CHEMICAL ENGINEERING TRANSACTIONS

VOL. 48, 2016

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Eddy de Rademaeker, Peter Schmelzer

ISBN 978-88-95608-39-6; **ISSN** 2283-9216

DOI: 10.3303/CET1648053

Models to Estimate the Lower Explosion Limits of Dusts, Gases and Hybrid Mixtures

Emmanuel Kwasi Addai*, Dieter Gabel, Ulrich Krause

Otto-von-Guericke University, Institute of Instrumental and Environmental Technology, Department of System Engineering and Plant Safety, Universitätsplatz 2, 39106 Magdeburg, Germany.

emmanuel.addai@ovgu.de

The present paper reports on the experimental and theoretical investigations on the lower explosion limits of single dusts, gases as well of two phase mixtures such as gas/dust, vapor/dust, spray/vapor and vapor/gas. The materials used were corn starch, lycopodium, toner and high density polyethylene as dusts, methane and hydrogen as combustible (perfect) gases and acetone and isopropanol as sprays or vapours (real gases). The experiments were performed in the standardized 20-lters spherical explosion chamber where modifications were done to allow input of spray, solvent and gas. The test protocol was according to EN 14034 with an electrical ignition source. The experimental results demonstrate a significant enhancement in explosion likelihood by solvent, gas or spray admixture with dust and vice versa. They also confirm that a hybrid mixture explosion is possible even when the concentrations of both components are lower than their minimum explosion concentration (MEC) respectively lower explosivity limit (LEL). For example, the MEC of starch decreases from 150 g/m^3 decrease to 20, 30, 125g/m^3 and 125g/m^3 when small amounts of isopropanol spray, acetone vapor, methane gas and hydrogen gas respectively were added. These concentrations were all below the LEL of the individual substance. Comparisons have been done between the lower explosible limit of the experimental data and classical models such as those developed by Bartknecht, Le Chatelier, MKOPSC and our newly proposed models. With the exception of the Le Chatelier and MKOPSC model, the other models were in agreement with the experimental result for safety point of view.

1. introduction

Hybrid mixtures are mixtures of at least two combustibles in different state of aggregation, e.g. dust with a flammable gas, solvent vapor or spray. They are usually encountered in industrial processes that handle dust, flammable gases, sprays or vapours such as paint factories (pigments and solvents), mining (dusts and gas), grain elevators (small grains and fermentation gases) or pharmaceutical industries (dust and solvent vapor). It has long been known that the explosion sensitivity and severity of hybrid mixtures differ from that of the single components. Unlike solitary dust, gas or solvent explosions, which have been widely studied in the past decades, data on explosion characteristics of hybrid mixtures are relatively few. However, these kinds of mixtures are usually encountered where gases, solvents and dusts are either handle or process. Some recent studies on the explosion sensitivity and severities of hybrid mixture explosion include; Dufaud et al., (2009), Amyotte et al., (2010), Garcia-Agreda et al., (2011), Addai et al.., (2015) etc.). The main conclusions of the previous studies could non-exhaustively be summarized by the following assertions that the ignition sensitivity of the powder can be strongly increased by the addition of a few percent of combustible gas or vapour, even with contents lower than their LEL. It has notably been shown that hybrid mixtures can also be explosible when the concentrations of the dust and the gas are both below their respective MEC and LEL. Nevertheless, performing experimental studies on these mixtures are time consuming that is more than a half day to deal with one test sample. Moreover, the costs for the dust samples as well as labour are considerable. It is therefore necessary to introduce simple models for estimation of the LEL of dusts, gases and hybrid mixtures using only the basic known parameters. Hence this paper present three dusts models and three gas models as well as three hybrid mixtures models to predict the LEL and MEC. Furthermore, three new models based on the single component models were proposed by the author to predict the LEL of hybrid mixtures. The

Please cite this article as: Addai E., Gabel D., Krause U., 2016, Models to estimate the lower explosion limits of dusts, gases and hybrid mixtures, Chemical Engineering Transactions, 48, 313-318 DOI:10.3303/CET1648053

comparison with these models with experimental results were also done. Two perfect gases (methane and hydrogen) and two real gases (acetone as vapour and isopropanol as spray) as well as four combustible dusts (toner, starch, lycopodium and high density polyethylene) were used for this work.

