STUDYING THE DUST CLOUD MINIMUM IGNITION ENERGY OF AMINO ACIDS

AND THEIR FMOC'S

A Thesis

by

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ABSTRACT

Fmoc groups are base labile functional groups attached to amino acids to reduce undesirable reactions in peptide synthesis. As with ordinary amino acids, Fmoc-protected amino acid dusts are combustible, and exhibit the potential for a dust explosion. Dust explosions are a continuing challenge in the process industries and has been the subject of much research. Industrial dusts are usually evaluated for explosion hazard probability on the basis of their minimum ignition energy, the minimum energy an ignition source must supply in order to ignite a dust cloud. Such data is often used in risk assessments and to compare combustible dusts to each other, but there is a lack of data in the literature for minimum ignition energies for both ordinary amino acid dust and Fmoc-protected amino acid dusts. This study experimentally determined minimum ignition energies for the following amino acids and their corresponding Fmoc-protected versions: L-serine, L-proline, glycine, L-glutamic acid, and L-alanine. By comparing the Fmoc-protected amino acid dusts to their ordinary amino acid counterpart, it becomes apparent that the protected variants are much more combustible than the parent molecules. From a perspective of loss prevention, this publication attempts to bring immediate awareness and takes the first step in filling a gap in the published information addressing this topic and contextualize these findings as they pertain to process safety.

DEDICATION

This thesis is dedicated to my parents,

Mr.Gopalakrishnan Varadharajan and Mrs. Nirmala Banu

for their support and guidance.

ACKNOWLEDGEMENTS

NOMENCLATURE

ASTM	American Society for testing and Materials
CSB	Chemical Safety Board
KSt	Deflagration Index
MEC	Minimum Explosible Concentration
MIE	Minimum Ignition Energy
NFPA	National Fire Protection Association
OSHA	Occupational Safety and Health Administration
P	Pressure
Pmax	Maximum deflagration pressure
R	Universal gas Constant
SDSs	Safety Data Sheets
T	Temperature
FMOC	Fluorenyl Methoxy Carbonyl
PSD	Particle Size Distribution

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1. INTRODUCTION

In the solids processing industries, materials with particle size less than 1000 µm (16 BS mesh size) [1,2] belong to a category called Powders. When the diameter is less than 76 µm (200 BS mesh size), they are called as 'Dust'. As per NFPA [3] , any solid that is 420 µm or less in diameter is considered to be 'Dust'. 70% of the dusts processed in various industries are combustible, which emphasizes the fact that industrial solids processing equipment is subjective to a dust explosion potential [5]. Rapid combustion of flammable particles suspended in air is termed a 'Dust explosion'. The smaller the particle size, the more a dust cloud resembles a vapor or gas with respect to combustion. As particle size reduces both the thermodynamic (maximum pressures generated) and kinetics (rate of pressure rise and flame speed) of the explosion are enhanced [4]. If the ignited cloud is not confined , then a flash fire is likely to happen. In case of confinement, the heat of combustion may result in flame propagation and pressure increase, thereby confining the evolving of heat, conveying energy to unreacted materials, thereby accelerating the reaction resulting in an explosion [6].

1.1   Dust accidents

There are numerous historical as well as recent incidents involving dust explosions which have demanded awareness of the field of dust explosions and challenged process safety experts. Some of them are:

The 1972 Bremanger, Norway incident involved a silicon powder grinding plant, in which a dust explosion killed five workers and injured four. The explosion occurred in the milling section which resulted in a rupture of the entire process, blowing out all the walls of the facility [7].

On April 11th,1981, an incident in Corpus Christi, Texas killed 9 people and injured 30 [8]. This catastrophic explosion happened in a large grain silo, with the ignition source being smoldering lumps of sorghum, that entered a bucket elevator with the grain causing the dust to explode.

On February 20th, 2003, an explosion damaged the CTA Acoustics manufacturing plant in Corbin, Kentucky, fatally injuring seven workers. This explosion happened when a accumulated resin dust was accidently ignited in a production line that had been partially shutdown for cleaning. A thick cloud of dust was ignited, and the resulting explosion propagated throughout the facility causing a secondary explosion where resin dust acted as a fuel [9] .
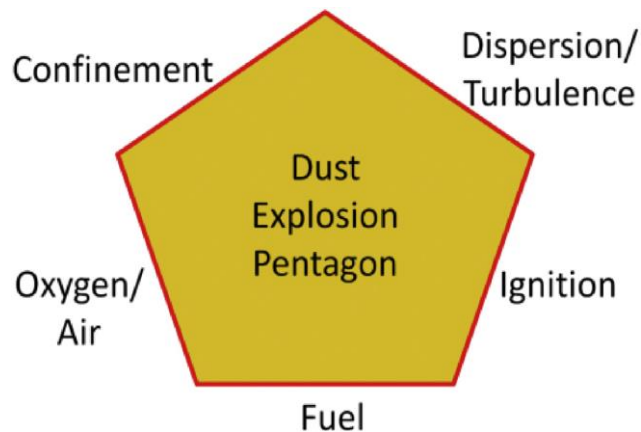
1.2   Dust pentagon

Figure 1: Dust Pentagon [X].

A fire triangle has an oxidant, ignition source and fuel. With the presence of all three parameters, a fire is likely to happen. A dust explosion requires two other additional parameters compared to the fire triangle. These are mixing of air and dust or dispersion and confinement of

the dust. Together these parameters are needed for a dust explosion to happen. The parameters for dust explosions are [10]:

i. Finely divided dust particles

ii. Presence of oxygen

iii. Presence of an ignition source

iv. Mixing of dust and air in proportion quantities

v. Degree of confinement of the dust

Two parameters that are important in a fire pentagon which are not present in the fire triangle are dispersion and confinement of the dust. The intensity of the dust explosion is solely dependent on the confinement. An unconfined dust explosion may lead to a flash fire which is less lethal when compared to the dust explosion caused by confined dust particles which can cause deflagration with higher temperatures and pressures. The particle size of the dust in another parameter that plays a major role in determining the effect of a dust explosion. The smaller the average the particle size is, the lower the energy requirement is to ignite it, thus a lower MIE value.

1.3   Dusts in process industries

The key industries that process solids on a large scale and are affected by dust explosions include the following [11]:

I. Pharmaceutical Plants – chemical dusts, reactive intermediates

II. Food Processing Plants – grains, powdered milk, sugar, egg whites, etc.

III. Manufacturing Plants – rubbers, plastics, etc.

IV. Metal Processing Plants – aluminum, magnesium, chromium, iron, etc.

V.   Wood Processing Plants – sawdust

1.4   Classification of dusts

Not all combustible dusts are explosive, but all explosive dusts are combustible. If an external source ignites a dust cloud, then it is combustible, and the pressure propagated is sufficient after the source is taken away [12]. The dust explosibility at room temperature (25°C) can be divided into two main categories:

1. **Group A :** Dust ignites and propagates into a flame

2. **Group B :** Dust does not propagate into a flame

Group B dusts can explode with an increase in temperature. The combustion class is one of the factors in the ignitability of a dust layer. The dust characteristic depends on its nature and reaction of the dust when an ignition source is provided. The following represents a combustion classification [13][14]:

i.   CC1: no ignition, no self-sustained combustion

ii.   CC2: localized combustion of short duration

iii. CC3: local sustained combustion with no propagation

iv.   CC4: propagation, smoldering combustion, spreading of fire

v.   CC5: propagation of open fire with open flames

vi.   CC6: explosive combustion with explosive burning

Dust moisture content, ambient temperature, atmospheric humidity, oxygen accessibility, particle size and oxidizer/reducer ratio (oxygen from air/dust fuel) are some of the factors that affect dust ignition. Different dust samples of the same chemical can have diverse explosive

characteristics depending on these factors. An experimental parameter called the deflagration index (KSt) is related to the kinetics or of a dust deflagration and is called the deflagration index. It is the relative measure of the explosion severity compared to other dusts [14]. The concept of KSt was introduced by a German scientist Bartknecht, utilizing the so-called cube root law. The deflagration index shown below is found by experimentally measuring the rate of pressure rise in a known volume. The resulting deflagration index can then be used in the same equation below to find the rate of pressure rise at the process scale. The deflagration index is used as a tool for sizing relieve panels for safely venting deflagrative dust explosions.

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

$$dP/dt = Rate\ of\ rise\ of\ pressure$$

$$V = Volume$$

Dust explosion class and Kst values for common dusts [14]:

Table 1: Dust explosion class and deflagration index for typical materials.

Dust Explosion Class	Kst (bar-m/sec)	Characteristic*	Typical Material
St 0	0	No explosion	Silica
St 1	> 0 and ≤ 200	Week explosion	Powdered milk, charcoal, sulfur, sugar, etc.
St 2	> 200 and ≤ 300	Strong explosion	Cellulose, wood flour, etc.
St 3	>300	Very strong explosion	Aluminum, magnesium, etc.
*OSHA CPL 03-00-008 – Combustible dust national emphasis program			

1.5   Factors affecting the explosivity of dust clouds

1.5.1   Particle size

One of the foremost critical variables influencing the explosivity is particle size. As mentioned previously, the smaller the particle size, the lower the minimum ignition energy required for ignition. This is because as particle size reduces it becomes easier and more probable for a dust cloud to be created [37] and smaller particles have a greater specific area leading to more contact with oxygen lowering the input energy to initiate an explosion.

1.5.2   Moisture content

Several studies have proven that increased dust moisture content can decrease the explosivity of dust clouds and increases the ignition sensitivity [15]. The vapors generated from the moisture tend to act as an inert, thereby self inerting the atmosphere, reducing the explosion strength of the dust cloud explosions. Additionally, moisture tends to increase the cohesiveness of the particles leading to agglomeration, effectively resulting in larger particle size.

1.5.3   Agglomeration

Agglomeration is the self-assembly of small particles into a larger unit. The shift to larger agglomerates shifts the net surface area of the dust to a lower value. The increase in particle size due to agglomeration reduces surface area contact with oxygen and provides an inert if water is forming the agglomeration. Both of these contribute to increasing the required ignition energy and decreasing the explosion severity [15].

1.5.4 Turbulence in the cloud

In general, an increase in dust cloud turbulence results in a stronger explosion due to an increase in forced convective mass and heat transfer between reacted an unreacted species.

1.5.5 Oxygen concentration

Oxygen is essential component for explosions and combustion in general. Similarly, dust cloud explosions also require oxygen (or and oxidizer), typically supplied by air. The scarcity of oxygen in the atmosphere can inhibit the effectiveness of a dust cloud. Thus, for materials very low minimum ignition energy, the atmospheric oxygen is reduced through inerting to mitigate the dust explosion potential.

1.6 US regulations for dust explosions

The chemical safety board (CSB) is an independent agency that investigates industrial accidents, including dust explosions. Major findings of these investigations include:

i. Over 100 individuals have died and more than 700 have been injured in 300 dust explosions within the last 25 years

ii. Dust explosion prevention and mitigation are not addressed in a comprehensive manner by the US safety regulations

iii. Most of the Material Safety data sheets (MSDS) lack dust explosion hazard information

1.6.1 OSHA standards and regulations

OSHA gives the mandatory recommended standards to be followed. Relevant standards with respect to dust hazards are as follows:

- OSHA 3644-04 2013: Combustible Dust - Fire Fighting Precaution at Facilities:

  This OSHA standard pertains to the Firefighting Safeguards at facilities with combustible dust. The main thrust of this regulation is to protect the emergency responders from injury by giving them essential pre-incident information around any hazard and secure safe working strategies. It identifies the firefighters and other emergency responders who may be called upon in the event of a incident. This control does not provide specifics techniques or measures to be utilized in an emergency situation. The control is restricted to the fire and the hazardous danger of the combustible dust [16].

- OSHA 3674-2013: Combustible Dust - Precaution for Fire Fighters to Prevent Dust Explosions: Firefighters can inadvertently induce a dust explosion by presenting atmospheric air or by unsettling dust creating dust clouds, resulting in an ignition. This regulation the above mentioned issues. It clarifies a standard working strategy to be taken by the firefighters if a dust explosion is plausible [17].

