Influence of the ignition source on the Safety Characteristics of hybrid dust-gas mixtures

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Abstract

Safety characteristics like the lower explosion limit, the highest concentration for a given substance mixed with air that does not result in a self-propagating flame, or the maximum explosion pressure, the highest pressure that can be reached after ignition for a given combustible substance mixed with air at any concentration, are widely used in the industry to either prevent an explosion or to mitigate the effects of it. Safety characteristics are not physical constants, are determined experimentally and depend on the chosen experimental parameters such as the ignition energy or turbulence.

For the determination of the safety characteristics lower explosion limit (LEL), limiting oxygen concentration (LOC), maximum explosion pressure (p_{max}) and maximum rate of pressure rise ($(dp/dt)_{max}$) of gases and vapors the gas is filled via partial pressures into a test vessel and then ignited under quiescent conditions with a weak (2 J - 20 J) ignition source. For dusts, the same safety characteristics are determined under turbulent conditions to elevate the dust homogeneously and it is ignited with two chemical igniters with an ignition energy of 1000 J each (LEL and LOC) or 5000 J each (p_{max} and $(dp/dt)_{max}$). For the determination of safety characteristics of hybrid mixtures (a mixture containing a combustible dust and a flammable gas) there is no existing standard.

In the last 40 years most of the research on their safety characteristics was performed with dust testing equipment that was modified for the addition of flammable gas. Because of the different mixing procedures of gases and dusts with air and because of different ignition energies and sources that are normally used for the standard tests of gases or dusts, the results were hardly reproducible. Statements about the different safety characteristics were contradictory and left the reader or the person responsible for designing safety measures for a process plant or a facility behind with no clear suggestion about the behavior of hybrid mixtures.

This thesis is aimed on determining the influence of the different ignition sources and energies on the safety characteristics p_{max}, $(dp/dt)_{max}$, lower explosion limit, and limiting oxygen concentration of hybrid mixtures.

Several test series were conducted to characterize different standardized ignition sources, that are already in use for the determination of safety characteristics of single-phase substances (gases, liquids, dusts). The burning duration, the igniting volume and the net energy were investigated.

It was shown, that the chemical igniters and the exploding wire are suitable ignition sources for the determination of safety characteristics of hybrid mixtures in general. Their burning duration was long enough to ignite dusts and quick enough, that the decay of the turbulence or sedimentation of the dusts did not occur. Both ignition sources produced comparable results for the determination of p_{max}, LEL and $(dp/dt)_{max}$ of dusts when they had the same ignition energy. A reduced ignition energy of the exploding wire and the chemical igniters did not affect the p_{max} and $(dp/dt)_{max}$. The LEL changed with lower energies. However, for the determination of the LOC of hybrid mixtures the exploding wires with an overall energy of 2 kJ produced the best results.

The influence of the different mixing procedures that have already been used for hybrid mixtures and the requirements for them were also investigated experimentally for the gas concentration and the determined safety characteristics and compared to each other. It was shown, that the partial pressure method works for mixing hybrid mixtures but the pressures should be measured very accurately and the gas concentration should be validated.

Furthermore, the influence of the turbulence that is inevitable when testing dusts, on the safety characteristics of gases was determined. It was found that the chemical igniters and exploding wires produced comparable results for the determination of p_{max}, LEL and $(dp/dt)_{max}$ under turbulence. For the LOC only exploding wires with two times 1 kJ worked.

Finally, the safety characteristics of hybrid mixtures were determined with different ignition energies and sources and the data were compared. It was discovered, that the p_{max} of hybrid mixtures was the same value than the higher determined one of the single substances while $(dp/dt)_{max}$ of hybrid mixtures was about 10 % to 25 % higher than the value of the stoichiometric gas mixture under turbulence. The point was found at the stoichiometric gas concentration with very little amounts of dust.

To prove the key findings of this work and for the establishment of a standardized procedure for the determination of safety characteristics of hybrid mixtures, an international round robin test was conducted with eleven participating facilities in seven countries. The results were comparable within a reasonable range and are presented in this dissertation in an extra chapter.

Based upon the observations in this work a reliable solution for a new standardizable ignition source to determine the safety characteristics of hybrid dust-gas-mixtures is proposed.

Zusammenfassung

Sicherheitstechnische Kenngrößen wie die untere Explosionsgrenze, die höchste Konzentration eines mit Luft vermischten Stoffes, der nicht zu einer sich selbst ausbreitenden Flamme führt, oder der maximale Explosionsdruck, der höchste Druck, der nach der Zündung eines mit Luft vermischten brennbaren Stoffes in beliebiger Konzentration erreicht werden kann, werden in der Industrie häufig verwendet, um entweder eine Explosion zu verhindern oder ihre Auswirkungen zu mildern. Die sicherheitstechnischen Kenngrößen sind keine physikalischen Konstanten, sondern werden experimentell ermittelt und hängen von den gewählten experimentellen Parametern wie Zündenergie oder Turbulenz ab.

Zur Bestimmung der sicherheitstechnischen Kenngrößen untere Explosionsgrenze (UEG), Sauerstoffgrenzkonzentration (SGK), maximaler Explosionsdruck (p_{max}) und maximaler Druckanstiegsrate ($(dp/dt)_{max}$) von Gasen und Dämpfen wird das Gas mittels Partialdruckmethode in ein Prüfgefäß gefüllt und dann unter ruhenden Bedingungen mit einer schwachen (2 J - 20 J) Zündquelle gezündet. Bei Stäuben werden die gleichen sicherheitstechnischen Kenngrößen unter turbulenten Bedingungen ermittelt, um den Staub möglichst homogen in der Luft zu verteilen und er wird mit zwei chemischen Zündern mit einer Zündenergie von je 1000 J (UEG und SGK) oder je 5000 J (p_{max} und $(dp/dt)_{max}$) gezündet. Für die Bestimmung der sicherheitstechnischen Kenngrößen von hybriden Gemischen (Gemisch aus brennbarem Staub und brennbarem Gas) gibt es derzeit keine Norm.

In den letzten 40 Jahren wurden die meisten Untersuchungen zu deren sicherheitstechnischen Kenngrößen mit Staubprüfgeräten durchgeführt, die für die Zugabe von brennbarem Gas modifiziert wurden. Wegen der unterschiedlichen Mischverfahren von Gasen und Stäuben mit Luft und wegen der unterschiedlichen Zündenergien und Zündquellen, die normalerweise für die Standardprüfungen von Gasen oder Stäuben verwendet werden, waren die Ergebnisse kaum reproduzierbar. Aussagen über die unterschiedlichen sicherheitstechnischen Kenngrößen waren widersprüchlich und gaben dem Leser bzw. den Verantwortlichen für die sicherheitstechnische Auslegung einer verfahrenstechnischen Anlage keinen eindeutigen Hinweis auf das Verhalten hybrider Gemische.

Ziel dieser Arbeit ist es, den Einfluss der verschiedenen Zündquellen und -energien auf die sicherheitstechnischen Kenngrößen p_{max}, $(dp/dt)_{max}$, untere Explosionsgrenze und Sauerstoffgrenzkonzentration von hybriden Gemischen zu ermitteln.

Es wurden mehrere Versuchsreihen zur Charakterisierung verschiedener genormter Zündquellen durchgeführt, die bereits zur Bestimmung der sicherheitstechnischen Kenngrößen von einphasigen Stoffen (Gase, Flüssigkeiten, Stäube) eingesetzt werden. Untersucht wurden die Brenndauer, das Zündvolumen und die Nettoenergie.

Es wurde gezeigt, dass die chemischen Zünder und der explodierende Draht geeignete Zündquellen für die Bestimmung der sicherheitstechnischen Kenngrößen von hybriden Gemischen im Allgemeinen sind. Ihre Brenndauer war lang genug, um Stäube zu entzünden, und schnell genug, dass das Abklingen der Turbulenz oder die Sedimentation der Stäube nicht eintrat. Beide Zündquellen lieferten vergleichbare Ergebnisse für die Bestimmung von p_{max}, UEG und $(dp/dt)_{max}$ von Stäuben, wenn sie die gleiche Zündenergie hatten. Eine reduzierte Zündenergie des explodierenden Drahtes und der chemischen Zünder hatte keinen Einfluss auf p_{max} und $(dp/dt)_{max}$. Die UEG änderte sich bei niedrigeren Energien. Für die Bestimmung der SGK von hybriden Gemischen lieferten die explodierenden Drähte mit einer Gesamtenergie von 2 kJ jedoch die besten Ergebnisse.

Der Einfluss der verschiedenen Mischverfahren, die bereits für hybride Gemische verwendet wurden, und die Anforderungen an sie wurden ebenfalls experimentell für die Gaskonzentration und die ermittelten sicherheitstechnischen Kenngrößen untersucht und miteinander verglichen. Es zeigte sich, dass die Partialdruckmethode zum Mischen von hybriden Gemischen funktioniert, jedoch sollten die Drücke sehr genau gemessen und die Gaskonzentration validiert werden.

Außerdem wurde der Einfluss der Turbulenzen, die bei der Prüfung von Stäuben unvermeidlich sind, auf die sicherheitstechnischen Kenngrößen von Gasen ermittelt. Es wurde festgestellt, dass die chemischen Zünder und die explodierenden Drähte vergleichbare Ergebnisse für die Bestimmung von p_{max}, UEG und $(dp/dt)_{max}$ unter Turbulenz liefern. Für die SGK funktionierten nur explodierende Drähte mit zwei mal 1 kJ.

