

# STUDY OF DUST – GAS HYBRID MIXTURE EXPLOSIONS

A Dissertation

By

JIAOJUN JIANG

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Chair of Committee,	M. Sam Mannan
Committee Members,	Zhengdong Cheng
	James Holste
	Eric Petersen
Head of Department,	M. Nazmul Karim

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## ABSTRACT

Hybrid mixtures are widely encountered in industries such as coal mines, paint factories, pharmaceutical industries, or grain elevators. Hybrid mixtures explosions involving dust and gas can cause great loss of lives and properties. 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 36 L dust explosion apparatus including mixtures of methane/niacin, methane/cornstarch, ethane/niacin and ethylene/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.

This work also studied the effect of varying the ignition energy and turbulence intensity to the proposed formula. For ignition energy effect, results from methane/niacin mixture demonstrated that the MEC and LFL will not be affected by changing ignition energy.

There is no distinguishable difference among gas explosion index ( $K_G$ ) and dust explosion index ( $K_{St}$ ) derived from tests with every ignition energy (2.5 kJ, 5 kJ and 10 kJ) in a 36 L vessel. The proposed formula is independent of ignition energy. For turbulence effect, the proposed formula can have a good prediction of the explosion and non-explosion zone if the ignition delay time is within a certain range. The formula prediction is good as the ignition delay time increases up to 100 ms in this work. Propane/niacin and propane/cornstarch mixtures are also tested to validate the proposed formula. It has been confirmed that the proposed formula predicts the explosion and non-explosion zone boundary of such mixtures.

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## **CHAPTER I**

### **INTRODUCTION**

Many combustible materials, which are virtually non-flammable in the bulk form, can become highly explosive if dispersed and mixed with air in the presence of an ignition source in a confined space [1, 2]. Chemical Safety Board (CSB) reports published in 2006 show that over 200 explosions happened in the US from 1980 to 2005 [3]. These types of accidents still happen and cause a great loss of lives and properties. A recent case is the coal mine explosion in Upper Big Branch Mine in West Virginia, April 2010, in which 29 miners lost their lives [4]. It is considered as one of the most disastrous mining accidents in US history. Since methane coexists with coal, this type of explosion usually involves dust and gas explosions together, named as a hybrid mixture explosion [5, 6]. Aside from the mining industry, hybrid mixtures are also encountered in industries such as paint factories (pigments and solvents), pharmaceutical industries or grain elevators (small grains and fermentation gases) [7]. Unlike pure 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 [8-10]. Because of this, continued research on hybrid mixtures explosions is needed. Hybrid mixtures are a special class of explosible fuel, and their explosible behavior cannot be predicted from knowledge of dust alone. Research on hybrid mixtures is one of three most attractive research branches for dust explosion [11, 12].

## 1.1 Motivations

Recently, several studies have been performed toward the basic understanding of hybrid mixture systems. Risk is the function of severity and probability [13]. For a hybrid mixture explosion, the severity can be characterized by explosion index ( $K_{St}$ ), maximum explosion pressure ( $P_{max}$ ), and maximum rate of pressure rise ( $[dP/dt]_{max}$ ), while the probability can be represented by minimum ignition energy, lean flammability limits, and minimum ignition temperature.

On the possibility side, one of the most interesting characteristics is the lower flammability limit (LFL) of hybrid mixtures. The LFL 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 done by Cashdollar, *et al.* [14]. For this system, it was found that Le Chatelier's Law can be applied to distinguish between flammable and non-flammable zones. If extended to hybrid mixtures, Le Chatelier's Law is a linear relationship between the LFL of gas and the minimum explosible concentration (MEC) of dust, and the weighting factor for each fuel is its fractional content in the mixture as represented in Eq. 1.

$$\frac{c}{MEC} + \frac{y}{LFL} = 1 \quad \text{Eq. (1)}$$

where  $c$  is the concentration of the combustible dust,  $\text{g/m}^3$ ; MEC is the minimum explosible concentration of such dust,  $\text{g/m}^3$ ;  $y$  is the volume concentration of the flammable gas, % v/v; LFL is the lower flammability limit of such gas, % v/v.

However, some deviation from Le Chatelier's Law was found when applied to the low volatility Pocahontas coal with methane by Cashdollar [15]. The similar deviation was also found by Bartknecht, *et al.* [16] in PVC dust mixed with methane or propane. The LFL of hybrid mixtures decreases with increasing the gas concentration by a second order equation, named the Bartknecht curve as represented in Eq. 2.

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

Cornstarch dust with hydrogen was tested by Gaug and referred to by Cashdollar, *et al.* [14]. It was shown that more dust is required to render the system flammable, which significantly deviates from either the linear relationship defined by Le Chatelier's Law or the second order curve as defined by Bartknecht.

Pilão, *et al.* [17] studied the effect of the addition of methane to a flammable mixture of cork-air in a 20 L vessel, using 2500 J ignitors. They found the mixture can be flammable when the concentration of each fuel is below its lean flammability limit. However, similar to the cornstarch and hydrogen system, more cork dust is needed to render the system flammable.

Attempting to understand this deviation, the LFL of different hybrid mixtures reported in the literature was summarized and compared with regards to the heat capacity and the deflagration index of each fuel by Prugh [18]. 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.

Generally, it is known that hybrid mixtures can be flammable when the concentration of each fuel is below its lean flammability limit. Le Chatelier's Law and the Bartknecht curve can be used to predict the LFL of such mixtures, but deviations still exist, especially in the case where more dust/gas is needed to render the system flammable. Thus, a more accurate correlation to predict the LFL for hybrid mixtures is necessary.

## **1.2 Objectives**

The objective of this research is to study the explosion behavior of hybrid mixtures through doing systematic experiments. Based on solid experimental results, the current work aims to develop a formula which can have a more accurate prediction on the LFL for a hybrid mixture than Le Chatelier's Law and Bartknecht curve. Several hybrid mixture representatives including cornstarch and methane mixtures, niacin and methane mixtures, *etc.* are selected to be tested in different conditions (ignition energy, ignition delay times). These tests are not only to provide solid data for the correlation but also to be used to validate its applicability in various conditions.

Specifically, the objectives of this research include:

- 1) Modifying the dust explosion test apparatus by designing and installing a new gas supply system to extend its capability for testing dust/gas hybrid mixtures;
- 2) Developing a correlation of the lower flammability limit for hybrid mixtures based on experimental results;
- 3) Studying the influence of ignition energy and ignition delay times on the developed formula and validating it with other hybrid mixtures.

### **1.3 Organization of dissertation**

This dissertation is based on a current, on-going research program in the dust laboratory of the Mary Kay O'Connor Process Safety Center at Texas A&M University. Parts of the work in the dissertation were published in peer-reviewed publications.

This dissertation includes six chapters. Chapter I presented the gap between existing research and the needs on the determination of LFL for hybrid mixtures. It has been an accepted fact that the hybrid mixtures research is one of the important branches in the dust explosion area. A more accurate correlation for LFL prediction is of importance and can be beneficial to industries that have potential hybrid mixtures hazards in terms of protecting and preserving health and safety through appropriate prevention method.

Chapter II presented the background of the dust explosion, hybrid mixtures explosion as well as other concepts used often in this research. A literature review has also been summarized in Chapter II represented the current state of knowledge on the topics in this research, including research progress in hybrid mixtures explosion, and the comparison



of dust and gas explosion. The knowledge is considered necessary for understanding the scope and the methodology in this research.

Chapter III introduced the 36 L dust explosion vessel and the modification of such apparatus in the dust explosion laboratory of Mary Kay O'Connor Process Safety. The operation procedure of normal dust explosion test and the partial pressure method for hybrid mixtures test were also discussed. A typical experimental result and the criteria to determine explosion or non-explosion has also been represented. At the end of this chapter, the methodology of varying turbulence by changing ignition delay times has been introduced.

Chapter IV and Chapter V represented all the experimental results and discussion. Chapter IV focused on the developing of the correlation of LFL for a hybrid mixture. In this chapter, results from tests of pure dust and pure gas, as well as their combination were analyzed. These data together with other data from the literature were fitted into a correlation to predict the explosion and non-explosion zone of such hybrid mixtures. The explosion and non-explosion zone predicted by proposed formula were also compared with results from Le Chatelier's Law and Bartknecht curve. The uncertainty of the proposed formula was also discussed in this chapter.

Chapter V summarized the validation of the formula developed in Chapter IV in terms of the applicability with varying ignition energy and turbulence which affected by ignition delay times. Additional hybrid mixtures including cornstarch and propane, niacin and propane were also tested and such results were used for validating the proposed formula.

Finally, this dissertation wrapped with Chapter VI, which including the conclusions from this research, and some recommendations for future work.

## CHAPTER II

### BACKGROUND

#### 2.1 Dust explosion

A dust explosion can occur when the particulate solid material is suspended in air and a sufficient energetic ignition source is present [19]. Any solid material that can burn in air will do so with a violence and speed that increases with the degree of sub-division of the material [2]. Higher the degree of sub-division, which also means smaller the particle size, more rapid and explosive the burning, till a limiting stage is reached when particles too fine in size tend to agglomerate in a group. If the dust cloud ignited in an unconfined space, it would only cause a flash fire. But if such dust cloud ignited in a confined space, even partially, the heat of combustion may result in rapid development of pressure, with flame propagation across the dust cloud and the release of large quantities of heat and reaction products [20].

The consequences of dust explosions are often similar to those arising from a gas explosion in terms of impact on people and environment, damage on physical assets and interruption to business. The first recorded dust explosion was an explosion of flour in a warehouse occurred in 1795 [2]. Systematic records available from the early 20<sup>th</sup> century show that dust explosion was a serious issue in several industries, *e.g.* flour, cornstarch and other grain dust in the food industry, coal in the mining industry [20]. Fast-forwarding to the 21<sup>st</sup> century, dust explosions remain a persistent and damaging

industrial occurrence. The US Chemical Safety Board published a report in 2006. It researched the history of 281 major combustible dust explosions in the US from 1980 to 2005. The 281 incidents resulted in 119 worker deaths, 718 injuries, and destroyed many industrial facilities [21]. But it does not thoroughly wake the industry up, several catastrophic disasters still recently occurred. One of them is the sugar explosion occurred at the Imperial Sugar refinery in 2008 resulted in 14 fatalities and 36 injuries [22]. Another one is the Upper Big Branch (UBB) mine disaster occurred at West Virginia in 2010 which resulted in 29 fatalities. This incident was the worst in the US since 1970 [23]. Moreover, three combustible dust incidents occurred over a six-month period in a same company in 2011 at the Hoeganaes facility resulted in 5 fatalities and 3 injuries [24]. Hence, dust explosion is still a serious industrial problem.

## **2.2 The dust explosion pentagon**

A fire is caused when three factors – fuel, oxidant, and ignition – come together. These three factors make a triangle (Figure 1) what has been named as ‘the fire triangle’. Differently, a dust explosion demands two more elements: mixing of dust and air to form the dust cloud, and confinement of the dust cloud. These five factors together form the ‘dust explosion pentagon’ (Figure 2).

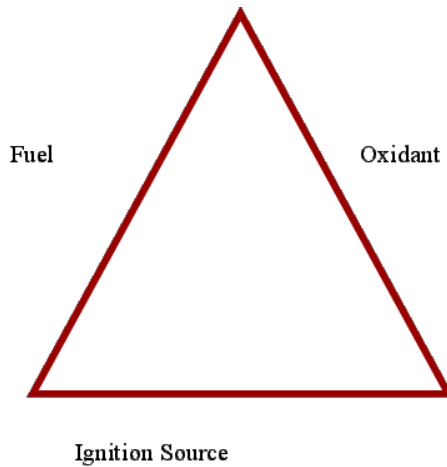


Figure 1 Fire triangle

The first of the additional factor – mixing of dust and air – reflects the key difference between dust and gas explosions, a solid rather than a gaseous fuel. A gas explosion therefore involves a homogeneous system in which the smallest entities of fuel and air are separated only by molecular distances and the gravitational effects are negligible. However, the dust particles are strongly affected by gravity in dust and air mixture. An essential prerequisite is the formation of a dust cloud for a dust explosion [6]. The comparison of dust and gas explosion and other in-depth of dust explosion will be discussed later in this research.

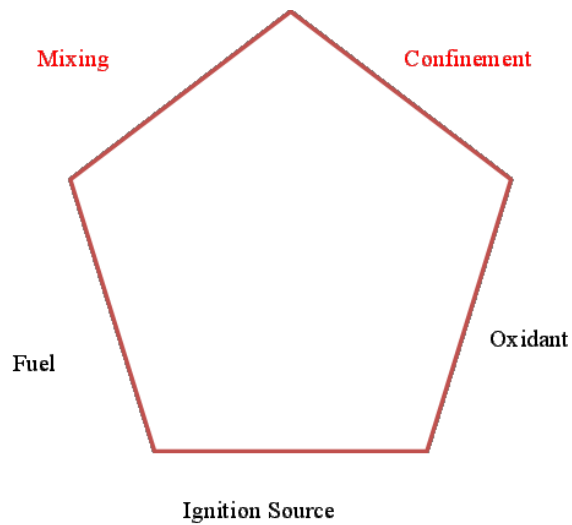


Figure 2 Dust explosion pentagon

The second of the additional factor – confinement – can be in a complete or partial form. It is important to note that even in a partial confinement of an ignited dust cloud is sufficient to cause a severe damage. It is because the reactions caused by combustion are so fast that pressure builds up in the dust cloud faster than it can be dissipated at the edge of the cloud [1].

### 2.3 Classification of dust

Generally, all explosible dust shall be combustible, but not all combustible dust are easily explosible [2]. A dust is combustible means such dust can be ignited with a foreign source and the local fire thus generated propagates sufficiently after the outside source is taken away [25]. Hence, a dust can be characterized into different classes according to its explosibility. A widely accepted categorization of dust is based on the value of  $K_{St}$ , which represents the maximum rate of pressure rise in 1 m<sup>3</sup> vessel when a

dust is ignited. The  $K_{St}$  concept was introduced by Bartknecht [16] who reported that so-called cube root law (Eq. 3):

$$\left(\frac{dP}{dt}\right)_{\max} \bullet V^{1/3} = \text{constant} \equiv K_{St} \quad \text{Eq. (3)}$$

According to the value of  $K_{St}$ , the explosibility of dust can be ranked into four groups classified by NFPA 68 [26] as shown in Table 1.

Table 1 Hazard classes of dust deflagration

$K_{St}$ (bar·m/s)	Group	Explosibility
$K_{St} = 0$	St-0	Non-explosible
$0 < K_{St} \leq 200$	St-1	Weak
$200 < K_{St} \leq 300$	St-2	Strong
$K_{St} > 300$	St-3	Very Strong

It must be emphasized that the cube root law is valid only in geometrically similar vessels if the flame thickness is negligible compared to the vessel radius, and if the burning velocity as a function of pressure and temperature is identical in all volumes [2]. ASTM E1226 requires that  $K_{St}$  shall be determined in approximately spherical calibrated test vessel of at least 20 L capacity.

## 2.4 Explosibility parameters

The purpose of this section is to provide a guide to some of the more important and commonly used dust explosion parameters in this dissertation. As listed in Table 2, most of the parameters are self-explanatory.

Table 2 Important dust explosibility parameters and their determination [19]

Parameter	Typical units	Description	Risk component addressed	Example test methodology
$P_{\max}$	bar(g)	Maximum explosion pressure in constant-volume explosion	Consequence severity	ASTM E1226-05
$(dP/dt)_{\max}$	bar/s	Maximum rate of pressure rise in constant-volume explosion	Consequence severity	ASTM E1226-05
$K_{St}$	bar m/s	Volume-normalized (or standardized) maximum rate of pressure rise in constant-volume explosion	Consequence severity	ASTM E1226-05
MEC	g/m <sup>3</sup>	Minimum explosible (or explosive) dust concentration	Likelihood of occurrence	ASTM E1515-07
MIE	mJ	Minimum ignition energy of dust cloud (electric spark)	Likelihood of occurrence	ASTM E2019-03
MIT	°C	Minimum ignition temperature of dust cloud	Likelihood of occurrence	ASTM E1491-06
LIT	°C	Minimum ignition temperature of dust layer or dust deposit	Likelihood of occurrence	ASTM E2021-06
MOC (LOC)	volume%	Minimum (or limiting) oxygen concentration in the atmosphere for flame propagation in dust cloud	Likelihood of occurrence	ASTM WK1680

These parameters basically address questions [19] such as: i) Can the dust be explosible when dispersed as a cloud in the air? ii) How high will the overpressure resulted from the explosion at constant volume? iii) How quickly does the pressure rise if an explosion occurs at constant volume? iv) What concentration of airborne dust is needed for an



explosion? v) How much energy, or how high a temperature, is needed to initiate the explosion? vi) What minimum percentage of oxygen in the atmosphere is needed to sustain flame propagation in the dust cloud?

## **2.5 Hybrid mixture explosion**

### **2.5.1 Hybrid mixture**

Hybrid mixture is a term used for mixtures of dust suspensions, gases and/or vapors, and air [27]. 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. [28]. The hybrid mixtures are encountered in different process industries such as food, pharmaceutical, and paint industries as well as chemical manufacturing [19]. Although it has attracted public and researcher's attention, accidental hybrid mixture explosion is still a big problem and continues to cause significant loss of life and property damages, and damage to the surrounding environment in the process industries [2, 29].

During the risk assessment phase and especially during the application of ATEX directives in Europe, hybrid mixtures are not frequently appreciated at their full value. On fact is that if the gas or vapour content is low, i.e. low than its LFL, their influences are often neglected. Another fact is that if the dust concentration is lower than its MEC, the analysis is usually done as if only gas was present [30]. Better than ATEX directives, the latest NFPA 68 takes hybrid mixtures into account. It points out that careful evaluation of the ignition and deflagration characteristics of the specific mixtures is

necessary. NFPA 68 also gives suggestion on the venting system design for hybrid mixtures: the vent size shall be based on the equivalent  $K_{St}$  as determined by test. If test data are not available for hybrid mixtures with gases that have combustion characteristics similar to those of propane (fundamental burning velocity less than 1.3 times that of propane) and St-1 and St-2 dust, the design shall be permitted to be based upon  $P_{max} = 10$  bar and  $K_{St} = 500$  bar·m/s [26]. Apparently, more research focuses on hybrid mixtures is needed.

### 2.5.2 Hybrid mixture explosion

The hybrid mixtures explosion is different from dust explosion. It involves a flammable gas or flammable gases. For dust explosion, the cloud contains only dust particle and air; for hybrid mixtures explosion, the cloud contains dust particles and such dust are surrounded with flammable gas and air. Figure 3 describes the process of a hybrid mixture explosion.

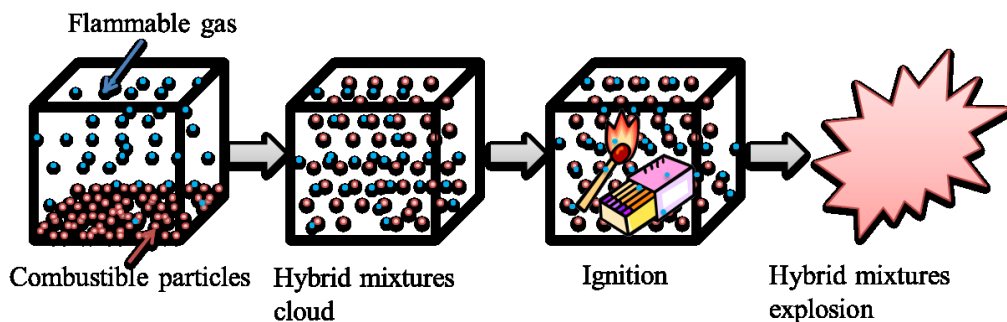


Figure 3 Demonstration of hybrid mixtures explosion

It is worth to point out that the hybrid mixtures explosion can be as the initial or first explosion in some process. Sometimes, it can be as the second explosion which usually results in more damage.

### **2.5.3 Recent research on hybrid mixtures explosion**

Many studies recently have been performed and have shown that specific behaviors of such mixtures. The effect of the addition of graphite dust to a flammable mixture of H<sub>2</sub> in a 20 L sphere was studied by Denkevits [31]. The ignitor was a weak electric spark. At each hydrogen composition different amounts of graphite were added to the mixture and the maximum pressure and deflagration index were compared to the pure H<sub>2</sub> explosion values. The author found that the explosion for H<sub>2</sub>/graphite can proceed in two stages depending on the fuel component concentration. At low H<sub>2</sub> and dust concentrations, the mixture ignition initiates first a fast hydrogen explosion followed by a slower phase of the dust explosion. With increasing dust concentration, the dust explodes faster and can overlap the H<sub>2</sub> explosion stage. At higher H<sub>2</sub> concentrations, the hybrid mixtures explode in one stage with gas and dust reacting at the same time.  $P_{\max}$  of a hybrid mixture is higher than that derived from pure H<sub>2</sub> or pure graphite tests.

Dufaud, *et al.* [7, 32] studied the influence of mixing pharmaceutical dusts (magnesium stearate, niacin and antibiotic) and solvents (ethanol, di-isopropyl ether, and toluene) on  $P_{\max}$  and  $(dP/dt)_{\max}$  obtained during their explosion. The experiments were performed in a 20 L vessel ignited by two pyrotechnic ignitors of 5 kJ each (ignition delay time equals to 60 ms). It was observed that the deflagration index for hybrid mixtures is significantly

higher than those of pure gas or dust. They concluded that there are more than simple additive effects on explosion severity.

Amyotte, *et al.* [13, 19] studied the explosion features of polyethylene admixed with propane, ethylene and hexane in a 20 L sphere with two 5 kJ chemical igniters. The experiments were performed by adding low gas concentrations (1-5%) of ethylene, propane and hexane to polyethylene dust at changing the dust concentration. It was found that a significant increase of the deflagration index by adding ethylene at a concentration higher than its flammability limit with respect to the dust alone.

Garcia-Agreda, *et al.* [8, 9] studied the explosion behavior of a mixture of niacin and methane at changing both the dust and the gas concentrations in the full flammable range in a 20 L vessel with an electric spark as the ignition source. They also tested the pure stoichiometric gas/air and dust/air mixtures in the same device. They found that the deflagration indexes of the niacin/methane mixtures are always lower than the stoichiometric methane/air values, no matter the relative amount of niacin and methane.