2. Models to predict the lower explosion limits of dusts, gases and hybrid mixtures

2.1 dust models

In order to prevent the risk associated with dust explosion, three different dust models proposed by; Shevchuk et al.., (1979), Schonewald; (1971), and Buksowicz and Wolanski's, (1983) base on different assumptions and condition to predict the MEC of dust are presented. Below are summaries of these models while the details could be found in the original articles mentioned in the above literature as well as in Eckhoff, (2003).

Shevchuk's model:

$$\mathrm{MEC} = \frac{(T_i - T_0)c_g\rho_g}{F\Delta H_{comb} - c_d(T_i - T_0)} \tag{1}$$

Schönewald Model:

$$\mathrm{MEC} = \frac{a''}{\Delta H_{comb}} - b'' \tag{2}$$

, a'' is -1.032 and b¨ is 1.207×10^6 for organic dust
Ht is the heat of combustion per unit mass

Buksowicz and Wolanski's model:

$$\mathrm{MEC} = 1.55 \times 10^7 \Delta H_{comb}{}^{-1.21} \tag{3}$$

2.2 Gas models

Furthermore, three different models to predict the LEL of gases proposed by: Zabetakis (1965), Shebeko et al.., (2002) and Spakowski (1952) are present. These models are summarized below while the details could also be found in the original articles in the above mentioned literature.

Zabetakis model:

$$\mathrm{LEL} = 0.55\frac{100}{1+1.193k} \tag{4}$$

$\mathrm{k = 4c + h + 4s - 2o - n - 2cl - 3f - 5br}$, where c, h, s, o, n, cl, f, br are number of atoms of carbon, hydrogen, sulphur, oxygen, nitrogen, chlorine, fluorine and bromine in the molecule respectively.

Shebeko et al:

$$\mathrm{LEL} = \frac{100}{1+n_a} \tag{5}$$

$$na = g_f\Delta H_f + g_C n_C + g_H n_H + g_O n_O + g_N n_N \tag{6}$$

Where 'na` is the number of moles of air per mole of fuel in the mixture at LEL

Spakowski model:

$$LEL = -\frac{4354}{\Delta H_{comb}} \tag{7}$$

2.3 Hybrid mixture models

Three existing models proposed by different authors as well as three new model are presented. Any possible combination of dust and gas mixture ($\mathrm{LEL}_{\text{-hybrid}}$) has the unit of g/m^3.

2.3.1 Already existing hybrid mixture model

Le Chatelier model

This model was proposed by Glassmann (1996) taking Le Chatelier law as origin that describes homogeneous mixtures by considering a constant flame temperature. It shows linear relationship between the LEL of gas and the MEC of dust, and the weighting factor for each fuel is its fractional content in the mixture as represented in equation (8).

$$LEL_{hybrid} = \frac{100}{\frac{X_{gas}}{LEL_{gas}} + \frac{X_{dust}}{MEC_{dust}}} \tag{8}$$

Bartknecht model

This model proposed by Bartknecht, (1981) is an empirical formula derived from a series of experimental measurements. The LEL of hybrid mixtures decreases with increasing the gas concentration by a second order equation, named the Bartknecht curve as represented (9).

$$LEL_{hybrid} = MEC_{dust}[\frac{y}{LEL_{gas}} - 1]^2 \tag{9}$$

MKOPSC model

This model was proposed by Sam Mannan et al.., (2014) to predict the LEL of hybrid mixture. It was based on a correlation between the Le Chatelier Law and the Bartknecht equation.