- OSHA 3878-2009: Combustible Dust: Protecting Workers from Combustible Dust Explosion Hazards: This directs the workers working in a dust explosion inclined industry, to relieve the impacts of explosion. It tells how to control the dust, duties of the managers to keep workers safe and the worker's rights. This regulation requires the employer to report and contact OSHA in case of an explosion [18].

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- OSHA 3371-2009: Hazard Communication Guidance for Combustible Dusts: The hazard communication standard comprehensively addresses the assessment of the potential risks of chemicals and the communication of hazard information to workers. It may be a performance-based standard that can be significant to any chemical industry, in which could be exposed to the risk of a dust explosion. This direction is planning to assist makers and merchants of chemicals recognize the potential of dust explosion to distinguish legitimate defensive measures as a portion of their hazard communication standard [14].

- OSHA Hazard Information: Improper Installation of Wood Dust Collectors: The above mentioned title gives non-compulsory controls with respect to moderation of potential fire and blast risks within the working environment related with installed cyclone dust collectors within the wood industry [19].

- OSHA Safety and Health Information - Combustible Dust in Industry: Prevention and Mitigating the effects of Fire and Explosions: This control could be a non-mandatory board that can be actualized within the process industry managing with combustible dusts It deals with the dangers related with the combustible dusts. Proper Measures & guidelines should be followed to decrease the risk of potential for a combustible tidy blast. It gives a preparing module for the laborers, which makes a difference in allowing them to recognize and secure themselves from the dust explosion hazards [21].

- OSHA Hazard Communication Standard: This OSHA's communicating tool mandates the chemical manufacturers or producers or handlers at their workplace for potential hazards, and to convey required Safety Data Sheets (SDSs) with the chemicals they process, in any form [20].

- OSHA General Duty Clause: This requires managers to supply a working environment with no potential risks giving a conducive environment and a sound working environment.

1.6.2 NFPA standards

The National Fire Protection Association (NFPA) is a regulatory body that provides codes/standards to prevent dust explosion hazards. Some of the major NFPA standards which deal with the hazards of dusts explosions are mentioned below:

- NFPA 61: Standard for the Prevention of Fires and Dusts in Agriculture and Food Processing Facilities: The standard is prepared with rules appropriate for food processing plants for moderating fire and risk of dust explosion. It gives the minimum recommended rules required for mitigation from fire and explosion dangers emerging from dusts related to agriculture plants [22].

- NFPA 484: Standard for Combustible Metals: This standard gives the prerequisite of the facilities required for the plants included within the generation, handling, finishing, handling, reusing, capacity and utilization of metals and amalgams that are competent of causing combustion or explosion. This standard is entirely implied only for plants working the above-mentioned activities, and the transportation of metals or alloys vulnerable to explosions [23].

- NFPA 652: The Fundamentals of Combustible Dust: The standard gives the desired least criteria required for the measures to be taken for overseeing fires, flash fires, explosions that can happen due to combustible dust. This code helps other NFPA standards for clean explosion moderation. Wherever other NFPA rules are not appropriate this standard may

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be considered as a thumb rule and ought to be followed. Though this standard could be a bit bland, unless and until indicated in NFPA, this should not be applied [24].

- NFPA 654: Prevention of Fire and Dust Explosion from combustible particulate solids: The standard gives relief measures for all the stages of fabricating, preparing, mixing, passing on, repackaging, and taking care of combustible particulate solids of its hybrid blend, independent of its concentration or particle size [3].

- NFPA 655: Standard for Prevention of Sulphur Fires and Explosions: The standard bargains with the dust hazards related with the diminishment within the size of Sulfur. The reason for the standard is to play down and relieve the inherent fire and explosion dangers related to preparing and taking care of Sulfur. In spite of the fact that this standard is entirely connected as it were to the dealing with the Sulfur, not to other forms like mining, recovery, or transportation. The standard commands the manager who is dealing with the method to comply with all the specified criteria [25].

- NFPA 664: Standard for Prevention of Fires and Explosions in Wood Processing and Woodworking Facilities: The standard gives fire and explosion prevention and relief measures for commercial, industrial, and other facilities which handle wood or make wood items including wood items or other materials having cellulose. The standard would give the plan criteria, operation criteria, and other support measures for carpentry and wood preparing facilities [26].

1.7   Dust explosion and fire mitigation measures

Designing and installation of explosion mitigation or preventive systems are usually undertaken using a prescriptive approach. Some of the most common protection methods are as follows:

1.7.1   Inerting

In some cases, inerting is referred to as blanketing or padding. In any case oxidant concentration reduction utilizes the understanding of NFPA 69 which includes introducing inert gas (such as Nitrogen, Argon, or CO_2) into the system in order to diminish the oxidant concentration to a point at which combustion cannot happen. This method requires that the limiting oxygen concentration (LOC) be known for the combustible dust, and instruments should be introduced to ensure and maintain the required oxidant concentration reduction within the protected system. Other dangers related to inerting ought to be considered as part of the overall approach such as suffocation which can be a threat to personnel in the event that they are not appropriately trained [27].

1.7.2   Explosion venting

Deflagration venting as outlined in NFPA 68 is a method of avoiding the overpressure of an vessel or building through the utilization of a blowout panel or comparable gadget which is designed to yield and discharge at low pressure (regularly 1.5 psig) and remove the fire ball out of the protected volume. Blast venting must redirect the resulting discharge external to the process facility away from personnel. The specified vent range of the blast vents are described by

calculations found in NFPA 68. The maximum dust cloud explosion pressure (Pmax) and the deflagration index (Kst) values for the combustible dust are required in order to design the venting system and these values can be found with the Explosion Severity Test (ASTM 1226).

1.7.3 Flameless venting

Deflagration venting through a recorded flame-arresting device in accordance with NFPA 68 could be a method comparative to standard explosion venting. In any case, instead of discharging a fireball into the zone surrounding the explosion vent opening, the flameless vent will extinguish the fire and expel only the combustion gases which makes it secure for use inside [27]. There are several distinctive types of flameless vents, but all depend on the same basic principle of utilizing stainless steel network as a fire arrestor. Like explosion venting, the objective of the flameless vent is to be in accordance with the calculations found in NFPA 68. Pmax, Kst, and Pred values will all be required for the complete design. Explosion confinement is required to be utilized in conjunction with this arrangement in accordance with NFPA 69. Flameless Venting can be a PASSIVE mitigation procedure.

1.7.4 Containment

Deflagration pressure control in accordance with NFPA 69 is a strategy in which the vessel handling combustible dust is built to withstand the pressure of a deflagration inside the vessel. In most cases, this means building the vessel to resist between 8 and 12 barg (115 to 175 psig) and the pressure that will have to be accounted for is found within the Pmax value obtained by the Explosion Severity Test (ASTM 1226) [28]. Typically, this method is utilized by producers of

milling equipment (e.g. hammermills) and with handing hardware utilized essentially within the pharmaceutical industry. It is vital to guarantee that a control technique utilizes fast-acting mechanical separation in agreement with NFPA 69 that is appropriate for containing pressures to avoid the pressure and fire from exiting through the inlet and outlet of the secured vessel [29]. Control can be passive or active, depending on the sort of confinement.

1.7.5   Explosion suppression

Deflagration suppression in accordance with NFPA 69 is a strategy for recognizing and quenching the deflagration in its early stages, before the pressure has a chance to build up. This is often accomplished by using pressure detectors and chemical suppression bottles to the protected vessel. The chemical suppressant bottles will typically contain powder suppressants such as sodium bicarbonate and a propellant such as nitrogen gas to move the suppressant into the protected volume. These suppression frameworks offer the advantage of not discharging any gas into the area surrounding the protected vessel but can malfunction and trigger if it is not designed, installed, and maintained properly. When planning a chemical suppression arrangement, the Kst, and Pmax of the material must be known (ASTM 1226), while the reduced pressure (Pred) of the vessel must be selected, and the conditions must be considered to guarantee that the sensors will not falsely activate the system due to ordinary working conditions [27].

1.7.6   Dilution

This mitigation technique includes the expansion of a noncombustible solid into a combustible dust mixture to form a mixture that is non-combustible as a whole. An illustrative case

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of where dilution is utilized is within the mining industry where limestone will be spread as a layer on the coal dust in the underground mine shaft passages. When planning a dilution scheme, it is critical to affirm that the resulting mixture is inside the noncombustible zone by having the mixture tested utilizing the Go/No-Go Screening Test over a range of mixture concentrations [27]. One potentially important drawback is the fact that it is difficult to separate the dilution component from the combustible downstream in the process with the dilution method of prevention.

2.   AMINO ACIDS

The minimum ignition energy (MIE) of a flammable substance is the minimum amount of energy an ignition source must supply to initiate combustion. Combustible dusts pose a significant explosion threat in an industrial setting, and the combustion behaviors and safety hazards of such dusts have been the subject of much research [30]. Given the prevalence of solid materials processing in many industries (energy, pharmaceuticals, food, agriculture, chemicals), the dust explosion hazard is of great interest to risk assessment and managerial safety efforts [31]. Despite a lengthy precedent of research on the topic, as well as increased scrutiny of such hazards in the process industries, fatal dust explosions continue to occur on regular intervals [32]. Published research efforts in response to these incidents have addressed many facets on the topic, including experimental determination of MIEs, flammability limits, dust dispersion patterns, and flame propagation [32]. Publications that holistically usually invoke the importance of further fundamental research, which is supported by the continuing trend of incidents [33].

Amino acids are ubiquitous in the industrial preparation of health products, including pharmaceuticals, cosmetics, medicine, and supplements [34]. Industrially applicable amino acids are often stored and handled in the solid phase in the form of a powder. Like many industrial solids, amino acid dusts are combustible under the right conditions. No industrial accidents due to amino acid dusts have been reported, although some groups in the scientific community have anticipated the hazard [35]. For purposes of productivity, the fluorenylmethoxycarbonyl (FMOC) protecting group is often added to amino acids to chemically protect them from undesired reactions, and

permit peptide synthesis with improved methods [36]. Figure 2 below shows a molecular schematic of an FMOC protecting group attached to an amino acid.
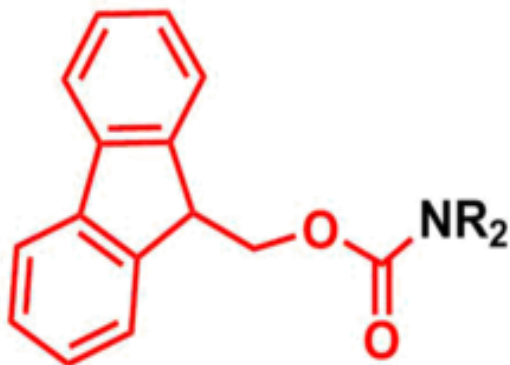

Figure 2: Molecular schematic of Fmoc-protected amino acid.

Although the MIEs of some amino acids dusts have been reported in the literature [37], no significant attention has been paid to the ignition characteristics of Fmoc-protected amino acid dusts. Many applications of FMOC-protected amino acids have been presented in the recent literature, a sample of which are cited here [38].This is a situation where the safety-related research has not yet caught up to the application research, and this shortcoming in the literature is one of the motivators of this study. The results of this study suggest that FMOC-protected amino acids exhibit markedly different combustion behavior than ordinary amino acids, and they are also much more easily ignited. This study applied the widely-known ASTM E2019 [39] standard for the determination of ignition energies of combustible dusts to compare the ignition energies of some amino acids with and without FMOC-protection. Although there are shortcomings recognized in the scientific efficacy of such methods, the ASTM method is widely used, and the MIE is considered the best quantitative metric for characterizing flammable dusts [40].

