

# A Correlation of the Lower Flammability Limit for Hybrid Mixtures

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## Abstract

Hybrid mixtures explosions involving dust and gas can cause great loss of lives and properties. A recent coal mine explosion in Upper Big Branch Mine, West Virginia, in April 2010, resulted in the loss of 29 miners' lives. Hybrid mixtures are also widely encountered in industries such as paint factories, pharmaceutical industries, or grain elevators. The lower flammability limit (LFL) is a critical parameter when conducting a hazard assessment or developing mitigation methods for processes involving hybrid mixtures. Unlike unitary dust or gas explosions, which have been widely studied in past decades, only minimal research focuses on hybrid mixtures, and data concerning hybrid mixtures can rarely be found. Although methods to predict the LFL have been developed by using either Le Chatelier's Law, which was initially proposed for homogeneous gas mixtures, or the Bartknecht curve, which was adopted for only certain hybrid mixtures, significant deviations still remain. A more accurate correlation to predict an LFL for a hybrid mixtures explosion is necessary for risk assessment. This work focuses on the study of hybrid mixtures explosions in a 36L dust explosion apparatus using a mixture of methane/niacin in air. By utilizing basic characteristics of unitary dust or gas explosions, a new formula is proposed to improve the prediction of the LFL of the mixture. The new formula is consistent with Le Chatelier's Law or the Bartknecht curve.

## 1. Introduction

A hybrid mixture is the result of a combination of a combustible dust and a flammable gas or vapour (Worsfold *et al.*, 2012). In a hybrid mixture, the gas may be present below its LFL, and the dust may be present below its minimum explosible concentration (MEC), the combination becoming an explosible mixture (Amyotte *et al.*, 2010; Amyotte *et al.*, 1993; Denkevits, 2007; Dufaud *et al.*, 2009; Eckhoff, 2005; Garcia-Agreda *et al.*, 2011). A recent case is the coal mine explosion that occurred in Upper Big Branch Mine, West Virginia, in April 2010, which resulted in the loss of 29 miners' lives. This incident is considered the worst coal mine incident since the 1970s in the U.S. (Mann, 2012). The hybrid mixture explosion not only can happen in the coal mining industry, but also occur in other industries such as food, pharmaceutical, paint, as well as chemical manufacturing (Amyotte and Eckhoff, 2010). Accidental hybrid mixture explosion is still a big problem and continues to cause significant losses of lives and properties, and damages to the surrounding environment in the process industry (Benedetto *et al.*, 2013; Eckhoff, 2003).

The addition of a flammable gas results in hybrid mixtures being a higher dust explosion risk. Adding flammable gases to a dust mixture increases the explosion pressure and rate of pressure rise on the consequence side, as well as reduces the MEC of dust on the likelihood side. Because of the possibilities concerned with the formation of hybrid mixtures, several studies have been performed toward the basic understanding of such systems. One interesting topic is on the LFL determination of hybrid mixtures since it is a critical parameter when conducting a hazard assessment or developing mitigation methods for processes involving such mixtures. The most extensive work on the LFL of hybrid mixtures is the coal and methane system (Cashdollar *et al.*, 1987). For this system, it was found that Le Chatelier's Law, which was originally developed and adopted for homogeneous gas mixtures, can be applied to distinguish the explosion zone from the non-explosion zone. If extended to a hybrid mixture, Le Chatelier's Law is a straight line between the LFL of gas and the MEC of dust, and the weighting factor for each fuel is its fractional content in the mixture. However, a significant deviation from Le Chatelier's Law was found when applied to the low volatile Pocahontas coal with methane (Cashdollar, 1996). Similar deviation was also found in PVC dust mixed with methane or propane (Bartknecht *et al.*, 1981). The LFL of hybrid mixtures decreases with increasing the gas concentration by a second order equation named the Bartknecht curve.

The effect of the addition of methane to a flammable mixture of cork-air was studied in a 20L vessel, using 2500J ignitors (Pilão *et al.*, 2006). The experiment showed that such hybrid mixtures can explode when each fuel is less than its lean flammability limit, but more cork dust is needed to render the system flammable as predicted by either Le Chatelier's Law or the Bartknecht curve.