$$LEL_{hybrid} = MEC_{dust}\left[1 - \frac{y}{LEL_{gas}}\right]^{(1.12\pm0.03)\frac{K_{St}}{K_G}} \tag{10}$$

2.3.2 Proposed models to predict the LEL of hybrid mixtures

The above models to predict the LEL of hybrid mixtures have proving themselves to some extent. However, some deviation from Le Chatelier Law was found when applied to the low volatile Pocahontas coal with methane by Cashdollar (1996). Similar deviation was also found by Bartknecht et al.., (1981) in PVC dust mixed with methane or propane. Furthermore, Addai et al.., 2015 also found a deviation in both Le Chatelier and Bartknecht equation when they applied methane and corn starch. Moreover, the parameters used in the above equation are obtained experimentally which is very expensive in terms of equipment, material and labour cost. Base on the above mentioned reasons, there is need to develop a simple model to predict the LEL of hybrid mixture which needs only the basic parameter from the single substances. Hence three new models have been proposed by the present authors by combining the models to predict the LEL for both dusts and gases. These new models are based on Le Chatelier law as presented in equation (8) while LEL of gas and MEC of dust are calculated from both gas and dust models and not from experimental values.

Model 1

This model was proposed by combining the models developed by Shevchuk et al.., (1979) and Shebeko et al.., (2002) to predict the lower explosion limits for both dust and gas using the Le Chatelier Law as the basis. From equ. (1) $\mathrm{MEC}_{dust} = \frac{(T_i - T_0)d_g Cp}{[F\Delta H_{comb} - c_d(T_i - T_0)]}$ and equ. (5) $\mathrm{LEL}_{gas} = \frac{100}{1+n_a}$, and by inserting them into Le chatelier's equation, equ. (11), could be obtained

$$LEL_{hybrid} = \frac{100}{\frac{X_{dust}}{\frac{(T_i - T_0)d_g c_v}{[F\Delta H_{comb} - c_d(T_i - T_0)]}} + \frac{X_{gas}}{\frac{100}{1+n_a}}} \tag{11}$$

Where $na = g_f \Delta H_f + g_C n_C + g_H n_H + g_O n_O + g_N n_N$

Simplifying the equ. (11), produces equ. (12). Hence the LEL-hybrid could be calculated from equ. (12)

$$LFL_{hybrid} = \frac{100}{\frac{X_{dust}[F\Delta H_{comb} - c_d(T_i - T_0)]}{(T_i - T_0)d_g c_v} + \frac{X_{gas}(1 + g_f \Delta H_f + g_C n_C + g_H n_H + g_O n_O + g_N n_N)}{100}} \tag{12}$$

Model 2:

In a similar way, the models developed by Schonewald; (1971): $\mathrm{MEC}_{dust} = \frac{a''}{\Delta H_{comb}} + b''$ and Zabetakis (1965), $\mathrm{LELgas} = 0.55\frac{100}{1+1.193k}$ could also be combined using Le chatelier's equation as the basis to produce equ. (13)

$$LEL_{hybrid} = \frac{100}{\frac{X_{dust}\Delta H_{comb}}{1.207*10^7 - 1.032\Delta H_{comb}} + \frac{X_{gas}(1+1.193k)}{55}} \tag{13}$$

Hence the lower explosion limit of hybrid mixture could be calculated using equ. (13)

Model 3:

Finally, model developed by Spakowski (1952) in equ. (1) and Shevchuk et al.., (1979) in equ. (7), could also be combined to produce equ. (14).

$$LFL_{hybrid} = \frac{100}{\frac{X_{dust}[F\Delta H_{comb} - c_d(T_i - T_0)]}{(T_i - T_0)d_g c_v} - \frac{X_{gas}\Delta H_{comb}}{4345}} \tag{14}$$

A comparison of these models against experimental results as well as the models according to Le Chatelier, Bartknecht and MKOPSC was done.