Additional to researches mentioned above, there are several other studies have been performed. These researches, on one hand side, deal with the severity of the explosion. The hybrid mixtures result in an increase in the severity of the explosion over that of the dust or gas alone [8, 13, 32, 33]. Apart from the severity, several research have been conducted toward the understanding of the likelihood of hybrid mixtures explosion [5, 8, 17, 32, 34]. The main conclusion of these studies could be summarized as following:

- i) The hybrid mixtures can be explosive when both the concentrations of dust and the gas are lower than their respective MEC and LFL. The ignition sensitivity of the dust can be strongly increased by the addition of flammable gases, even with a small amount which is less than its LFL [8, 11, 13, 31, 32, 35].
- ii) The maximum rate of the explosion of the pure gas or pure dust is significantly affected by the presence of a few amount of dust or gas. Synergistic effects have been found, and the maximum pressure rise rate of a hybrid mixture can be higher than that of the pure gas under peculiar conditions [31, 32].
- iii) If the dust concentrations are greater than the MEC, the addition of few amount of flammable gas has only a minor effect on the  $P_{\max}$  [9, 36].
- iv) The explosion regimes of hybrid mixtures can be represented as a function of the dust concentration/MEC and gas concentration/LFL ratios [8].

One aspect of the likelihood is the lower flammability limit of hybrid mixtures, which is a critical parameter for hazard assessment or mitigation method development in an unexpected hybrid mixtures explosion event.

Cashdollar, *et al.* [14] performed the most extensive work on the LFL of coal and methane hybrid mixtures. For this system, it was found that Le Chatelier's Law (Eq. 1) can be applied to separate the flammable and non-flammable mixtures. Le Chatelier's Law was originally developed and adopted for homogeneous gas mixtures based on the concept of a constant limit flame temperature for a given class of fuels [37]. If extended

to hybrid mixtures, 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. In the case of a coal and methane mixture, such temperatures are comparable and then the linear trend is valid. However, some deviation from Le Chatelier's Law was found when applied to the low volatile Pocahontas coal with methane by Cashdollar [15].

The similar deviation was also found by Bartknecht [16] in PVC dust mixed with methane or propane. The LFL of hybrid mixtures decreases with increasing the gas concentration by a second order equation named the Bartknecht curve (Eq. 2).

Additionally, cornstarch dust with hydrogen was tested by Gaug and referred to by Hertzberg and Cashdollar [14]. It was shown that more dust is required to render the system flammable, which significantly deviates from either the linear relationship defined by Le Chatelier's Law or the second order curve as defined by Bartknecht.

Pilão, *et al.* [17, 38] studied the effect of the addition of methane to a flammable cork/air mixture in a 20 L vessel ignited by a pyrotechnic ignitor with 2500 J of energy. Explosion tests on the hybrid mixture were performed at methane concentrations lower than the lower flammability limit. It was found that the addition of methane enhances the deflagration index of the cork dust alone. They also found the mixture can be flammable when the concentration of each fuel is below its lean flammability limit. However, similar to the cornstarch and hydrogen system, more cork dust is needed to render the system flammable.

Sanchirico, *et al.* [39] studied the niacin/acetone mixtures in a standard 20 L vessel. Similar to the cornstarch/hydrogen, cork/methane mixtures, more niacin dust is required to render the system flammable.

Addai, *et al.* [40] studied the LFL of hybrid mixtures in a standard 20 L vessel. Permanent spark with ignition energy of 10 J was used as the ignition source. Samples are different dust such as toner, polyethylene, starch, and lycopodium mixed with hydrogen and methane, respectively. The results obtained so showed that there are some combination dust and gas where the proposed mathematical formula such as Le Chatelier's Law and Bartknecht curve to predict the LFL of hybrid mixtures are not safe enough.

Prugh [18] compared the LFL of different hybrid mixtures reported in the literature with respect to the heat capacity and the deflagration index of each fuel. Prugh [18] concluded that the straight-line relationship applies only to mixtures where the ratio of the heat capacities of the dust and gas/vapor are similar, and where the deflagration indices are roughly equivalent.

To summarize above discussion, it is well known that hybrid mixtures can be flammable when the concentration of each fuel is below its lean flammability limit. Le Chatelier's Law and the Bartknecht curve can be used to predict the LFL of hybrid mixtures, but deviations still exist, especially in the case where more dust/gas is needed to render the system flammable. Therefore, a more accurate correlation to predict the LFL for hybrid mixtures is necessary.

## 2.6 Comparison of gas and dust explosions

Some of the significant differences between gas and dust explosion in terms of explosion characteristics are summarized in Table 3.

Table 3 Comparison of gas and dust explosion [41]

Characteristic	Gas explosions	Dust explosions
Type of explosion	Deflagrations or detonations	Usually deflagrations; detonations have been observed under special laboratory conditions. <sup>33-35</sup> Detonations and DDT have recently been observed in large-scale tests. <sup>16</sup>
Flame speed	Up to 3000 m/sec	Usually up to 10 m/sec. In long galleries flames can accelerate up to 1000 m/sec, and when detonations occur the flame speed can reach 2500 m/sec.
Maximum explosion pressure	Same order of magnitude (typically 8 bar or less)	
Maximum rate of pressure rise	Usually greater for gases than for dusts	
Flammability limits	Usually narrow, but varies with material	Generally very wide, with upper limit several times stoichiometric concentration
Minimum ignition energy	0.2-10 mJ	10-60 mJ

When comparing gas and dust explosions, the major difference is that only one phase exists in the former type. Gas combustion is a homogenous process in which the distance between the smallest entities of fuel and air is in the molecular level. The fuel and air can be well mixed, and the gravitational influences are negligible. But in a dust and air mixture, the dust particles are heavily affected by gravity. Therefore, a critical prerequisite for a dust explosion is the formation of a dust cloud in which dust mixed



with air. A uniform dust cloud may not occur which could lead to local variations in concentration [6].

Apart from the uniformity difference, the dust explosion can also be affected by other factors such as particle size, shape and distribution. Because the evolution of volatiles from and heat transfer into the particles depend on the exposed surface area, variation in any of these factors can affect the dust explosion characteristics.

Additionally, for dust explosion, the solid phase in combination with gas phase leads to a complicated combustion process which becomes a step-wise procedure and is dependent on the nature of the combustible material. There are three distinct mechanisms for a pure dust explosion as follows: i) a reaction on the solid or liquid surface, forming gaseous products; ii) a reaction on the solid or liquid surface, forming solid or liquid products; and iii) a reaction in the gas phase, forming solid, liquid or gaseous products [41]. Dust explosion generally occurs through two main paths: the heterogeneous and the homogeneous combustion path (Figure 4). The devitalization followed by gas-phase combustion has been proposed by some researchers as the dominant mechanism of flame propagation. Evidence also suggests that heterogeneous surface oxidation may be responsible for flame propagation in some materials.

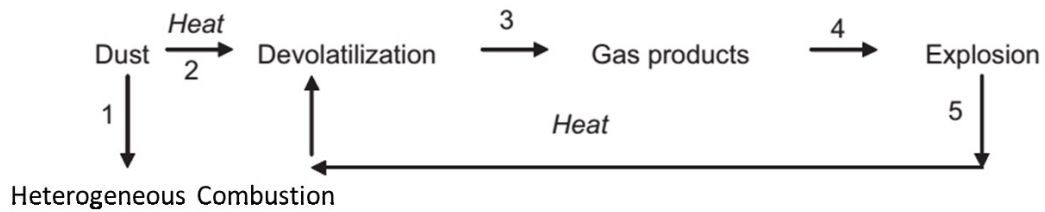


Figure 4 Schematic representation of the paths occurring during dust explosion[42]

## 2.7 Role of turbulence

Because of the differences between dust and gas, the dust particles should be in a cloud form to be able to be explosible. The dust particles movement within the cloud is controlled by inertial forces, including gravity, rather than by random molecular motion. Additionally, the collisions between dust particles in a dust cloud may lead to the agglomeration and then enhance the settling-out of such particles [43]. Therefore, the dust kept in suspension is necessary for a dust explosion. This suspension is usually initiated and maintained by turbulence.

Turbulence plays a critical role in determining explosion characteristics of a dust and is a dominant concern in dust explosion research [6]. On one hand side, a highly turbulent cloud will have evenly distributed dust in it. Once such a dust cloud catches ignition source, the turbulence will play an import role during the explosion: mixing the hot burnt/burning part of the cloud with the unburnt parts, generating a three-dimensional laminate of alternating hot burnt/burning and cold unburnt zones [20]. In other words, a violent explosion will be formed because a flame will propagate very quickly through a

dust cloud if such cloud has a high degree of turbulence. Turbulence affects the maximum rate of pressure rise much more than the maximum pressure [34, 44]. On the other hand side, once ignited, a less turbulent dust cloud releases an initial large amount of heat. Because of the low rate of heat dissipation, the amount of heat will be locally concentrated. Any further propagation of flame produced in the dust cloud is based on the degree of the dust dispersion. It is usually that a more evenly dispersed dust burned more easily.

There are two types of turbulence. In a dust explosion test, the dust cloud is usually generated by means of pneumatic dust dispersion system. Therefore, some degree of turbulence is required in dust cloud before ignition. This type of turbulence is defined as pre-ignition turbulence. It can also be generated by other dust production operations such as a mixer, air jet mill, and pneumatic transport pipe and bucket elevator. Pre-ignition turbulence can keep suspending the dust as in cloud form. Its intensity will decay as time lapse. Another form of turbulence is generated after ignition by the combustion in the presence of vessel walls, obstacles and other restrictions such as vent holes. It is an expansion-induced flow of unburnt dust cloud ahead of the propagating flame [20].

The grade of turbulence can be expressed in terms of turbulent Reynold number,  $Re_t$  (see Eq. 4):

$$Re_t = \frac{\rho \cdot \mu' \cdot R_{sphere}}{\mu} \quad \text{Eq. (4)}$$

where  $\rho$  and  $\mu$  are respectively the density and the viscosity of the un-burned fuel; and  $R_{\text{sphere}}$  is the radius of the sphere vessel.

In this research, a dust cloud is ignited at a defined ignition delay time from the beginning of dust dispersion and, hence, at a given initial level of turbulence. More details on how to control this ignition delay time will be discussed in the following parts.

## 2.8 Models for determining the lower flammability limit of dust/gas

Since the lower flammability limit is critical important for a hybrid mixture, besides experimental method and the empirical equation such as Le Chatelier's Law (Eq. 1) and the Bartknecht curve (Eq. 2), researcher also tried to build models which can be able to calculate the LFL with basic characteristics of the dust and gas. A typical example is a model updated on Jaeckel's theory [45] as show in Eq. 5. This theoretical expression is applicable for the minimum explosion concentration of dust in a space of a constant volume.

$$MEC \cdot \Delta_c H_{\text{dust}} = (T_{\text{ign-dust}} - T_0) \cdot (C_{p\text{-air}} \cdot \rho_{\text{air}} + C_{p\text{-dust}} \cdot MEC) \quad \text{Eq. (5)}$$

where  $\Delta_c H_{\text{dust}}$  is the heat of combustion of the dust,  $C_{p\text{-dust}}$  is the heat capacity of the dust and  $T_{\text{ign-dust}}$  is the adiabatic flame temperature reached during the explosion of the lowest flammable concentration of such dust. On one hand side, such space should be with a plane hot surface of a similar initiating source. One dimension heat transfer from a plane flame front to the adjacent layer of dust cloud was considered. The explosion of dust cloud was proposed to start by heating and ignition of the dust particles in the air layer

parallel with and adjacent to the hot surface. The energy released by this combustion in turn heated and ignited the next dust/air layers, and in this manner the explosion propagated throughout the dust cloud [46]. On the other hand side, it was considered that in a lower limit mixture there were just enough particles in each parallel layer to produce the heat (of combustion) required to bring the adjacent layer to the ignition temperature and to take care of heat loss by radiation and conduction to the surroundings.

The same approach can be applied to define the LFL for a gas (Eq. 6):

$$\rho_{gas} \cdot LFL \cdot \Delta_c H_{gas} = (T_{ign-gas} - T_0) \cdot (C_{p-air} \cdot \rho_{air} + \rho_{gas} \cdot C_{p-gas} \cdot LFL) \quad \text{Eq. (6)}$$

If applied to a hybrid mixture, Jaeckel's model should be in the form of Eq. 7:

$$\begin{aligned} & \rho_{gas} \cdot y_{gas} \cdot \Delta_c H_{gas} + MEC \cdot \Delta_c H_{dust} \\ & = (T_{ign-hybrid} - T_0) \cdot (C_{p-air} \cdot \rho_{air} + \rho_{gas} \cdot y_{gas} \cdot C_{p-gas} + C_{p-dust} \cdot MEC) \end{aligned} \quad \text{Eq. (7)}$$

In Eq. 7,  $T_{ign-hybrid}$  is the adiabatic flame temperature reached during the hybrid mixture explosion. If an exponential relationship is assumed between temperatures, it can be estimated from  $T_{ign-dust}$  and  $T_{ign-gas}$  as for instance (Eq. 8).

$$T_{ign-hybrid} = T_{ign-dust} \cdot \exp \left[ -\frac{C_{gas}}{C_{dust}} \cdot \ln \left( \frac{T_{ign-dust}}{T_{ign-gas}} \right) \right] \quad \text{Eq. (8)}$$

in which  $T_{ign-dust}$  and  $T_{ign-gas}$  can be derived from Eq. 5 and Eq. 6, respectively.

## CHAPTER III

### APPARATUS AND EXPERIMENTAL METHOD

This chapter will provide an overview of the dust explosion apparatus and the modification made for this research. The methodology on both dust explosion and hybrid mixtures explosion are also discussed.

#### 3.1 Overview of 36 L dust explosion apparatus

The dust explosion apparatus used in this research is a 36 L device developed by Mary Kay O'Connor Process Safety Center. It had already been carefully calibrated with round robin tests and the results were comparable to such ones obtained from 20 L and 1 m<sup>3</sup> standard devices [47].

This device (see Figure 5) was designed based on ASTM E1226 standard. It originally consisted of an explosion chamber, the dust dispersion system, an ignition system, a vacuum system, and a control and data acquisition system. In order to test hybrid mixtures for this research, a gas supply system was introduced.

The explosion vessel has a capacity of 36 L and is in semi-spherical. It is made with stainless steel. The maximum allowed working pressure (MAWP) is 1000 psi.

The dispersion system is equipped with an air reservoir, a fast open valve, the dust sample container and a rebound nozzle. During the experiment, the pressurized air from

the reservoir will blow the dust through the rebound nozzle to disperse the dust into the vessel.

The ignition system has two electric rods in the center of the vessel. Chemical ignitors with different energy (1 kJ, 2.5 kJ, or 5 kJ) which consists a certain amount of pyrotechnical mixture (40 wt% zirconium, 30 wt% barium nitrate, 30 wt% barium peroxide) are placed on the electric rods. The ignitor is manufactured by Fr. Sobbe GmbH in Germany and distributed in the U.S. and Canada by Cesana Corporation. During the experiment, the chemical ignitor will be triggered by electricity, then the ignitor explosion will trigger the dust explosion.

The vacuum system is essential to the dust explosion test. According to ASTM E1226 and ASTM E1515, the dust explosion tests should start with pressure at 1 atm. Since the dust cloud is generated by the pressurized air from the air reservoir, which means the additional air will be introduced to the system before dispersion. Hence, it is important to evacuate a certain amount of air out of the system before the dispersion step. For a hybrid mixture test, the flammable gas concentration will be determined by the partial pressure method, and the accuracy of the gas concentration is highly dependent on the vacuum system as well as gas supply system. Both the partial pressure method and the gas supply system will be discussed in Section 3.3 and 3.4.

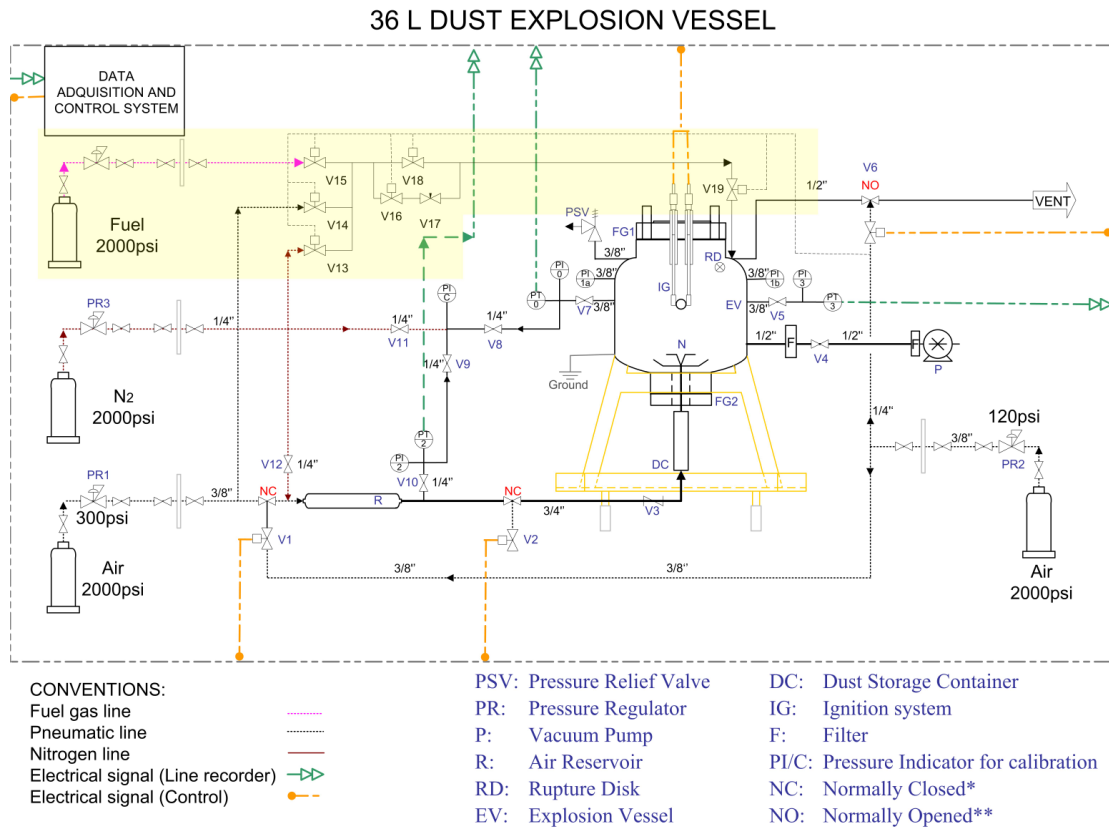


Figure 5 Diagram of 36 L dust explosion apparatus

### 3.2 The operation procedure of a normal dust explosion

For a pure dust test, after the dust sample was loaded into the dust sample container, the rebound nozzle and an ignitor(s) were installed in the chamber. The number and energy of the ignitor were determined by the experiment. Then the flange was bolted on and the chamber was partially evacuated to 10.30 psia which was calibrated by MKOPSC based on a mass balance calculation. The pressurized air in the reservoir used to sweep the dust sample into the chamber established a pressure of 14.70 psia prior to ignition of the dust.



The air reservoir was pressurized with compressed air to 314.70 psia. At the start of the test, the dust was injected by air through a rebound nozzle by opening a fast-acting valve for 50 ms. The chemical ignitor was then activated 25 ms after the valve was closed. The 50 ms time is a fixed value which determines the amount of gas entered into the chamber from the reservoir. The 25 ms delay can vary based on the needs *i.e.* study the ignition delay times effect.

### 3.3 The partial pressure method to determine the flammable gas concentration

Table 4 Set pressures for preparation of flammable gas/air mixture in the vessel

$P_2$ (psia)	$P_1$ (psia)	$P_{\text{ignition}}$ (psia)	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

For the hybrid mixture test, the partial pressure method was employed to prepare flammable-air mixtures inside the vessel before the test. The vessel was evacuated to  $P_2$ , and then pure flammable gas (*e.g.* methane, ethane, and ethylene) was fed until 10.30 psia ( $P_1$ ) was reached. The value of  $P_2$  is determined by different flammable gas concentrations to be tested and is reported in Table 4. The air from the reservoir with flammable gas in the vessel generated the initial test mixture at 14.70 psia ( $P_{\text{ignition}}$ ).

### **3.4 Modifications of the 36 L dust explosion apparatus**

The partial pressure method employed in the research is fulfilled by the newly designed gas supply system as shown in highlighted area in Figure 5. It mainly includes two feeding paths. One path is for fast feeding via V18, which is an air activated solenoid valve. Another path is for slow feeding via V16 which is also an air activated solenoid valve followed by V17 which is a needle valve. All these valves are mounted on a manifold (see Figure 6). The switches are installed to the control box.

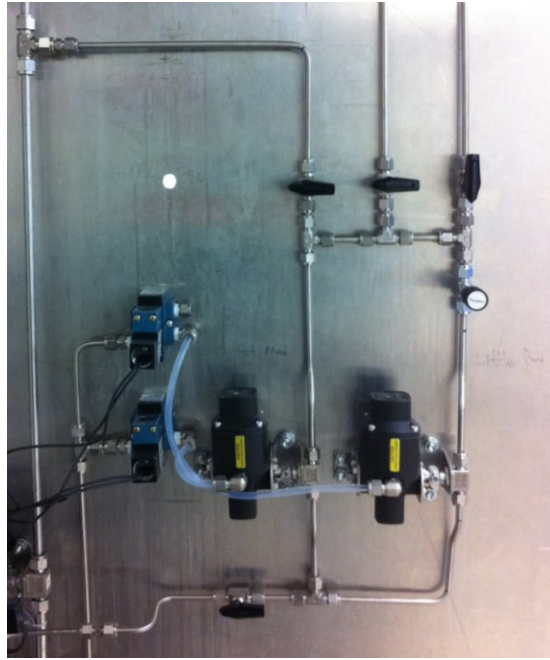


Figure 6 Gas supply system

Before feeding the flammable gas, V19 will be open in the vacuum step to evacuate the residual flammable gas in the line to eliminate the potential dead volume effect. After the vacuum procedure, at least 5 min will be held for checking if there is a leakage. This 5 min slot also to stabilize the pressure reading. During the feeding process, the fast feeding path will be used first to reach 90% of the partial pressure. The rest 10% of such pressure difference will be slowly fed through the needle valve. In some cases, if the pressure difference is very small, only the slow feeding path will be employed.