Schließlich wurden die sicherheitstechnischen Kenngrößen von hybriden Gemischen mit unterschiedlichen Zündenergien und Zündquellen bestimmt und die Daten verglichen. Es wurde festgestellt, dass der Wert für p_{max} von hybriden Gemischen derselbe wie der höhere ermittelte p_{max} der Einzelsubstanzen war, während $(dp/dt)_{max}$ von hybriden Gemischen etwa 10 % bis 25 % höher war als der Wert des stöchiometrischen Gasgemisches unter Turbulenz. Dieser Höchstwert wurde stets bei der stöchiometrischen Gaskonzentration mit sehr geringen Staubanteilen gefunden.

Zum Nachweis der wesentlichen Ergebnisse dieser Arbeit und zur Etablierung eines standardisierten Verfahrens zur Bestimmung der sicherheitstechnischen Kenngrößen von hybriden Gemischen wurde ein internationaler Ringversuch mit elf Teilnehmern in sieben Ländern durchgeführt. Die Ergebnisse waren vergleichbar und werden in dieser Dissertation in einem Extrakapitel vorgestellt.

Auf der Grundlage der in dieser Arbeit gemachten Beobachtungen wird eine zuverlässige Lösung für eine neue standardisierbare Zündquelle zur Bestimmung der sicherheitstechnischen Kenngrößen von hybriden Staub-Gas-Gemischen vorgeschlagen.

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List of abbreviations and technical terms

Abbreviation	Unit	Description
ADC		Analog-Digital-Converter
BAM		Bundesanstalt für Materialforschung und -prüfung Berlin
CIS1		1^{st} Capacitor Ignition System
fps	1/s	frames per second
LEL		Lower explosion limit
LOC		Limiting oxygen concentration
PIPD	bar	Post-ignition pressure drop
PIPR	bar	Pre-ignition pressure rise
SOP		Standard operating procedure
$1m^3$		The old standard test vessel for dust explosion testing with a volume of 1000 litre

In the literature usually the term "flammable" is used for gases, that can burn within a certain concentration in air and "combustible" is used for dusts, that can burn above a certain concentration in air when dispersed. The term "burnable" is also found in the literature, but in this thesis the two more common are used. For hybrids or when in general it is referred to a substance that can be gaseous, solid or liquid the term "combustible" is used throughout this thesis.

List of Symbols

Symbol	Unit	Description
A_{cable}	mm^2	Cable cross section
C	Farad	Capacitance
dp/dt	bar/s	Rate of pressure rise
$(dp/dt)_{Ex}$	bar/s	Highest rate of pressure rise for one test
$(dp/dt)_{max}$	bar/s	Maximum rate of pressure rise over all tests for a given substance
$(dp/dt)_{Leakage}$	bar/min	Leakage-rate of the 20L-sphere
E	Joule	Energy
G	-	Gas
H	-	Hybrid
I	Ampere	Current
$I_{meas.}$	Ampere	Measuerd Current
K	bar*m/s	Volume-normalized rate of pressure rise
l_{cable}	m	Cable length
p	bar	Pressure
p_{Ex}	bar	Measured explosion pressure for one test absolute for gases, overpressure for dusts
p_{Gas}	bar	Partial pressure of the flammable gas
p_{max}	bar	Measured explosion pressure over all tests for a given substance; absolute for gases, overpressure for dusts
p_m	bar g	Corrected explosion pressure
PV	bar g	Partial Vacuum before the injection process starts
St	-	Staub (German word for dust)
t	seconds	Time
U	Volts	Voltage
U_{res}	Volts	Resulting Voltage
$U_{meas.}$	Volts	Measured Voltage
ρ_{copper}	Ω * m	Specific electrical resistance of copper = 0.017 Ω * m

1. Introduction

1.1. History of Research on Hybrid Mixture Explosions

Hybrid mixtures consist of more than one combustible phase (gaseous, liquid and solid) mixed with air. Their safety characteristics are unpredictable and until now, there has been no broadband screening of various gases and dusts and there is no reliable database or reference values. For single substances and single aggregates standards exist to determine the safety characteristics. For hybrid mixtures there is no existing standard[1] or method, even though the first observations are almost 200 years old, when Faraday and Lyell commented in 1844 on the explosion of the Haswell colliery: "In considering the extent of the fire for the moment of explosion, it is not to be supposed that fire-damp is its only fuel; the coal dust swept by the rush of wind and flame from the floor, roof, and walls of the works would instantly take fire and burn, if there were oxygen enough in the air present to support the combustion." ([2], page 27)
The first scientific work was published almost 150 years ago in 1876 by William Galloway who proved the following hypothesis right experimentally: "Air mixed with certain proportions of firedamp and dry coal-dust would be explosive at ordinary pressure and temperature, although the presence of the same proportion of one of the combustible ingredients, or the other, alone, might be insufficient to confer this property on the mixture." Galloway describes this thesis further: "Combustible gases can supplant each other in certain equivalent proportions in mixtures which will just ignite at given temperatures and finely divided combustible solids have probably the same property to some extent." ([3], page 355 f.) Galloway built an apparatus to prove this thesis of the behaviour of the lower explosion limit (LEL) of hybrid mixtures, here with methane and coal dust. On a smaller scale, the experimental investigations of the hybrid LEL were performed again: C. Engler observed in 1907 that hybrid mixtures of coal dust and methane form explosive atmospheres under the lower explosion limits of the single substances [4]. First tests were already conducted and in a short communication reported by Engler in 1885 [5]. For some reason Englers work is usually cited as the first hybrid mixture tests, even though Galloway made the experiments nine years earlier and published them eye-catching in the Royal Society Proceedings.[2]
In 1887 Th. Walther published a book about the role of coal dust in minery (methane)

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[1] There used to be a standard: ISO 6184-3 [1] but it is officially under review since 2005

[2] In 1882 Frederick Augustus Abel published an article in Nature where he states, that the knowledge about hybrid mixture explosions was common at the time Galloway investigated them and there were earlier researchers doing similar experiments [6]. However, that this was not common knowledge, even years later, can be seen in a report from George S. Rice who stated in 1913, that coal dust is probably more inflammable with a small quantity of methane but that this has not been investigated before. ([7], page 8)

explosions. In this book the author assumes, that the accident of the mines Quaregnon-Paturages in Belgium on the 4^{th} of May 1887 causing over 140 deaths was a hybrid mixture explosion [8]. For one century of hybrid mixture explosion research the only two substances tested were methane and coal until Richard Siwek tested other substances in 1977 [9].

Two challenges increased the difficulty in obtaining a robust knowledge about hybrid mixtures explosions and their safety characteristics. One is, that most safety characteristics are dependent on the testing apparatus and the testing parameters including

- pressure at the moment of ignition
- turbulence
- ignition energy
- ignition source
- number of ignition sources
- precise characterisation of the dust
- concentration of gas

A direct comparison is only possible when all parameters are kept constant. The other challenge is that these parameters are often not described completely: In the literature survey about hybrid mixtures the gas amount was verified only in four of them. None of them stated how large the deviation and scattering was and they were published between 1964 and 1987 ([10], [11], [12], [13]). Today, even though laboratory equipment is cheaper, the gas amount is typically not verified. In many articles the safety characteristics of two different substances were compared with two different methods, both having an influence on them, because only one substance was tested while the other one was cited from earlier works using different testing conditions ([14], [15]). A comparison of the different findings was not done. Apart from that, it was often not really clear what a hybrid mixture is: In some of the articles it is assumed, that the gas simply ignited the dust, others refer to them as dust explosions and just mention that some gas might have been around. Sometimes it is not really clear, what was tested at all, like the above mentioned "fire-damp", an old word for the gas that arises in coal mines and consists mainly but to a non-specified amount of methane. The term "hybrid mixture" was also not used before 1975 [16] and many research articles afterwards did not call the mixtures hybrid.

While research on hybrid mixure explosions was scarce until 1970 (only 18 articles were found before) it became more frequent in the 1980s with one or two articles per year. A clear rise is observed from 2010 on and the number of articles is still rising. For example in the first three months of 2022 eight articles were published (for a full overview see Appendix C).

1.2. Importance of hybrid mixtures for industrial processes

Most research about hybrid mixtures was and still is about methane and coal dust with the typical field of colliery explosions. But in the modern industry hybrid mixtures play an increasing role in an expanding number of processes. With progressively faster, specialised and overlapping production methods the production can not be separated in unit operations of every single substance anymore. In some processes this is not possible at all, because the step of operation comprises several phases.

Spray-drying and coating processes are typical examples where hybrid mixtures occur and can't be avoided because the process itself is based on the evaporation of the liquid component. The gasification of wood or synthetic materials is another process where the formation of a hybrid gas-dust atmosphere is inevitable. In other cases the admixture of small amounts of dust to a gaseous atmosphere or vice versa may occur. The following list may give a (non-complete) overview how diverse the processes are in which hybrid mixtures might occur:

- Accidental admixture of coal or aluminium dust because of abrasion to hydrogen in fusion reactors ([17], [18])
- Mixture of soy flour and hexane in the soy-oil extraction process [19]
- Metals and hydrogen for the storage of hydrogen in metal hydrides [20]
- Cork dust and vapors arising from glue with a high volatile content in vineyards or cork factories [21]
- While recycling metal oxides with hydrogen when using the metals as energy carriers [22] or in the production process of steel [23]
- On the 9th of July in 1994 a preshredder in a waste processing plant became wedged by phenolic resin-impregnated paper waste between the cavities of the missing cutting blades. The friction-induced heating initiated the outgassing of combustible components of the phenolic resin and, together with the dust in air, formed a hybrid mixture that lowered the minimum ignition energy [24]

Even though the potential hazards of hybrid mixtures are known, in some cases dusts and gases are still looked at separately. In the German compulsive policy for the classification about explosion-zones it says "If, during the formation of a hazardous explosive atmosphere, dusts can occur together with gases, vapors or mists (hybrid mixtures), the hazardous area is classified according to zones 0, 1 and 2 as well as zones 20, 21 and 22." ([25], page 6). It is later described how to prevent explosive atmospheres and there it is described for the single components. So according to that, both aggregates are checked alone instead of checking both together what might lead to an explosive atmosphere even though the single phases are outside their explosive region.