3. Experimental procedure

Before each experiment was performed, all the dusts sample underwent initial analysis such as the determination of particle size distribution, volatile content, moisture content and heat of combustion as presented in table 1.

Table 1: preparatory analysis for the dust used

Materials	Media diameter(µm)	Volatile Content (% mass)	Moisture Content (% mass)	Heat of combustion (KJ/Kg)
Toner	13.4	91.1	0.92	35792
Lycopodium	31.6	93.7	0.35	28447
Starch	29.2	90.1	0.50	15302
PE-HD	41.0	99.8	0.23	42740

3.1 Experimental description

Experiments were performed in a 20-liters sphere standard apparatus to determine the maximum explosion pressure (Pmax), maximum rate of pressure rise (dp/dt) max and K-value, lower explosion limit (LEL) and limiting oxygen concentration (LOC). Measurements were performed in accordance with EN 14034 1-4. Detail experimental procedure could be referred to Addai et al.., (2015, a & c)

4. Results and discussion

The Lower Explosible Limit of gases or Minimum Explosible Concentration of dusts is the concentration of fuel in a mixture with air below which the self-sustained propagation of a flame is not possible. In order to prevent or mitigate the risk associate with gas, dust or hybrid mixture explosion, it is therefore vital to know the lowest concentration of these mixture at which explosion can occur. Knowing these limit can help to set a limit for a system so that the concentration could not exceed the limit. Usually, determination of these limits are done experimental which is time consuming and costly. With respect to dust, Shevchuk et al.., (1979), Schonewald; (1971), and Buksowicz and Wolanski's, (1983) have propose different models to predict the minimum explosion concentration. These models were computed and compared with experimental results as shown in table 2. It could be seen that, the results from the experiments were all below the results obtained from the models with a maximum deviation of 86 g/m^3 for high density polyethylene.

Table 2: Comparison between experimental results for the MEC of four dusts and the three models

		Experimental	Shevchuk	Schonewald	Buksowicz
MEC (g/m^3)	Starch	150	84.6	77.8	133.9
	Lycopodium	100	51.0	41.4	62.2
	Toner	60	42.5	32.7	47.9
	HDPE	120	41.4	24.3	33.8

Furthermore, in the case of combustible gases; Zabetakis (1965), Shebeko et al.., (2002) and Spakowski (1952) have also proposed models to predict the LEL of gases. Comparison between the experimental and the computational results of these models were performed as presented in table 3. It could be seen that the results obtained from the computational models are almost the same as the experimental results with deviations of not more than 0.4 vol. %

Table 3: Comparison between experimental results for LEL of three gases and the three models

		Experiment	Spakowski	Zabetakis	Shebeko
LEL (vol. %)	Methane	5.0	4.9	5.2	4.7
	Acetone	2.5	2.5	2.7	2.1
	Isopropanol	2.1	2.4	2.5	1.8

With respect to hybrid mixture, the lower explosion limit could be defined as the concentration of fuel mixtures of two or more substances with different state of aggregate with air below which the self-sustained propagation of a flame is not possible. It has been well noted that the lower explosion limit of hybrid mixtures cannot be predicted by simply overlapping the effects of the single dust or gas Addai et al.., (2015).

Table 4: Comparison of experimental results for LEL hybrid mixture with six models (g/m^3)

component of mixture			Exp. LEL	Le Chatelier	Bartknecht	MKOPSC	Model 1	Model 2	Model 3
Gas	conc. vol.%	Dust							
methane	3	starch	100	109	62	178	65	64	68
	2	lycopodium	50	77	50	185	48	40	49
	2	toner	42	46	21	48	39	34	40
	3	HDPE	100	109	75	168	39	45	40
hydrogen	2	starch	125	189	122	184	76	71	76
	2	lycopodium	60	52	22	162	30	26	33
	2	toner	30	46	21	48	35	28	39
	3	HDPE	50	52	40	180	26	29	27
isopropanol	1	starch	35	156	90	117	65	72	75
acetone	1.5	starch	60	101	40	194	65	73	62