After the feeding step is done, V19 will be close. Then at least 5 min will be hold for the system to be stable. Once the pressure in the vessel is stable, the dust explosion

procedure will be followed. It is assumed in our research that the dust cloud will be mixed very well with the flammable gas in the vessel.

### 3.5 Typical pressure-time profile

A typical pressure-time profile in an explosion test is shown in Figure 7, where  $(dP/dt)_{ex}$ ,  $P_{ex}$  is obtained for a specific concentration of pure dust or pure gas or a combination of both.  $(dP/dt)_{ex}$  is multiplied by the cubic root of the vessel volume to obtain  $(dP/dt)_{ex}V^{1/3}$ .  $P_{max}$  is the maximum value of  $P_{ex}$ .  $K_{St}$  and  $K_G$  are the maximum values of  $(dP/dt)_{ex}V^{1/3}$  at varying dust or gas concentrations.

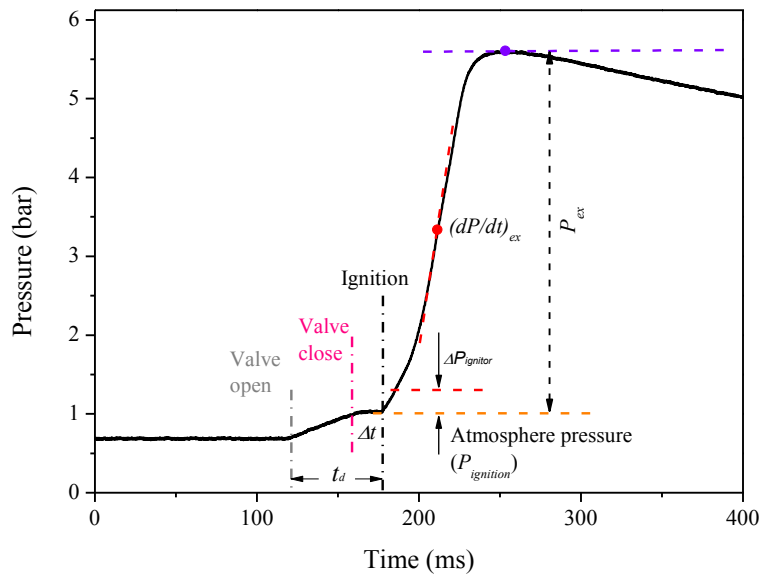


Figure 7 A typical pressure-time profile during one explosion test

### 3.6 Criteria to determine the explosion and non-explosion

In this research, chemical ignitors were used as the ignition source. It can generate a certain amount of pressure rise in the chamber. In some tests, if a low  $dP/dt$  is obtained, a weak deflagration may have occurred. Under these conditions, it is important that the  $dP/dt$  measurement is not taken from the chemical ignitor but from the dust or hybrid mixtures. In order for a test to be considered a deflagration, and differentiate a test from the ignitor explosion, criteria must be set.

Generally, there are two criteria to determine whether deflagration occurred or not in the chamber. One criterion is the pressure ratio which is defined as  $(P_{ex,a} - \Delta P_{ignitor})/P_{ignition}$  [48].  $P_{ex,a}$  is the maximum absolute pressure obtained from the pressure-time curve (Figure 7). If PR is no less than 2, the test will be defined as an explosion. Otherwise, no explosion occurred inside. Another criterion is dependent on the pressure rise  $(P_{ex,a} - P_{ignition} - \Delta P_{ignitor})$ : if such value no less than 1 bar, the test will be considered deflagration. In this research, we use the first criteria to analysis the test.

### 3.7 How to change the turbulence by controlling the ignition delay time

In this research, the dust cloud is generated by means of pneumatic dust dispersion system. Therefore, some degree of turbulence is generated in dust cloud before ignition. This type of turbulence is a type of pre-ignition turbulence. Although the magnitude of such turbulence is not quantified in this research, the level of turbulence is associated with the ignition delay time. The ignition delay time ( $t_d$ ) is defined as the time interval

between the initiation of the dust dispersion procedure and the activation of the ignition source (see Figure 7). The ignition delay time can be separated into two intervals in this research. The first interval is from the time the dispersion air starts to enter the chamber to the time at which such dispersion stops. The amount of air added into the chamber is controlled by this time interval. The second interval ( $\Delta t$ ) is from the time at the end of air dispersion to the activation of the ignitor. The ignitor was triggered at different ignition delay times, usually by varying the second time interval ( $\Delta t$ ). This enabled tests to be carried out at different turbulence levels.

### **3.8 MEC test method**

The MEC test follows ASTM E1515 standard. For each sample, an initial concentration of  $100 \text{ g/m}^3$  is tested first. If the initial concentration produces a deflagration, decrease the concentration until no deflagration occurs. If the initial concentration does not produce a deflagration, increase the concentration in steps of  $10 \text{ g/m}^3$  until a deflagration is obtained. Plot the explosibility data from individual tests versus dust concentration as shown in Figure 8.

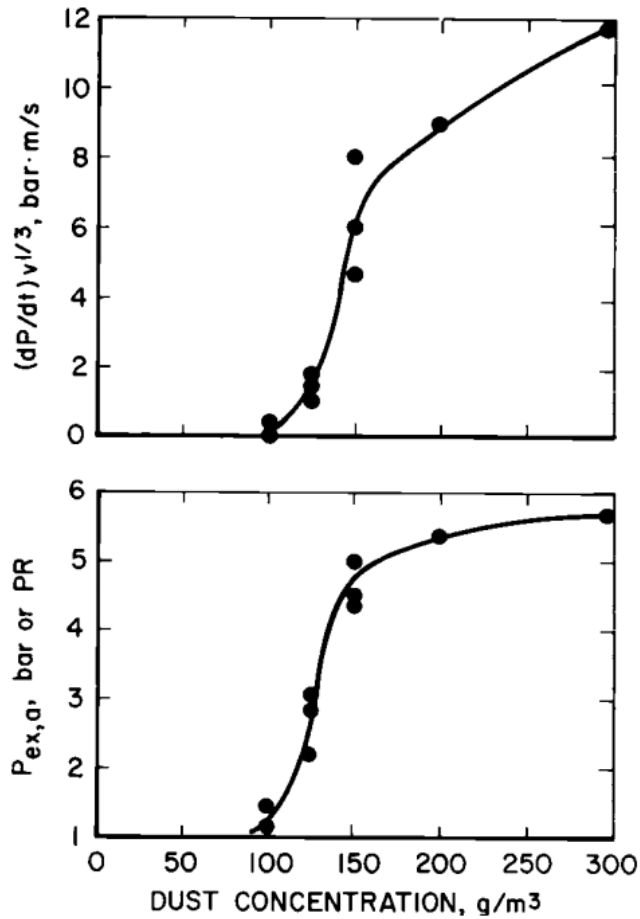


Figure 8 Explosibility test data as a function of concentration for a typical dust[48]

In Figure 8, the minimum explosible concentration is defined as the lowest concentration for PR value no less than 2. The MEC is usually rounded to the nearest 5 g/m<sup>3</sup> or 10%, whichever is larger. Another point is that, for the final determination of the MEC, the concentration increments should be no greater than 25% of the MEC. It is necessary that at least two tests be made at each concentration near the MEC.

## CHAPTER IV

### A CORRELATION OF THE LOWER FLAMMABILITY LIMIT\*

This chapter focused on the developing of the correlation of LFL for a hybrid mixture. In this chapter, results from testes of pure gas including methane, ethane and ethylene were analyzed regarding the LFL verification of such gases, the explosion test following the dust explosion procedure, as well as the turbulence effect on gas explosion. For pure dust explosion, niacin and cornstarch were tested following the ASTM E1226 and ASTM E1515 to derive their deflagration index ( $K_{St}$ ) and  $P_{max}$  as well as MEC. Then the hybrid mixture which is a combination of one type of dust and one type of gas was tested to find the lower flammability limit. For all critical tests in this chapter, they were repeated at least three times. A critical test means the test is near (below and above) the lower flammability limit. The ignitor used in these tests is a single one with 2.5 kJ. The ignition delay time is 75 ms in most tests except for some in the turbulence effect on the gas explosion study.

These data together with other data from the literature were then fitted into a correlation to predict the explosion and non-explosion zone of such hybrid mixtures. The explosion and non-explosion zone predicted by proposed formula were also compared with results from Le Chatelier's Law and the Bartknecht curve. The uncertainty of the proposed formula was also discussed in this chapter.

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\* Part of this chapter is reprinted from "A correlation of the lower flammability limit for hybrid mixtures" by Jiang, J., Liu, Y., & Mannan, M. S. (2014). *Journal of Loss Prevention in the Process Industries*, 32, 120-126, with permission from Elsevier



#### 4.1 Flammable gas explosion

The explosibility of methane, ethane and ethylene has been widely studied and reported in literature [5, 49, 50]. In these experiments, they are tested under quiescent status. However, the turbulence which plays an important role in the hybrid mixtures explosion usually results in a different gas explosion behavior.

In order to compare the pure fuel explosion behavior with the hybrid mixtures behavior, each flammable gas explosion is conducted under the same conditions as the dust runs: flammable gas injection followed by a generation of turbulence inside the vessel before ignition.

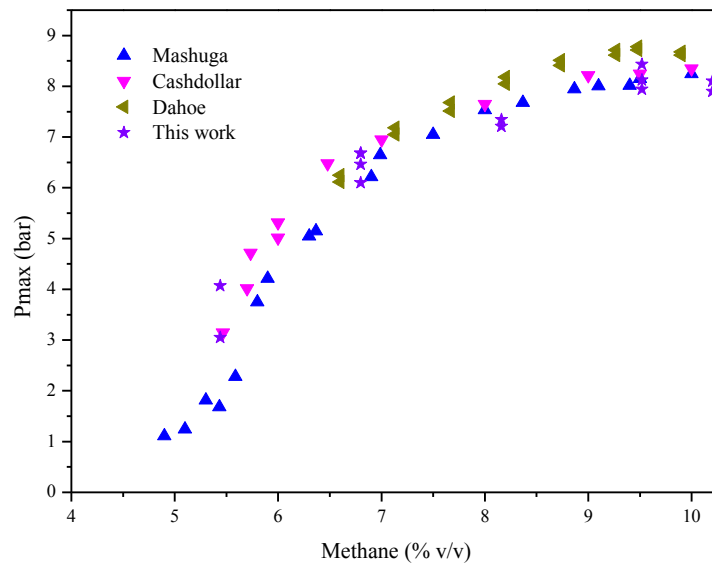


Figure 9  $P_{max}$  as a function of methane concentration from experiments and literature data

The  $P_{\max}$  and  $K_G$  of methane/air in a 36 L apparatus and published results from experiments performed in a 20 L apparatus are reported in Figure 9 and Figure 10 respectively. The  $P_{\max}$  of methane generally increases as the concentration increases from 5.44% v/v to 9.52 % v/v then it drops a little, this is because of the amount of oxygen in the chamber. At a low gas concentration, the oxygen is rich enough for all the gas to burn out, thus the maximum pressure is proportional to the gas concentration. Once the gas amount is beyond the supply of oxygen in the chamber, partial combustion will occur, the maximum pressure will no longer increase even decrease. The  $P_{\max}$  of methane is 7.9 bar in a 36 L vessel, and it agrees well with the result obtained from the 20 L vessel. The  $K_G$  of methane has been found as 290 bar-m/s when the concentration is 9.52% v/v in this work.

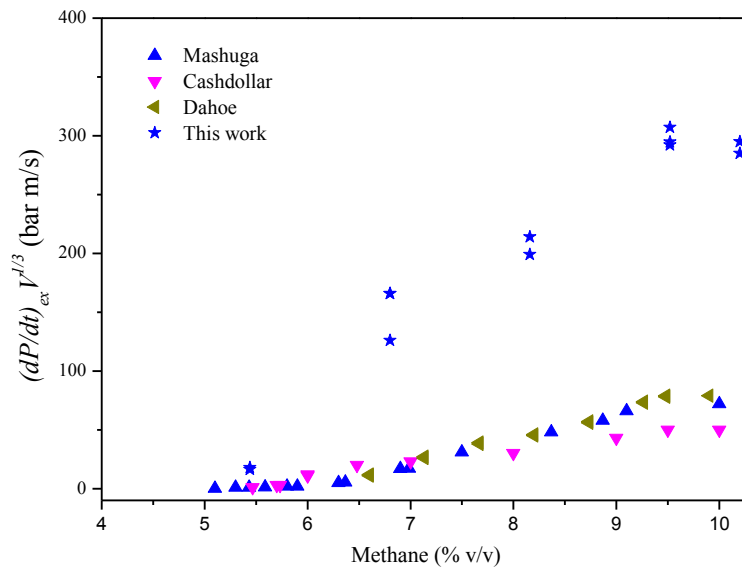


Figure 10  $K_G$  as a function of methane concentration from experiments and literature data

Similarly, the  $K_G$  of ethane and ethylene has been found as 360 bar·m/s and 400 bar·m/s respectively in a turbulence environment (see Figure 11 and Figure 12). These  $K_G$  values are significantly higher than the results from the literature in a quiescent status [50-52]. This phenomenon is caused by the turbulence inside the vessel mostly determined by the ignition delay time.

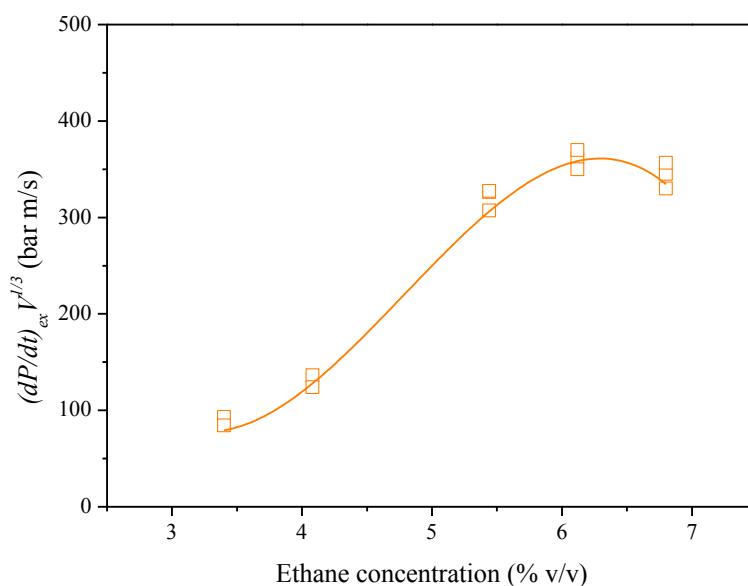


Figure 11  $(dP/dt)_{ex} V^{1/3}$  of ethane explosion as function of concentration

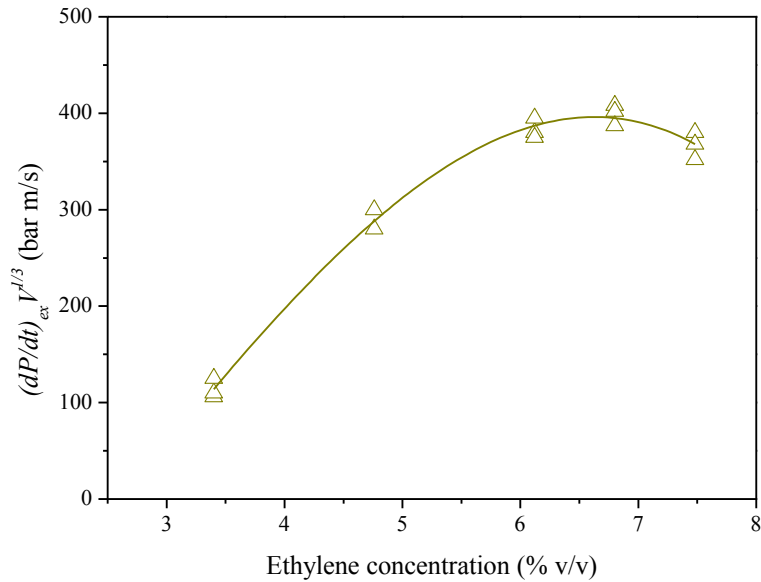


Figure 12  $(dP/dt)_{ex} V^{1/3}$  of ethylene explosion as function of concentration

Figure 13 shows the results of  $(dP/dt)_{ex} V^{1/3}$  of methane along with different ignition delay times. The  $(dP/dt)_{ex} V^{1/3}$  dramatically decreases from 290 bar·m/s to 120 bar·m/s when the ignition delay time extends from 75 ms to 300 ms. It then drops to 70 bar·m/s as the ignition delay time reaches 1000 ms. Similar trends have also been found by Garcia-Agreda, *et al.* [8]. Values of  $(dP/dt)_{ex} V^{1/3}$  in this work are higher than those from their work because of the methane concentration in this work (9.52% v/v) is higher than that in their work (8.60% v/v).

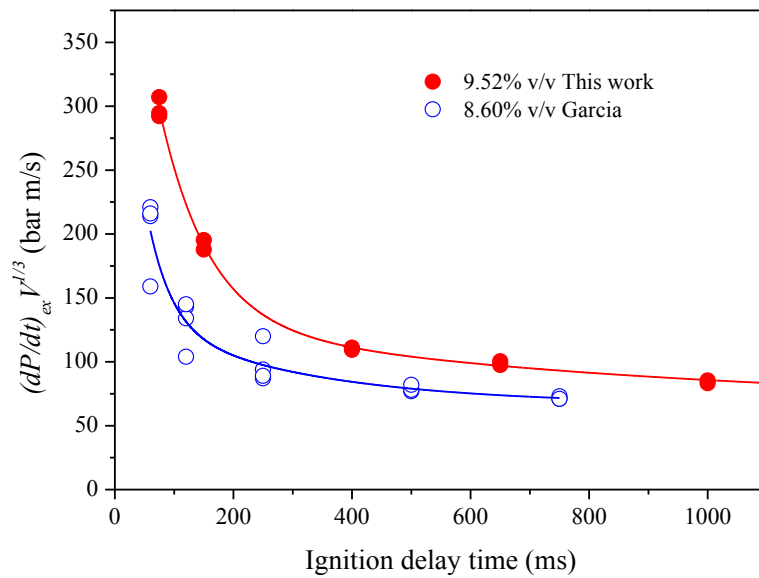


Figure 13  $(dP/dt)_{ex} V_{ex}^{1/3}$  of methane explosion differed with the ignition delay time

The lower flammability limit of methane, ethane and ethylene given 75 ms ignition delay time has been verified. In Figure 9, only the GO tests are plotted. For example, 4.08% v/v, 5.44% v/v and higher concentrations of methane are tested. 5.44% v/v of methane or above is a GO test while 4.08% v/v of methane is a NO-GO test. This means the LFL of methane will be within 4.08% v/v and 5.44% v/v. The turbulence effect on LFL of methane was also studied by Cashdollar, *et al.* [51]. They tested the LFL of methane in quiescent and turbulence conditions. They concluded that the LFL of methane shows very close agreement, regardless of the turbulence. In all cases, the LFL for methane in air is close to 5.0% v/v. Neglecting the turbulence effect, the lower

flammable limit for methane, ethane and ethylene used in this work is 5.0% v/v, 3.0% v/v and 2.7% v/v respectively cited from the literature [53].

## 4.2 Dust explosion

Cornstarch and niacin are organic compounds and have been widely studied. In our experiments, the explosion and the MEC tests have been done following ASTM E1226 and ASTM E1515 standard. The maximum pressures of cornstarch explosion at different dust concentrations are plotted in Figure 14. Data found from the literature are also plotted in the same figure for comparison. Clear, the maximum pressure will increase along increasing the dust concentration, then will keep constant even decrease a little once the concentration reaches to  $750 \text{ g/m}^3$ . This is because of the fixed amount of oxygen in the closed vessel. The similar trend can also be found in Figure 15 which represents  $(dP/dt)_{ex} \cdot V^{1/3}$  of cornstarch explosion. The  $P_{max}$  is 7.9 bar, and the  $K_{St}$  is 175 bar·m/s for cornstarch. Figure 16 summarizes the MEC tests of cornstarch. Based on pressure ratio criteria, the MEC of cornstarch is found at  $100 \text{ g/m}^3$ .

Similarly, the experiments associated with niacin are plotted in Figure 17, Figure 18 and Figure 19. The  $P_{max}$  is 8.2 bar, and the  $K_{St}$  is 160 bar·m/s of niacin. The MEC of niacin is  $75 \text{ g/m}^3$ .