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3.   METHODOLOGY

3.1   Materials

The materials under investigation in this study were the following five amino acids, which are commonly used in peptide synthesis in the pharmaceutical and other industries: serine, proline, glycine, glutamic acid, and alanine. To complement these amino acids, the Fmoc-protected versions of these amino acids were also examined. All of these materials were obtained in a powdered form. Before measuring MIEs of the study samples, a niacin sample from an international round robin (CaRo17) was tested to verify that the experimental instrument and methodology produced results consistent with previously published values. The dusts used in this study were stored in a desiccant chamber, since adsorbed moisture can cause particle agglomeration and raise dust MIE's [48]. The gas used for the dust dispersion in the experimental apparatus was analyzed by the supplier and found to have 20.6 % oxygen, 0.144 ppm water and the balance nitrogen conforming with ASTM E2019.

3.2   Experimental apparatus

The commercially available Kühner MIKE3 MIE apparatus was used to perform the minimum ignition energy experiments in this study. This device is manufactured to meet the experimental specifications of the ASTM E2019 standard and has been used in many research efforts [49][50][51]. The device features a 1.2 L glass Hartman tube that acts as the test chamber. A nozzle integrated into the tube's housing deploys a pulse of air at 7 bar, which generates a dust dispersion within the tube. After a delay time, electrodes within the tube create a spark within the

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cloud, which may ignite the dust if the spark's energy is greater than the dust's MIE. Table 1 shows the programmable options for the device's inductance, spark energy, and spark delay time. Due to a fixed number and capacity of capacitors in the device, the device is only able to deliver spark energies at the values shown in the table. For this study, zero circuit inductance was selected for all tests, as suggested by ASTM E2019. A delay time of 120 ms (between dispersion and ignition) was selected as a focus point in this study, as for many dusts tested in various studies, this delay time has been found to result in the lowest possible ignition energy in the Kühner MIKE3 MIE apparatus [52].

Table 2: Kühner MIKE3 spark parameters.

Inductance [mH]	Spark Energy [mJ]	Delay Time [ms]
0	1	90
	3	120
1	10	
	30	150
	100	
	300	180
	1000	

For the sake of consistency between experiments, a modification was made to the device, which allows for the utility air to purge the Hartman tube after each experiment. A valve and a flowmeter are monitored by the operator to ensure an adequate purge. Figure 3 below shows a schematic of MIKE 3.
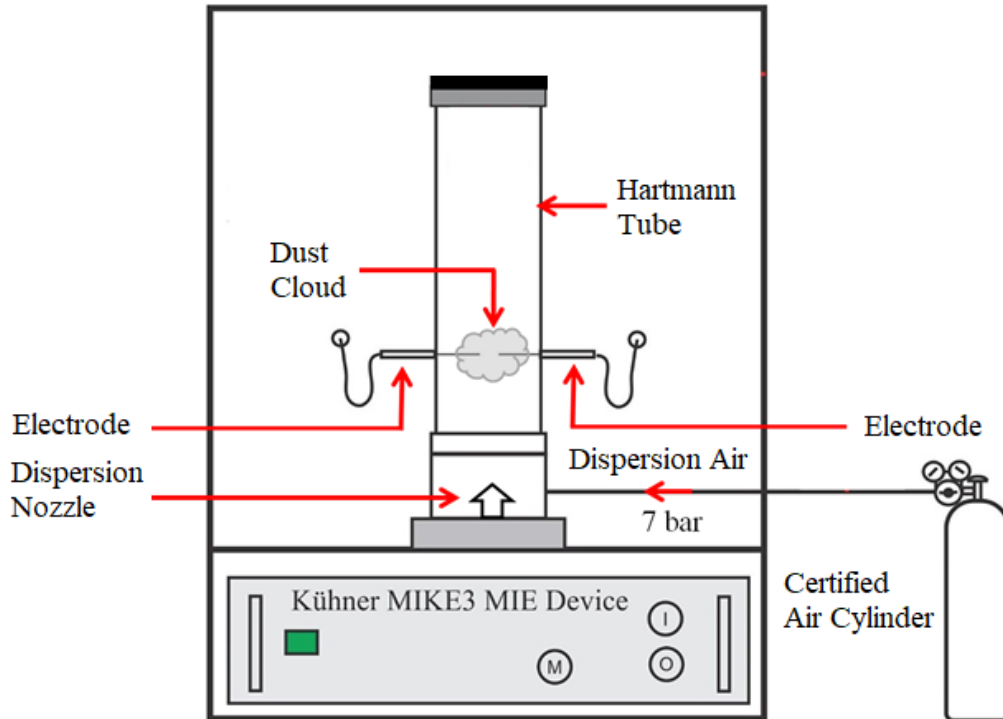
Figure 3: Schematic of MIKE3 minimum ignition energy device.

3.3 Factors effecting the MIE

The Minimum Ignition energy (MIE) of a combustible dust cloud is influenced by the following parameters:

3.3.1   Inductance in the discharge circuit

Dust cloud minimum ignition energy data is dependent on the physics of the capacitive discharge supplying energy for ignition. If capacitors are also discharged through a circuit inductance, the results obtained are different than a capacitive discharge without inductance. The delivered energy can be identical with a non-inductive spark fast while an inductive spark has a longer duration. Hence to assess the electrostatic discharges with respect to dust/air mixtures, the MIE value without inductance should also be found [41]. Figure 4 shows the MIE with and without inductance in the test circuit.
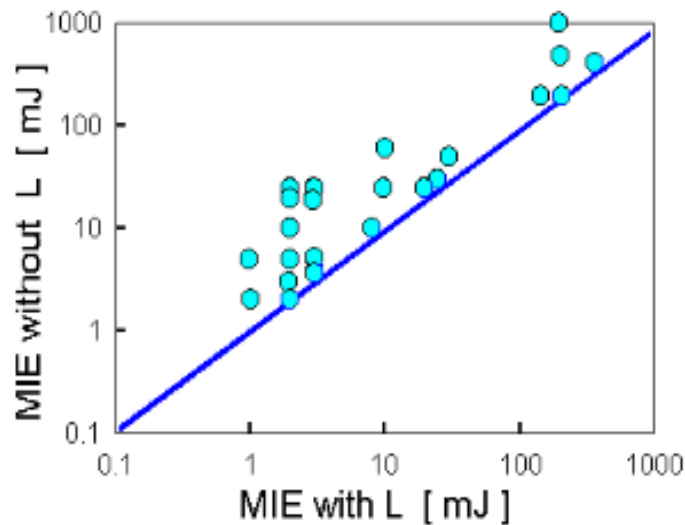
Figure 4: Effect of inductance in a spark circuit on MIE values [60].

3.3.2   Turbulence, ignition delay time

The measurement of a dust cloud MIE should be performed with as low a turbulence as conceivable [42]. Effectively the degree of the turbulence of the dust/air mixtures is the ignition

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delay time (tv) between activation of the outlet dispersion valve and the initiation of a spark. Short delay times result in high turbulence and long delay times in low turbulence. In the event that delay times are long, a partition of the dust can occur, and the result is not meaningful. The ideal delay time which results in the most reduced value of the MIE is not steady but depends on the dust sample. The start delay time must in this manner be changed step by step until the minimum value of the ignition energy is found. Figure 5 shows a relationship between the level of turbulence and the MIE value. Delay times that produce low to medium turbulence levels (typically 120 ms) will result in the lowest MIE values.
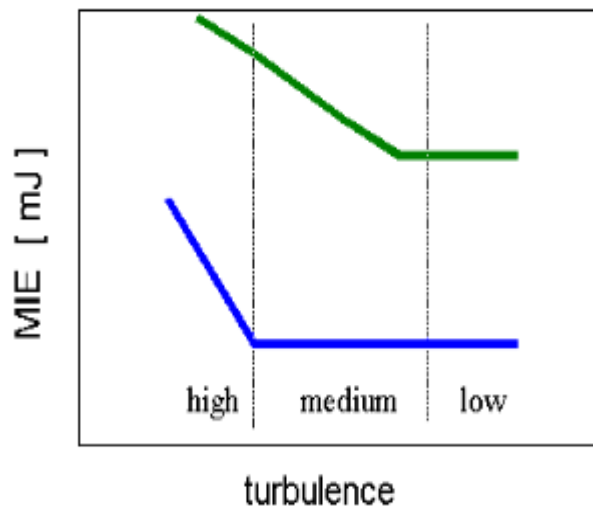
Figure 5: Effect of turbulence on MIE [60].

3.3.3 Particle size

The particle size or the median value can have a dramatic impact on the minimum ignition energy. This energy is related to the cube of the median diameter value of dust. The finer the dust,

the easier it can be lighted [43]. An estimation of an MIE value (MIE_2) at a second mean size (M_2) can be found from a known MIE value and its mean particle size. The estimation equation is as follows:

$$MIE_2 = MIE_1 \cdot (M_2 / M_1)^{2.5}$$

Index 1 : Measured

Index 2 : Estimated
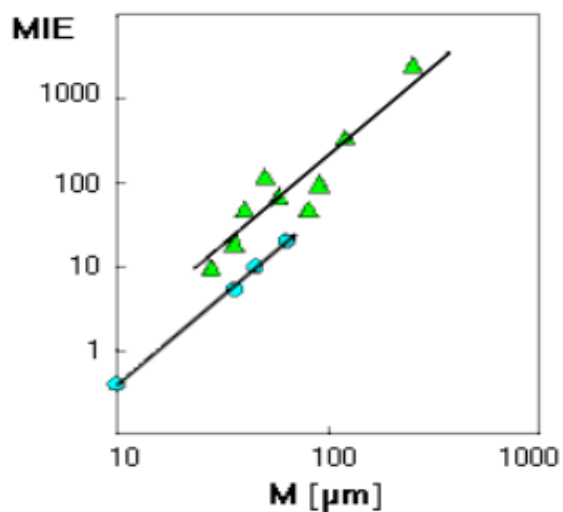
Figure 6: Effect of Particle size on MIE [60].

3.3.4 Dust concentration

There is a parabolic relationship between the dust concentration and the ignition energy. MIE testing must therefore be determined over a wide range of dust concentrations and energy levels [44]. Figure 7 shows a range of dust ignition tests at various concentrations and energy levels in

order to map out an ignition region (above the top parabola – red line) and a no ignition region (below the bottom parabola – blue line).
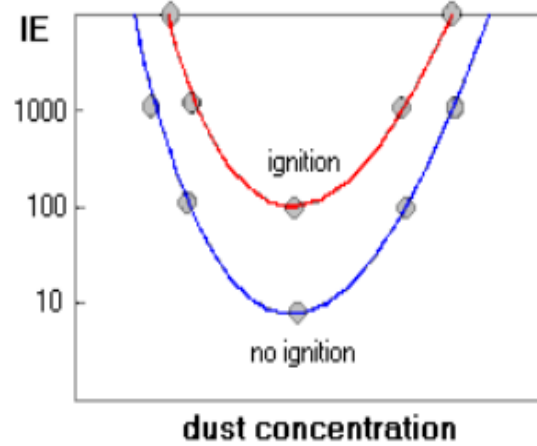
Figure 7: Effect of Dust Concentration on MIE [60].