Glassmann (1996), Bartknecht, (1981) and Sam Mannan et al.., (2014) have proposed various models to predict the lower explosion limit hybrid mixture. However, deviations from these models have been noticed by applying various gas and dust mixtures Cashdollar (1996) and Addai et al.., (2015). Moreover, application of these models is expensive and time consuming since all the input data are obtained from experimental results. Hence three new models were proposed by the current author of whom the input data are the basic parameter of individual substance which can easily be obtained from general thermodynamic book or material safety data sheets of the substance. A summary of the comparison of the three existing models and the newly proposed model against experimental result are also shown in table 4. It could be seen from the table that the models according to Le Chatelier's, and Sam Mannan et al. was not able to give a good prediction of the LEL hybrid mixture. Almost all the computed results were above the experimental result with a maximum deviation more than 100 g/cm^3. On the other hand, Bartknecht models as well as the newly proposed models gave results below the experimental value but the three newly models were able to give a very good prediction of the lower explosion limits of hybrid mixtures for safety point of view.

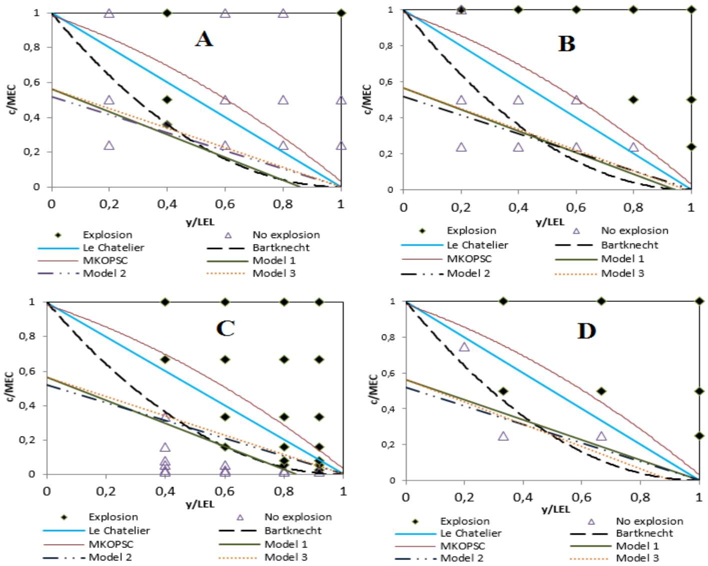

Figure 1: Diagram showing a comparison between experimental result and three models: (a) starch/isopropanol; (b) starch/hydrogen; (c) starch/acetone; (d) starch/methane.

Unlike lycopodium, toner and HDPE which were test with only methane and hydrogen, starch was further tested with two additional gases which include; acetone (vapours) and isopropanol (mist or spray). Figure 1 shows the results of starch with four gases as well as the comparison between the models Glassmann (1996), Bartknecht, (1981), Sam Mannan et al.., (2014) and the three newly proposed models with experimental results. The y-axis is dimensionless dust concentration (c/MEC), and the x-axis is dimensionless flammable gas content (y/LEL). The solid diamond represents explosions, while the triangle stands for no explosions. The Le Chatelier's Law, Bartknecht curve, MKOPSC curve as well as the three newly proposed models are also plotted in the same diagram. These curves delimit the explosion region versus the non-explosive region. With the exception of starch/hydrogen mixture, which did not violate any of the models, all the other three mixtures violated one or more of the models. For example, both starch/acetone and starch/ isopropanol mixture, explosion were obtained at the non-explosion region of the three already existing models.