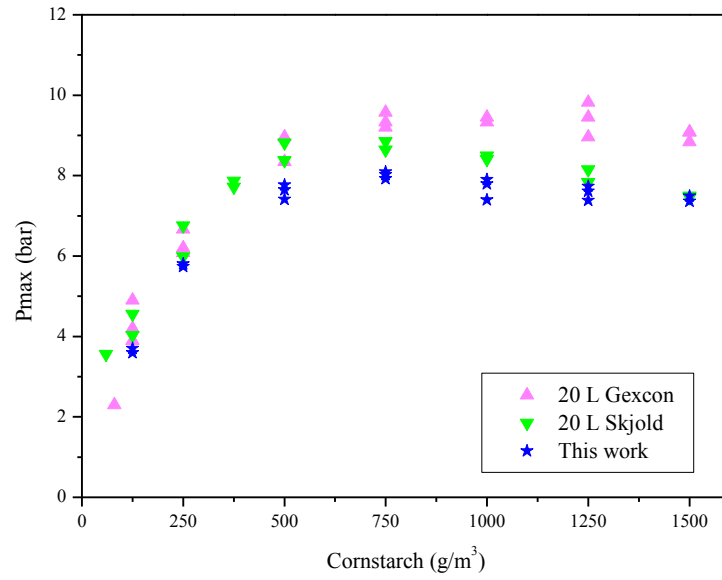


Figure 14  $P_{max}$  of cornstarch explosion

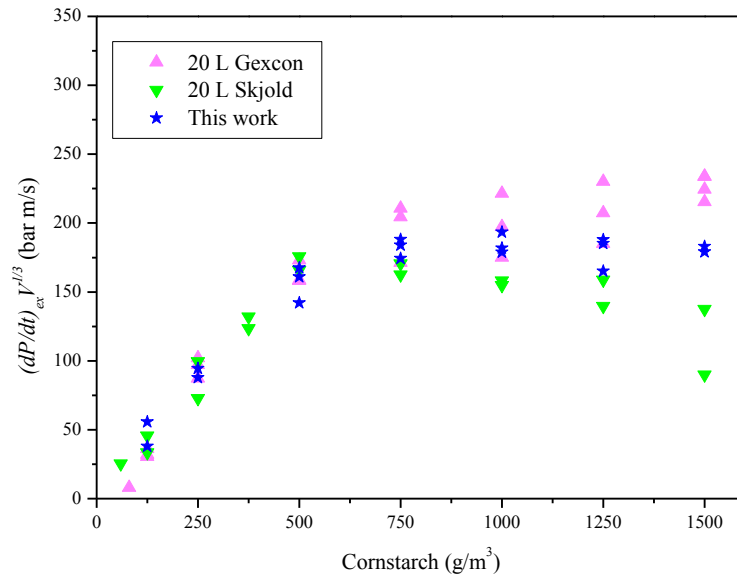


Figure 15  $(dP/dt)_{ex} \cdot V^{1/3}$  of cornstarch explosion

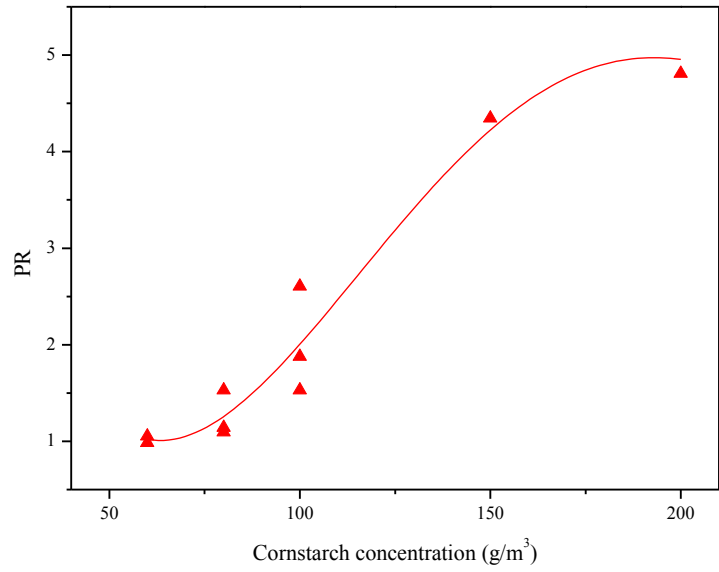


Figure 16 MEC test of cornstarch

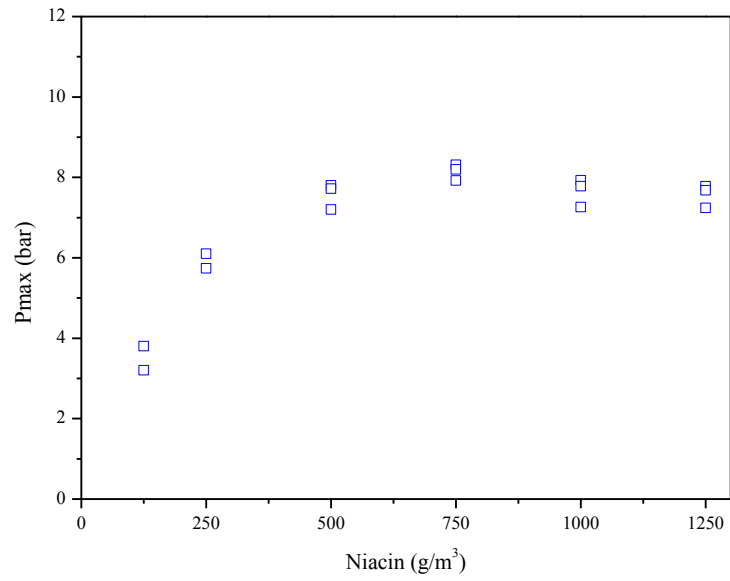


Figure 17  $P_{\max}$  of niacin explosion



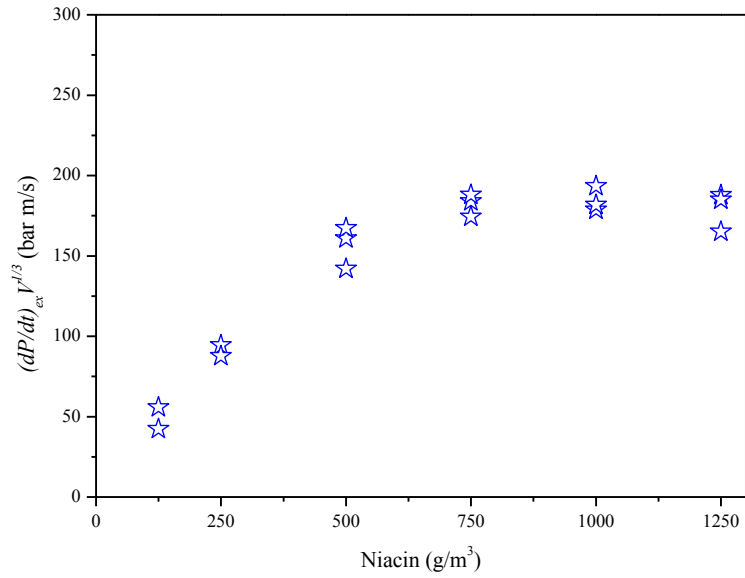


Figure 18  $(dP/dt)_{ex} \cdot V^{1/3}$  of niacin explosion

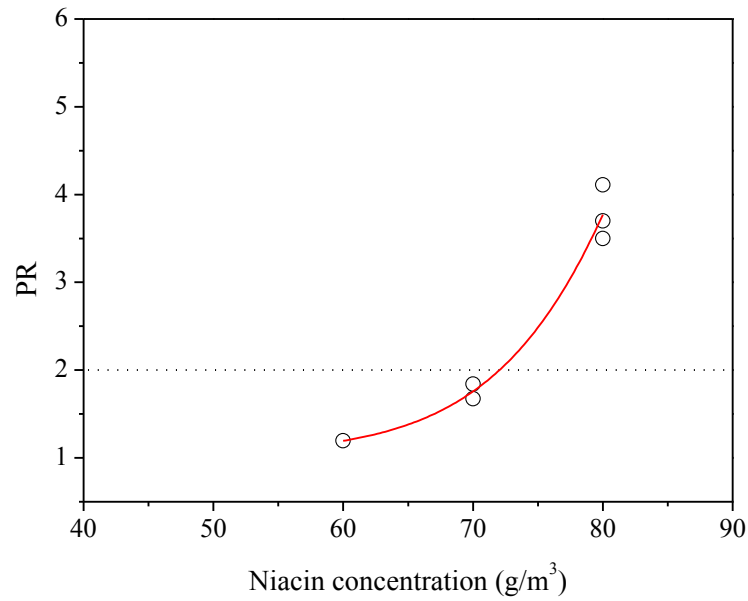


Figure 19 MEC test of niacin

### 4.3 Hybrid mixtures explosion

In order to rationalize all the data, a map of the explosion behavior of the methane/cornstarch mixtures has been developed as shown in Figure 20. The x-axis is the dust concentration ( $c/MEC$ ), and the y-axis is the methane content ( $y/LFL$ ) respectively. In the figure, the deflagration indexes are represented by circles in which diameter is proportional to the value of  $K_{St}$ .

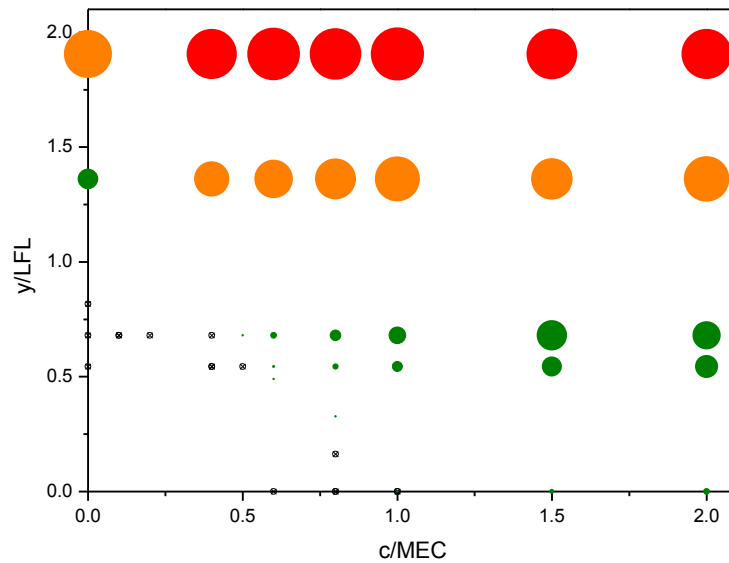


Figure 20  $K_{St}$  in the plane methane content/cornstarch concentration

The hazard of the dust deflagration is divided into three classes by NFPA 68. Red circles refer to a  $K_{St}$  value higher than 300, which is located in class St-3. Yellow circles are in the range of 200 to 300 and are located in class St-2. Green circles are less than

200 and are in class St-1. The empty circles represent experiments where no explosion occurred. Compared to the pure dust in class St-1, the cornstarch can easily be transferred into St-2 and St-3 by adding methane. The effects of the gas cannot be neglected, and the result shows that the hybrid mixture is much more dangerous than pure gas or dust.

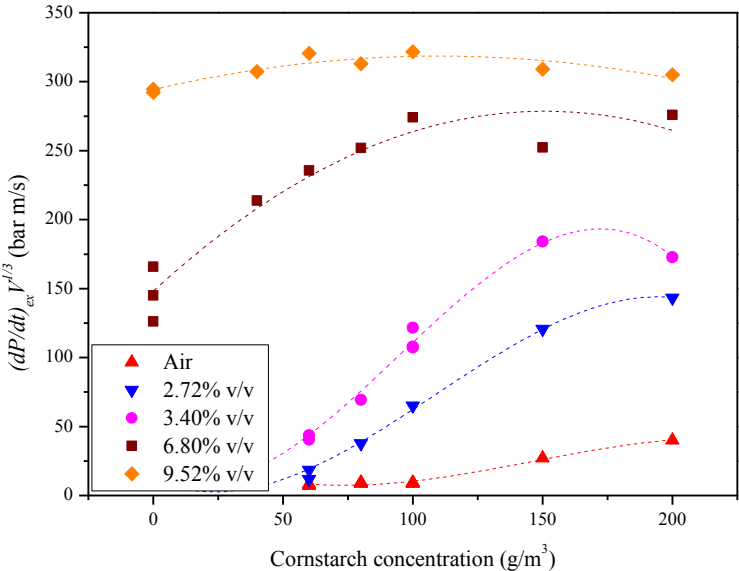


Figure 21  $K_{St}$  as a function of cornstarch concentration at different values of the methane concentration

Figure 21 represents in detail the  $K_{St}$  values for the cornstarch/methane mixtures. When the methane concentration is lower than its LFL (2.72% v/v and 3.40% v/v), the  $K_{St}$  values dramatically increase with the increase of cornstarch content. When methane concentration is equal to 6.80% v/v, the  $K_{St}$  will increase to 270 bar-m/s as dust

concentration increased to  $100 \text{ g/m}^3$ . Then it appears to remain steady or even decrease as dust content increases. When the methane concentration is increased to 9.52% v/v, the  $K_{St}$  appears to be nearly independent of the dust content. Similarly, at cornstarch concentrations below the MEC ( $100 \text{ g/m}^3$ ), it is not able to be ignited, but it could be easily ignited along with methane. The presence of methane has a significant influence on the deflagration index ( $K_{St}$ ).

At a dust concentration above MEC, the deflagration index will increase with the presence of methane, but the impact of methane will be less. Particularly, at a cornstarch concentration equal to MEC, the  $K_{St}$  increases from 10 to 340 bar·m/s when the methane content increases from 0 to 9.52% v/v.

These phenomena are also found in other systems such as niacin/methane systems as reported by Garcia [9], and cork/methane systems as reported by Pilão [17]. They can be explained by the oxygen competition between the gas and dust during the explosion. For high dust concentrations, the deflagration index is imposed by the oxygen content and the increase of gas content also has little impact on the deflagration index due to the same reason.

Since the scope of this work is to develop a correlation to predict the explosion and non-explosion boundary for hybrid mixtures, the following part will only focus on the left bottom area of Figure 20 where both the gas and dust concentration are less than their LFL or MEC, respectively.

Explosion behavior of studied hybrid mixtures has been developed as shown in Figure 22 - Figure 25. The x-axis is dimensionless dust concentration ( $c/\text{MEC}$ ), and the y-axis is dimensionless flammable gas content ( $y/\text{LFL}$ ). The solid markers represent explosions where pressure ratio (PR) is larger than 2 while the empty ones stand for no explosions, where PR is less than 2. From these explosion tests, it has been confirmed that the hybrid mixtures can be explosive with dust and gas concentration less than each MEC or LFL.

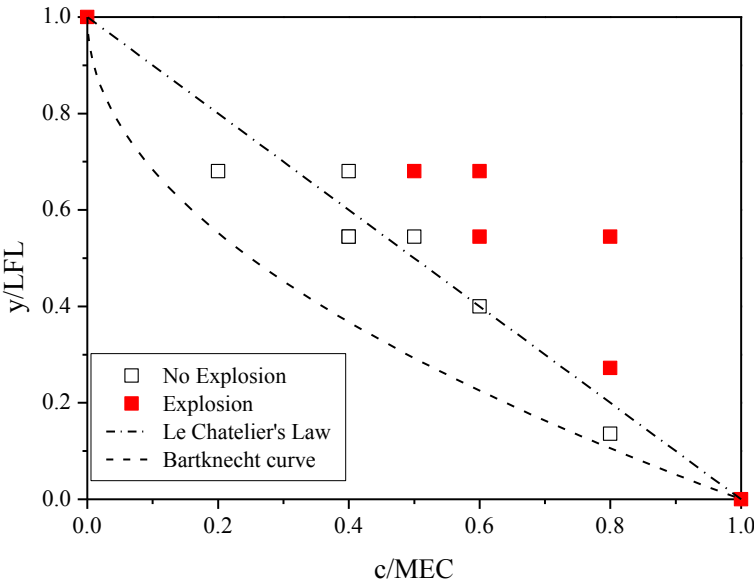


Figure 22 Explosion tests for methane/cornstarch

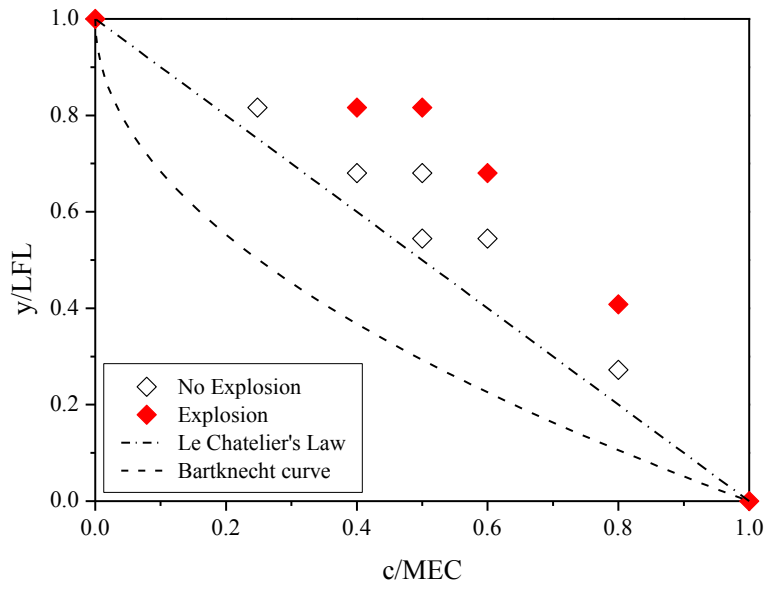


Figure 23 Explosion tests for methane/niacin

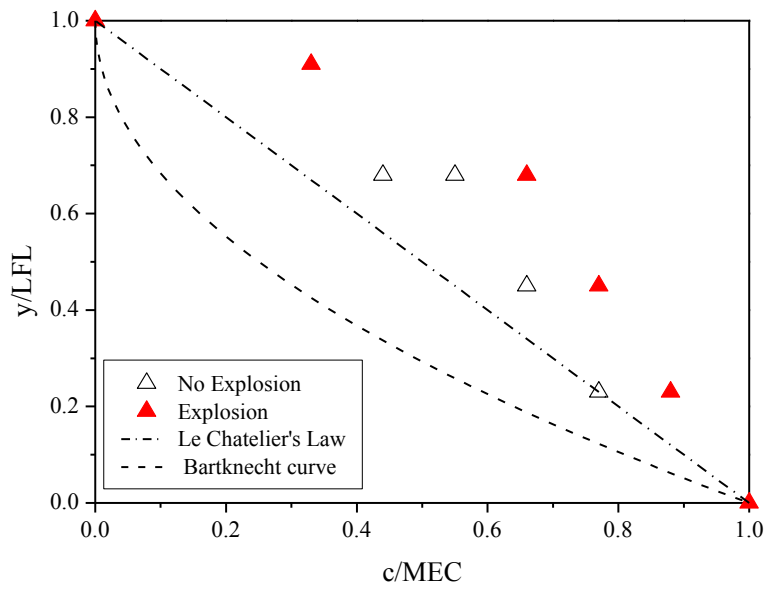


Figure 24 Explosion tests for ethane/niacin

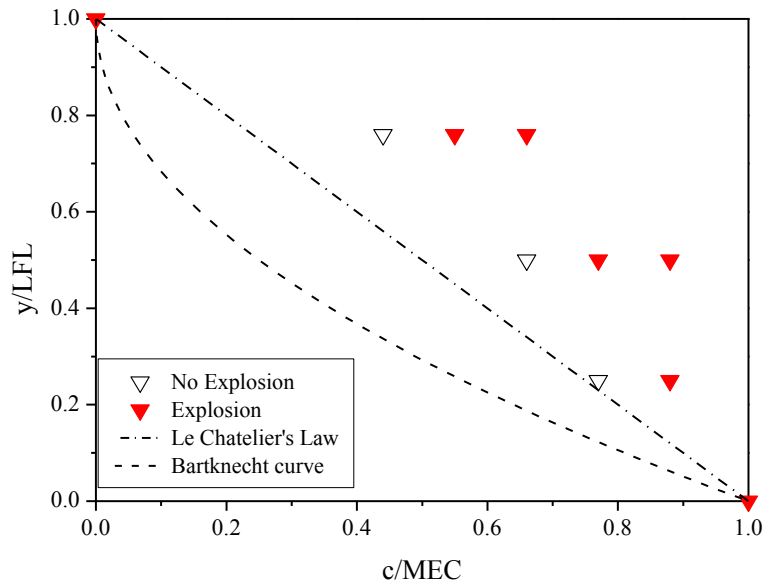


Figure 25 Explosion tests for ethylene/niacin

In the same figure, both Le Chatelier's Law and the Bartknecht curve are plotted. These curves delimit the explosive region versus the non-explosive region. It is clear that neither of them can be applied to the studied hybrid mixtures. For example, in Figure 23, 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. Le Chatelier's Law derives from the well-known concept of limit flame temperature for gas mixtures. If the flame temperatures for the dust and gas are of comparable magnitude,

there is not a significant change in the flame temperature or in the combustion propagation velocity when the system goes from gas mixtures to hybrid mixtures [1]. The results obtained with studied systems may be because the limit flame temperature of the studied hybrid mixtures is higher than the linearly weighted averages of the lean limits for pure dust and pure gas. This means more gas or dust is needed to render the system flammable, as predicted by either Le Chatelier's Law or the Bartknecht curve.

Not only have the studied system in this work, but also data of other hybrid systems from literature found similar fact. Figure 26 and Figure 27 also summarized results on niacin and acetone mixtures in a 20 L vessel tested by Sanchirico, *et al.* [39]. In their test experiment, a pure acetone explosion was tested in the same condition as a niacin explosion test. They also performed the lower flammability limit test for acetone/niacin hybrid mixtures. The difference between the test in Figure 26 and Figure 27 was the ignition delay time, 30 ms for Figure 26 and 60 ms for Figure 27, respectively.



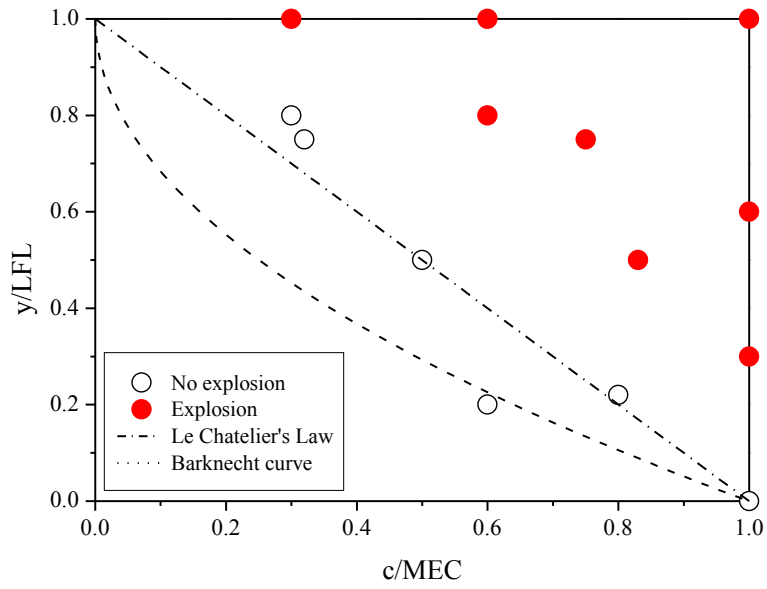


Figure 26 Explosion tests for acetone/niacin (ignition delay times = 30 ms)

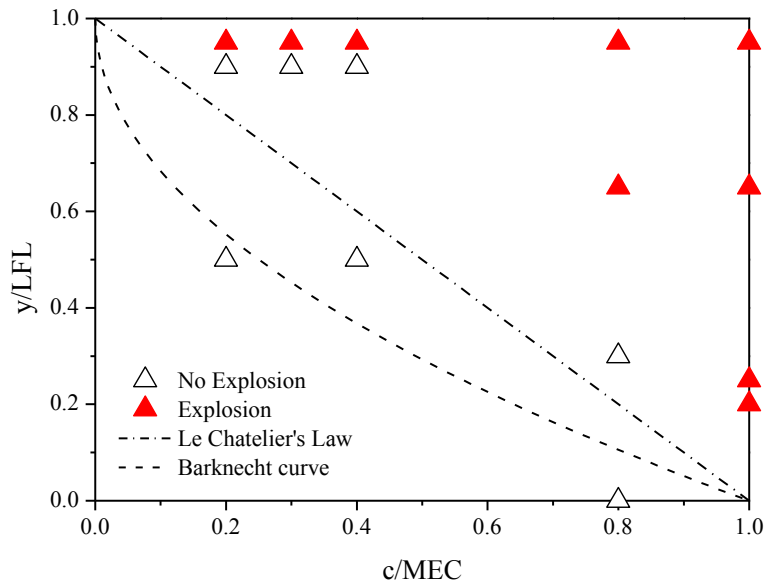


Figure 27 Explosion tests for acetone/niacin (ignition delay times = 60 ms)

#### **4.4 Effect of different hydrocarbon-air mixtures on dust MEC**

From the experiments above, with regards to the MEC of dust, it is dramatically decreased in the presence of flammable gas which has also been found by several other researchers in different hybrid mixtures such as coal/methane, niacin/methane, cork/methane, and cornstarch/methane. However, the effect of adding flammable gas on decreasing the dust MEC is still not well studied. It is not only because the research on hybrid mixtures is so limited that the data can be rarely found in literature, but also because this limited research generally focused only on one kind of hybrid mixture. Most of the gas is methane, which is the simplest hydrocarbon with a single atom and saturated bond. The explosion characteristics for different hydrocarbons on the same dust mixture are still lacking. Based on the experiments which have been conducted in this work, this section will summarize the MEC test of niacin in the presence of different hydrocarbons including methane, ethane, and ethylene to discuss the flammable gas effects on dust MEC. The dust is niacin, and the flammable gases discussed in this section include methane, ethane, and ethylene. For each gas, two different concentrations are tested at 1.4% v/v and 2.0% v/v.