3.3.5   Temperature

The minimum ignition energy is also influenced by temperature. It is lowered by an increase in temperature to an extent which depends on the ignitability of the dust [45]. In Figure 8 a log-log plot of temperature and MIE for several dusts consists of straight lines which meet at a point (1000°C; 0.088 mJ). In case the minimum ignition energy of dust is known at room temperature, a straight line interpolation can be made to find the minimum ignition energy of the dust-up to temperatures of 300°. The extrapolation formula below can be used to find the MIE in a temperature range from 25 to 300°C:

$$MIE(T) = 10^{-4.056 + (1.873 - 0.624 \log T) \cdot (\log MIE(25°C) + 4.056)}$$
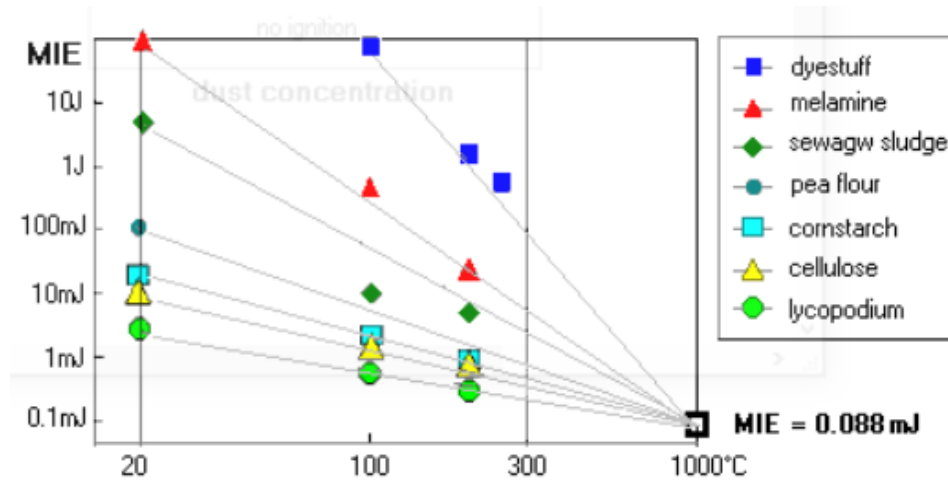
Figure 8: Effect of Temperature on MIE [60].

3.3.6   Moisture content

Figure 9 shows the effect of dust moisture content on the MIE value. As moisture content increases, the dust can form larger agglomerates and the water acts as an inert, both of which increase the energy required for ignition. In general, as shown in Figure 9 below 5% moisture the impact on MIE is minimal [43].
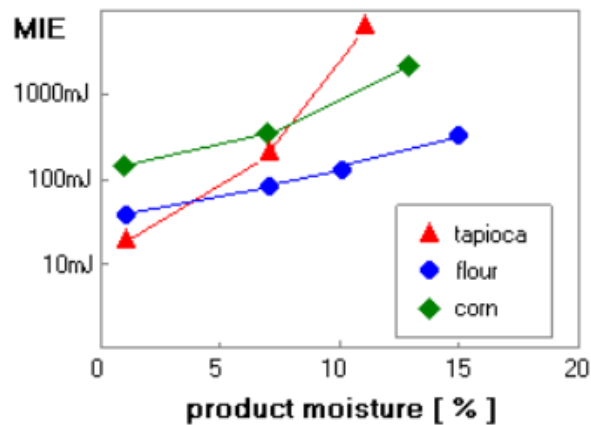

Figure 9: Effect of Moisture on MIE [60].

3.3.7   Oxygen concentration

The oxygen content of the dust cloud dispersion air has an impact on the minimum ignition energy as shown in Figure 10 which depend on the given dust material [45]. In this semi-logarithmic plot, the MIE rises linearly at low oxygen concentrations [47]. At higher oxygen concentrations the MIE tends be less dependent on the oxygen concentration. The overall slope of MIE with oxygen concentration below 21% oxygen is an important concept in partial inerting of dust processing equipment's with both the proper experimental technique and modeling has been proposed [53].
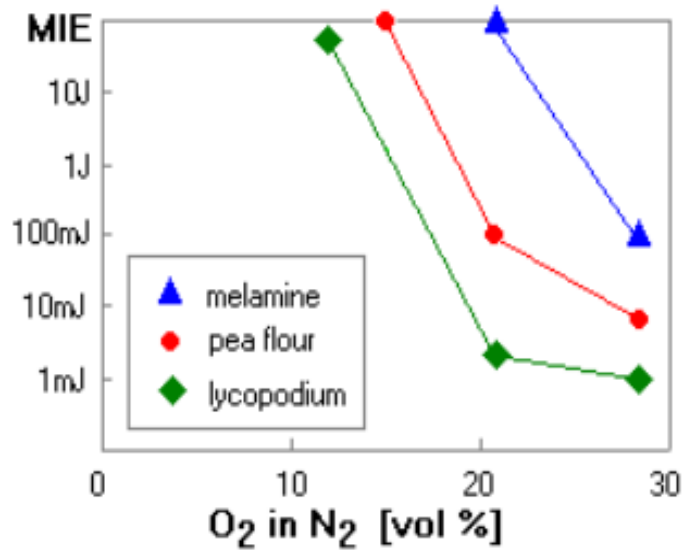
Figure 10: Effect of O_2 concentration on MIE [60].

3.3.8   Addition of flammable gases

The addition of combustible gasses to the dispersion air lowers the minimum ignition energy of combustible dusts and are known as hybrid dust explosions [46]. In Figure 11 a semi-logarithmic plot of the MIE against the included combustible propane gas results in straight lines which meet at a point characteristic of the minimum ignition energy of the specific combustible gas. Plot of MIE for various size coal dusts with added methane are of particular concern for the coal mining industry [61].
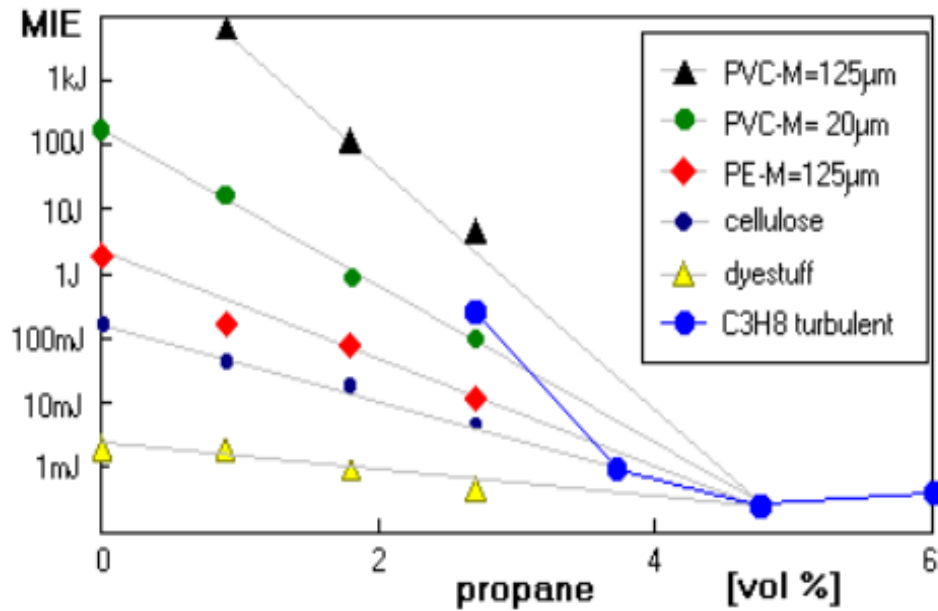
Figure 11: Effect of Addition of flammable gases on MIE [60].

3.4   Procedure

The procedures for sample preparation and operation of the Kühner MIKE3 MIE apparatus closely follow the ASTM E2019 standard. The raw samples were first dried in a nitrogen-purged

oven at 50 °C, then sieved with a 63 μm sieve. The sieving step was done to ensure that the dust particles were of sufficiently small size to meet the requirements in the ASTM standard (≥ 95 volume percent of the sample having diameters of less than 75 microns). After drying and sieving, the dust samples underwent size measurement in a Beckman-Coulter Particle Size Analyzer (model LS 13 320), which generated a particle size distribution (PSD) plot for each dust sample. This information was used to verify that the sample met the ASTM particle size criteria. After the particle size analysis, the sieved dusts were stored in a desiccant chamber until testing in the MIKE3 apparatus.

Each experiment in the MIKE3 device began by collecting and weighing a portion of a previously sieved and dried dust sample. This experimental sample was then loaded into the MIKE3 at the bottom of the Hartmann tube. The operator would then program the MIKE3 device with appropriate inductance, spark energy, and spark delay. Next, the operator instructs the program to deploy a 7 bar pulse of air within the Hartmann tube, which causes the dust sample to become dispersed within the tube, resulting in a dust cloud of a nominal concentration. The capacitive spark would initiate automatically after the appointed delay time, which would result in either a "Go" (dust cloud ignition) or a "No-Go" (failure to ignite the dust cloud). In the event of a No-Go, the dust was carefully brushed from the electrodes and Hartmann tube walls, returning it to the bottom nozzle area of the Hartmann tube, such that it could be retested. In this study, samples were replaced if they resulted in three consecutive No-Go dispersions. Experiments for a given sample quantity and spark energy were repeated up to ten times under the same conditions to ensure that such conditions would not result in ignition. If all ten trials resulted in a No-Go, then the conditions were considered to be preclusive for ignition and were recorded collectively as a

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No-Go [53]. However, if any of the up to ten trials resulted in a Go, then the conditions were considered conducive to ignition, and were recorded collectively as a Go. This approach is consistent with loss prevention principles, as the most conservative MIE should be reported to assess risk.

Spark energy and dust mass (or nominal dust cloud concentration) are the two experimental variables typically reported in ASTM E2019 experiments. After the ignition capabilities of a particular experimental condition were resolved, one or both of these variables was changed, and the new conditions were tested. The goal of the experimental routine was to mark enough conditions as either Gos or No-Gos such that the minimum ignition energy could be graphically ascertained, following the guidelines outlined in the Kühner MIKE3 operation manual and discussed further in subsequent sections.

4.   RESULTS AND DISCUSSION

4.1   Particle size distribution

Although the particle size distributions of this study's dust samples are not the primary result of this work, it is necessary to present them to contextualize the resulting MIE values. As explained in the methodology section, all amino acid and Fmoc-protected amino acid samples were received as dusts, before being dried, ground and analyzed in the Beckman-Coulter particle size analyzer. Drying was performed to prevent moisture from raising the experimental MIE values. The grinding and sieving are performed to meet ASTM standard E2019 criteria of the dust particles being ≥ 95% by volume smaller than 75 microns. It is worth noting that the grinding and sieving was, in some cases, an iterative process, as a single round of grinding and sieving did not always result in a PSD that satisfied the ASTM requirement.

It has been recognized in the study of flammable dusts that MIEs decrease with decreasing dust particle size. This is supported by principles of reaction kinetics and heat transfer   (Bagaria et al., 2019b), as very fine dusts will have more surface area over which to undergo pyrolysis, resulting in a lower required energy threshold for ignition. The ASTM requirement that ≥ 95 volume percent of the particles be less than 75 microns in diameter is meant to address this issue, and to provide some standardization to the dusts being tested in independent projects. However, the ASTM standard provides no criteria for the PSD shape; in other words, any PSD is acceptable, as long as the sample meets the size requirement. Figs. 3a and 3b show the PSDs for L-serine and Fmoc-protected L-serine, respectively, and represent typical PSDs for samples in this study. Table

30

2 shows a statistical summary of the particle size distributions for all of the samples in this study while Supplementary Information contains data showing the PSD curves.
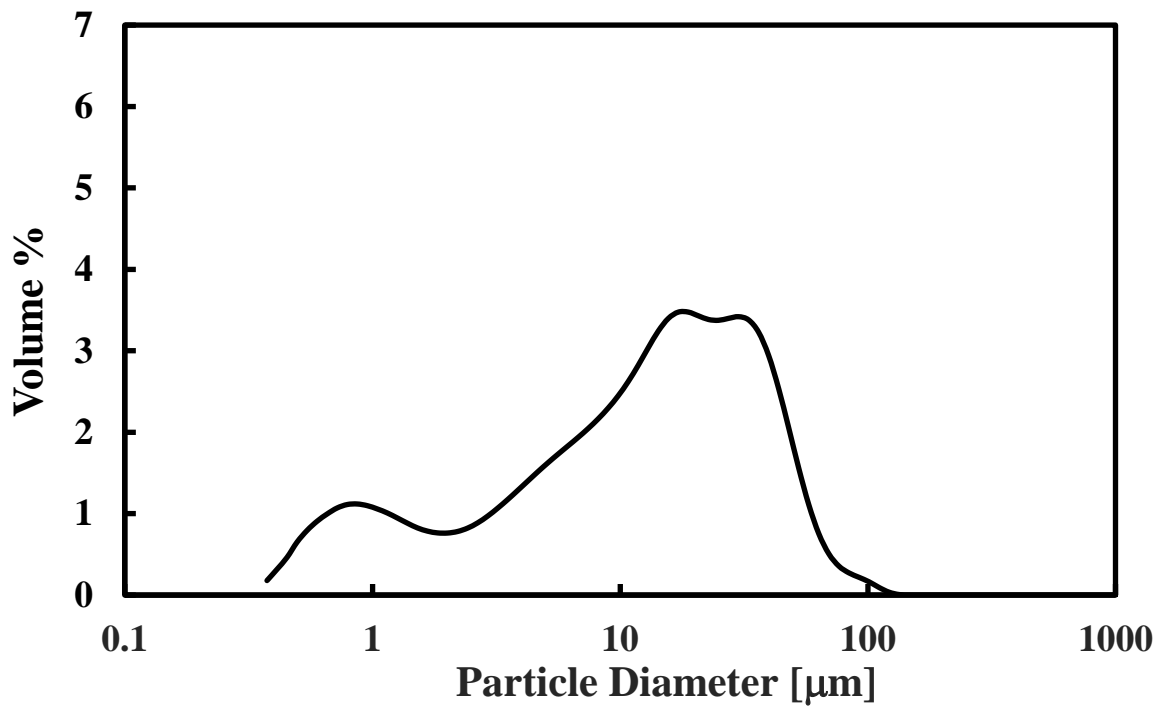