1.3. Hybrid mixture research and demand

In the literature survey (see also Appendix C), general statements about the different safety characteristics of hybrid mixtures and their behaviour are hard to find and partly conflict with each other.

Especially when it comes to an often-used safety characteristic, the maximum rate of pressure rise (dp/dt)$_{max}$ or rather the volume-normalised K-value (for both see chapter 2.1.2) the statements in the rare literature are more confusing than clarifying (see table 1.1) and the conclusions vary and leave the reader or the person responsible for designing safety measures for a process plant or a facility behind with no suggestion about the behavior of hybrid mixtures. This problem is intensified, since there are no standardized testing methods [3] and hardly any testing laboratories for determining the (dp/dt)$_{max}$ of hybrid mixtures. For the limiting oxygen concentration (LOC), another safety characteristic, that is used in industry processes, there are just two research papers published yet, all from the same institute ([29], [30]). In their work, it is stated that no significant change was observed for the limiting oxygen concentration of hybrid mixtures, if the experimental parameters were chosen right. Even though this work relies on a broadband screening with 15 dusts and 3 different gases this knowledge shall still be checked and verified by at least one more facility.

Table 1.1.: Selected conclusions about the rate of pressure rise of hybrid mixtures

Statement	Dust/Gas/Vapor	Reference
The (dp/dt)$_{max}$ of the hybrid mixture is 2.3 times greater than of the hydrogen-air mixture alone and 10.4 times greater than of activated carbon alone	Activated carbon/ Hydrogen	Khalil (2013) [14]
The (dp/dt)$_{max}$ of hybrid mixtures is usually as high as of the stoichiometric gas mixture under turbulence. It might be 15 % higher*,**	Many tested	Bartknecht (1985) [26]
The (dp/dt)$_{max}$ of methane/coal dust mixtures at any methane concentration are higher than those of pure coal dust but lower than those of pure methane*	Coal dust/ Methane	Wang et. al. (2020) [27]
The optimum (e.g. worst-case-value) of the pure compounds for (dp/dt) is approximately 800 $\frac{bar}{s}$ for 750 $\frac{g}{m^3}$ of niacin, 1300 $\frac{bar}{s}$ for 2.5 % of diisopropyl ether and 1600 $\frac{bar}{s}$ for certain hybrid mixtures (e.g. 23 % higher)*	Niacin/ Diisopropyl ether	Dufaud (2008) [28]

*all statements are shortened by the author, the values and core findings were not changed
**translation by the author

The maximum explosion pressure p$_{max}$ is another safety characteristic for which the statements vary significantly in the research literature.

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[3] ISO 6184-3 is officially under revision since 2005 and with 4 pages too short to be applicable [1]

- "...the maximum explosion pressures p_{max}...for the hybrid mixtures at any flammable gas concentrations are **smaller** than those of the pure flammable gas..."[31]
- "In all the cases examined, p_{max}- values of the activated carbon dust-hydrogen-air hybrid mixture **exceed** p_{max} of the near stoichiometric hydrogen air mixture."[14]

Research about the p_{max} of hybrid mixtures is also rare and again, the person in charge of the risk assessment is left behind with no clear advice.

It was carved out that the contradicting statements about the safety characteristics of hybrid mixtures arise from different experimental parameters, mainly the different mixing procedures sometimes leading to deviating gas concentrations than the aimed ones, the different levels of turbulence (highly turbulent for dusts vs. quiescent for gases) and the different ignition sources and energies. Their influence is neglected in most literature simply because there is no standard yet on which all institutes can agree or rely on.

This work provides laboratories with insights on these parameters and gives advice, how the safety characteristics can be determined in a way, that other facilities can reproduce them.

1.4. Alternative ignition sources

The ignition source and energy affect the determined values of the safety characteristics [32]. The standardized ignition sources that are used for gas explosions are too weak to ignite dusts under turbulence and with that might lead to non-conservative safety characteristics. The chemical igniters, the only standardized ignition source for the determination of the maximum explosion pressure and maximum rate of pressure rise of dusts, have an unspecified burning duration and might cause an overdrive of gaseous mixtures, leading to highly conservative safety characteristics and with that to overpriced safety measures. They are also not available in some parts of the world due to restrictions (see Appendix E.6).

Other laboratories are also investigating the influence of the ignition sources and developing new ones for the determination of safety characteristics.

There are currently at least four different approaches to a new ignition source:

- The Technical University of Bratislava is working on alternative chemical [33] and various other types of ignition sources [34]
- The University of Pardubice together with OZM Research is investigating squibs for the activation of airbags as alternative ignition source [35]
- The University of Orleans is working with an adjustable permanent spark ignition source ([36], [37], [38])
- The University of Lorraine in Nancy and INERIS are developing a new ignition device with an adjustable permanent spark [39]

For hybrid mixtures and for precise results the requirements are even stricter so a new ignition source was developed and tested in this thesis.

2. State of the art

2.1. Safety Characteristics for gases and dusts

Safety characteristics for explosion protection are used to estimate the hazard potential of substances and their mixtures. They can be found in databases (e.g. [40], [41]) for many individual substances, usually at ambient conditions (1 bara and 20° C). There are standardized procedures for determining safety characteristics of flammable gases ([42], [43], [44]) or dusts ([45], [46], [47], [47]). But there are no applicable standard procedures for the determination of safety characteristics of hybrid mixtures containing combustible substances in different phases (gaseous, liquid or solid).

The determination methods of safety characteristics of combustible substances in different phases differ in some extent. Generally, in the case of dusts it is particularly complicated because of the following additional influencing parameters [48]:

- Different particle sizes and particle size distributions for the same type of dust
- Non-uniform moisture content within the dust sample
- Non-uniform density within the dust sample (especially for organic compounds)
- Aging ability of dusts
- Homogeneity of the particle distribution in the dust-air-mixtures

While the influence of these first three points can be reduced significantly with additional measures (sieving, drying, stirring), the last two points present a great challenge. If pronounced aging is present, it should be identified, and the consequences named. The last point could only be remedied in weightlessness (zero-gravity conditions), since here no sedimentation of the dust would take place. However, this is almost impossible due to the great effort involved.[1]

2.1.1. Primary Explosion protection - Explosion Limits

The term primary explosion protection refers to all precautions which prevent the formation of an explosive atmosphere. This can be achieved by avoiding combustible substances, combustible mixtures or inertization [48].

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[1] Though there is an attempt to investigate the flame velocity of dust air mixtures under defined flow conditions with low turbulence ([49], [50]). However, the device is not suitable for the determination of p_{max} and $(dp/dt)_{max}$

The lower explosion limit (LEL) is the highest concentration of a substance in air at which a self-sustaining flame propagation can just not be triggered by a defined ignition source [48]. On a microscopic scale this can be seen as the tipping point at which the combustion heat that is released by the reaction (triggered by an external ignition source) in one particular unit of volume is not sufficient to heat the vicinity up to the required temperature for the propagation of the reaction, so that no chain reaction occurs anymore. In figure 2.1 this is displayed for a mixture of hydrogen (green circles) in air. The blue circles represent the oxygen. For better visibility the nitrogen is not displayed. The reddish circle is the impact zone of the initial reaction which releases an energy of 5.92 eV per mol oxygen with two moles hydrogen. On the left side the initial reaction would trigger three other molecules leading to a chain reaction, on the right side nothing happens. Though the green particles would be magnitudes bigger, the same mechanism accounts for dusts.

In American standards for dusts the LEL is called minimum explosible concentration (MEC)[51]. In this thesis LEL is used since it is the more common term for hybrid mixtures. The limiting oxygen concentration (LOC) is another safety characteristic that aims at the formation of a combustible atmosphere respectively the prevention of it. In theory, it works similar to the UEL displayed in figure 2.2: If there is not enough oxygen around the combustible substance no chain reaction can go off. This safety characteristic exists for dusts (EN 14034-4 [47], ASTM E2931 [52]) and gases (EN 1839 [42], ASTM 2079 [44]).