The calculated PR values of the experiment with methane, ethane, and ethylene are represented in Figure 28, Figure 29, and Figure 30, respectively. Results with air are also included in each figure for comparison. The straight dash line crossing the y-axis at 2 in each figure represents the criteria for determining MEC. The MEC is the average value

of two dust concentrations nearest the PR criteria (e.g. 2.0% v/v methane, MEC =  $(50+60)/2 = 55 \text{ g/m}^3$ ).

As shown in Figure 28, the MEC of niacin in the air is  $75 \text{ g/m}^3$ . This value agrees well with the result reported by other researchers [8]. The MEC of niacin decreases to  $62 \text{ g/m}^3$  when adding 1.4% v/v methane into the system. This also confirms that an explosion can occur when both combustible dust and flammable gas concentrations are lower than their MEC and LFL, respectively. The MEC of niacin decreases to  $55 \text{ g/m}^3$  by continuing to add methane up to 2% v/v. It is reasonable to conclude that with adding more methane in, the MEC of niacin will continue decreasing. When methane concentration reaches its LFL, the explosion for the mixture will occur no matter if niacin exists or not. The same trend can also be found in ethane/niacin and ethylene/niacin systems as shown in Figure 29 and Figure 30, respectively.

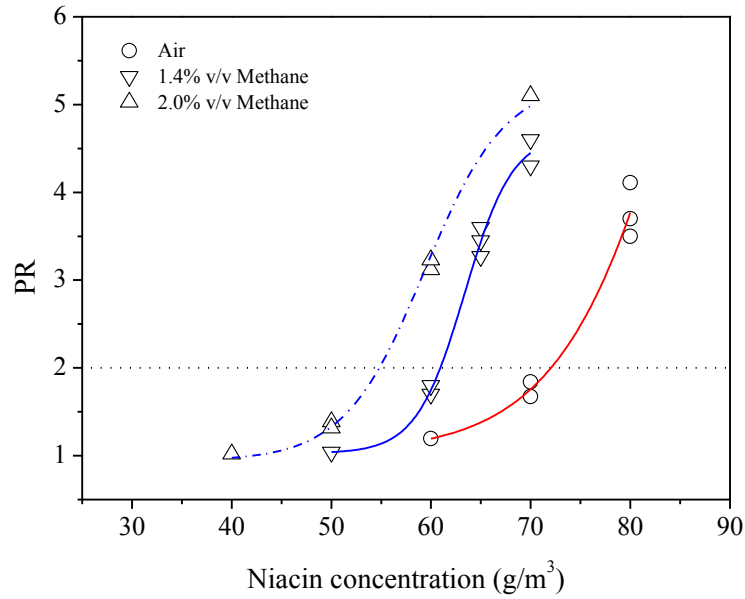


Figure 28 Pressure ratios in niacin MEC test with methane at 1.4% v/v and 2.0% v/v

It can also be found that the pressure ratio does not vary too much at the same dust concentration or at the same gas concentration when it is lower than 2. For example, in Figure 29, the PR with ethane at 1.4% v/v is similar to 2.0% v/v when dust concentration is at 40 g/m<sup>3</sup>; in Figure 30, the PR with ethylene at 1.4% v/v does not change too much when dust concentration increases from 40 g/m<sup>3</sup> to 50 g/m<sup>3</sup>. This phenomenon may be due to no explosion occurring in the vessel. The  $P_{\max}$  used in calculation PR is mostly affected by the explosion of the 2500 J chemical ignitor.

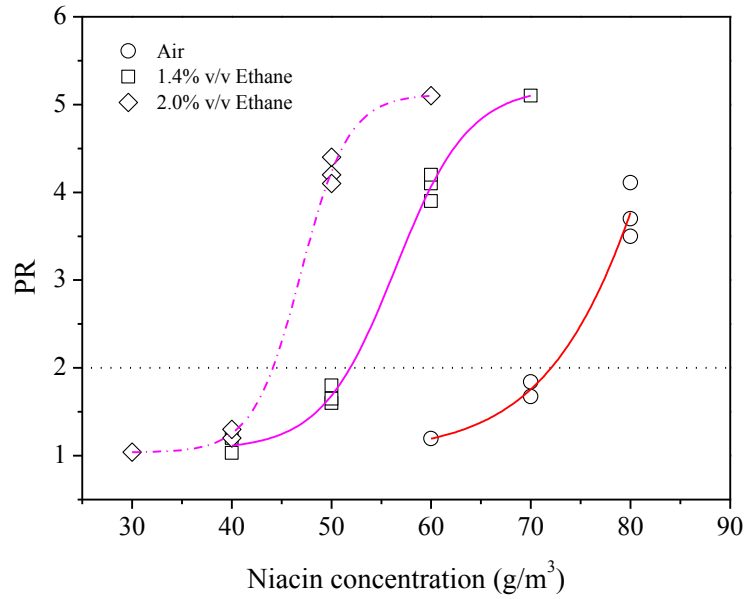


Figure 29 Pressure ratios in niacin MEC test with ethane at 1.4% v/v and 2.0% v/v

When the PR is greater than 2, which indicates an explosion happening, the PR value increases as flammable gas is added at the same dust concentration. For example, in Figure 29, the PR with ethane at 2.0% v/v is much higher than 1.4% v/v when the dust concentration is 60 g/m<sup>3</sup>. This is because more flammable gas involved in the reaction of combustion generates more gas product and heat. The gas product and heat heavily affect the  $P_{\max}$ .

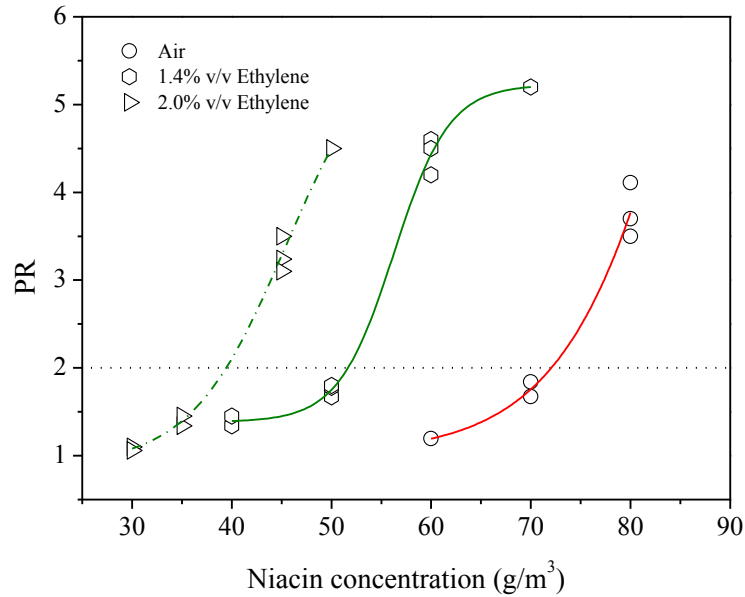


Figure 30 Pressure ratios in niacin MEC test with ethylene at 1.4% v/v and 2.0% v/v

Pressure ratios were plotted in Figure 31 and Figure 32 at concentration 1.4% v/v and 2.0% v/v respectively in order to compare the effect of different gases to the MEC of niacin. As shown in Figure 31, the MEC of niacin in ethane and ethylene is much lower than it is in the same concentration of methane. But the MEC values in the same concentration of ethane and ethylene are close to each other. Similar trends can also be found in Figure 32 where all the flammable gases are at 2.0% v/v. This may be because of the LFL differences between them. As summarized in Table 5, methane's LFL is 5% v/v as reported by Zabetakis [53]. It is higher than the LFL of ethane and ethylene while the latter two gases have similar ones.

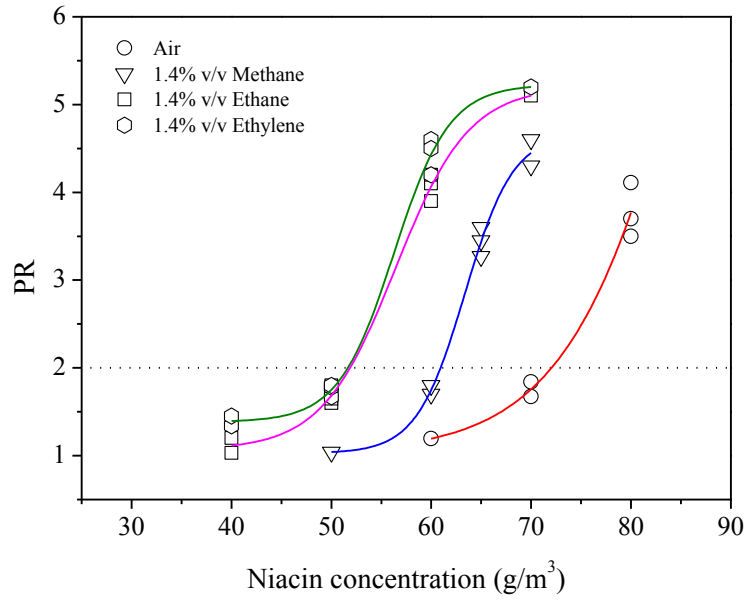


Figure 31 Pressure ratios in niacin MEC test with methane, ethane, and ethylene at 1.4% v/v

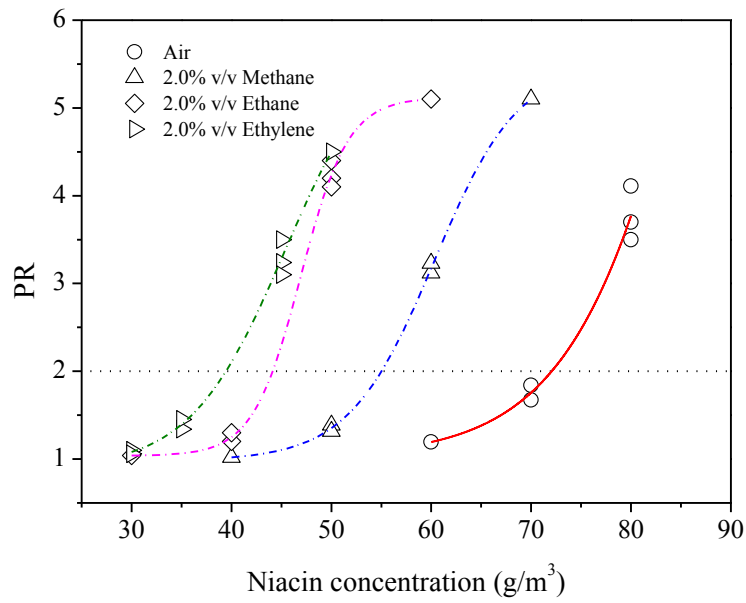


Figure 32 Pressure ratios in niacin MEC test with methane, ethane, and ethylene at 2.0% v/v

The pressure ratios with ethane and ethylene are close to each other but much higher than with methane when an explosion occurs at the same dust concentration. For example, the pressure ratios with ethane and ethylene are 5.2 and 5.1 while it is averaged at 4.5 with methane when niacin concentration equals to  $70 \text{ g/m}^3$  in Figure 31. Similar trends can be found in Figure 32 where experiments have been done at dust concentrations located at  $50 \text{ g/m}^3$  or  $60 \text{ g/m}^3$ . The pressure ratio is mainly controlled by the  $P_{\max}$ . Under the condition of experiments done in this part, it is assumed that both niacin and flammable gas will burn out if an explosion occurs.

Table 5 LFL, heat of combustion of methane, ethane, and ethylene

Name	LFL(% v/v)	Heat of Combustion (Kcal/mole)
Methane	5.0	191.8
Ethane	3.0	341.3
Ethylene	2.7	316.2

The maximum pressure is affected by two factors. The first factor is the moles of gas change before and after the explosion. For methane and ethylene, the mole of gas keeps constant, while, for the ethane, it decreases a little. The second factor is the heat



generated in the explosion. Ethane and ethylene have a similar heat of combustion which is much higher than methane's as indicated in Table 5. Compared with the moles of gas change, heat is the control factor for  $P_{\max}$  of these three gases. Thus, ethane and ethylene have a similar pressure ratio which is higher than methane's.

#### 4.5 Correlations

In order to develop a more accurate formula which can improve the prediction, Le Chatelier's Law and the Bartknecht curve are reformatted into Eq. 9 and Eq. 10.

$$\ln \frac{c}{\text{MEC}} = \ln \left( 1 - \frac{y}{\text{LFL}} \right) \quad \text{Eq. (9)}$$

$$\ln \frac{c}{\text{MEC}} = 2 \times \ln \left( 1 - \frac{y}{\text{LFL}} \right) \quad \text{Eq. (10)}$$

This is the case assuming the result of this work keep the same format as following:

$$\ln \frac{c}{\text{MEC}} = C \times \ln \left( 1 - \frac{y}{\text{LFL}} \right) \quad \text{Eq. (11)}$$

The explosion and non-explosion points in Figure 33 - Figure 38 are obtained by plotting the absolute values of corresponding ones transformed from Figure 22 - Figure 27 using Eq. 11. The point ( $c/\text{MEC} = 0$ ,  $y/\text{LFL} = 1$ ) is excluded because it cannot be plotted in logarithmic coordinates. Both Le Chatelier's Law and the Bartknecht curve are also plotted as straight lines in Figure 33 - Figure 38, but again neither of them can be used to distinguish the explosion and non-explosion zone in the studied hybrid mixtures.

However, such zones can be separated by another line in Figure 33 - Figure 38. To determine the slope of this line, only explosion and non-explosion data near the boundary are employed for linear regression. For example, in Figure 33, eight points were used for the regression, while two higher points (points A and B) and two lower points (points C and D) are considered outliers. This similar approach is applied to the other three samples as showed in Figure 34 - Figure 38.

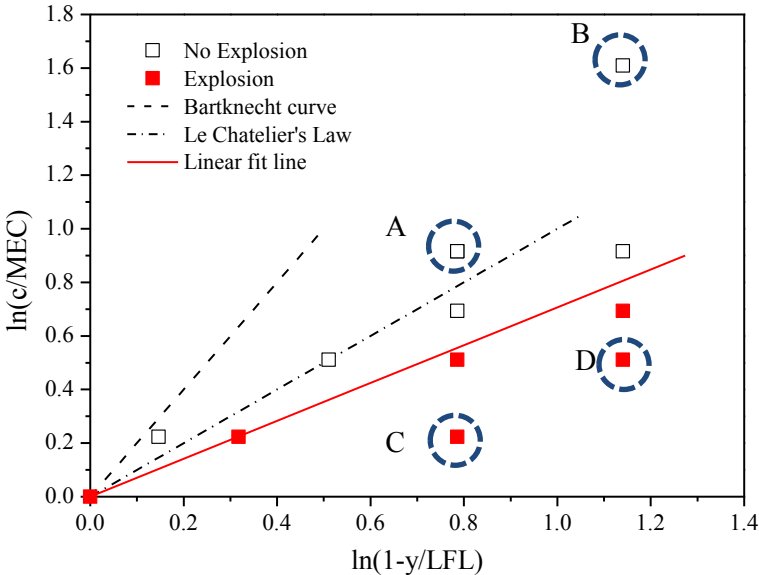


Figure 33 Experiment data on hybrid mixtures plotted in logarithmic coordinate: methane/cornstarch

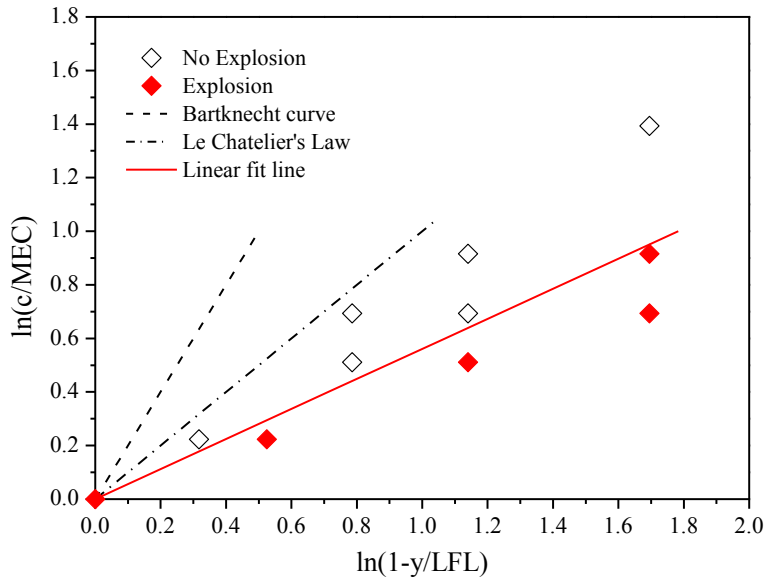


Figure 34 Experiment data on hybrid mixtures plotted in logarithmic coordinates: methane/niacin

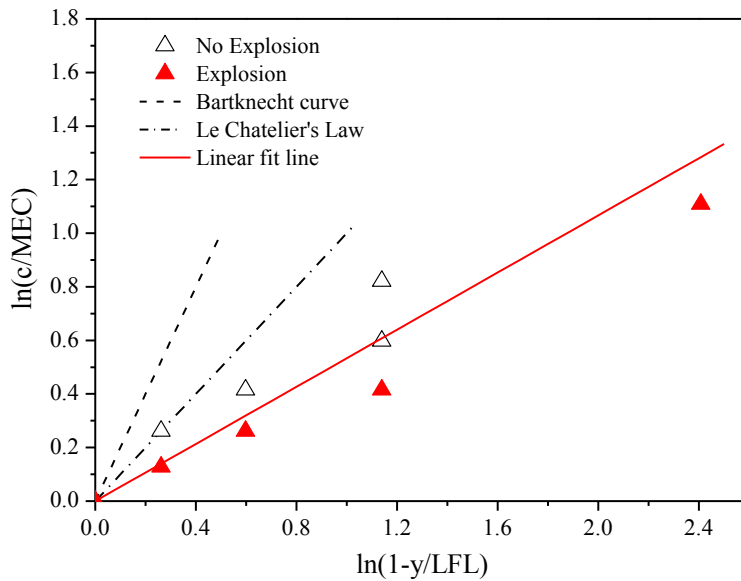


Figure 35 Experiment data on hybrid mixtures plotted in logarithmic coordinates: ethane/niacin

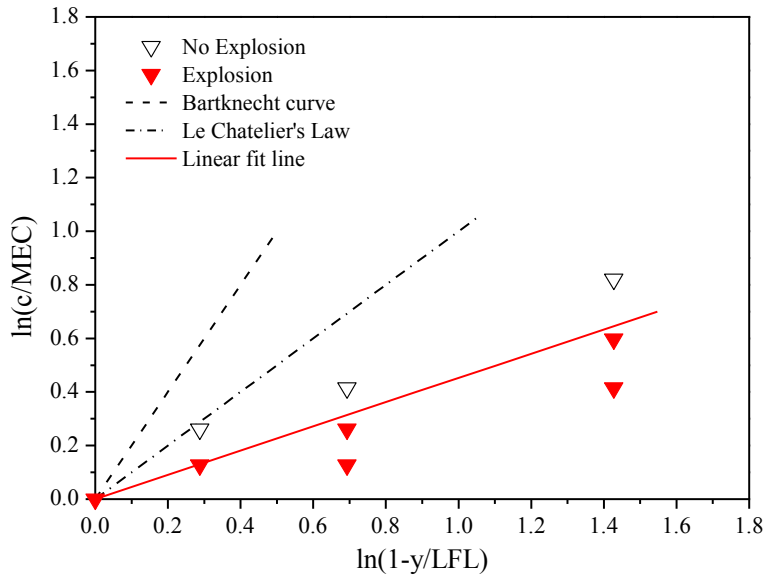


Figure 36 Experiment data on hybrid mixtures plotted in logarithmic coordinates: ethylene/niacin

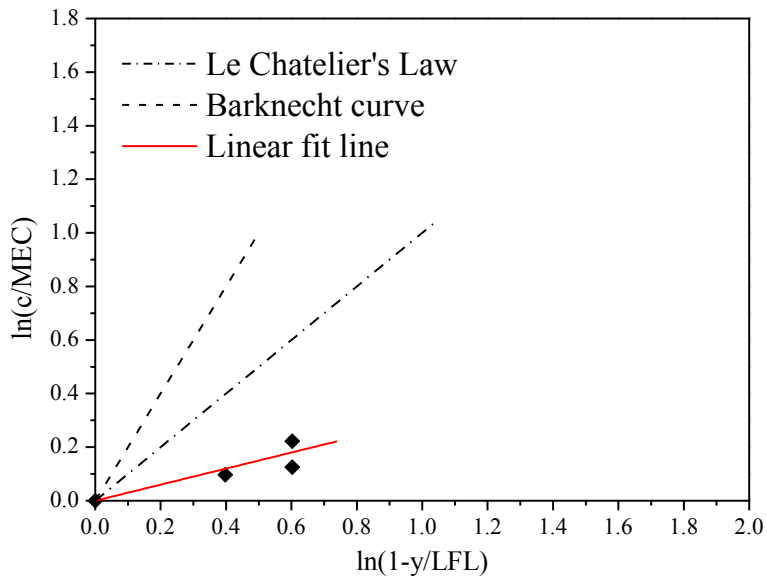


Figure 37 Experiment data on hybrid mixtures plotted in logarithmic coordinates: acetone/niacin (ignition delay times = 30 ms)

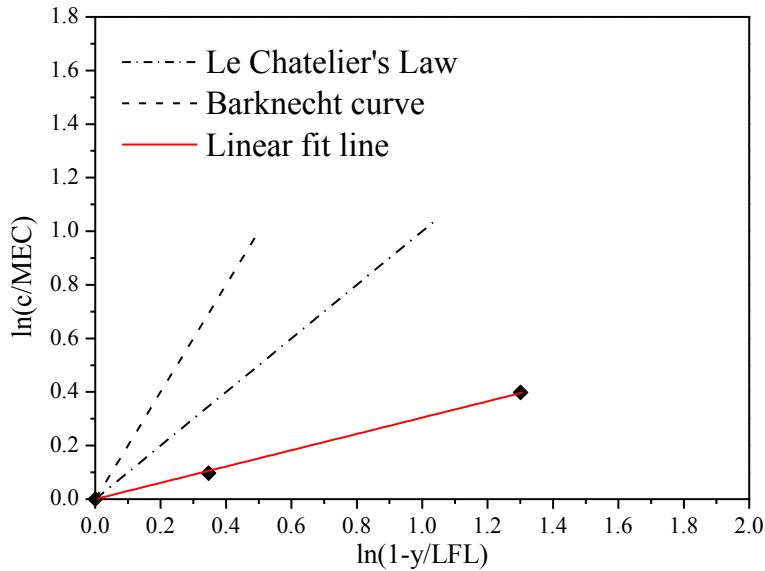


Figure 38 Experiment data on hybrid mixtures plotted in logarithmic coordinates: acetone/niacin (ignition delay times = 60 ms)

Table 6 listed all slopes as well as the experimental results of pure dust and pure gas. Table 6 also summarized results on niacin and acetone mixtures in a 20 L vessel tested by Sanchirico, *et al.* [39]. A pure acetone explosion was tested in the same condition as a niacin explosion in their tests. They also performed the lower flammability limit test for acetone/niacin hybrid mixtures. The difference between test (e) and test (f) was the ignition delay time, 30 ms for (e) and 60 ms for (f). The slopes were derived following the same approach used in this work. Rarely can much more data be found in literature since the explosibility data for hybrid mixtures are limited, especially for data including the pure gas explosibility test in the equipment under the same turbulence condition as a dust test.