Figure 12: L-Serine particle size distribution (after drying, grinding, and sieving).
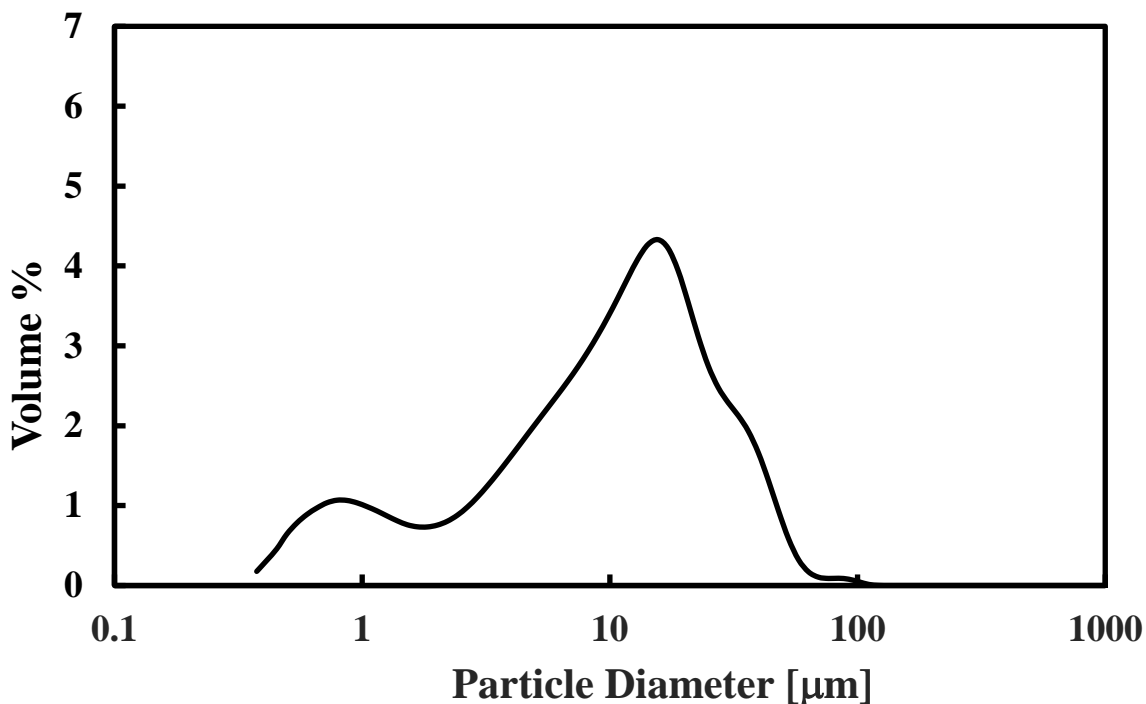
Figure 13: F-moc L-serine particle size distribution (after drying, grinding, and sieving).

Note that despite the internally consistent dust processing techniques used in this study, the PSDs for L-serine and Fmoc-protected L-serine are markedly different, although they both satisfy the ASTM E2019 requirements. Considering the fact that PSDs are highly subject to dust manufacturing, collection, and preparation processes, it is unlikely that two samples of the same dust species, when used in independent studies, will have similar PSDs [54]. The lack of any perceivable vertical pattern between the rows of Table 2 speaks to this difficulty. Vast differences in amino acid dust MIEs with discrepant particle sizes have been observed [37] This is not such a problem in the context of loss prevention and risk management, as samples of hazardous dusts might be taken as-is from a process wherein they are accumulating, sieved in bulk, and tested directly.

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Table 3: Statistical summary of particle size distributions.

	Mean [μm]	S.D. [μm]	D_{10} [μm]	D_{50} [μm]	D_{90} [μm]	D(3,2) [μm]
L-Analine	19.87	17.00	1.425	16.49	42.25	4.554
L-Glutamic Acid	29.06	21.65	3.336	27.29	54.20	7.135
Glycine	23.15	21.23	1.728	18.39	48.89	5.074
L-Proline	21.78	31.65	4.596	13.72	40.44	6.579
L-Serine	18.97	17.90	1.175	14.18	43.22	3.963
Fmoc-Analine	17.58	10.51	5.399	16.09	31.88	8.058
Fmoc-Glutamic Acid	15.31	11.26	1.917	13.24	31.58	4.875
Fmoc-Glycine	11.88	21.05	21.05	4.054	32.70	1.960
Fmoc-Proline	14.35	8.214	4.622	13.51	24.91	6.554
Fmoc-Serine	14.50	13.18	1.218	11.36	32.34	3.868

4.2   Amino acid MIEs

The MIE values of ordinary amino acids were measured first, so as to have a meaningful starting value to initiate Fmoc-protected amino acid testing and to contrast the MIE values. Following the procedure outlined in the previous section, the MIE behavior for each amino acid was characterized for several cloud concentrations. Figure 14 a-b shows L-proline and Fmoc-protected L-proline MIE behavior, and similar graphs were also constructed for the eight other amino acid and Fmoc-protected amino acid dusts and can be found in the Supplementary Information.
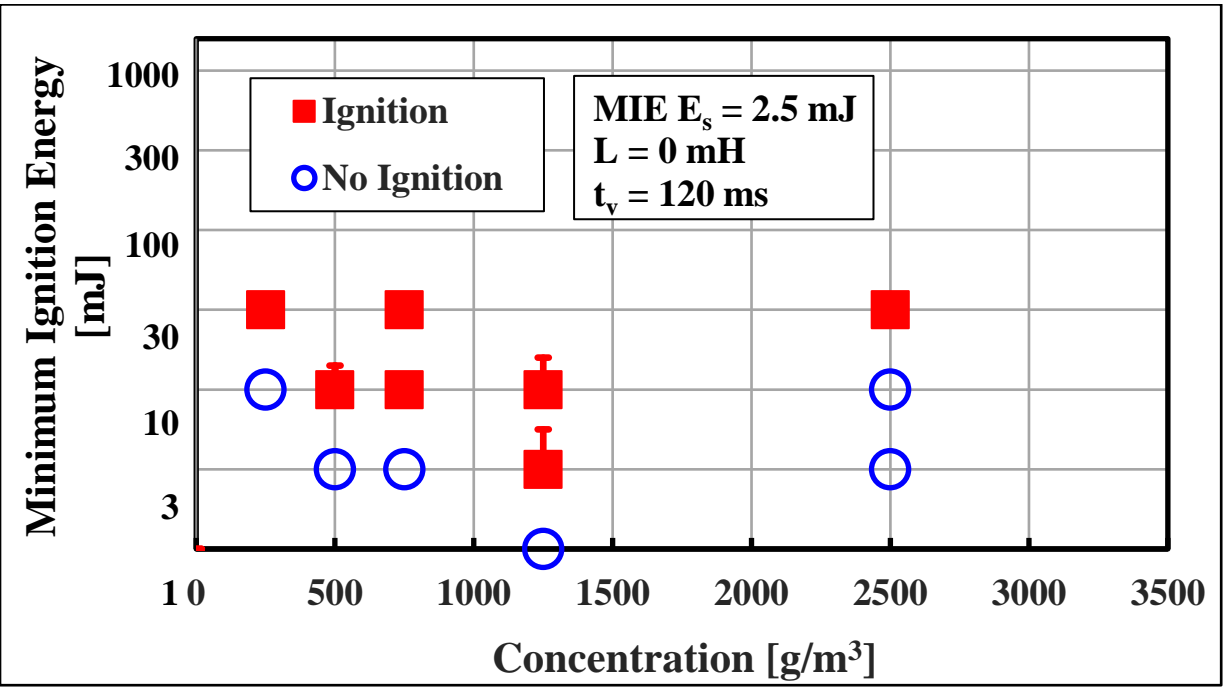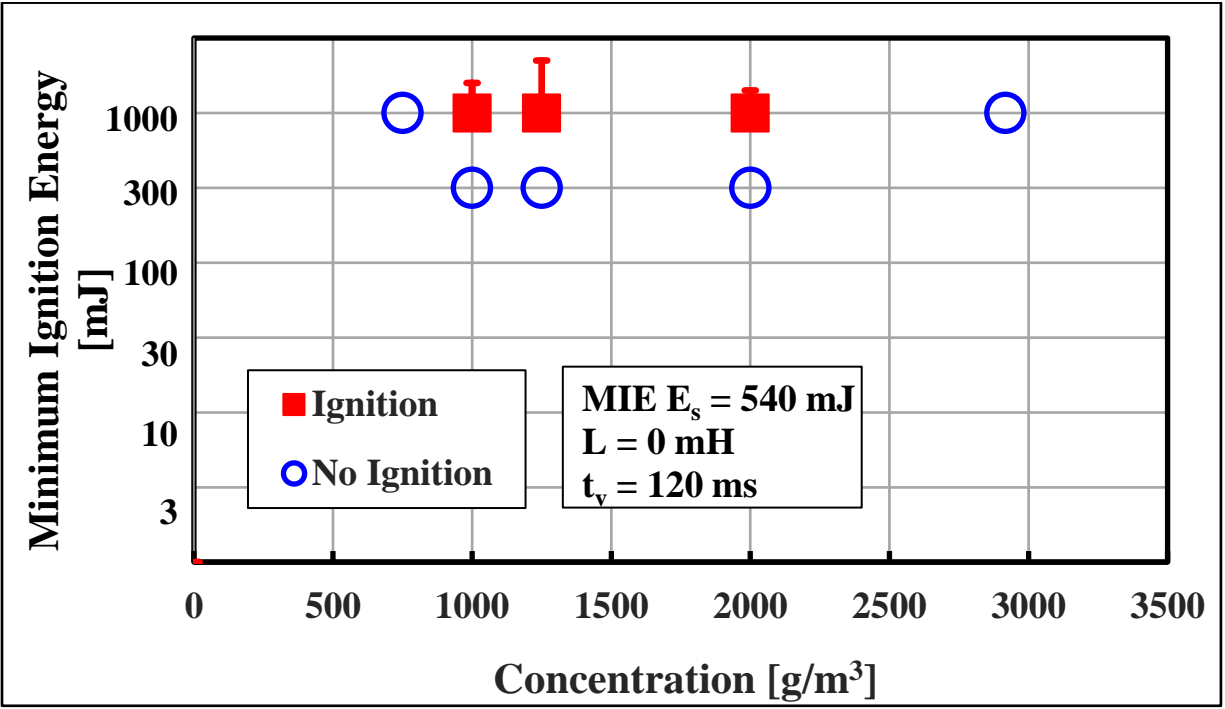
Figure 14: (a) L-serine and (b) Fmoc-protected L-serine minimum ignition energy region.