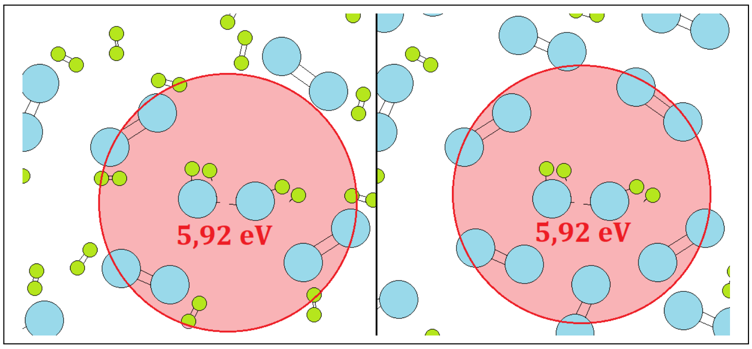

Figure 2.1.: Schematic of stoichiometric mixture (chain reaction starts) and mixture below the LEL (not enough hydrogen for a chain reaction to go off); Oxygen in blue, hydrogen in green

The type and strength of the ignition source are important influencing factors for the determination of explosion limits. This was investigated by Askar and Schröder for methane and difluoromethane where the explosion range widened with higher ignition energies [53]. This effect is rather unpredictable. For methane the upper explosion limit was higher with stronger ignition sources, for difluoromethane the lower explosion limit was lowered and the upper explosion limit was stable with higher ignition energies. Mynarz et. al. investigated the effect of the ignition energy on the safety characteristics of hydrogen, methane and propane [54]. They observed a widening of the explosive range for all three gases. In the SAFEKINEX Del. No. 2 the general effect of the widening of the explosion range with higher ignition energies is also described for gases [55]. Kuai et. al. investigated the influence

of the ignition source on the lower explosion limit of sweet potato, magnesium and coal dust [56]. They also observed lower values for the concentration with higher ignition energies.
In particular, the energy that is released by the ignition source on the one hand and the forced combustion in the direct vicinity of the ignition source that is triggered by the ignition source causes a pressure rise in a closed vessel without the occurrence of self-sustaining flame propagation. The extent of the pressure rise is also dependent on the type and strength of the ignition source. Since the standardized ignition sources, particularly their strength and burning duration, differ significantly for gas and dust testing and because of the high turbulence in the dust test leading to a higher scattering, the ignition criteria are different:

- Gas (European Standard): Pressure rise of the ignition source plus 5 % pressure rise of the pressure at the beginning [42], criterion is also valid for the upper explosion limit and the limiting oxygen concentration
- Dust (European Standard): Pressure rise of more than 0.5 bar [46]
- Dust (American Standard): Pressure rise of more than 1 bar [57]
- Dust (International Standard): Pressure rise of the ignition source plus 0.3 bar [58]

This is one reason, why the comparison of literature values for hybrid mixtures is difficult. The development of a standard for hybrid dust-gas mixtures primarily needs a proper definition of the ignition criterion.
The upper explosion limit (UEL) is the lowest concentration above the explosion region of a substance in air at which there is no explosion observed anymore [42]. The concentration of the substance is sufficient but there is not enough oxygen within the sphere of influence of a potential starting point (see figure 2.2) and thereby no chain reaction would take place.
The UEL is usually not determined for dusts. Because of the natural behavior of sedimentation the hazard of the concentration in air to fall below the upper explosion limit can not be excluded. There is neither a European nor an American standard for the determination of the UEL for dusts. It was also not tested for hybrid mixtures in this thesis.

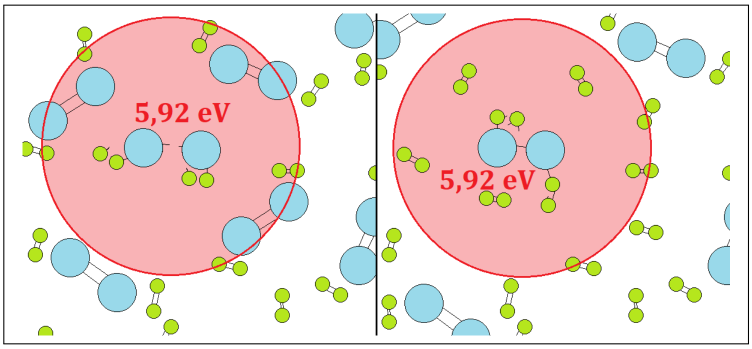

Figure 2.2.: Schematic of stoichiometric mixture (chain reaction starts) and mixture above the UEL (not enough oxygen for a chain reaction to go off); Oxygen in blue, hydrogen in green

2.1.2. Constructive explosion protection - p$_{max}$ and (dp/dt)$_{max}$

If it is not possible to certainly avoid an explosive atmosphere (primary explosion protection) and if the absence of an ignition source can not be ensured either (secondary explosion protection) constructive measures have to be taken to mitigate a possible explosion (tertiary or constructive explosion protection). Safety characteristics that are necessary to implement measures of tertiary explosion protection are maximum explosion pressures and maximum rates of pressure rise of combustible substances.

The highest pressure that occurs in an explosion is called p$_{ex}$. The rate of pressure rise (dp/dt)$_{Ex}$ is the highest slope of the explosion pressure recorded in an explosion test (see figure 2.4).

If these values are recorded for a combustible substance and the concentration is varied over a wide range, the maximum of these values is called the maximum explosion pressure p$_{max}$ and (dp/dt)$_{max}$. p$_{max}$ and (dp/dt)$_{max}$ are defined differently for gases and dusts according to international standards. For dusts they are the average of the maximum values of three test series. The concentration steps are defined in the standards ([45], [59]). For gases they are the highest recorded values of all tests for the given substance and the concentration is variably adjusted to find the optimal concentration [43].

Another difference for p$_{max}$ is that the pressure is stated in absolute pressures for gases [43] and in relative pressures for dusts ([45] and [57]).

Furthermore, if p$_{max}$ for dusts is determined in the 20L-sphere it is corrected to match the values obtained with the 1m^3 with the following equations 2.1 and 2.2 as stated in the standards for dusts, EN 14034-1 [45] and ASTM 1226a [57]:

If the measured overpressure is below 5.5 bar g the pressure rise of the ignition source is partially substracted:

$$p_{Ex}[barg] = 5.5 * \frac{p_{Ex,20L} - p_{CI}}{(5.5 - p_{CI})}[barg] \tag{2.1}$$

with p$_{CI}$ [bar g] = 1.6 * $\frac{IgnitionEnergy(J)}{10000(J/bar)}$

If the measured overpressure is above 5.5 bar g the stated pressure is higher, than the recorded one. The European standard says this is due to heatlosses in the 20L-sphere [45] while Bartknecht stated, that this is a matter of the elevated starting pressure in the standard 1m^3-vessel of 1.1 bara [60]:

$$p_{Ex}[barg] = 0.775 * p_{Ex,20L}^{1,15}[barg] \tag{2.2}$$

This correction (see figure 2.3) is not done when testing safety characteristics of flammable gases and is one source of confusion when comparing data from different sources since the correction is carried out by most of the testing software automatically and it is not stated in databases and literature.

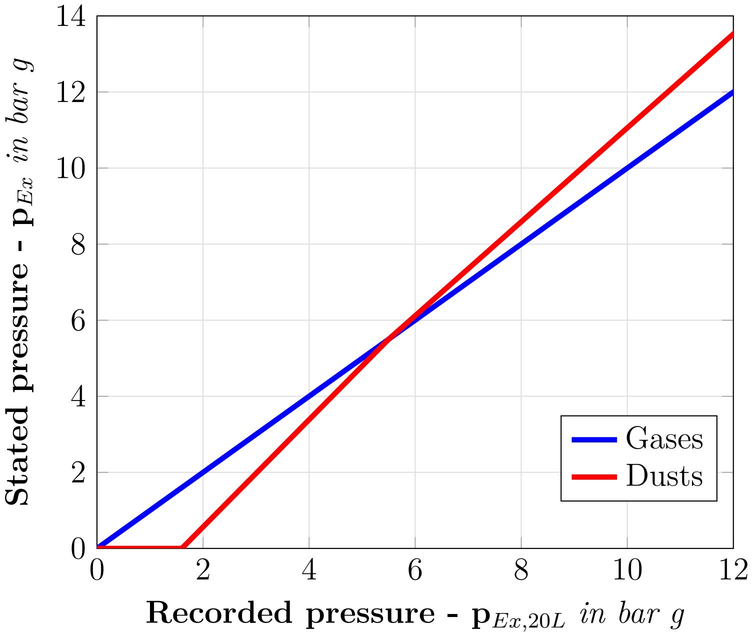

Figure 2.3.: Recorded pressures ($p_{Ex,20L}$) against stated pressures (p_{Ex}) for gases and dusts determined in the 20L-sphere

It was observed that the maximum rate of pressure rise depends on the size of the test vessel [61]. Since this safety characteristic was developed with a standardized 1 m^3 test vessel for dusts but is today often determined in smaller volumes, the value is normalized with the following equation, the so called cubic root relationship to the values K_G for gases, K_{St} for dusts ("St" for german: Staub) and K_H for hybrid mixtures [62].

$$K_H[bar * m/s] = (dp/dt)_{max}[bar/s] * (V_{Testvessel}[m^3])^{1/3} \tag{2.3}$$

This characteristic has the unit bar*m/s ([43], [46], [57]).