Table 6 Summary of experimental results I

Reference	Dust	MEC g/m <sup>3</sup>	$K_{St}$ bar·m/s	Gas	LFL % v/v	$K_G$ bar·m/s	$C$	$\frac{K_{St}}{K_G}$
(a)	This Cornstarch	100	175	Methane	5.0	290	0.707	0.603
(b)	This Niacin	75	160	Methane	5.0	290	0.561	0.552
(c)	This Niacin	75	160	Ethane	3.0	360	0.523	0.440
(d)	This Niacin	75	160	Ethylene	2.7	400	0.452	0.400
(e)	Sanchirio Niacin	125	160	Acetone	2.5	600	0.304	0.267
(f)	Sanchirio Niacin	125	140	Acetone	2.5	500	0.300	0.280

The ratio of  $K_{St}$  to  $K_G$  for each dust and gas tested under the same ignition delay time is also calculated and listed in Table 6.  $K_{St}$  and  $K_G$  are fundamentally determined by the laminar burning velocity, which can be associated with the limit flame temperature [49].  $K_{St}$  and  $K_G$  can also be significantly affected by the testing procedure, especially the turbulence in the vessel associated with the ignition delay time. When  $K_{St}$  and  $K_G$  are roughly equivalent to each other, Le Chatelier's Law can be applied [18]. Hence, it is reasonable to correlate the lower flammability limit of hybrid mixtures to  $K_{St}/K_G$ .

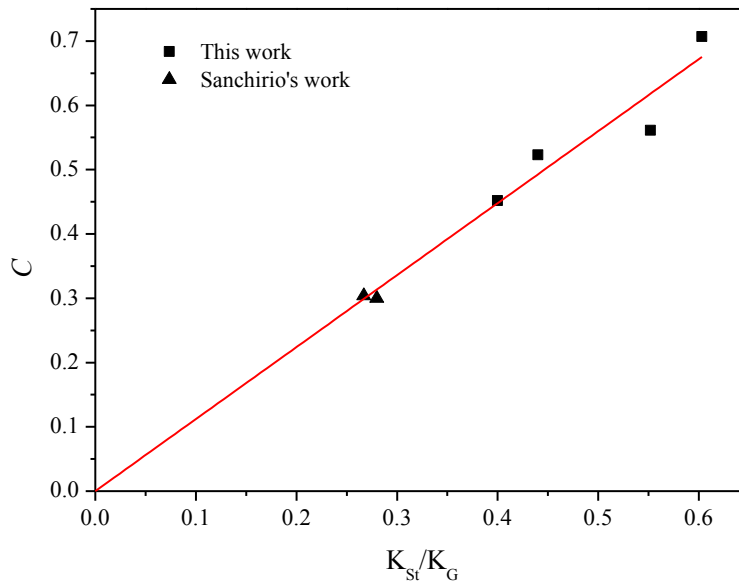


Figure 39 Relationship between the coefficient C and the ratio of  $K_{St}$  to  $K_G$

The slope C and  $K_{St}/K_G$  from Table 6 are plotted in Figure 39. It shows that C linearly depends on  $K_{St}/K_G$ , which can be represented as  $C = (1.12 \pm 0.03) K_{St}/K_G$ . Thus, Eq. 12 can be rewritten as:

$$\frac{c}{MEC} = \left(1 - \frac{y}{LFL}\right)^{(1.12 \pm 0.03) \frac{K_{St}}{K_G}} \quad \text{Eq. (12)}$$

The new formula has more accuracy corresponding to the experimental results. As shown in Figure 40 - Figure 45, when plotting the new formula back to Figure 22 - Figure 27, the non-explosion zone will be larger than predicted by either Le Chatelier's

Law or the Bartknecht curve, but the explosion or non-explosion zones can be well predicted by the proposed formula. The shading belt represents the error from the regression combined with the variance during  $K_{St}$  and  $K_G$  testing. To ensure safety, it is better to keep the hybrid mixtures below this shading belt.

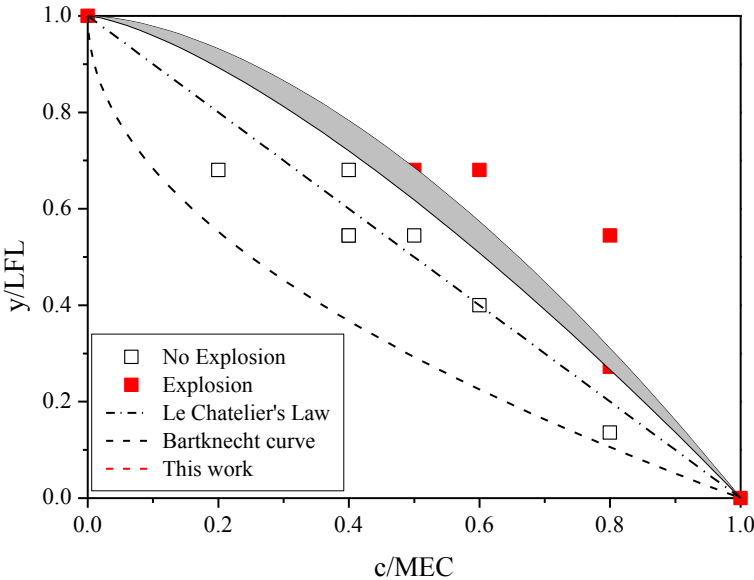


Figure 40 Confidence interval of the new formula: methane/cornstarch



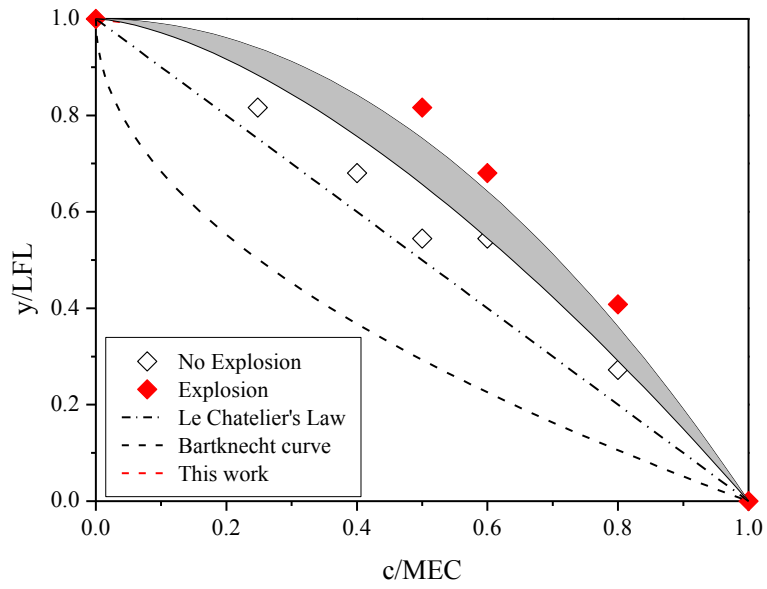


Figure 41 Confidence interval of the new formula: methane/niacin

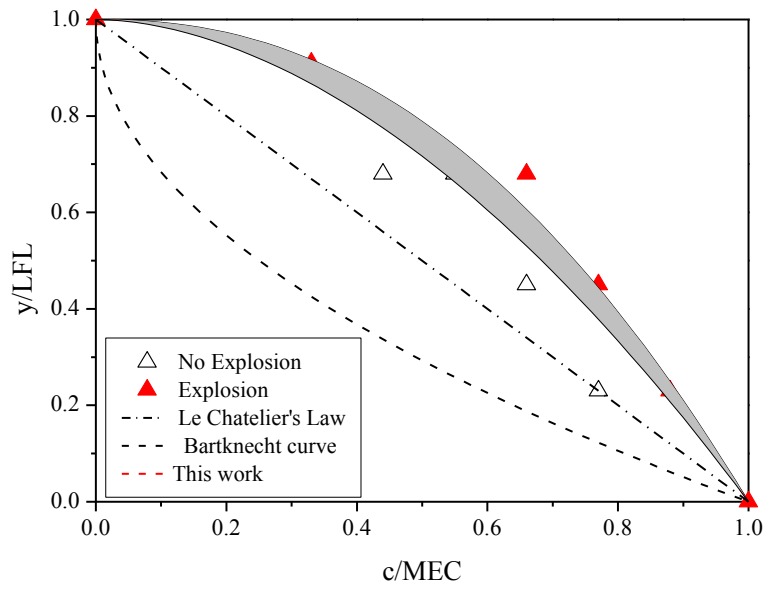


Figure 42 Confidence interval of the new formula: ethane/niacin

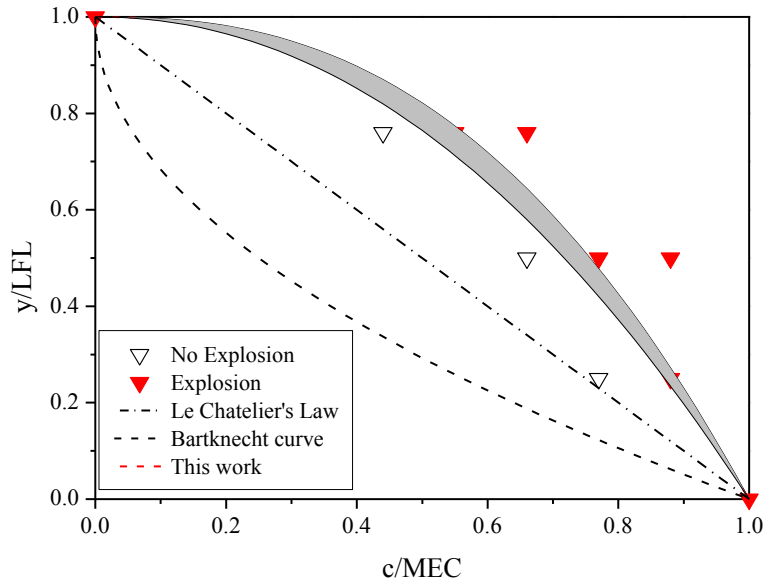


Figure 43 Confidence interval of the new formula: ethylene/niacin

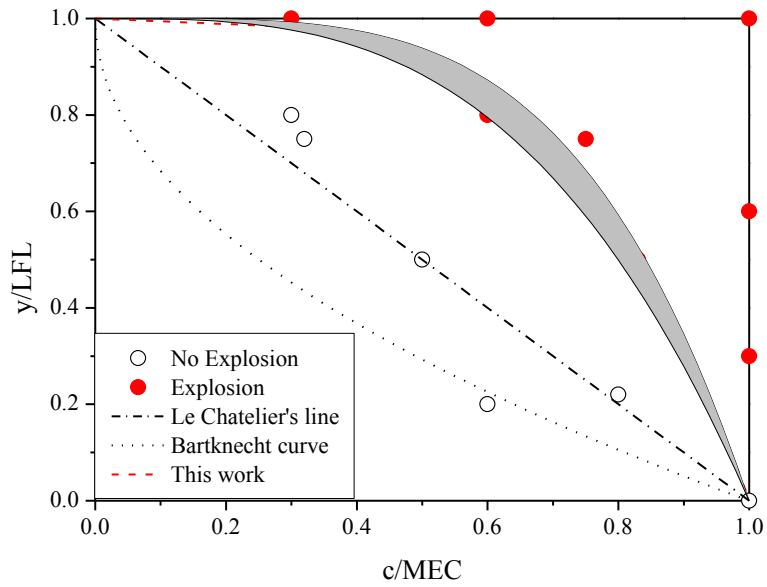


Figure 44 Confidence interval of the new formula: acetone/niacin (ignition delay times = 30 ms)

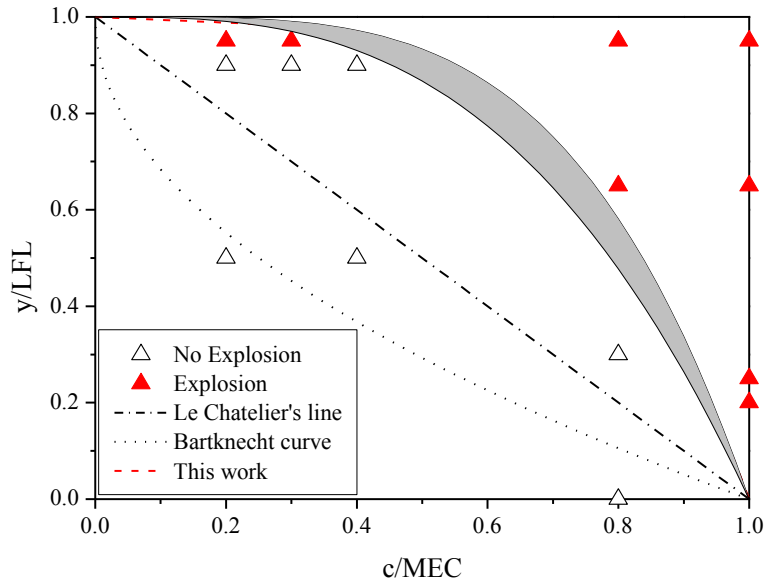


Figure 45 Confidence interval of the new formula: acetone/niacin (ignition delay times = 60 ms)

Eq. 12 can be used to divide the explosion zone from the non-explosion zone of the hybrid mixtures by utilizing basic characteristics of unitary dust or gas explosions. In Eq. 12, 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  $K_G$ , which means the flame temperatures for the dust and gas are of comparable magnitude, this formula can be simplified close to Le Chatelier's Law. Since the studied gases vary from one carbon to two carbons, or from saturated to unsaturated

bond, the new formula is supposed to be able to extend to other hybrid mixtures explosion.

#### **4.6 Conclusion**

This chapter studied hybrid mixtures explosion in a 36 L dust explosion apparatus using a series of hybrid mixtures. From the results obtained, conclusions can be made as follows: The  $K_G$  of flammable gases have been found to be significantly higher than results from literature due to the high turbulence inside the vessel, established by the ignition delay time. More gas or dust is needed to render the studied hybrid system flammable than that would be predicted by either Le Chatelier's Law or the Bartknecht curve. It is clear that neither of these two relationships can provide an accurate prediction on such systems. The new proposed formula can improve the prediction of the LFL of the mixture by utilizing basic characteristics of unitary dust and gas systems. The new formula is consistent with Le Chatelier's Law. Further study may be done to extend it to more hybrid mixtures.

## CHAPTER V

### VALIDATION OF THE PROPOSED FORMULA\*

A correlation of the lower flammability limit for hybrid mixtures was proposed in Chapter IV. The experimental conditions including ignition energy and turbulence which play a primary role in a gas or dust explosion were at fixed values. The sensitivity of such experimental conditions to the accuracy of the proposed formula was not thoroughly discussed in the previous chapter. Therefore, the work in this chapter studied the effect of varying the ignition energy and turbulence intensity to the proposed formula. For ignition energy effect, results from methane/niacin mixture demonstrated that the MEC and LFL will not be affected by changing ignition energy. There is no distinguishable difference among gas explosion index ( $K_G$ ) and dust explosion index ( $K_{St}$ ) derived from tests with every ignition energy (2.5 kJ, 5 kJ and 10 kJ) in a 36 L vessel. The proposed formula is independent of ignition energy. For turbulence effect, the proposed formula can have a good prediction of the explosion and non-explosion zone if the ignition delay time is within a certain range. The formula prediction is good as the ignition delay time increases up to 100 ms in this work. Propane/niacin and propane/cornstarch mixtures are also tested to validate the proposed formula. It has been confirmed that the proposed formula predicts the explosion and non-explosion zone boundary of such mixtures.

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\*Part of this chapter is reprinted from “Validation of a new formula for predicting the lower flammability limit of hybrid mixtures” by Jiang, J., Liu, Y., Mashuga, C. V., & Mannan, M. S. (2015), *Journal of Loss Prevention in the Process Industries*, 35, 52-58, with permission from Elsevier.

## 5.1 Background

The new formula proposed in Chapter IV is correlated with series hybrid mixtures experiments (methane/cornstarch, methane/niacin, ethane/niacin and ethylene/niacin in air) in a 36 L dust explosion apparatus. Unlike Le Chatelier's Law or the Bartknecht curve, this new formula utilizes basic characteristics of unitary dust or gas explosions including LFL, MEC, and the ratio of  $K_{St}$  and  $K_G$ . Since the previous work aimed to use a straight method to derive the correlation with essential experimental results, the sensitivity of the experimental conditions (*e.g.*, ignition energy, turbulence, *etc.*) to the accuracy of the proposed formula is not thoroughly discussed.

Generally, the energy and type of ignition sources has been found to have a primary role on the explosion behavior of a flammable gas, combustible dust or their hybrid mixtures [54, 55]. Several works have been done to study the effect of different energy values on the gas-air, dust-air, and hybrid mixture explosion parameters, such as maximum pressure and deflagration index [30, 44]. It has been found that inappropriate ignition energy can cause under or over-driving of the explosion in a 20 L dust explosion vessel. Thus, the ignition energy is an important factor which can affect the initiation of a gas or dust explosion and subsequent flame propagation [56, 57]. In our previous work, only one 2500 J chemical ignitor was used. The sensitive of the proposed formula to the ignition energy has not been studied.

In addition to ignition energy, turbulence can significantly affect  $K_{St}$  and  $K_G$ . Experiments performed at increasing ignition delay times which decreases turbulence

show that the deflagration index ( $K_G$ ) significantly decreases for gas explosions [34, 44]. With regards to a dust explosion test, the dispersion is an essential prerequisite. The dust cloud is formed by the pneumatic dust dispersion system where the blast of compressed air transports the sample into the test vessel and generates turbulence within the dust/air suspension. Because a blast of air is used to disperse the dust instead of a continuous flow, the turbulence intensity inside the vessel decays once the injection of air stops. Therefore, the ignition delay time determines turbulence intensity in the dust cloud at the moment of ignition. Studies show that longer ignition delay times result in a lower degree of pre-ignition turbulence and thereby a lower value of  $K_{St}$  [6, 58-61]. In our previous work, we only did experiments with one ignition delay time and emphasized the  $K_{St}$  and  $K_G$  in the proposed formula should be derived under the same turbulence intensity.

The objective of the work in this chapter work is to discuss the sensitivity of the proposed formula to ignitor energy and turbulence with experimental results. Additionally, new hybrid mixtures are also tested to further validate the proposed formula.

## **5.2 Methods**

The experiments were conducted in the same 36 L spherical vessel used in Chapter IV. Attempts were made to study the effect of ignition energy. Ignitors with different energies (2.5 kJ, 5 kJ and 10 kJ) were used. The 10 kJ ignitor was a combination of two 5 kJ ignitors. The ignitor was positioned at the centre of the vessel and directed with its

output horizontally. In order to compare the pressure generated ( $\Delta P_{\text{ignitor}}$ , see Figure 7) by ignitor itself, tests with only ignitor were conducted. The selected hybrid system is niacin/methane. The lower flammability limit of both niacin (MEC) and methane (LFL) was assumed to be constant with respect to ignition energy. More discussing can be found in the following sections.  $K_G$  and  $K_{St}$  were tested with 5 kJ or 10 kJ ignitor. These parameters were then inserted into the proposed formula (Eq. 12) to predict the lower flammability limit for such hybrid mixtures. Several additional tests in either the explosion zone or the non-explosion zone were conducted to check the accuracy of the formula.