It can be seen in Figure 4 that all ignition energies tested were at fixed energy levels as listed in Table 1. This is not a requirement of the ASTM E2019 standard, but rather a constraint in the capabilities of the MIKE3 device. Due to this equipment constraint, it is only possible to characterize the dust ignition energies within a certain resolution. To counter this, the apparatus' software provides an approach for interpolative estimation based on the equation below.

$$log(E_s) = log(E_2) - I_2 \frac{log(E_2) - log(E_1)}{T_2}$$

Where E_s is a dust concentration's likely minimum ignition energy, E_2 is the lowest spark energy resulting in ignition, E_1 is the highest spark energy failing to cause ignition, I_2 is the number of tests at E_2 that resulted in ignition, and T_2 is the total number of tests at E_2. By applying this equation, the likely MIE values were obtained for each amino acid. Literature on the topic of amino acid dust ignitions is very sparse, and mostly limited to several papers published by a team at Hiroshima University in Japan [35][37][55].

Table 4: Amino acid MIE values for this work and those in literature.
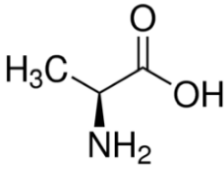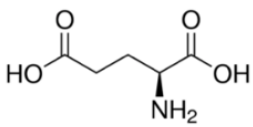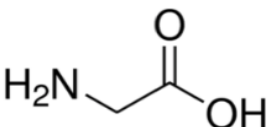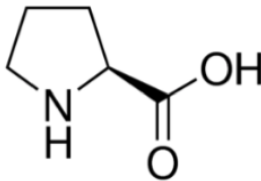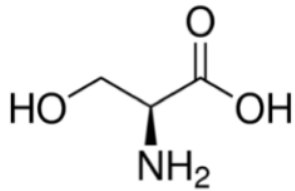
Amino Acid	Structure	Kim et. al., 2019b [mJ]	This Work [mJ]
L-alanine		55	79
L-glutamic acid		No value	540
glycine		540	>1000
L-proline		No value	16
L-serine		700	540

Table 3 shows the MIE values for each amino acid value for this work, compared to values published by the Hiroshima team, and showing that the corresponding values are roughly

equivalent. However, Kim followed the International Electrotechnical Commission (IEC) standard [56] which calls for inductance in the ignition circuit, while this work followed ASTM E2019, which calls for zero inductance [39]. The presence of inductance is known to cause a spark of longer duration, thereby lowering the MIE value [57]. It is also worth noting that Kim used a much smaller particle sieve (15-28 microns) than was used in this study (< 63 microns), which accounts for the comparatively lower MIE for L-alanine and glycine. The comparatively higher MIE for L-serine, despite the smaller particle size and presence of inductance, is not accounted for. It is possible that this discrepancy is due to a different number of tests at different spark energies, which would affect the outcome of Eqn. 1. As far as experimental error goes, the challenges of experimental combustion research are always many, and have been discussed with respect to MIE experimentation in the literature [40].

4.3   Fmoc-protected amino acid MIEs

No literature adequately addresses the topic of the ignition behavior of F-moc-protected amino acids. In all five cases tested in this study, the MIE was observed to be lower for the F-moc protected material than for the parent amino acid. Fig 15 shows the minimum ignition energy characteristics for the F-moc L-proline. Table 3 summarizes the MIE values for each of the amino acids and F-moc Protected amino acids. Figures for the rest of the FMOC-protected amino acids can be found in the Appendix.

Table 5: Amino acid and Fmoc-protected amino acid MIEs of this study.

Amino Acid	MIE [mJ]	Fmoc-protected MIE [mJ]
L-alanine	79	15
L-glutamic acid	540	2.1
glycine	>1000	17
L-proline	16	6
L-serine	540	2.5

It is clear that the Fmoc-protected amino acid dusts are much more easily ignited. It was originally thought that the Fmoc-protected amino acids might feature lower MIEs due to having comparatively smaller characteristic particle sizes. While the PSDs of the Fmoc-protected amino acids are skewed to a smaller particle diameter (see Supplementary Information), which would be indicative of more readily igniting dusts, they were not sufficiently different from the ordinary amino acids to cause such large decreases in MIE. A comprehensive analysis of the decrease in Fmoc-protected amino acid MIE is beyond the scope of this publication. However, it is hypothesized that the increase in ignitability of the Fmoc-protected amino acids is more likely due to molecular characteristics (nano-scale surface area, susceptibility to pyrolysis, etc.) than macroscale dust properties (dust dispersibility, PSD, etc.). The extended ring structure of the Fmoc protecting group likely adds to the molecule's flammability. It is known that dust MIEs are directly related to surface weighted average diameter (D(3,2)) [58], but the Hiroshima team showed data suggesting that this dependence alone would not account for this much discrepancy [59]. Several publications have discussed pyrolysis in the context of MIEs for organic molecules, and the high variability in MIEs of the ordinary amino acids suggests that pyrolysis kinetics may be significant in the ignition characteristics of such molecules [35].

5.   CONCLUSIONS

This work has presented the minimum ignition energies of five amino acid powders and their corresponding Fmoc-protected variants. It has been shown via experiments in the Kühner MIKE3 apparatus that the MIE values of the Fmoc-protected amino acids are significantly lower than their unprotected counterparts. In the context of process safety, the treatment of Fmoc-protected amino acid dusts as being equivalent to ordinary amino acid dusts would be a gross safety oversight, and it could be safely said that utilizing Fmoc-protected dusts is significantly more hazardous.   Although the applications of Fmoc-protected amino acids constitute only a specialized fraction of the industries previously mentioned, the novelty of this data has greater implications. The most important conclusion for the at-large process safety interest may be the novelty of the data in and of itself. While dust explosions are understood to be a significant threat to safety in solids processing, minimum ignition energy data is nearly nonexistent in the literature for amino acids, peptide chains, or protected organic molecules. This work begins to address this deficiency by presenting experimentally determined MIEs for a selection of amino acids, as well as the MIEs of their much more hazardous Fmoc-protected counterparts.

6.   RECOMMENDATIONS AND FUTURE WORK

The content of this paper invokes several recommendations for further research on the topic of amino acid ignition and MIEs in general. A great deficiency exists in the literature on the combustion characteristics of amino acid dusts, and a rather straightforward objective would be to characterize the MIEs and flammability limits for dusts of all twenty amino acids. The combustion characteristics of protected amino acids or simple peptide chains, and a comparison between such molecules and ordinary amino acids, would also be applicable. With respect to the ASTM standard, researchers on this topic should be aware of shortcomings to this experiment that have been pointed out in the literature, as well limitations on the capability of standardizing the all-important particle size distribution for such experiments. Although it was not possible using this study's methodology, a tighter resolution on spark energy values in the experimental apparatus would decrease uncertainty and would be useful when comparing very similar amino acids or making attempts to model ignition energy.

In the context of process safety and risk assessment, the vast MIE difference between amino acid dusts and their Fmoc-protected counterparts suggests a serious safety concern for any organization working with solid-state protected amino acids. More generally, the reported challenges to creating dust samples with similar PSDs suggests uncertainty in the entirety of dust explosion experimentation, and as such, it is recommended that particle size become the subject of increased scrutiny, and that MIE values be considered very conservatively. With respect to risk assessment, the discrepancy between the ordinary amino acids and the Fmoc-protected counterparts serves as a reminder that even seemingly benign substances, such as amino acid dusts,

can be made much more hazardous through routine chemical treatment, and complacency must be warily avoided.

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8. APPENDIXES

Appendix A: Amino Acid Dust Sample PSDs

Particle Size distributions for the ordinary amino acid dusts that were tested in the MIKE3

minimum ignition energy device in this study. (Fig. A.1 – Fig. A.5)

Fig. A.1. L-Alanine particle size distribution.

Fig. A.2. L-Glutamic acid particle size distribution.
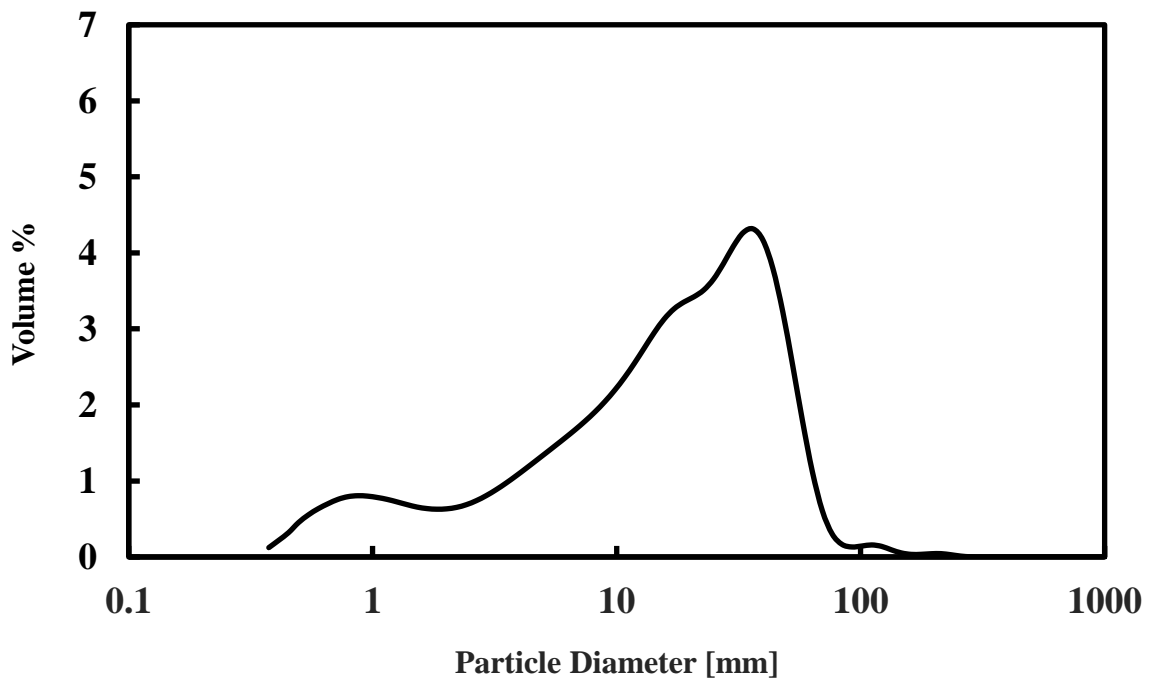
Fig. A.3. Glycine particle size distribution.
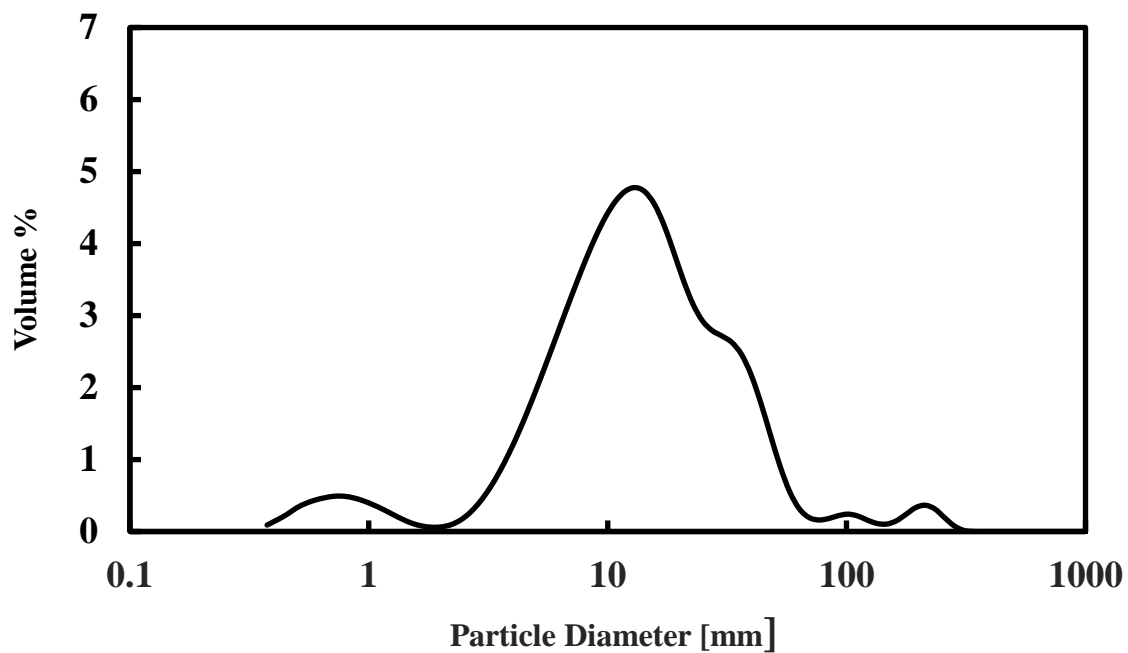
Fig. A.4. L-Proline particle size distribution.
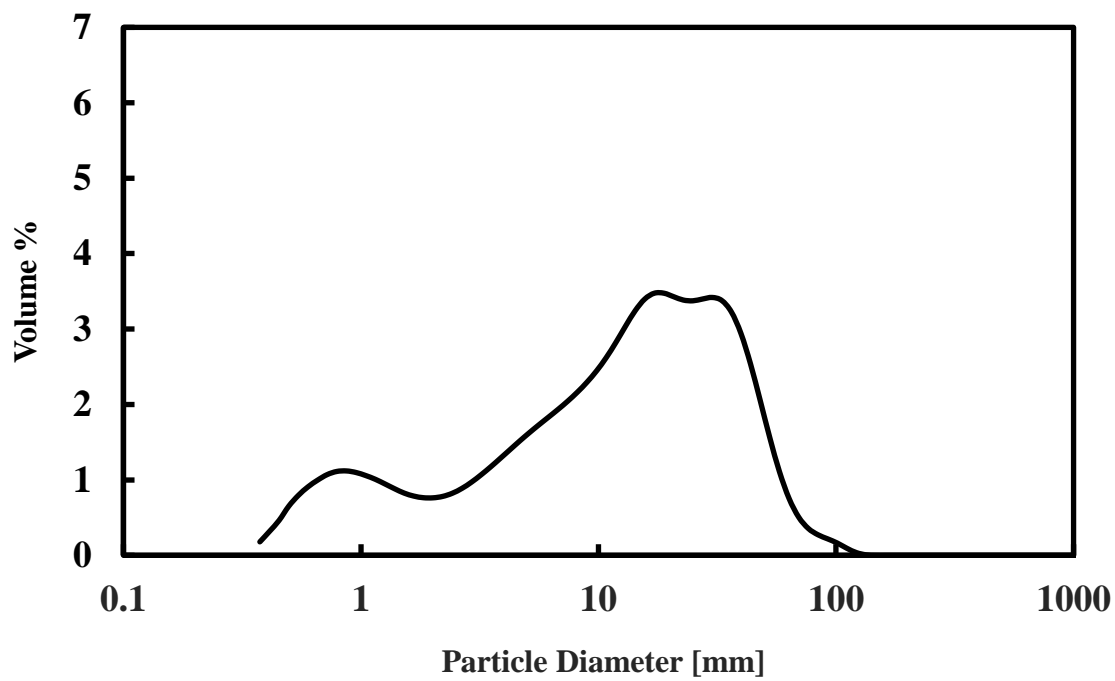
Fig. A.5. L-Serine particle size distribution.