Attempting to understand this deviation, the LFL of different hybrid mixtures reported in literature was summarized and compared with regards to the heat capacity and the deflagration index of each fuel (Prugh, 2008). The author concluded that the straight-line relationship applies only to mixtures where the ratio of the heat capacities of the dust and gas/vapour is similar, and where the deflagration indices are roughly equivalent.

In summary, it is known that hybrid mixtures can explode when each fuel is lower than its lean flammability limit. Le Chatelier's Law and the Bartknecht curve can be used to predict the LFL of such mixtures but the deviation still exists especially in the case where more dust/gas is needed to render the system flammable. As hybrid mixtures are a special class of dust explosion, and existing research on such a system is insufficient, further study to develop a more accurate correlation to predict the LFL for a hybrid mixtures explosion is necessary.

This work focuses on the study of hybrid mixtures explosions in a 36L dust explosion apparatus using a mixture of methane/niacin in air. The methane is selected as it has been well studied by several groups. The niacin is selected because it is also well studied by several groups, allowing the results to be compared with others.

## 2. Experiments

The experiments have been performed in a 36L apparatus. It was calibrated and the results agreed well with a standard 20L apparatus. For pure dust, the tests were performed based on the standard test procedure ASTM E1515 (ASTM, 2007). After the dust sample had been loaded into the container, the nozzle and 2500J igniter were installed in the chamber. Then the lid was bolted on and the chamber was partially evacuated to 10.3psi in order to start the ignition at 14.7psi. The air reservoir was pressurized with compressed air to 314.7psi. At the start of the test, the fast valve was triggered to open and lasted for 50ms. The chemical igniter was activated 25ms after the fast valve closed. The total ignition delay time is 75ms.

In order to test the hybrid mixture explosion, the partial pressure method was adopted to prepare flammable-air mixtures inside the chamber prior to the test. The chamber was evacuated to  $P_2$ , and then pure methane was fed until 10.3psi ( $P_1$ ) was reached. The value of  $P_2$  is determined by different methane concentrations and reported in Table 1. The air from the reservoir with the methane in the chamber generated the final test mixture at 14.7psi ( $P_0$ ).

| $P_2$ (psi) | $P_1$ (psi) | $P_0$ (psi) | Flammable gas concentration (% v/v) |
|-------------|-------------|-------------|-------------------------------------|
| 8.90        | 10.30       | 14.70       | 9.52                                |
| 9.10        | 10.30       | 14.70       | 8.16                                |
| 9.30        | 10.30       | 14.70       | 6.80                                |
| 9.50        | 10.30       | 14.70       | 5.44                                |
| 9.70        | 10.30       | 14.70       | 4.08                                |
| 9.90        | 10.30       | 14.70       | 2.72                                |