5. Conclusion

The LEL of various dusts and gases mixture have been investigated. Three models to predict the LEL of both dust and gases were presents as well as three exist existing models to predict the LEL of hybrid mixtures. Additionally, three new model to predict the LEL hybrid mixture were proposed. Based on the discussions, the following conclusion could be made.

- The present models to predict the MEC of dust gave results below the experimental values.
- The models to predict the LEL of gases were in agreement with the experimental results.
- The three existing models to predict the LEL hybrid mixture were not reliable for certain mixtures
- The three newly proposed LEL hybrid mixture models are more reliable for safety point of view.

List of symbols

MEC- the minimum explosible concentration of dust in g/m3	B- is the radiation factor given by $\mathrm{B} = \sigma\epsilon_2\epsilon_g F$
Ti- the temperature of ignition	Na– $(+g_f\Delta H_f + g_C n_C + g_H n_H + g_O n_O + g_N n_N)$
Cg- the specific heat of the gas molecules	LEL_hybrid- lower flammability limit of such mixture (g/m3)
Cd - the specific heat of the dust particles	LEL- lower flammability limit of such gas in %v/v
Cp and ρg are the heat capacity and the density of the gas	Kst- specific dust constant in bar m/s
F-special particle distribution factor resulting from this particular analysis	Xgas and Xdust is fractional content of gas and dust in the fuel mixture
	To is the ambient temperature
ΔH_{comb}-the heat of combustion in kJ/mol	KG- specific gas constant in bar m/s

Reference

Addai, E.K., Gabel, D, Krause, U. (2015) Lower explosion limit of hybrid mixtures of burnable gas and dust, Journal of Loss Prevention in the Process Industries,

Addai, E.K., Gabel, D, Krause, (2015) U, Ignition and explosion behavior of hybrid mixtures of two and three components in: 4. Magdeburger Brand- und Explosionsschutztag, HS- Magdeburg Stendal: Magdeburg, 2015, ISBN 978-3-00-048960-0, 26. und 27. März 2015.

Addai, E.K., Gabel, D, Krause, U (2015). Explosion characteristics of three component hybrid mixtures, Process Safety and Environmental Protection 9 8, 72–81

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

Buksowicz W., Wolanski P., Prog. (1983) Astronautics and Aeronautics 87 pp. 414-425

Bartknecht, W., (1981) Explosions, course, prevention, protection Springer-Verlag

Cashdollar, I. (1996), Coal dust explosibility Journal of Loss Prevention in the Process Industries, 9(1), p.65

Dufaud, O., Perrin, L., Traore, M., Chazelet, S., Thomas, D., Explosions of vapours/dust hybrid mixtures: a particular class Powder Technology, 190 (2009), pp. 269–273

Eckhoff, R., (2003) Dust Explosions in the Process Industries, 3rd ed. Gulf Professional Publishing, Elsevier Science, pp. 25–141, 251–424

EN 14034, European standard test method for explosibility of dust clouds

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

Glassman, I. (1996) Combustion (3rd, Ed.) Academic Press, San Diego, California

Jiaojun J, Yi L, Mannan S, A (2014) correlation of the lower flammability limit for hybrid mixtures, Journal of loss prevention in the process industries, 32 (2014), pp. 120–126

Schonewald, I.; Staub explosion (1971): 31, pp .376 -378

Shebeko, Y., N., Fan W., Bolodian, I. Navzenya, V. Y., (2002) “An analytical evaluation of flammability limits of gaseous mixtures of combustible-oxidizer-diluent,” Fire Safety J. 37 549-568

Shevchuk, V. G, E. N. Kondrat’ev, A. N. Zolotko, et al. (1979) “Effect of the structure of a Gas Suspension on the Process of Flame Propagation, shock wave. 15, no. 6, pp. 41-45

Spakowski, E. A. (1952) Natl. Advisory Committee Aeronautics (NACA)

Zabetakis, M.G. (1965) Flammability Characteristics of Combustible gases, Bureau of Mines 627, p16