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Particle Size distributions for the Fmoc protected amino acid dusts that were tested in the

MIKE3 minimum ignition energy device in this study. (Fig. A.6 – Fig. A.10)

Fig. A.6**.** Fmoc L-Alanine particle size distribution.
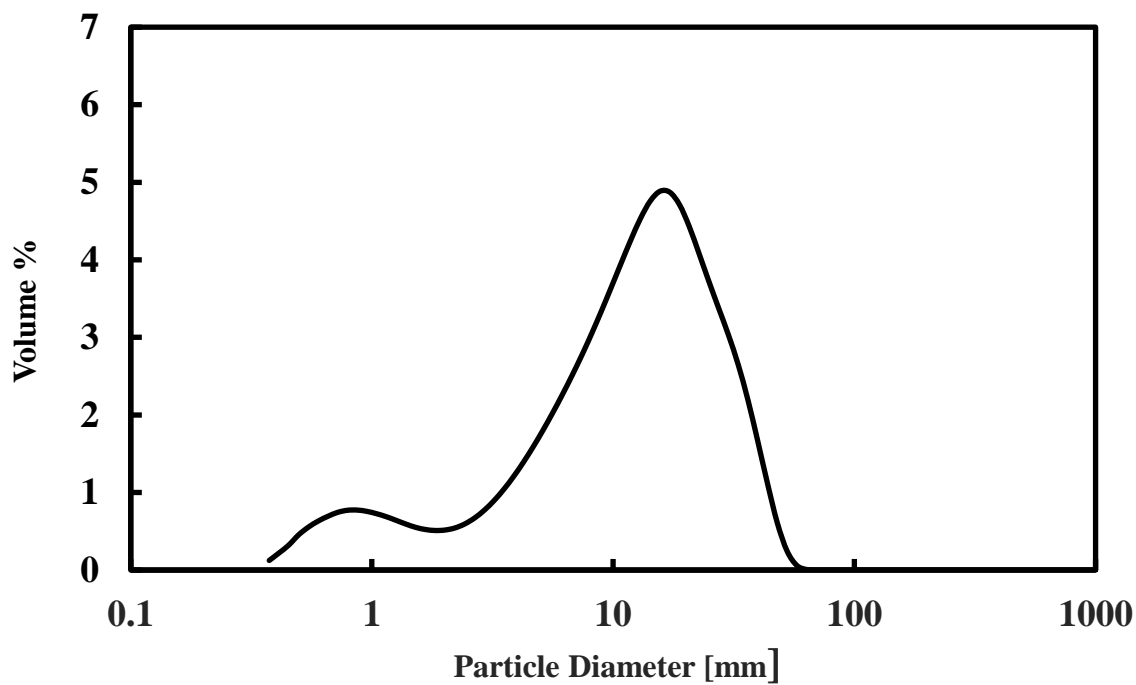
Fig. A.7. Fmoc L-Glutamic acid particle size distribution.
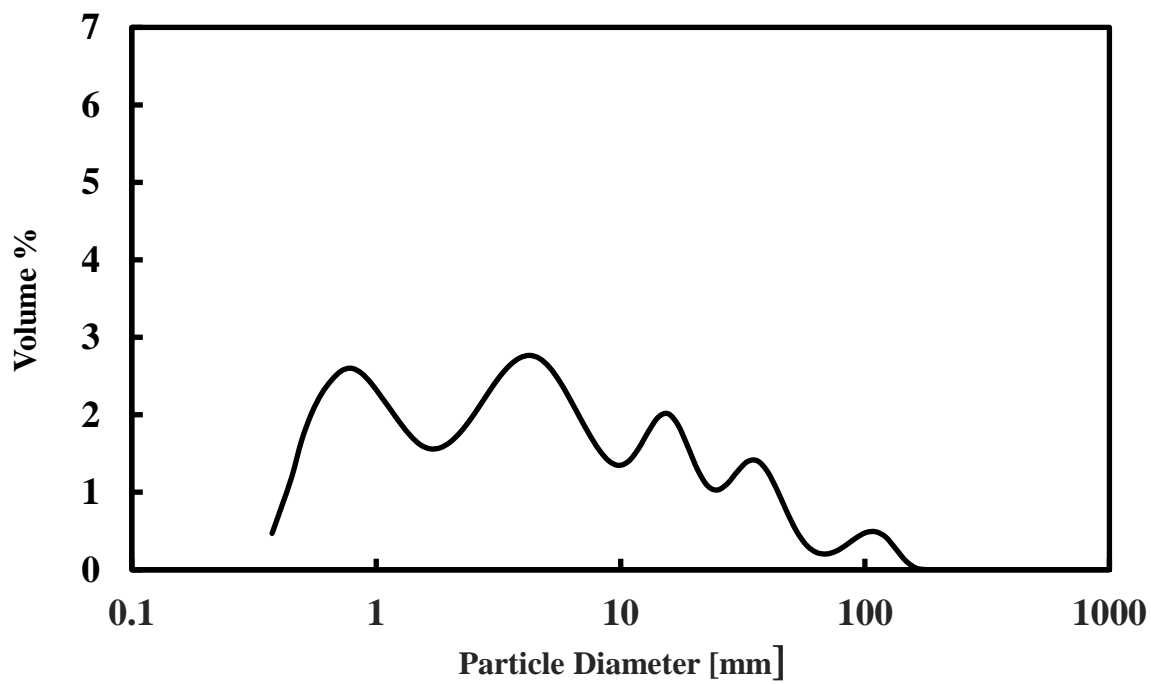
Fig. A.8. Fmoc Glycine particle size distribution.
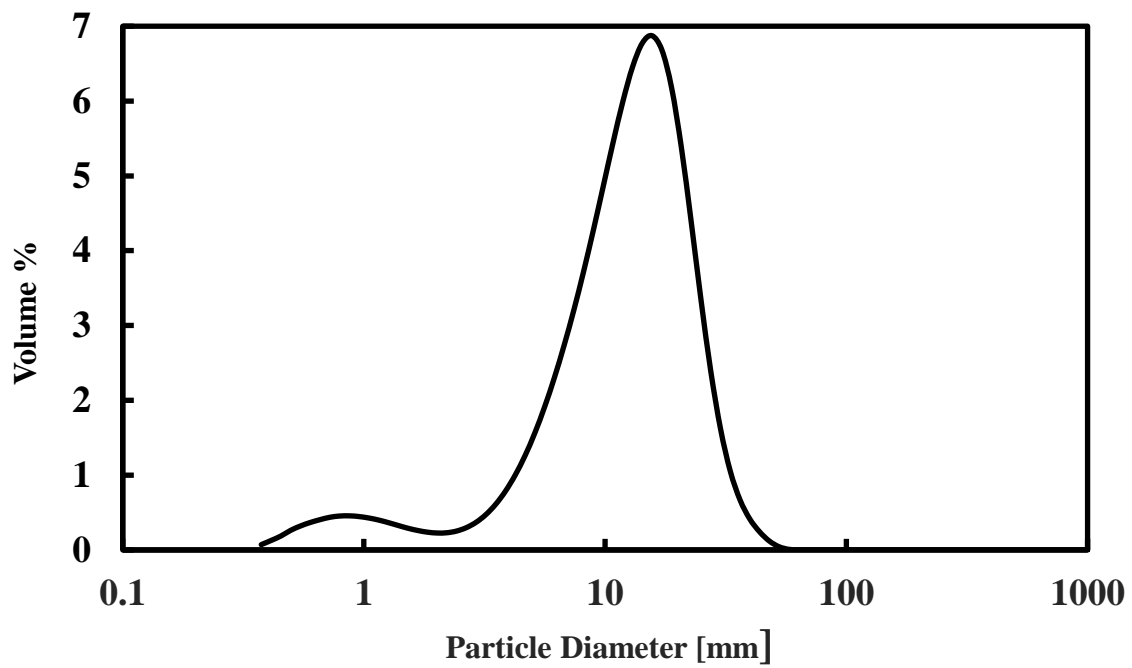
Fig. A.9. Fmoc L-Proline particle size distribution.
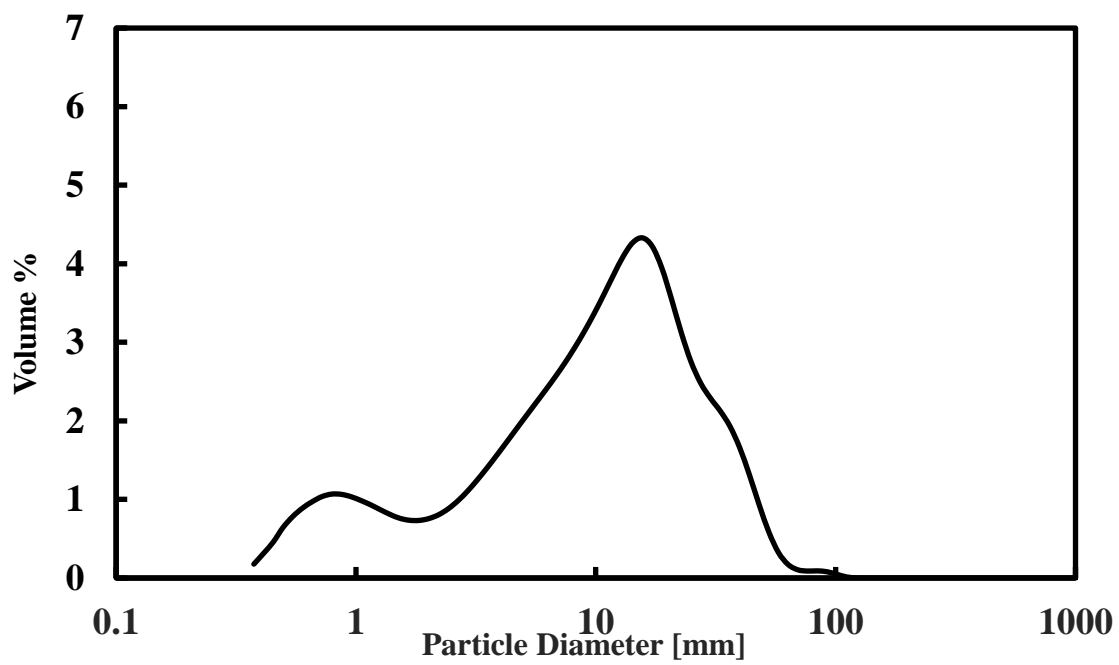
Fig. A.10. Fmoc L-Serine particle size distribution.