### 3. Results and discussion

#### 3.1 Methane explosion and niacin explosion

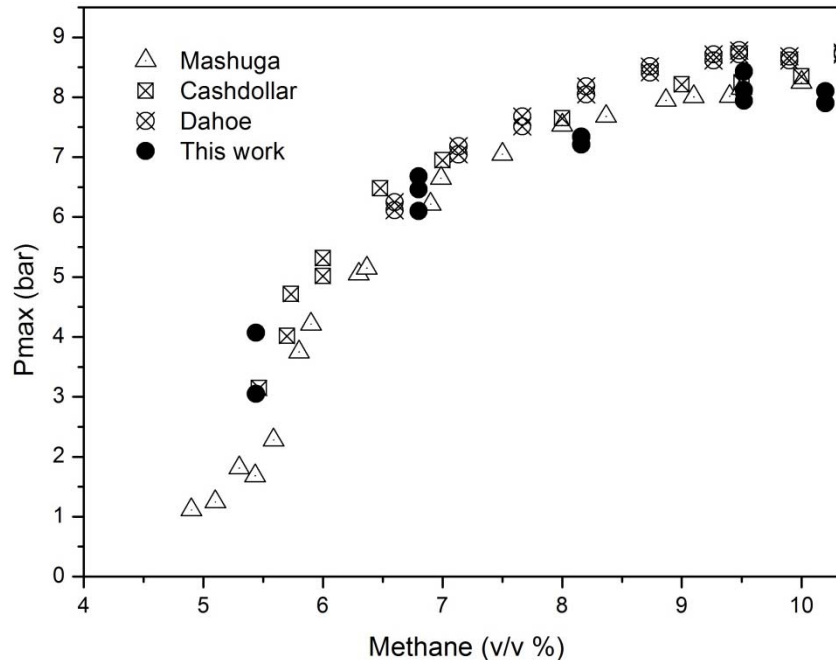


Figure 1.  $P_{max}$  as a function of methane concentration from experiments and literature data

The explosibility of methane has been widely studied and reported in literature (Cashdollar and Hertzberg, 1985; Dahoe and De Goey, 2003; Mashuga, 1999). In these experiments, methane is tested under quiescent status. In order to compare the pure fuel explosion behavior with the niacin/methane/air behavior, the methane/air explosion is conducted under the same conditions as the dust runs. The  $P_{max}$  and  $K_G$  of methane/air in a 36L apparatus and published results from experiments performed in a 20L apparatus are reported in Figures 1 and 2 respectively.

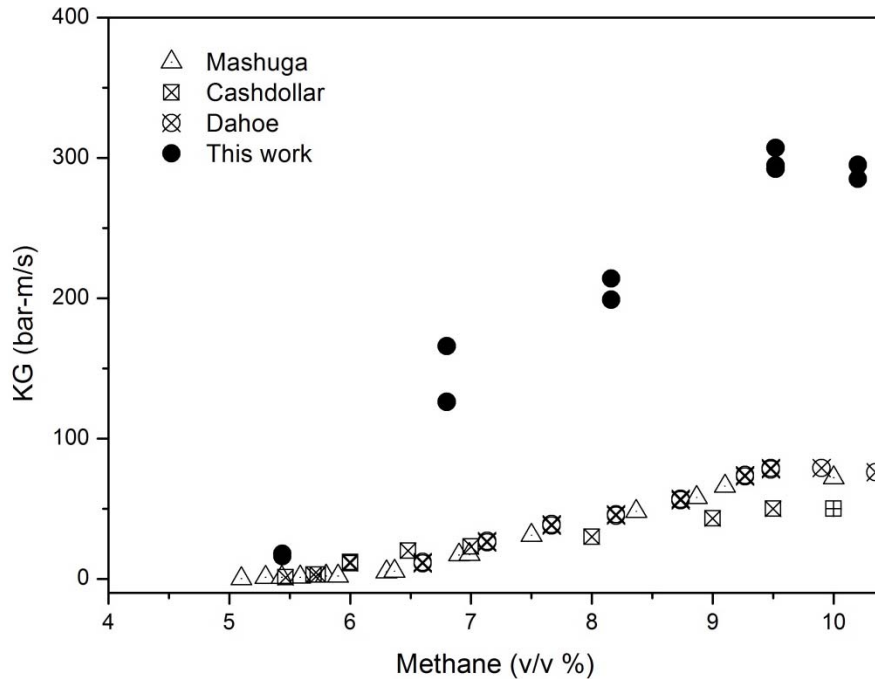


Figure 2.  $K_G$  as a function of methane concentration from experiments and literature data

The  $P_{max}$  of methane is 7.9bar in a 36L vessel, and it agrees well with the result obtained from the 20L vessel. The  $K_G$  of methane has been found as 290bar-m/s when the concentration is 9.5% v/v in this work, which is extremely higher than results from literature.