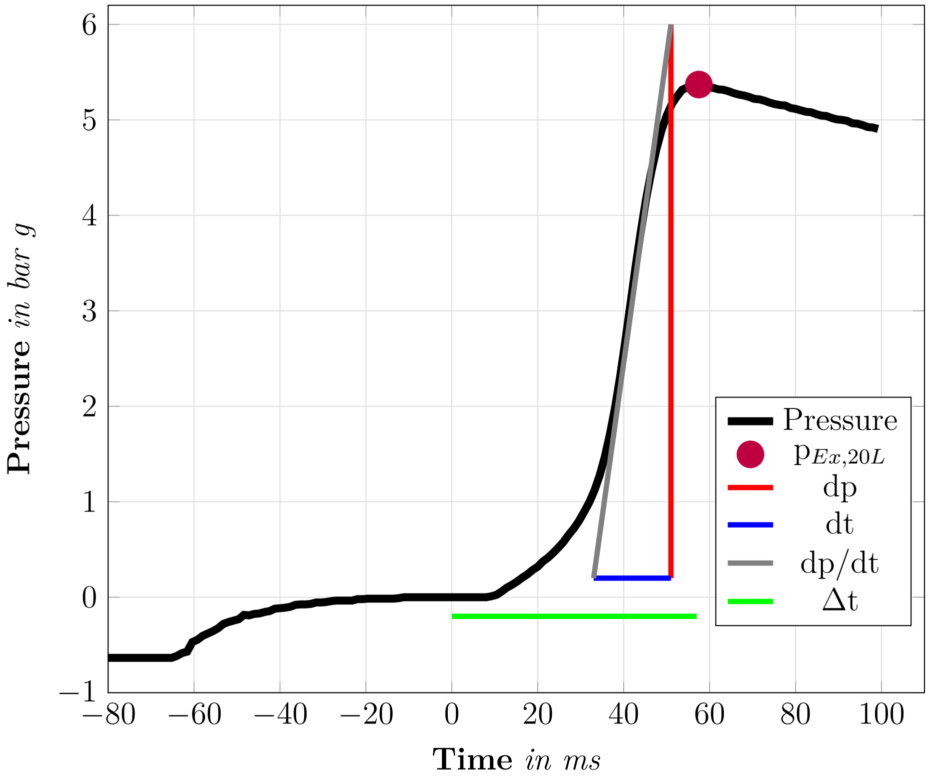

Figure 2.4.: Pressure vs. time curve of an explosion measured in the 20L-sphere with the highest explosion pressure ($p_{Ex,20L}$), the time until this pressure occurs after activation of the ignition source (Δt) and the highest (dp/dt) outlined

2.2. Ignition sources

In most cases, the chemical reaction that results in an explosion requires an activation energy. In the laboratory, this is provided by various ignition sources. Table 2.1 compares standardized ignition sources for the determination of safety characteristics with their main features.

Safety characteristics of gases, vapors and dusts are often investigated without considering the influence of the ignition source in more detail, even though it is found to have an impact on them ([63], [53], [64], [65], [66]). Other standards say, that the "delivered ignition energy" (= net energy) must be specified in the test report but do not give a hint how to measure it [44]. This is caused by the fact, that for most ignition sources it is hard to measure the real energy and ignition duration and volume under laboratory conditions and almost impossible during tests. Rough estimates such as the gross energy for all electrical igniters based on capacitors given as

$$E = 0.5 * C * U^2 \tag{2.4}$$

are known to be unprecise ([63], [67]) because of energy losses in the circuit but are still widely used. Therefore, the net energy is unknown. It is depending on cable resistance and length, ignition duration and other technical parameters, and varies between 20% to 80% of the gross energy for electrical ignition sources [63].

In addition to the ignition energy that is actually introduced into a system, there are several other specifications of the ignition source that might influence the effectivity of an ignition source, particularly the ignition duration and the initial volume that is affected by the ignition source, which is also dependent on the distance and the orientation of the electrodes.

For explosion tests on dusts mainly chemical igniters are used (ASTM 1226 [57], EN 14034-series[45] [59] [46] [47], ISO 80079 [58]).

Table 2.1.: Standardized ignition sources

Ignition source	**Energy Range [J]**	**Adjustable Energy**	**Application (example)**	**Used / Found in**	**Affecting chemical reaction**	**Suitable for high pressures**
Exploding Wire	Low to high 2-5000	Yes	Determination of LEL, UEL, LOC, p$_{max}$ and (dp/dt)$_{max}$ of gases and vapors	EN1839 [42] ASTM E918 [68] ISO 10156 [69]	No	Yes, Tested up to 100 bar g
Chemical Igniter	Moderate to high, 100-10 000	No, stepwise	Determination of LEL, p_{max}, (dp/dp)$_{max}$, K$_{St}$ of dusts	EN 14034 series [45][59][46][47]	Yes	Yes
Induction spark	Low, < 10 J	Yes	Determination of LEL, UEL, LOC, p$_{max}$ and (dp/dt)$_{max}$ of gases and vapors	EN 1839 [42] ASTM E681 [70]	No	No, Just up to 5 bar g
Surface-gap spark	Low 10-40	Yes	Determination of LOC of gases and vapors under non-atmospheric conditions	ASTM 2079 [44] EN 17624 [71]	No	No, Just up to 25 bar g

Pellmont investigated the influence of the ignition energy and source on p_{max} and $(dp/dt)_{max}$ of dusts. With chemical igniters, condenser discharge sparks (from about 5 J to 500 J) and the induction spark he concludes that "Only the permanent spark gap (=induction spark), hitherto commonly used in the Hartmann-tube, underestimates the explosion violence (=(dp/dt)-value) by about 60 %. This result has been proven for more than 50 dusts..." [72]. It might have been the case, that the induction spark does not work under the highest states of turbulence, igniting the dust-air mixture later and at a lower level of turbulence. This might also explain that the recorded explosion pressure is lower for this ignition source since some of the dust has already settled.
Chatrathi et. al. [32] investigated the influence of the ignition source on hybrid mixtures with chemical igniters and exploding wires (they called it "fuse wire" in the paper). The ignition energy of the two chemical igniters is stated with 5 kJ each but no statement about the energy of the exploding wire is given.
It shall be mentioned, that the glowing coil, stated in ISO 80079-2 [58] has not been tested extensively and is not part of this thesis.

2.2.1. Chemical Igniters

There are pre-fabricated chemical igniters with defined energies varying in steps from 100 J up to 10 000 J but the energy cannot be adjusted fluently, and the net energy that is introduced into the system (and their variation) as well as the ignition duration and volume show a non-negligible scattering.
The chemical igniters consist of a small plastic or aluminum bucket filled with an explosive mixture consisting of 40 % zirconium, 30 % barium nitrate and 30 % barium peroxide. A sealing cap keeps the firing charge inside. An electrical fuse head is connected to two wires for a precise electrically controlled ignition from the outside of the apparatus (see figure 2.5).
This type of ignition source is stated in many standards for the identification of combustible dusts [58] or for the determination of safety characteristics of dusts (DIN EN 14034-series

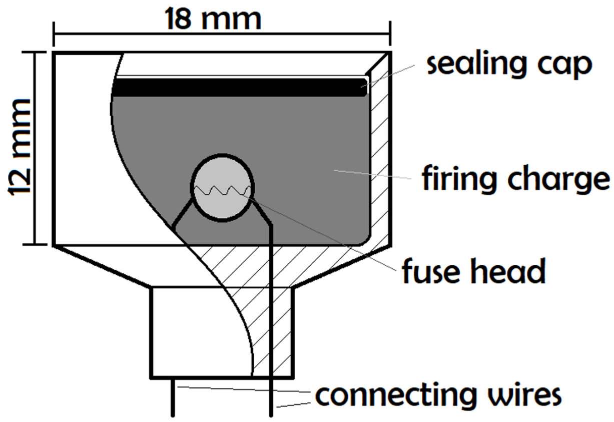

Figure 2.5.: Structure of a chemical igniter

[45], [59], [46], [47], ASTM 1226 [57] and ISO 6184-1 [73]). The two common ignition energies of the chemical igniters are 1 kJ and 5 kJ with a mass of the firing charge of 0.24 g [74] and 1.2 g. In all the standards for the determination of safety characteristics of dusts two chemical igniters are used. They are placed in the center of the sphere pointing in opposite directions.

2.2.2. Induction spark

The induction spark (figure 2.6) is the most common ignition source for gas testing. It is characterized by a rather low ignition energy (< 10 J) and long burning duration of 200 ms – 500 ms in which a series of sparks is introduced into the system. Measuring the actual net ignition energy of the induction spark is difficult because of the electro-magnetic radiation of the cables. Contrary to the exploding wire igniter it can only be used at atmospheric or slightly elevated pressure. It consists of a high voltage transformer with an open-circuit voltage of 15 kV and a short circuit current of 30 mA. A suitable material for the electrodes is stainless steel and the electrodes should not exceed a diameter of 4 mm. The electrodes have a distance of 5 ± 1 mm, a point angle of 60° ± 3° and the ignition duration, in which multiple sparks are released, is set to 200 ms according to the European standard EN 1839 [42]. In other standards the specifications vary and are sometimes presumably stated in wrong units. The transformers in EN 1839 [42] and EN 10156 [69] are obviously the same but one states the power as 10 Watts, the other 10 Joule per spark leading to a power of 1000 Watts (one spark per half cycle at 50 Hz; in the USA with 60 Hz this would lead to a power of 1200 Watts). The confusion in the different standards and the fact, that some specifications are missing, are an indicator, that little attention has been paid to the specifications of the ignition source in the past. The length, capacity, cross section and resistance of the cables is not specified in the standards (for a full overview see Appendix E.7).