Appendix B: Dust Sample Ignition Behaviors

This appendix features a side-by-side comparison of the ignition behaviors for the ordinary and FMOC-presented amino acids. (Fig. A.11 – Fig. A.20)
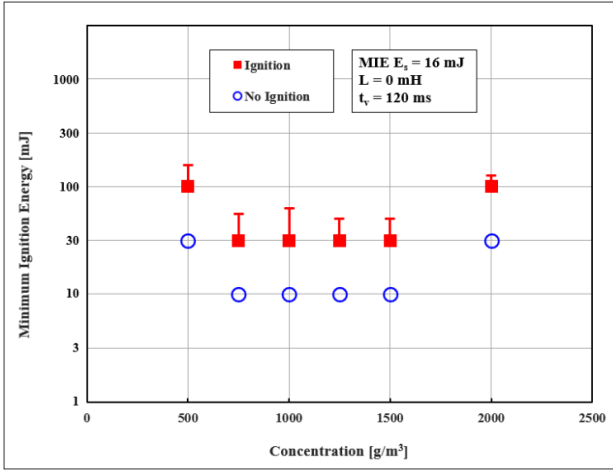
Fig. A.11. L-Proline ignition region.
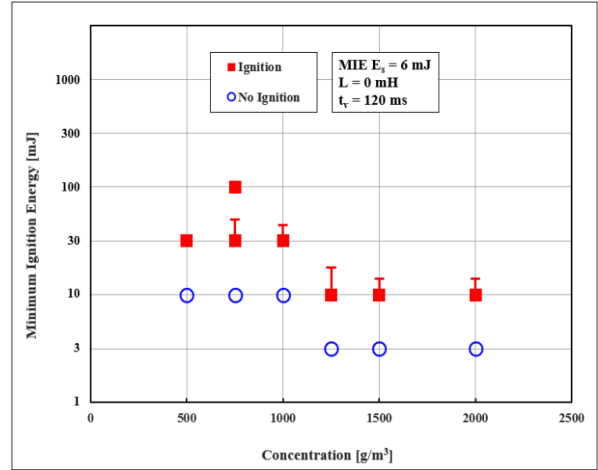
Fig. A.12. Fmoc L-Proline ignition region.
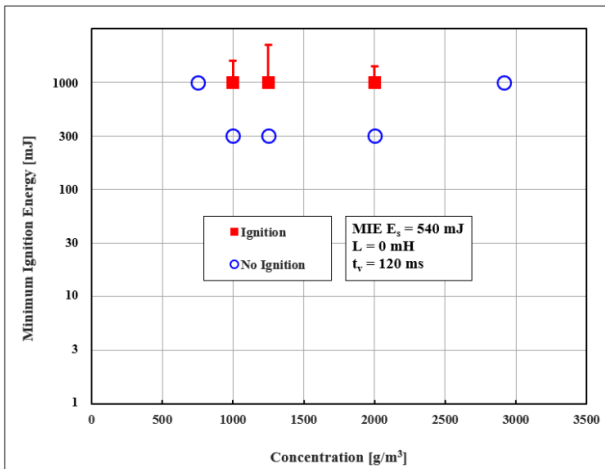
Fig. A.13. L-Serine ignition region.
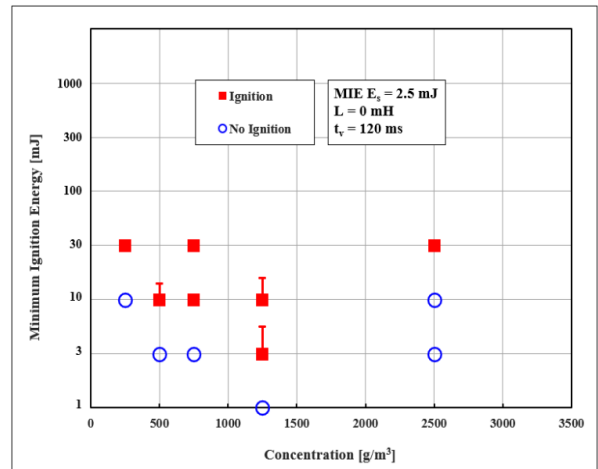
Fig. A.14. Fmoc L-Serine ignition region.
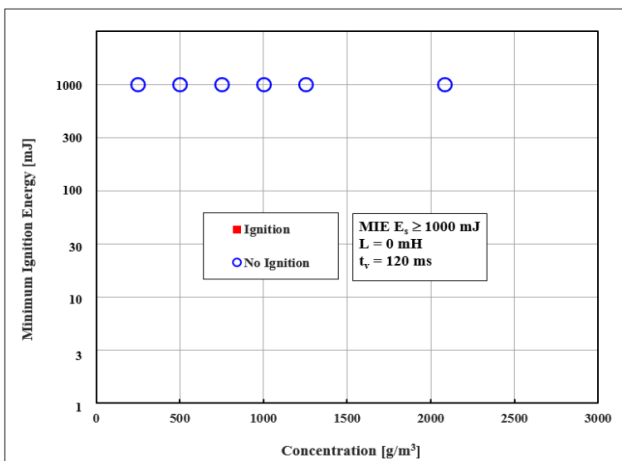
Fig. A.15. Glycine ignition region.
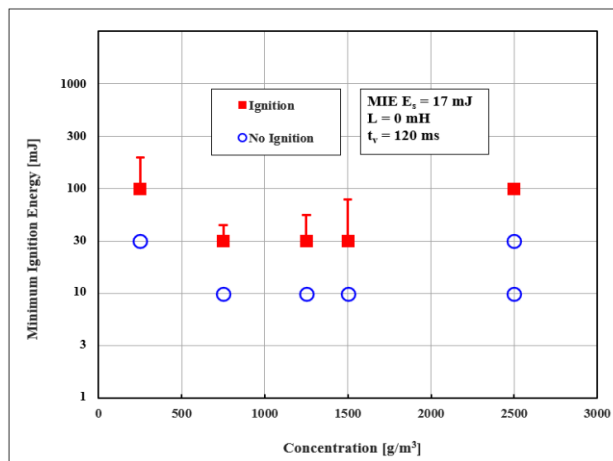
Fig. A.16. Fmoc Glycine ignition region.
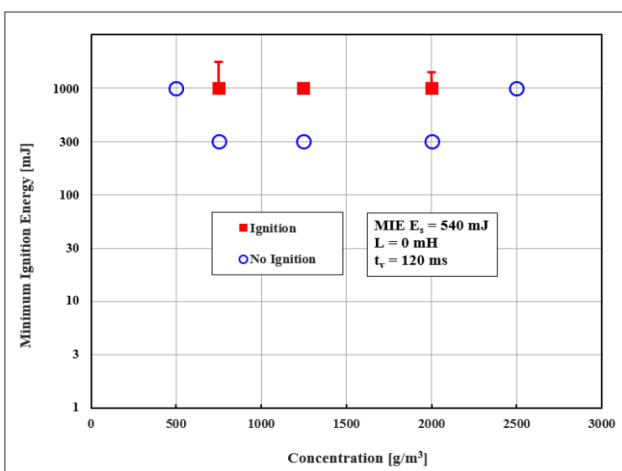
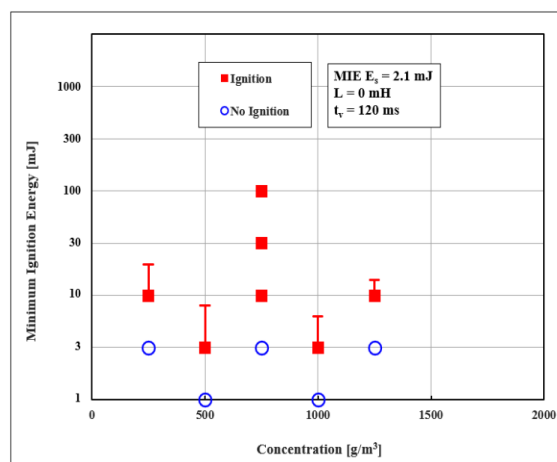Fig. A.17. L-Glutamic acid ignition region.

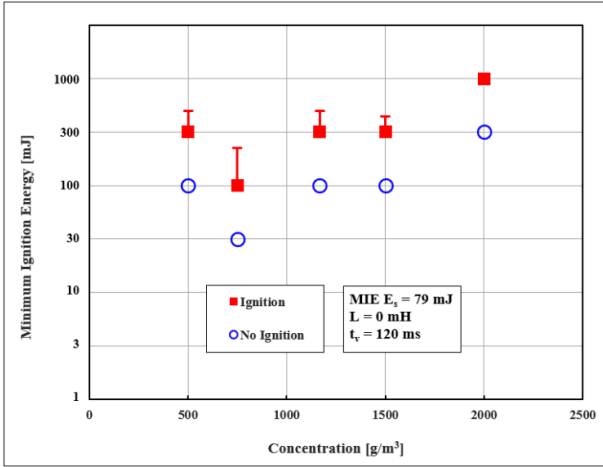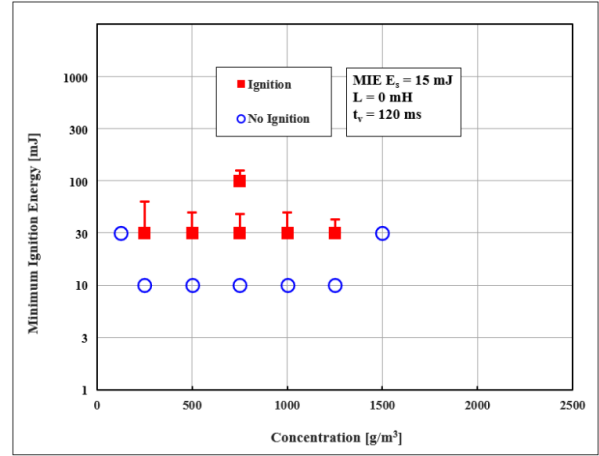Fig. A.18. Fmoc L-Glutamic acid ignition region.

Fig. A.19. L-Alanine ignition region.

Fig. A.20. Fmoc L-Alanine ignition region.