To validate whether the correlation can be used under other turbulence or not, a new ignition delay time ( $t_d = 100$  ms,  $\Delta t = 50$  ms) is used in this work. In Chapter IV, the dust, gas or hybrid mixtures were tested under turbulence with a short ignition delay time ( $t_d = 75$  ms,  $\Delta t = 25$  ms). The selected hybrid mixture systems are cornstarch/methane, and niacin/methane. Similar to the sensitivity study on the ignition energy, the lower flammability limit of dust and gas was assumed constant in the ignition delay time study range. With a new ignition delay time,  $K_G$  and  $K_{St}$  were tested and inserted into Eq. 12 to resolve the explosion zone and non-explosion zone. Then, several random tests near the boundary were conducted to check the accuracy of this prediction. In addition to the experimental work done in this study, data published by another group was also analysed using the proposed formula to study the sensitivity of ignition delay time.



Besides the sensitive study of ignition energy and ignition delay time, niacin/propane and cornstarch/propane were selected to validate if the proposed formula can be extended to other hybrid mixtures. These tests followed by the approach provided in our previous paper [34].

### **5.3 Ignitor effect**

The MEC of dust and LFL of gas are key parameters in the proposed formula. According to the work of Hertzberg [1], several factors can affect the accurate determination of the dust MEC including: careful control of the dust particle size distribution, uniform dispersion of the dust throughout the test apparatus, use of a sufficiently strong ignition source, and selection of suitable limit criteria. Among these factors, the only variable changed in this study was the ignitor energy. Typically, the minimum ignition energy for gas explosions is 0.2 - 10 mJ. For dust explosions, the MIE is 10 - 60 mJ [6]. The ignitors used in this work are significantly higher than the minimum ignition energy required to initiate the explosion. For dust explosions, the ignitor is to deliver enough energy to the dust/air mixture to create a kernel of hot gas. An explosion will occur if the rate of heat generation is greater than the rate of heat loss in this kernel. The minimum ignition energy is the minimum amount of energy that must be delivered to the dust/air mixture to generate a hot kernel of a critical size in which the flame propagates unaided after the ignition energy delivery has ceased. Thus, the minimum ignition energy will be heavily affected by varying the turbulence intensity. However, the true MEC should be independent of ignition energy [14]. Similarly, the

LFL of a gas should also be independent of ignition energy. Therefore, as shown in Table 7, the MEC and LFL reported in Chapter IV will not be tested again with changing ignitor energy in this study.

In addition, a 2.5 kJ, 5 kJ or 10 kJ ignitor was used to ignite the pure gas or dust in this study. Generally, higher energy ignitors have the potential to overdrive an explosion, especially in small diameter vessels. This may be due to the pyrotechnic ignitors influence on flame dispersion and added turbulence due to its explosion speed. During the process of explosion, part of the flame fronts can reach the wall of vessel far before the real end of explosion process. This effect can lead to a less realistic experimental pressure-time curve. In this work, no distinguishable  $K_G$  or  $K_{St}$  could be derived (See Figure 46 and Figure 47). Variation with ignitor energy is within  $K_G$  or  $K_{St}$  variability. This is due to our test being performed in the larger radius 36 L vessel. When testing dust explosions in a larger vessel, the ignition energy effect on the calculation of explosion index becomes smaller.

The explosion and non-explosion zone of niacin/methane mixtures can be plotted by substituting MEC, LFL, as well as  $K_G$  and  $K_{St}$  with the ignition energy of 5 kJ and 10 kJ into the proposed formula (see Figure 48 and Figure 49). Several verification tests were randomly done in both the explosion zone and non-explosion zone for each ignition energy. Firstly, if comparing the validation tests with the prediction boundary for one ignition energy, the validation test results are well separated by the boundary predicted by the proposed formula (see Figure 48 and Figure 49).

Table 7 Summary of experimental results II

Ignition energy (kJ)	Ignition delay times	Dust	MEC (g/m <sup>3</sup> )	$K_{St}$ (bar·m/s)	Gas	LFL (%)	$K_G$ (bar·m/s)	$\frac{KSt}{KG}$
2.5	75	Niacin	75	160	Methane	5.0	290	0.552
5	75	Niacin	75	164	Methane	5.0	294	0.557
10	75	Niacin	75	165	Methane	5.0	300	0.550
2.5	100	Niacin	75	130	Methane	5.0	250	0.520
2.5	75	Cornstarch	100	175	Methane	5.0	290	0.603
2.5	100	Cornstarch	100	140	Methane	5.0	250	0.560
Spark*	30	Niacin	125	160	Acetone	2.5	600	0.267
Spark*	60	Niacin	125	140	Acetone	2.5	500	0.280
Spark*	120	Niacin	125	60	Acetone	2.5	300	0.200
2.5	75	Niacin	75	160	Propane	2.1	410	0.390
2.5	75	Cornstarch	100	175	Propane	2.1	410	0.427

\* These data are compiled from work done by Sanchirico, *et al.*[39].

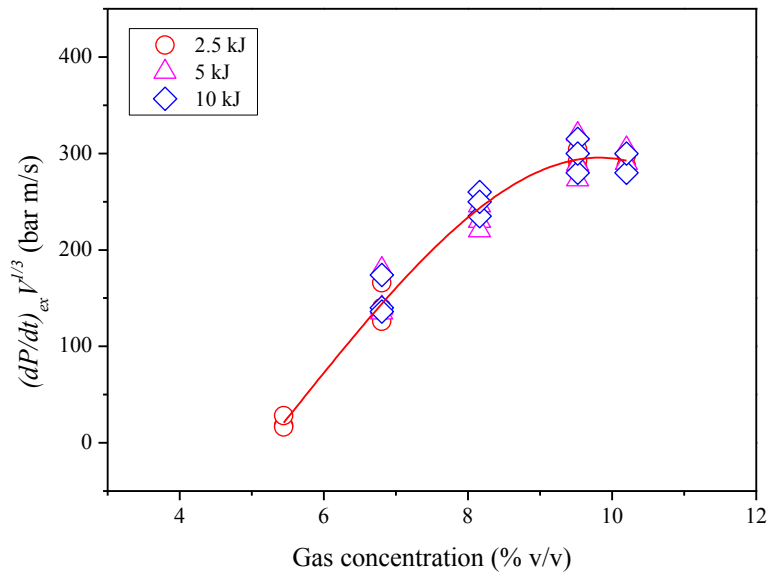


Figure 46  $(dP/dt)_{ex} V^{1/3}$  of methane explosion with variable ignition energy

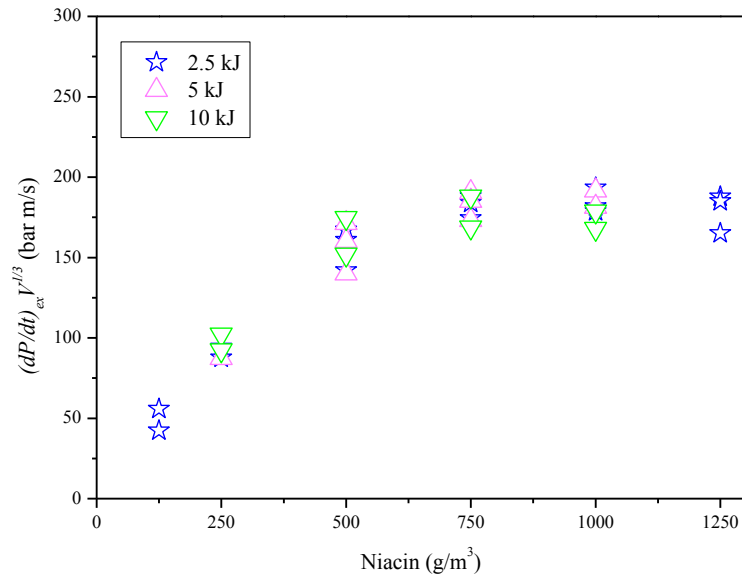


Figure 47  $(dP/dt)_{ex} V^{1/3}$  and concentration for niacin explosion with variable ignition energy

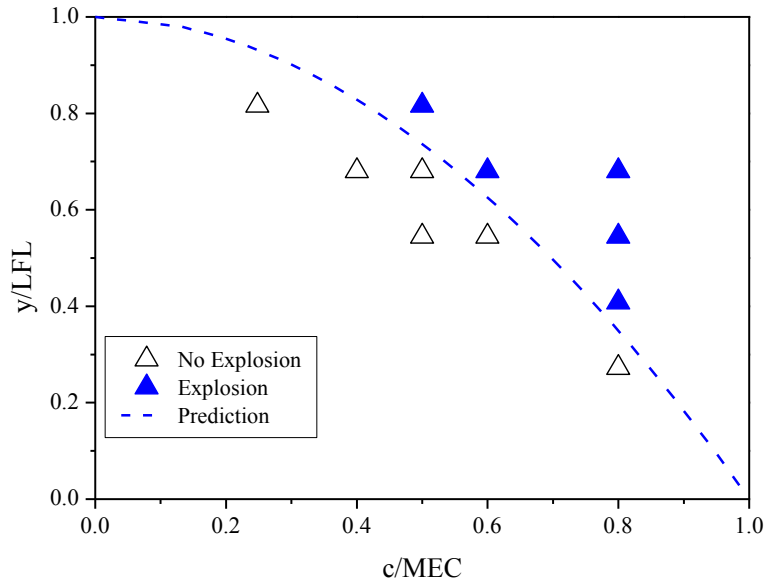


Figure 48 Explosion and non-explosion zone of niacin/methane mixture ( $t_d = 75$  ms, ignition energy = 5 kJ)

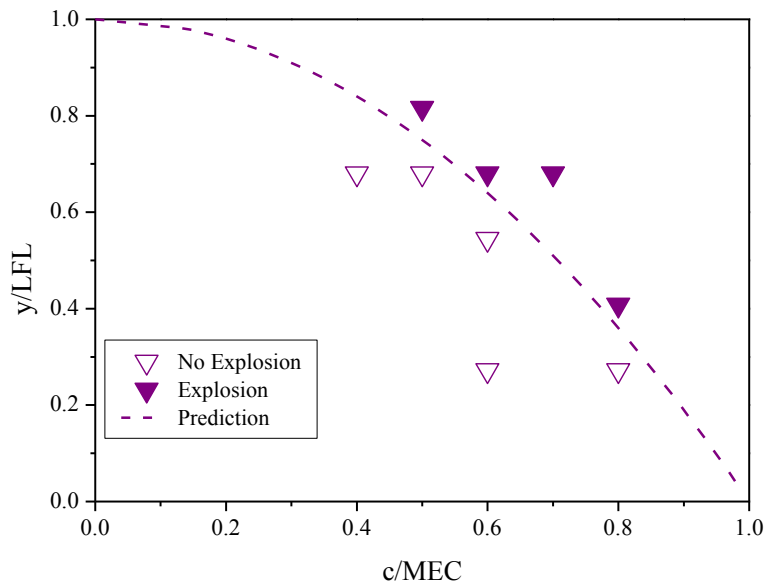


Figure 49 Explosion and non-explosion zone of niacin/methane mixture ( $t_d = 75$  ms, ignition energy = 10 kJ)

Moreover, if comparing the  $K_{St}/K_G$  ratios derived from ignition energy of 5 kJ and 10 kJ with the one from 2.5 kJ. They are close to each other meaning that all of them will give a similar prediction for explosion zone and non-explosion zone for the methane/niacin hybrid mixture. These two phenomena conclude that the proposed formula is independent of ignitor energy (2.5 kJ, 5 kJ or 10 kJ). This could be because of the explosion mechanism. For a pure dust explosion, there are three distinct mechanisms as follows: I) a reaction on the solid or liquid surface, forming gaseous products; II) a reaction on the solid or liquid surface, forming solid or liquid products; and III) a reaction in the gas phase, forming solid, liquid or gaseous products [41]. Niacin is a carbonaceous material which follows type I mechanism: devolatilization followed by gaseous combustion. With the addition of methane, the niacin particles will be surrounded by flammable gas atoms which are easily ignited before the dust particle devolatilization process. This new mechanism is equivalent to type III. The heat generated in the reaction of the gas phase will enhance the devolatilization process. Thus the minimum ignition energy for such hybrid mixture will be typically determined by the flammable gas, which is consistent with experiments [30]. The ignition energy in this study (2.5 kJ, 5 kJ or 10 kJ) is much higher than the MIE for methane as well as that of niacin through the pyrolysis process. Therefore, the proposed formula is not affected by the ignition energy (2.5 kJ to 10 kJ).

## 5.4 Turbulence effect

As discussed in Chapter III, turbulence is recognized as a primary factor among all variables affecting the explosion behavior of fuel-dust mixtures [44, 58, 60, 63]. Turbulence generation in hybrid mixtures is not limited to mechanical agitation. Blast waves from a primary explosion, caused by either pure dust or pure gas, can lift layered surface dust and form a turbulent dust/gas cloud. A typical 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. The investigation showed that the accumulated methane was ignited first followed by a massive coal/methane explosion [28]. For a given hybrid mixture and ignition energy, the level of pre-ignition turbulence has a primary influence on the development of hybrid mixture explosions.

For pure methane explosion, the turbulence effect on LFL of methane was studied in the work done by Cashdollar, *et al.* [51]. The LFL of methane was tested in both quiescent and turbulence conditions and found to be 5.0% v/v for both conditions. The conclusion was that the methane LFL values found with different turbulent conditions show very close agreement with that in a quiescent condition, regardless of the turbulence intensities or the short ignition delay. Hence, the LFL of the gases in this work associated with 75 ms or 100 ms ignition delay time is assumed the same. For dust explosions, it is required to have a minimum turbulence intensity to maintain the dust as a cloud. However, the MEC of such dust should be independent of the turbulence level [6]. Hertzberg and Cashdollar [14] found that the flammability limits of combustible

dusts would apparently narrow at high turbulence levels. This is actually a narrowing of the ignitability limits, not the flammability limits [6]. In this work, therefore, the same values for MEC of niacin and cornstarch are used in this work as in Chapter IV (see Table 7).

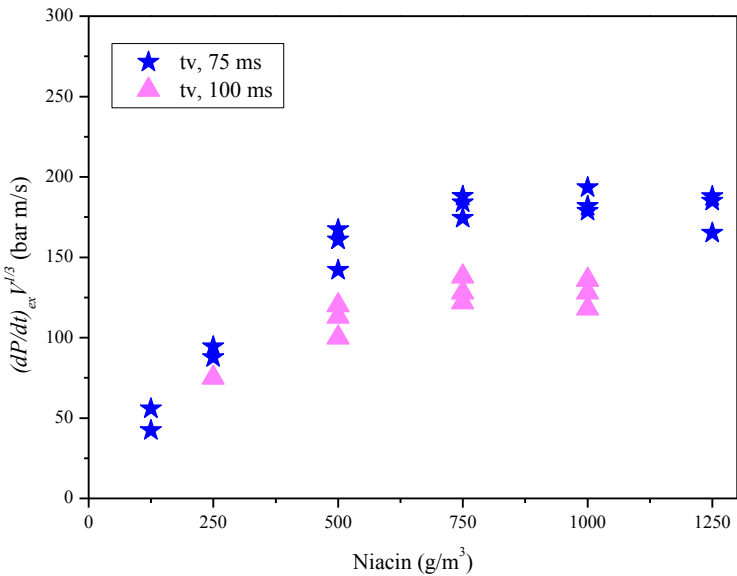


Figure 50  $(dP/dt)_{ex} V^{1/3}$  and concentration for niacin explosion with variable ignition delay time



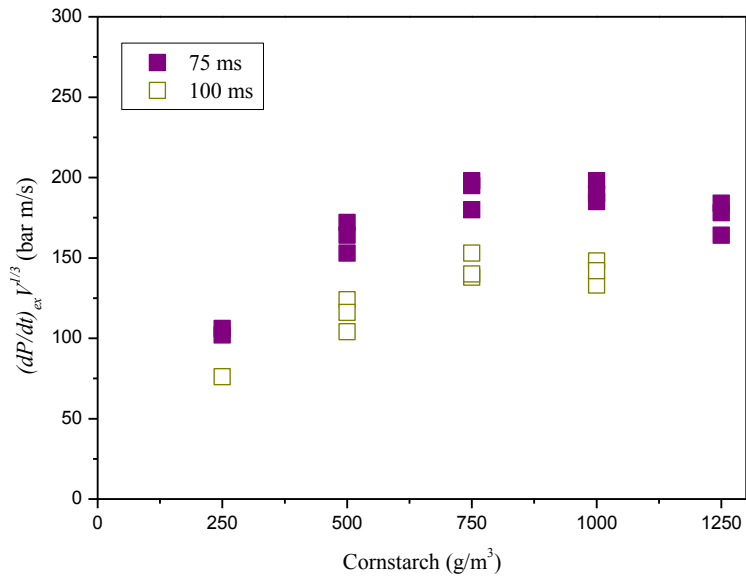


Figure 51  $(dP/dt)_{ex} V^{1/3}$  and concentration for cornstarch explosion with variable ignition delay time

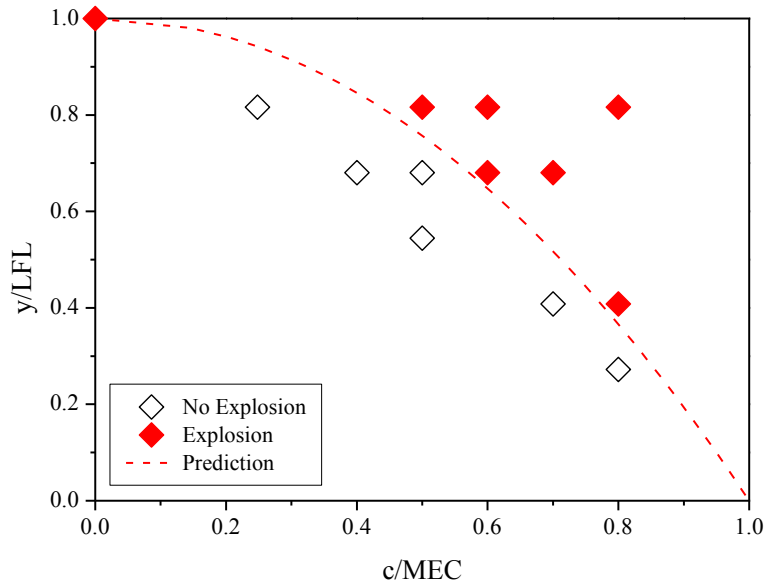


Figure 52 Explosion and non-explosion zone of methane/niacin mixture ( $t_d = 100$  ms, ignition energy = 2.5 kJ)

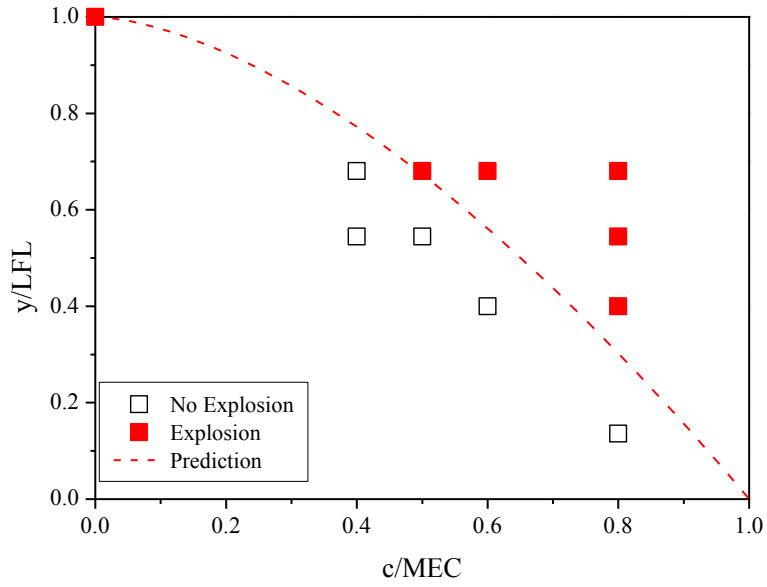


Figure 53 Explosion and non-explosion zone of methane/cornstarch mixture ( $t_d = 100$  ms, ignition energy = 2.5 kJ)

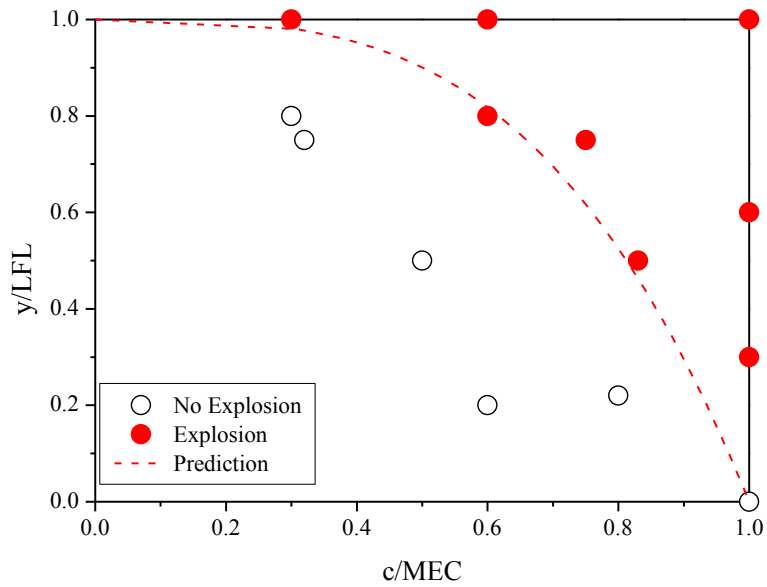


Figure 54 Explosion and non-explosion zone of acetone/niacin mixture ( $t_d = 30$  ms, ignition energy  $\approx 10$  mJ)