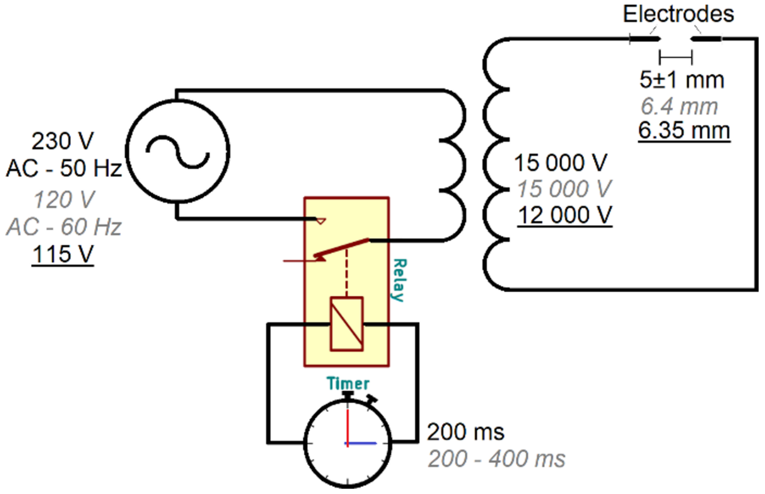

Figure 2.6.: Schematic of the induction spark, specifications according to DIN 1839:17 [42], *ASTM E681 [70]* and ASTM E789 [75]

2.2.3. Surface-gap spark

The surface gap spark is another alternative ignition source mainly for gas explosion tests ([44], [71]). Considering the ignition energies, that arise from the specifications stated in the standards, it introduces a higher ignition energy into the test vessel than the spark ignition, but not as much as the exploding wire.

However, the ignition duration is much shorter than all other ignition sources that are considered.

The surface-gap spark (Fig 2.7) is made of two electrodes, separated by a pencil lead mainly consisting of graphite with 6–10 mm in length and an electrical power supply. The emerging discrete spark is a surface discharge on the outside of the pencil lead.

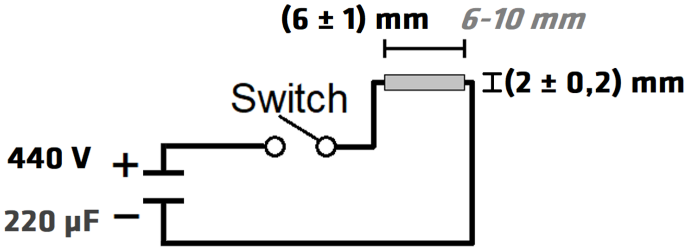

Figure 2.7.: Schematic of the surface-gap spark, with specifications according to EN 17624 [71] and *ASTM 2079 [44]*

2.2.4. Exploding Wire

Another common ignition source for gas explosion tests is the exploding wire [42], which has been approved to be suitable for gas testing [76].

It consists of a power source, connecting thick cables and a very thin wire, which evaporates when the power is switched on and donates a light arc into the system. One with a transformer as power source is already in use for the standardized determination of safety characteristics of gases [42], first tests on the suitability of an exploding wire with capacitors as power source for dust testing have also been carried out by Scheid et al. [77]. Using the exploding wire igniter, much higher ignition energies can be realized than with the induction spark and it is possible to calculate the actual net ignition energy in each test by measuring the ignition current and voltage, whereas the ignition duration of 5 ms - 10 ms is much shorter compared to the spark ignition.

The exploding wire consists of a thin wire that is stretched between two electrodes. An electric current is passed through the wire, causing it to melt, vaporize and then form a plasma arc between the two electrodes. The energy released by the arc depends on the duration and the amount of electrical energy supplied [78]. Typical specifications in standards for the determination of safety characteristics of gases are an electrode diameter greater than 3 mm and an electrode distance of (5 ± 1) mm. The connecting wire is typically made of Nickelin and shall have a diameter between 0.05 mm and 0.2 mm (typical: 0.12 mm). The electrical power for melting the wire and generating the arc is typically supplied by an alternating current isolating transformer with a power of 700 VA to 3500 VA and a secondary voltage of 230 V. The secondary winding of the transformer shall be switched by thyristors to control the time the voltage passes through the rods and the wire for adjustment of the ignition energy between 10 J and 20 J (EN 1839 [42] and ISO 10156 [69], see figure 2.8).

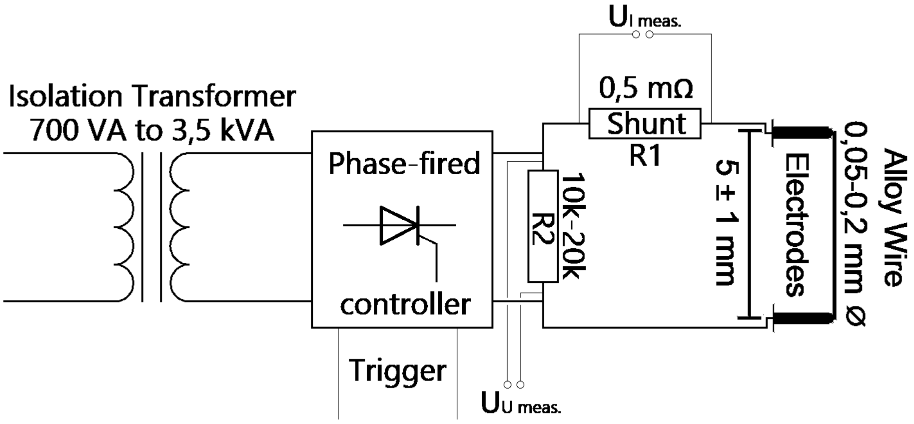

Figure 2.8.: Schematic of an exploding wire ignition source

First tests on the suitability of the exploding wire igniter for dust testing have been carried out by Scheid et al. [77]. Other benefits of the exploding wire are, that it can be used at high initial pressures and it is the only ignition source with an easily measurable ignition energy release.

2.3. Mixing procedures for the determination of safety characteristics of hybrid mixtures

2.3.1. 20L-Sphere

For the determination of safety characteristics there are several different apparatuses. One of the most common ones for the determination of several safety characteristics of dusts like the lower explosion limit [46], the limiting oxygen concentration [47], the maximum explosion pressure [45] and the maximum rate of pressure rise [59] is the 20L-Sphere (see figure 2.9).

It consists of a hollow metal sphere, with an inner volume of 20 liters that can withstand an overpressure of 20 bar g and a water jacket to keep it at defined temperatures (usually 20° C). The ignition source is placed in the center of the sphere and can be activated by electrodes that are sealed airtight to the lid of the sphere.

The 20L-sphere is not explicitly stated in the standards for the determination of safety characteristics of gases ([68], [42], [43]) but with the following requirements for the explosion vessel it is also possible to use it for gases.

- volume above 5 liters

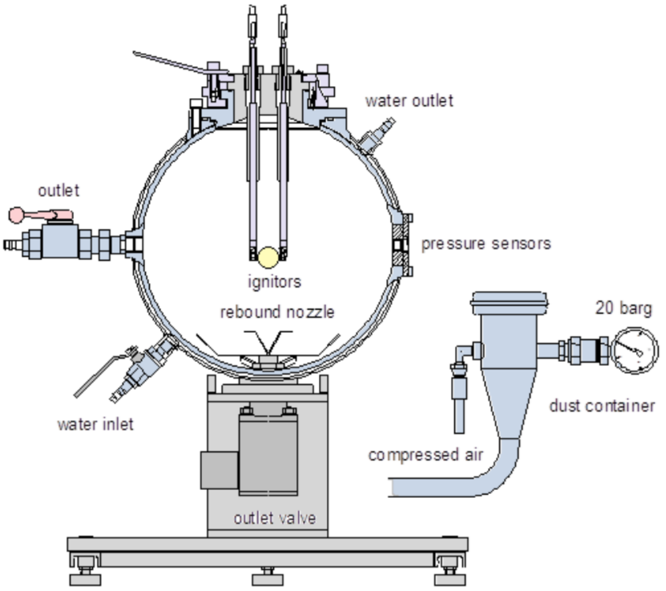

Figure 2.9.: Structure of the 20L-Sphere, taken from [79]

- spherical or cylindrical shape with a height to width ratio of 1 [43] or between 1 and 1,5 [42]
- the ignition source shall be placed in the center
- shall withstand 15 bar [42] or 20 bar [43] overpressure

This is the reason why most of the hybrid mixture research facilities are more experienced with dusts than with gases: With small modifications and adjustments from the generally accepted dust testing procedures the facilities can integrate gas components to the system while gas testing facilities would have to buy a new apparatus.

2.3.2. Mixing procedures

The mixing procedure for the determination of safety characteristics of hybrid mixtures in the 20L-sphere can be conducted in three different ways:

- Method I: A premixed gas-air mixture is used for both, the 20L-sphere and the dust container before ignition (see figure 2.10, left).
- Method II: The flammable gas is directly injected into the 20L sphere and dust is injected by pressurized air from the dust container (see figure 2.10, middle)
- Method III: The 20L-sphere is only filled with air and the dust container is pressurized by a mixture of flammable gas and air injecting the dust from the dust container (see figure 2.10, right)

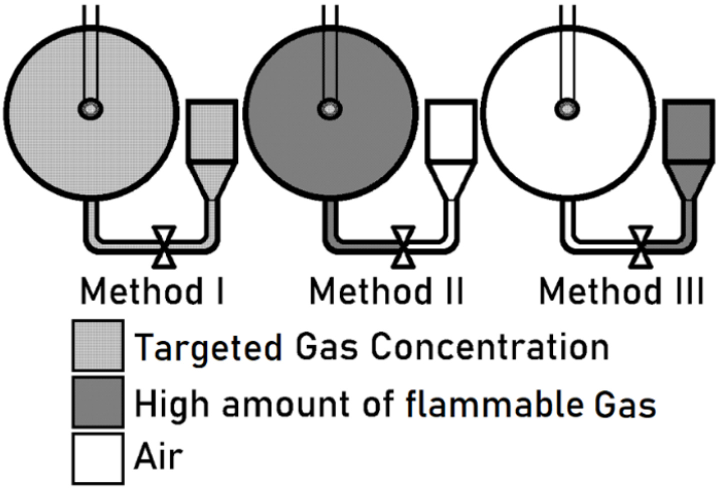

Figure 2.10.: Three different ways of mixing; Conditions before opening the fast-acting valve between 20L-sphere and dust container [80]

In none of the previous works on hybrid mixtures in the 20L-sphere the actual gas concentration is measured in the tests nor is the accuracy of the gas concentrations mentioned. The gas fractions are calculated based on the partial pressures usually measured with sensors that can withstand the typical explosion pressure of 10 bar g or more and with that have a high measuring uncertainty (typically 1 % of the measuring range). In most cases, other sources of errors are not mentioned at all and the accuracy of the gas preparation is hardly considered yet.