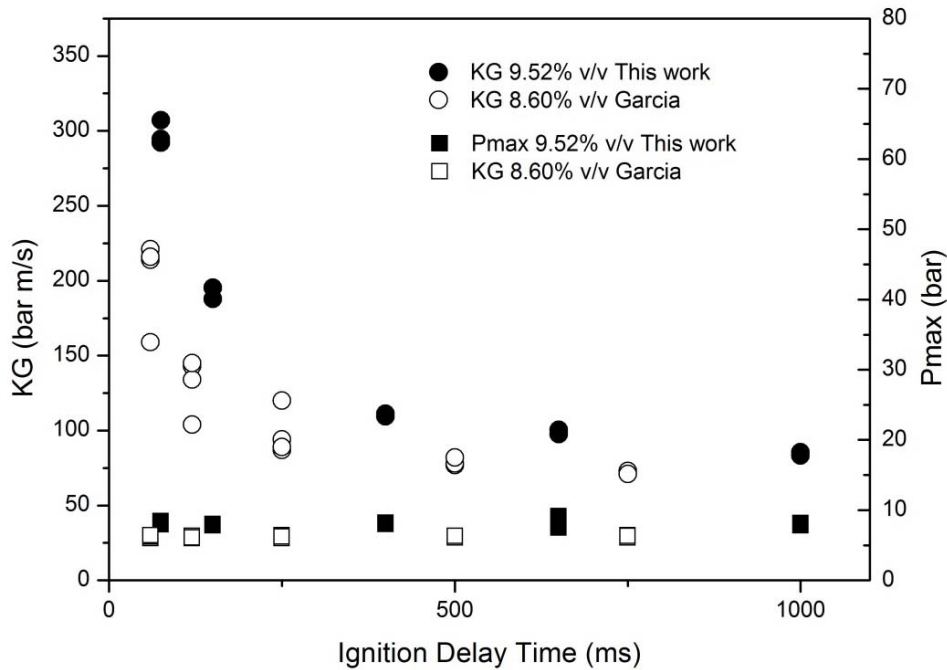


Figure 3. Deflagration index and explosion pressure of methane differed with ignition delay time

Figure 3 shows the results of maximum pressure and the deflagration index of methane along with different ignition delay times. Generally, the shorter the ignition delay time, the higher the deflagration

index is. This phenomenon is caused by the turbulence inside the vessel determined by the ignition delay time. However, the maximum pressure is independent from the ignition delay time. Similar trends have also been found in Garcia's work (Garcia-Agreda *et al.*, 2011). The methane concentration in Figure 3 is 9.52% v/v while it is 8.60% v/v in Garcia's work. Thus, both maximum pressure and deflagration obtained in this work are higher than those from Garcia's work. The lower flammable limit for methane is 5.0% v/v in this work.

The niacin is an organic compound and has been widely studied. In our experiments, the MEC of niacin is  $75\text{g/m}^3$ , and  $K_{St}$  is  $160\text{bar}\cdot\text{m/s}$ .

### 3.2 Hybrid mixtures explosion

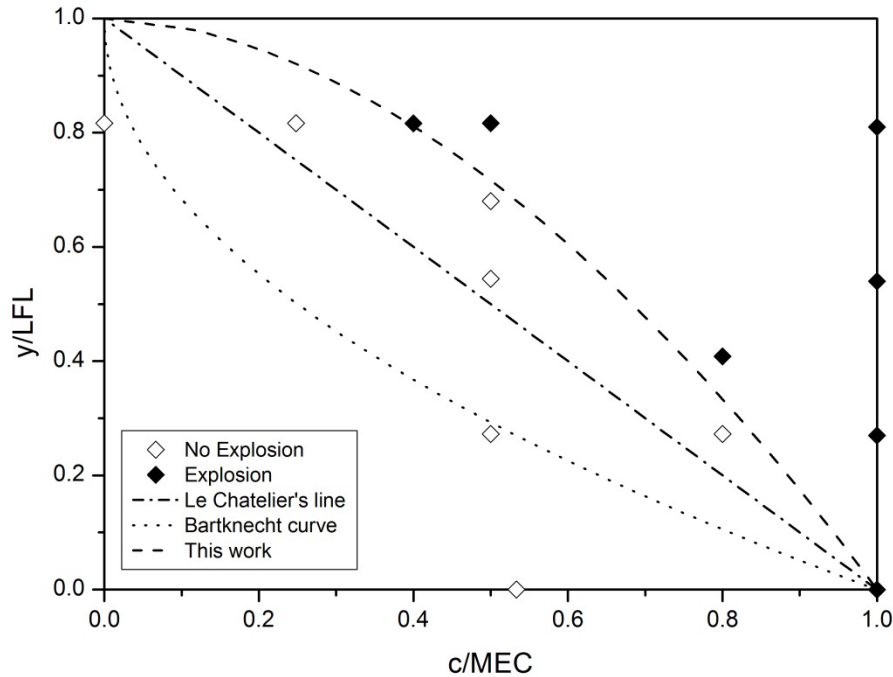


Figure 4. Explosion and no-explosion test of niacin and methane hybrid mixtures with each fuel less than its lean flammability limit