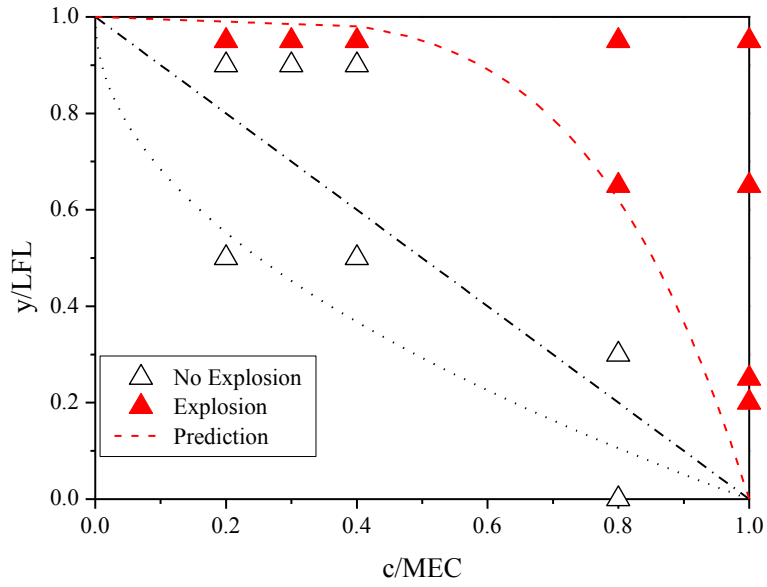


Figure 55 Explosion and non-explosion zone of acetone/niacin mixture ( $t_d = 60$  ms, ignition energy  $\approx 10$  mJ)

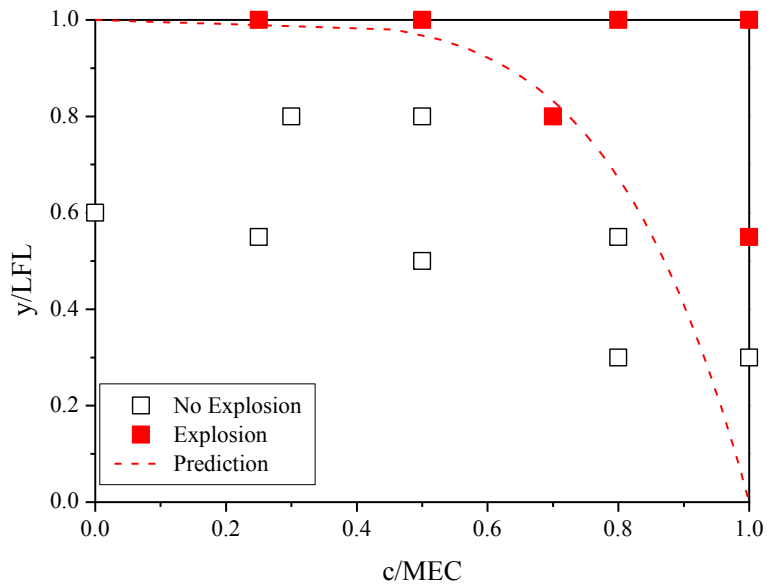


Figure 56 Explosion and non-explosion zone of acetone/niacin mixture ( $t_d = 120$  ms, ignition energy  $\approx 10$  mJ)

We have studied the turbulence effect on the deflagration index of methane in Chapter IV [34]. It was observed that the  $(dP/dt)_{ex}V^{1/3}$  dramatically decreases from 290 bar·m/s to 120 bar·m/s when the methane ignition delay time extends from 75 ms to 300 ms. At 100 ms ignition delay time, the  $K_G$  equals to 250 bar·m/s. In this work, experiments with both niacin and cornstarch were performed at increasing ignition delay times. These dusts show a similar trend as methane in that the dust explosion deflagration index significantly decreased with increasing delay times. Figure 50 represents the results of  $(dP/dt)_{ex}V^{1/3}$  of niacin as a function of concentration at different ignition delay times. The value of  $(dP/dt)_{ex}V^{1/3}$  decreases at every concentration as ignition delay time increases. The  $K_{St}$  (maximum  $(dP/dt)_{ex}V^{1/3}$ ) drops from 160 bar·m/s to 130 bar·m/s when the ignition delay time extends from 75 ms to 100 ms. Similar trends have also been identified for cornstarch explosion as shown in Figure 51.  $K_{St}$  decreases from 175 bar·m/s to 140 bar·m/s when the ignition delay time extends from 75 ms to 100 ms. This trend is in good agreement with the results found by other researchers [8, 39].

Figure 52 and Figure 53 represent the explosion and non-explosion zone of methane/niacin mixture and methane/cornstarch mixture at 100 ms ignition delay time, respectively. Several random tests were done for both mixtures and the results were also plotted in Figure 52 and Figure 53. Both demonstrate that the boundary predicted by the proposed formula can well separate the explosion zone from non-explosion zone.

Apart from the experiments done by ourselves, literature data are also employed to validate the turbulence effect on the proposed formula. Sanchirico, *et al.* [39] studied the

effect of pre-ignition turbulence by changing the ignition delay time (30 ms, 60 ms, and 120 ms) for the niacin, acetone, and acetone/niacin mixtures.  $K_{St}$  and  $K_G$  associated with each ignition delay time are summarized in Table 7. The MEC of niacin is reported as  $125 \text{ g/m}^3$  while the LFL of acetone is 2.5 % v/v. Both MEC and LFL should not change with extending ignition delay time from 30 ms to 120 ms.

By applying these parameters to the proposed formula, the explosion and non-explosion zone of acetone/niacin mixtures corresponding to each ignition delay time are represented in Figure 54 - Figure 56. Clearly, the explosion and non-explosion zone is well defined by the proposed formula in all figures. These means the effect of the ignition delay time (turbulence intensity) on the accuracy of the proposed formula can be neglected when such ignition delay time is not too long. The ratios,  $K_{St}/K_G$ , are similar to each other when ignition delay time is less than 60 ms (0.267 for 30 ms, 0.280 for 60 ms). It then decreased to 0.200 when ignition delay time is 120 ms. This is because  $K_G$  and  $K_{St}$  are determined by both concentration and turbulence. For gas explosions,  $K_G$  will only be affected by the turbulence. The gas concentration will keep constant regardless of varying the ignition delay time. For dust explosions, the action of varying ignition delay time will affect the actual dust concentration under the transient turbulent conditions. This will then further affect the behavior of the explosion parameters depending on the dust concentration. Due to dust sedimentation, the actual dust concentration will become lower with decreasing turbulence by increasing ignition delay time. As the ignition delay time increases, it eventually becomes the pure gas explosion instead of a hybrid mixture explosion.

In summary, the turbulence effect on the accuracy of the proposed formula depends on the duration of ignition delay time (turbulence intensity). The evidence presented shows the proposed formula provides a good prediction of the explosion and non-explosion zone if the ignition delay time is within a certain range. In our experiments, the formula provides a good prediction with an ignition delay time up to 100 ms. For the work done by Sanchirico, *et al.* [39], the formula works well up to an ignition delay time of 120 ms.

### **5.5 Other hybrid mixtures**

In addition to the study of ignition energy and turbulence effect on the proposed formula, two additional hybrid mixtures are tested and predicted in this work further supporting the validity of the proposed formula. The  $K_G$  of propane was found to be 410 bar·m/s (2.5 kJ ignitor,  $t_d = 75$  ms). Other parameters are summarized in Table 7.

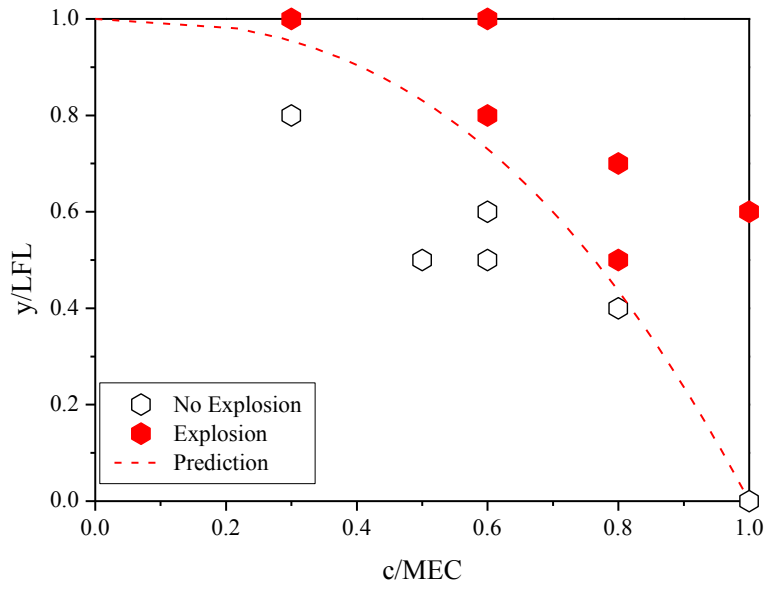


Figure 57 Explosion and non-explosion zone of propane/niacin mixture ( $t_d=75$  ms, ignition energy = 2.5 kJ)

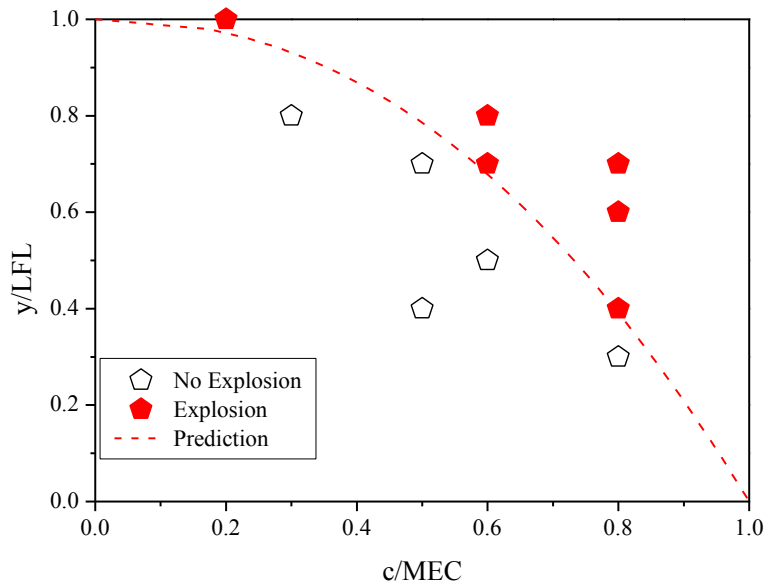


Figure 58 Explosion and non-explosion zone of propane/cornstarch mixture ( $t_d=75$  ms, ignition energy = 2.5 kJ)

Figure 57 and Figure 58 represent the predicted boundary as well as several random tests of propane/niacin mixtures and propane/cornstarch mixtures, respectively. These figures demonstrate clearly that the explosion and non-explosion zones distinguished by the proposed formula are consistently well predicted.

## 5.6 Conclusion

The work in this chapter studied the effect of variable ignition energy and turbulence on the formula proposed in Chapter IV. The proposed formula is shown to be independent of ignition energy over the range tested. This is supported by the fact that methane/niacin mixtures with 2.5 kJ, 5 kJ, 10 kJ ignitors all have consistent MECs and LFLs. Further, there is minimal difference within testing variability in gas explosion index ( $K_G$ ) and dust explosion index ( $K_{St}$ ) derived from tests with this range ignition energy in the 36 L vessel.

The proposed formula is also essentially independent of turbulence in the range examined in these tests. Evidence of good explosion/non-explosion prediction for variable ignition delay times (turbulence) is presented. Formula independence is demonstrated for methane/niacin and methane/cornstarch mixtures tested with 75 ms and 100 ms ignition delay time in a 36 L vessel. Data from literature for acetone/niacin mixtures at 30, 60 and 120 ms ignition delay time, 20 L vessel also supports the proposed formula in turbulence independence. In our work, the formula has a good prediction with ignition delay time up to 100 ms.



This work also tested additional propane/niacin and propane/cornstarch mixtures to validate the proposed formula. Results show that the proposed formula accurately predicts the explosion and non-explosion boundary.

## CHAPTER VI

### CONCLUSIONS AND FUTURE WORK

#### 6.1 Summary and conclusions

This work systemically studied a series of hybrid mixtures explosion in a 36 L dust explosion apparatus. From the results obtained, conclusions can be made as follows:

- 1) The  $K_G$  of flammable gases have been found to be significantly higher than results from literature due to the high turbulence inside the vessel, established by the ignition delay time.
- 2) More gas or dust is needed to render the studied hybrid system flammable than that would be predicted by either Le Chatelier's Law or the Bartknecht curve. It is clear that neither of these two relationships can provide accurate prediction on such systems.
- 3) The new proposed formula can improve the prediction of the LFL of the mixture by utilizing basic characteristics of unitary dust and gas systems.

Additionally, this work studied the effect of variable ignition energy and turbulence on the formula proposed. From the results obtained, conclusions can be made as follows:

- 1) The proposed formula is shown to be independent of ignition energy over the range tested. This is supported by the fact that methane/niacin mixtures with 2.5 kJ, 5 kJ, 10 kJ ignitors all have consistent MECs and LFLs. Further, there is minimal difference within

testing variability in gas explosion index ( $K_G$ ) and dust explosion index ( $K_{St}$ ) derived from tests with this range ignition energy in the 36 L vessel.

2) The proposed formula is also essentially independent of turbulence in the range examined in these tests. Evidence of good explosion/non-explosion prediction for variable ignition delay times (turbulence) is presented. Formula independence is demonstrated for methane/niacin and methane/cornstarch mixtures tested with 75 ms and 100 ms ignition delay time in a 36 L vessel. Data from literature for acetone/niacin mixtures at 30, 60 and 120 ms ignition delay time, 20 L vessel also supports the proposed formula in turbulence independence. In our work, the formula has a good prediction with ignition delay time up to 100 ms.

This work also tested propane/niacin and propane/cornstarch mixtures to validate the proposed formula. Results show that the proposed formula accurately predicts the explosion and non-explosion boundary. The new formula is consistent with Le Chatelier's Law. Further study may be done to extend it to more hybrid mixtures.

## **6.2 Future work**

Following on the current study, several future works can be done to further validate the proposed formula. More fundamental work could be done to better explain such empirical correlation. Then CFD modeling could be developed to study the consequence during a hybrid mixture explosion.

### **6.2.1 More hybrid mixtures need to be tested**

Although the hybrid mixtures in this study covered gases from one carbon atom to three carbon atoms, from single bond to double bonds, to further validate the developed equation, more hybrid mixtures need be tested by varying the dust or gas, *e.g.* polyethene and methane, polyethene and propane, niacin and propane, cornstarch and propane.

### **6.2.2 Other factors need to be studied**

All of the experiments in this study were conducted in 36 L dust explosion vessel. Although the 36 L device in MKOPSC was calibrated with Round Robin tests and the results were in very good agreement with results from standard 20 L/1 m<sup>3</sup> device, it would be better to validate the proposed formula in 20 L device or other device in a different volume.

Additionally, the current ignition system can only use chemical ignitors with a relatively high energy ignitor(s) than spark or electric discharge which are often the ignition source in industry. It is better to modify the current device to validate if the proposed formula can be able to be used at low ignition energy.

Furthermore, the current proposed formula uses  $K_{St}$  as one key parameter. Such value can be affected by the particle's shape, size, distribution, humidity as well as other factors. It is also interested to validate the proposed formula by varying these factors accordingly.

### 6.2.3 Correlation between $K_G$ and intensity of turbulence

Since the reported  $K_G$  values in literature are mostly under quiescent circumstance, the  $K_G$  coupled in proposed formula shall be tested under the same conditions as dust explosion. The main difference between them is the turbulence. A correlation between gas explosion index and turbulence is necessary. Once this relationship is built, the published gas explosion index will be employed into this equation instead of doing pure gas explosion experiments which will make the proposed formula more efficient.

### 6.2.4 Develop a correlation for $K_H$ determination

This work developed a correlation on the determination of LFL for hybrid mixtures, which is on the likelihood side of risk assessment. Similarly, on the severity side of risk, it would be useful to develop a correlation to determine the deflagration index of hybrid mixture explosion ( $K_H$ ) by using  $K_{St}$  and  $K_G$ .

Moreover, as we know, it is common practice to measure  $K_{St}$  in lab test vessels (1 m<sup>3</sup>, 20 L, 36 L) and to predict what would happen if the same mixture explodes in an industrial plant through the cubic relationship, as shown in Eq. 13.

$$K_{St} = \left( \frac{dP}{dt} \right)_{\max} V^{1/3} \quad \text{Eq. (13)}$$

where the maximum pressure rise ( $[dP/dt]_{\max}$ ) can be calculated by using the Eq. 14.

$$\left(\frac{dP}{dt}\right)_{\max} = \frac{3(P_{\max} - P_0)}{R_{\text{vessel}}} \left[ 1 - \left(\frac{P_0}{P}\right)^{1/\gamma} \frac{P_{\max} - P}{P_{\max} - P_0} \right]^{2/3} \left(\frac{P}{P_0}\right)^{1/\gamma} S_u \quad \text{Eq. (14)}$$

where  $P_{\max}$  is the maximum pressure during the explosion;  $P_0$  is the initial pressure before ignition;  $R_{\text{vessel}}$  is the radius of the 36 L vessel;  $\gamma$  is the ratio of specific heats;  $S_u$  is the laminar burning velocity.

One assumption for this methodology is the lab data can be applied to accidental explosions in industry. Another assumption is it can represent a conservative case even when the actual industrial circumstances are not reproduced in the lab tests. Many models of dust explosions, such as Bradley and Mitcheson [64], Dahoe, *et al.* [65], need to know the laminar burning velocity ( $S_u$ ). It is reasonable to derive a similar mode which can be considered to be applicable to hybrid mixtures to predict the  $K_H$  values.

Once the  $K_H$  can be predict either by correlations or by cubic relationship similar to Eq. 13, together with the proposed formula of LFL determination for hybrid mixtures developed in this work, a hybrid mixture explosion map could be derived as shown in Figure 59. This map will provide the necessary information for risk assessment as well as for developing mitigation methods for preventing hybrid mixtures explosion.

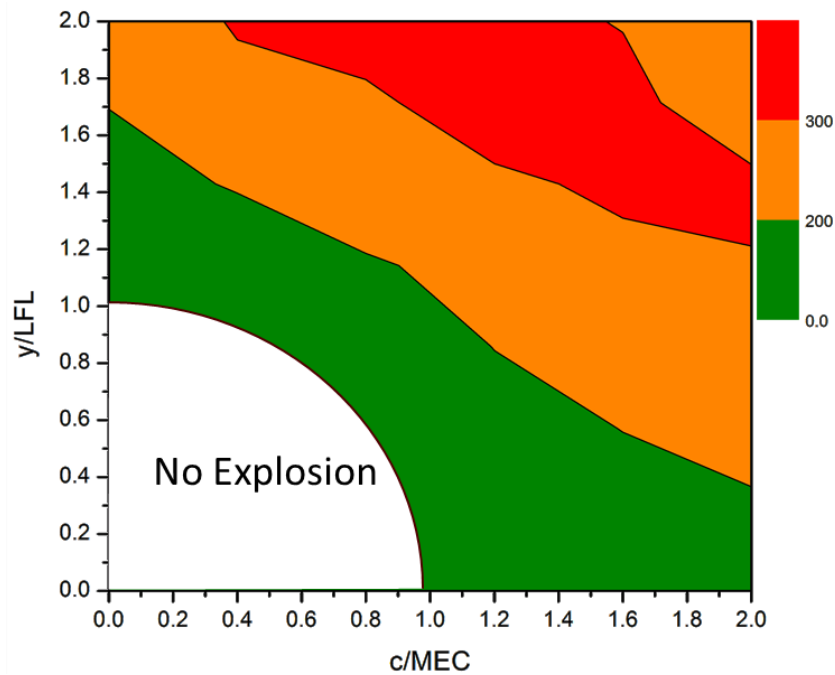


Figure 59 A hybrid mixture explosion map

### 6.2.5 Hybrid mixtures explosion modelling

Furthermore, the deflagration of a hybrid mixture could lead to the deflagration detonation transition (DDT) which is much more severe. The propagation of flames is of importance for revealing the explosion transition. This phenomenon in turbulent gaseous mixtures has been studied for a long time and several attempts have been done to pure dust; these aim to correlate turbulent burning velocity to turbulence intensity and basic flame propagation parameters like laminar burning velocity. For gases, a typical relationship is summarized by Abdel-Gayed and Bradley [66, 67] by an expression in this form:

$$S_T = C \cdot S_u^m \cdot (u'_{rms})^n \cdot l_0^p \quad \text{Eq. (15)}$$

where  $S_T$  and  $S_u$  are the turbulent and laminar burning velocities, respectively;  $u'_{rms}$  is the turbulent intensity;  $l_0$  is the length scale; and  $C$ ,  $m$ ,  $n$ , and  $p$  are the parameters which can be found based on an experiment. Computational Fluid Dynamic (CFD) models use Eq. 15 (or modifications thereof) to simulate flame propagation in gas-air mixtures. Note that the only input parameter necessary for the gas-mixture is the laminar burning velocity. Accurate methods for estimating this fundamental thermo-kinetic property exist for gases [68]. The turbulent flow field parameters,  $u'_{rms}$  and  $l_0$ , are obtained from the solution of the Navier-Stokes equation and a turbulent sub-model (such as  $\kappa$ - $\epsilon$  for example).

Similarly, Skjold has attempted to find the correlation between  $S_T$  and  $S_u$  for pure dust as the same form [69-71]. They have developed a new CFD-code based on FLACS-code and applied into pure dust (Dust Explosion Simulation Code or DESC). However, current CFD solvers cannot be applied to a hybrid system since the research on the flame propagation of hybrid mixtures can be rarely found compared with pure dust or gas. As a hybrid mixture combined with dust and gas, it is reasonable and necessary to do research to find a similar expression in order to assess the accidental hazard by CFD modeling.

Fundamentally, the turbulent burning velocity,  $S_T$ , is the primary controlling parameter that identifies the hazard in a hybrid mixture explosion. The increase in  $S_T$  as the deflagration progresses is also responsible for DDT. Thus from a safety perspective, it is



important to evaluate  $S_T$  given an input parameter such as gas concentration, dust size/concentration, and geometry effects. Not only is this correlation a scientific challenge but is also of practical importance for understanding the explosions of the hybrid mixture, modeling of the hybrid mixture flame propagation in industrial facilities, and assisting to choose adequate safety strategies for preventing accidents.

Hence, another future work of this research is to correlate the turbulent burning velocity  $S_T$  from the phenomenal side and the laminar burning velocity  $S_u$  from the hybrid mixture basic property side. The result will be able to be applied to CFD modeling.

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