2.3.3. Method I

The three different methods have their benefits and disadvantages: The most precise and homogeneous gas mixtures are obtained, if the explosion vessel and the dust container are both filled with the same premixture before injection of the dust. But, for hybrid mixtures of gas and dust this method is complicated and the common 20L-sphere for dusts must be modified slightly, because both, the sphere and the dust container, have to be evacuated to very low pressures before they are filled with the premixture. The latter is not possible, if dust is already in the dust container, but the residual air in the dust container can be considered for the determination of the final gas fraction. This method has the benefit, that the following sources of error are avoided:

- 1: Discrepancy between the calculated gas fractions, derived from the measured partial pressures with the pressure sensors installed in the test vessel and the actual fraction of the gas

- 2: Local concentration variations because of incomplete mixing at the ignition moment after 60 ms of ignition delay time (for 20L-sphere, 600 ms for 1 m^3)

The disadvantages of this mixing procedure are the dangerous explosive atmosphere in the dust container, if gas concentrations above the lower explosion limit are tested and the previous preparation of these mixtures. Either they are prepared at elevated pressure or the explosive mixture must be transferred by a compressor. Facilities that used this method so far are the Dortmund University (Germany, [81]) and the Dalhousie University (Canada, [82], with a 26L-sphere) but it is not applied anymore [83]. The latest article applying this method of mixture preparation was published in 2009 from the Northeastern University in Liaoning (China) but it seems it is not in use anymore, too [84].

2.3.4. Method II

Method II has the benefit that the common 20L-sphere can be used as it is without any complicated modifications. There are no explosive gas-air mixtures at high pressures during mixture preparation, which makes this procedure the safest one. It is valid for hybrid mixtures with a gas fraction of up to 40 %. However, this procedure is more prone to errors due to leakage of the 20L-sphere resulting in larger deviations to the desired concentration of flammable gas.

This method is recommended in the manufacturer's handbook for the most frequently used 20l-sphere for dusts (Kühner [79]) and applied by most of the research facilities like the Otto von Guericke University (Germany, [85]), Karlsruhe Institute for Technology (Germany, [17], [18]), Dalhousie University (Canada,[86]), Anhui University of Science and Technology Huainan (China, [87]), Henan Polytechnic University Jiaozuo (China, [27]), University of Napoli (Italy, [88]), Texas A & M University (USA, [15], with a 36L-sphere), University of Witwatersrand (South Africa, [89], with a 40L-sphere), the Italian National Research Council in Naples, Italy [90], Xi'an University 116 of Science and Technology in Shaanxi, China [91] and the University of Pardubice, Technical University of Ostrava and OZM Research (all three in Czech Republic, [92]), 20L sphere and 1m^3).

This mixing method assumes, that the gas-phase is homogeneous at the moment of ignition.

2.3.5. Method III

Method III has the disadvantage, that explosive gas-air mixtures are pressurized to 20 bar g in the dust container, so if an explosion occurs an overpressure of up to 200 bar g might occur inside the dust container which is not designed for these high pressures and might burst. Therefore, this mixing procedure is commonly applied with low amounts of flammable gas below the lower explosion limit (LEL) in the dust container. Thus, applying this method of mixture preparation, only hybrid mixtures with very little amounts of flammable gas can be tested. Usually, premixtures of flammable gas and air prepared in gas cylinders are used for pressurizing the dust container.

The benefits of this method are that there are no modifications needed on the standard dust sphere, the test procedure is comparably short, and the concentrations might be more

precise, because it is not dependent on potential leakages of the 20L-sphere. This method is applied by the University of Newcastle (Australia, [93], only gases under turbulence were tested, no hybrid mixtures and they used a 1 m^3 vessel), Dalian University (China, [94]), North University in Taiyuan (China, [95]) and Sichuan University (China, [96]).
It should be mentioned, that in some articles it is not mentioned at all, where the amount of flammable (or inerting) gas is added first, even though, this is crucial for a later interpretation of the data. It can be assumed, that if it is not stated or simply said, that the gas fraction was filled using the "partial pressure method" (which is actually true for all three methods) Method II was used [97].
This mixing method also assumes, that the gas-phase is homogeneous at the moment of ignition.

A comparison between the three mixing procedures has not taken place so far and with that the sources of error mentioned above have not been investigated either.

2.3.6. Pressure dependencies

Especially for hybrid mixtures containing a combustible dust as well as a flammable gas the pressure compensation and the mixing procedure can have a great influence on the test result, because they affect the gas composition significantly. The flammable (or interting) gases are usually filled in the 20L-sphere and the fraction is calculated from the partial pressure of the gas with the simple equation

$$x_{gas} = \frac{p_{gas}}{p_I} \tag{2.5}$$

with p_I as the pressure at the moment of ignition

Even though it has been known for a long time, that the explosion pressure is dependent on the initial pressure (Pilao et al. [98], Hertzberg et. al. [99], Glarner [100], SAFEKINEX Del. Nr. 8 [101], Lazaro and Torrent [102], Pascaud and Gillard [103]) the allowed pressure ranges and the requirements for the pressure measurement systems in the standards for the determination of the safety characteristics of dusts can lead to a wide variation of initial pressures in the tests. The pressure inside the 20L-sphere before injection of the dust, the difference between the pressure in the sphere at the time of ignition and before injection of the dust (or Pre-ignition pressure rise, PIPR) and the subsequent pressure drop, that occurs due to thermodynamic equilibration by dissipation of the heat induced previously by adiabatic compression inside the sphere have to be taken into account for calculating the amount of flammable gas correctly in case of hybrid mixtures and to obtain robust and reproducible results for the determination of safety characteristics. According to the American Standard ASTM 1226 [57] a pressure before injection of 0.4 bar a and a pressure at the ignition moment between 0.94 bar a and 1.06 bar a are demanded for the tests but no accuracy of the pressure measuring system is mentioned. According to the EN 14034 series a pressure before injection of 0.4 bar a and an accuracy of the pressure measuring system of

± 0.1 bar is suitable resulting in a pressure before injection of the dust of 0.3 bar a to 0.5 bar a ([45], [59], [46], [47]).

Pre-ignition pressure rise (PIPR)

Table 2.2 shows the pressures, that are relevant for the mixing procedure and their allowed ranges in different standards. The PIPR is only defined directly in the manufacturer's software of the 20L-sphere (from Kühner), which shows an error, if the PIPR is lower than 0.55 bar or higher than 0.7 bar. The American standard defines the allowed PIPR indirectly with the pressure before injection and the pressure at the moment of ignition resulting in an allowed range between 0.54 bar and 0.66 bar [57]. With a pressure of 400 mbara before injection and a definition for the ambient pressure at the moment of ignition of 1.013 bar a, the European standard EN 14034 series have a theoretical PIPR of 0.613 bar ([45], [46]). Considering the defined accuracy the allowed range is between 0.513 bar and 0.713 bar. The maximum measuring uncertainty of the pressure measuring system is also not stated.

Table 2.2.: Pressure specifications stated in the standards for determination of safety characteristics of dusts and in the standard software of a manufacturer of the 20L-sphere

Standard Procedure/ Source	Pressure before injection	Pressure at ignition	Accuracy of the pressure measuring system	PIPR
	in bar a	*in bar a*	*in bar*	*in bar*
EN 14034 [45][59][46][47]	0.4	1.013	± 0.1 (or better)	0.513-0.713*
ASTM 1226 [57]	0.4	0.94-1.06	Not defined	0.54-0.66
Manufacturer's software from Kühner[79]	0.4	1	Not defined	0.55-0.7

*Not defined explicitly, but calculated from the other specifications

Post injection pressure drop (PIPD)

After the fast injection of the dust via pressurized air from the dust container the pressure is recorded and the whole mixture should have 1 bar a [57] (or with 1.013 bar a close to that value [45]). Normally the ignition takes place shortly after the opening of the valve and this pressure shortly before ignition is usually taken as the initial pressure p_I and used for the calculation of the flammable gas fraction. However, the temperature rise due to the compression is not taken into account in the standard procedures. Especially, in case of hybrid mixtures, if this initial pressure is used for calculating the amount of flammable gas according to the partial pressures, this leads to wrong results. The effect of adiabatic compression is not mentioned in any standard and has not been found in research articles so far. Poletaev observed the temperature increase when air is added to the test vessel [104] and

Cashdollar observed the temperature increase while and decrease after the injection process [105], but both do not mention the pressure drop afterwards.[2]

2.4. The influence of turbulence on safety characteristics

During the quick injection process of the dust a high level of turbulence is created mixing the dust-gas mixture. If the ignition is not triggered, the turbulence decays over time and the gas eventually obtains a quiescent condition the dust settles. The behavior of turbulence is the same for all three mixing procedures while the ignition is usually initiated 60 milliseconds after a pressure rise is detected inside the test vessel.[3] The decay of the turbulence after injection has been investigated theoretically by Skrbek and Stalp [106] and described by Dahoe et. al. [107] who decsribed the decay of the root mean square velocity with the following equation, that was also used by Skjold to draw a connection between his measured values and the turbulence energy 2.11.

$$\frac{u^{|}_{rms}}{u^{|}_{rms,0}} = (\frac{t}{t_0})^n \tag{2.6}$$

It has also been investigated experimentally in the 20L-sphere by Skjold [108] and by Pu et. al. [109] (see figure 2.12).