A map of the explosion behavior of the methane/niacin mixtures has been developed as shown in Figure 4. The x-axis is the dust concentration ( $c/\text{MEC}$ ), and the y-axis is the methane content ( $y/\text{LFL}$ ). The solid circles represent explosions where pressure ratio (PR) is larger than 2, while the empty circles stand for no explosions where PR is less than 2. The flame propagation criteria PR is defined as  $(P_{\max} - \Delta P_{\text{ignitor}})/P_i$  according to ASTM E1515.  $P_{\max}$  is the maximum absolute explosion pressure obtained from the pressure-time curve.  $\Delta P_{\text{ignitor}}$  is the pressure difference promoted by the activation of the ignition source.  $P_i$  is the pressure before igniting the explosion which is equal to 14.7psi. Both Le Chatelier's Law and the Bartknecht curve are also plotted in. It is clear that neither of them can be applied to niacin/methane mixtures. For example, when niacin dust concentration is  $37\text{g/m}^3$  ( $c/\text{MEC} = 0.49$ ), 1.5% v/v ( $y/\text{LFL} = 0.30$ ) or 2.6% v/v ( $y/\text{LFL} = 0.51$ ) methane is required according to Le Chatelier's Law or the Bartknecht curve respectively. However, no explosion occurred even if the methane is up to 3.4% v/v ( $y/\text{LFL} = 0.68$ ) which is much higher than the predicted results. Thus, more gas or dust is needed to render the system flammable as predicted by both Le Chatelier's Law or the Bartknecht curve.

### 3.3 New formula to predict the LFL of hybrid mixtures

A dash curve shown in Figure 4 can well divide the explosion and non-explosion area compared with the existing two formulas. This new curve is fitted from the experimental data and can be represented as Equation 1.

$$\frac{c}{MEC} = \left(1 - \frac{y}{LFL}\right)^{0.53} \quad \text{Eq. 1}$$

The power is 0.53 which is close to the ratio of the deflagration indices ( $K_{St}/K_G = 0.55$ ). Thus a new formula is proposed as following:

$$\frac{c}{MEC} = \left(1 - \frac{y}{LFL}\right)^{\frac{K_{St}}{K_G}} \quad \text{Eq. 2}$$

In Equation 2, the gas deflagration index,  $K_G$ , shall be determined under the same turbulence as the dust explosion index,  $K_{St}$ , for the turbulence has a significant effect on them. If  $K_{St}$  is similar to  $K_G$ , this formula can be simplified to Le Chatelier's Law. This new formula can be used to predict the LFL of the hybrid mixtures by utilizing basic characteristics of unitary dust or gas explosions. It may also be extended to other hybrid mixtures with the same behavior as niacin and methane mixtures.

## 4. Conclusions

This work studied hybrid mixtures explosions in a 36L dust explosion apparatus using a mixture of methane/niacin in air. From the results obtained, it has been found the  $K_G$  of methane to be extremely higher than results from literature due to the high turbulence inside the vessel established by the ignition delay time. Additionally, more gas or dust is needed to render the niacin and methane system flammable as predicted by either Le Chatelier's Law or the Bartknecht curve. It is clear that neither of them can be applied to such hybrid mixtures. Furthermore, a new formula is proposed to improve the prediction of the LFL of the mixture by utilizing basic characteristics of unitary dust or gas explosions. Finally, the new formula is consistent with Le Chatelier's Law or the Bartknecht curve. It may be applied to other hybrid mixtures.

## 5. Acknowledgements

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