combustion, 67,159–184.

Denkevits A., 2007, Explosibility of hydrogen-graphite dust hybrid mixtures, Journal of Loss Prevention in Process Industries, 20, 698-707.

Di Benedetto A., Russo P., 2007, Thermo-kinetic modelling of dust explosions, Journal of Loss Prevention in Process Industries, 20, 303-309.

Di Benedetto A., Russo P., Amyotte P., Marchand N., 2010, Modelling the effect of particle size on dust explosions, Chemical Engineering Science, 65, 772-779.

Dufaud O., Perrin L., Traoré M., 2008, Dusts / vapours explosions: hybrid behaviours?, Journal of Loss Prevention in Process Industries, 21(4), 481-484.

Dufaud O., Perrin L., Traoré M., Chazelet S., Thomas D., 2009, Explosions of vapour/dust hybrid mixtures: a particular class, Powder Technology, 190(1-2), 269-273.

Dufaud O., Perrin L., Laurent A., 2010, State of art: promotion of early inherently safer design against dust explosions, Chemical Engineering Transactions, 19, 365-370.

Garcia-Agreda A., Di Benedetto A., Russo P., Salzano E., Sanchirico R., 2010, The role of ignition delay time on the deflagration index in a 20l bomb, In: Proceedings sixth fire and explosion hazards seminar (FEH6), University of Leeds, UK 11-16/04/2010, 684-694.

Garcia-Agreda A., Di Benedetto A., Russo P., Salzano E., Sanchirico R., 2011, Dust/gas mixtures explosion regimes, Powder Technology, 205, 81-86.

Glassman I., 1996, Combustion, 3rd ed., Academic Press, San Diego, USA.

Gordon S., McBride B.J., 1994, Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. NASA RP 1311, <www.grc.nasa.gov/WWW/CEAWeb/RP-1311.pdf>, Accessed 09/05/2012.

Pilão R., Ramalho E., Pinho C., 2006, Explosibility of cork dust in methane/air mixtures. Journal of Loss Prevention in Process Industries, 19, 17-23.

Sanchirico R., Di Benedetto A., Garcia-Agreda A., Russo P., 2011, Study of the severity of hybrid mixture explosions and comparison to pure dust-air and vapour-air explosions, Journal of Loss Prevention in Process Industries, 24, 648-655.