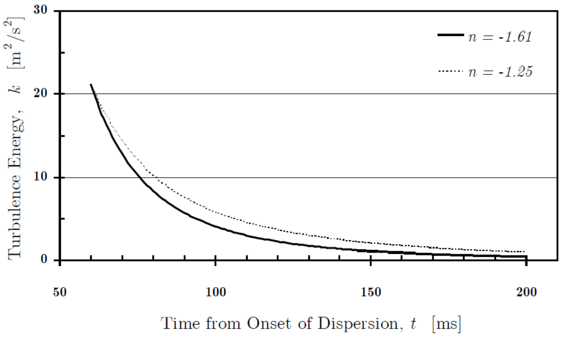

Figure 2.11.: Decay of the turbulent kinetic energy in a 20L-sphere, calculated from the measured root mean square velocity, taken from [108]

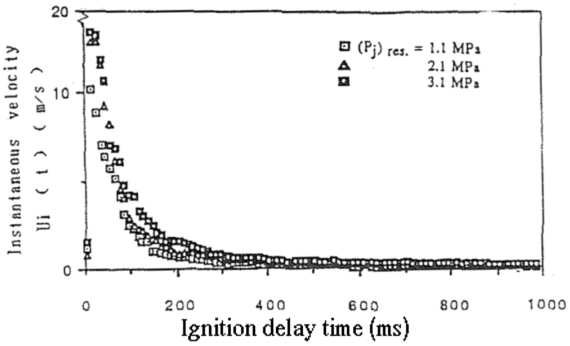

Figure 2.12.: Decay of the root mean square velocity in a 20L-sphere with different dispersion pressures measured with hot wire probes, taken from [109]

The initial turbulence at the moment of ignition has a significant influence on the measured values of $(dp/dt)_{max}$ of gases. The influence on p_{max} of gases is with about 10 % to

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[2] The cooling effect of the expansion in the dust chamber does not seem to play a role. Also, it has not been investigated how pure hydrogen behaves.

[3] This parameter was defined experimentally: It is the earliest moment, where the injection process is over. An activation of the ignition at an earlier moment would cause a combustion at a pressure lower than 1 bar a, a later activation would cause a further decrease of turbulence.

20 % smaller but clearly measurable.
The influence of the speed of a fan inside a 4-litre spherical test vessel on the flame propagation speed was systematically investigated by Richard Vernon Wheeler in 1919 for ethane (see figure 2.13 [110]). He cites an explanation from Mallard and Le Chatelier: "When the gas in which the flame is moving is in a state of agitation, the speed of propagation increases because the heat is transmitted not only by virtue of the conductivity of the gas mixture, but also by virtue of the differences in speed of the various parts of the mass. The surface of the flame, instead of keeping a constant and regular shape, is deformed at every moment, increases in width of width, multiplying the points of ignition and, consequently, making the progress of combustion more rapid." [110]

Wheeler further concludes that the explanation by Mallard and Le Chatelier has two consequences:

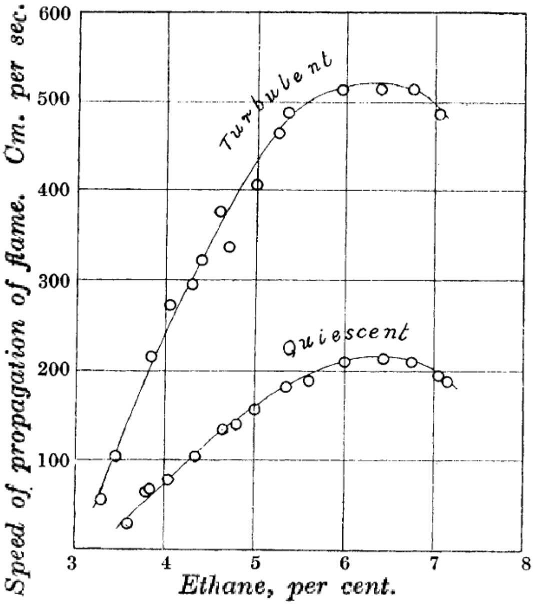

Figure 2.13.: Effect of turbulence on the flame propagation speed of ethane gas, taken from [110]

- The higher the level of turbulence, the more rapid the combustion
- A mixture with a low speed flame is more susceptible to the effects of turbulence than one in which the speed of the flame is high

A similar trend for the measured values of p_{max} and $(dp/dt)_{max}$ was also investigated by G. F. P. Harris in 1967 [111] for pentane. Harris also used a fan inside a 60 cubic feet (appr. 1.7 m^3) test vessel and varied the fan speed. While the values for p_{max} increased slightly for the near stoichiometric gas-air-mixture, it increased stronger for the lean mixture (see figure 2.14, left side). The reason for the increased explosion pressure seems to be experimental and is caused by a faster combustion and with that lower heat losses on the walls of the test

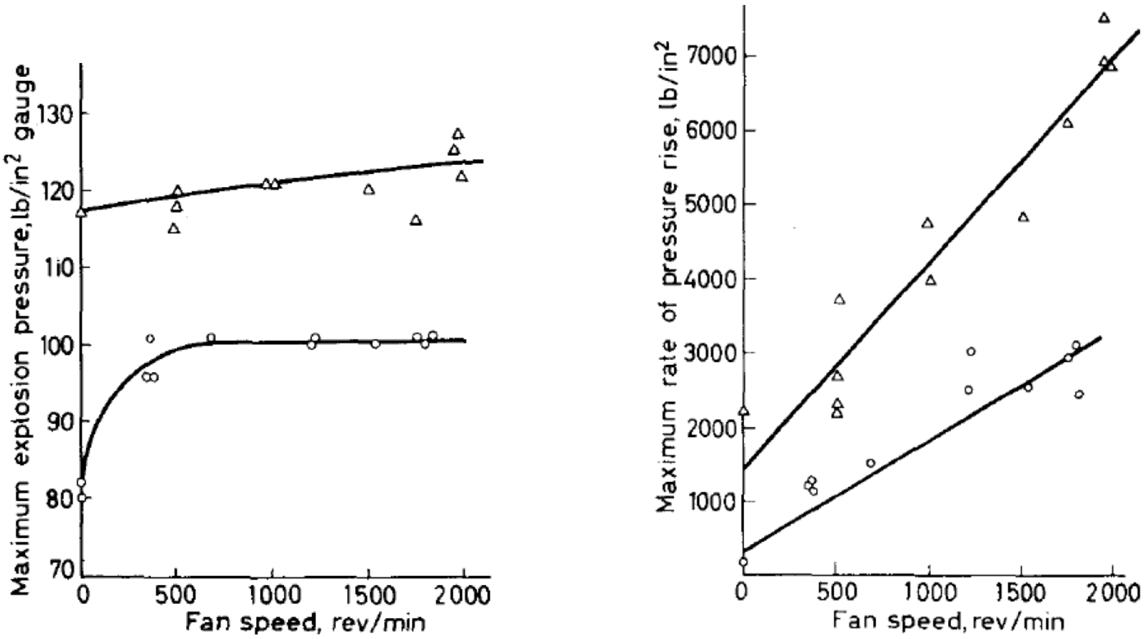

Figure 2.14.: Explosion pressure (left) and maximum rate of pressure rise (right) against fan speed in a 60 cubic feet vessel [111], Δ = 3 mol%, o = 1.7 mol%

vessel. While the effect on p$_{max}$ is rather small for all mixtures with an increase of 10 to 30 %, the maximum rate of pressure rise was increased by factors of ten and more (see figure 2.14, right side).

Investigations on the influence of the turbulence on the safety characteristics of dusts and gases were conducted with several approaches:

- The ignition delay time was varied ([112], [91], [113], [95], [114], [115], [116], [107], [117], [118], [119], [90], [120], [121])
- The pressure in the dust reservoir was varied [109]
- Fans were installed inside the test vessel (only for gases) [110], [111], [122]

The measurement techniques for the turbulences were also diverse. The particles were observed with a camera (Particle Image Velocimetry, only for dusts) [119], the injection process of a transparent 20L-sphere was filmed with a camera [123], the flow was measured with Hot Wire Anemometry ([109], only for gases) or Laser Doppler Anemometry (LDA) ([108], [124], [107]) or the safety characteristics were measured at different levels of turbulence caused by different fan speed or different times to ignition after injection drawing conclusions about the turbulence level at the moment of ignition ([125], [60], [120]).

The fact, that turbulence can not be measured directly and with that, the data can not be applied to the standard procedure, leaves no other option than comparing the safety characteristics of the gas in quiescent conditions to the agitated conditions when testing dust with high turbulence levels.

The most expedient comparisons of safety characteristics determined at turbulent conditions usually prevalent in the 20L-sphere with safety characteristics determined at quiescent conditions were made by Kundu et. al. [93] with a 1 m^3 test vessel and methane, Chang et. al. [112] with 100 ms instead of 60 ms ignition delay time using hydrogen and Skjold with a 20L-cubical vessel and propane [108]. The key findings, slight increase for p_{max} and increase by a factor of up to almost 10 for $(dp/dt)_{max}$ were the same (see 2.15).

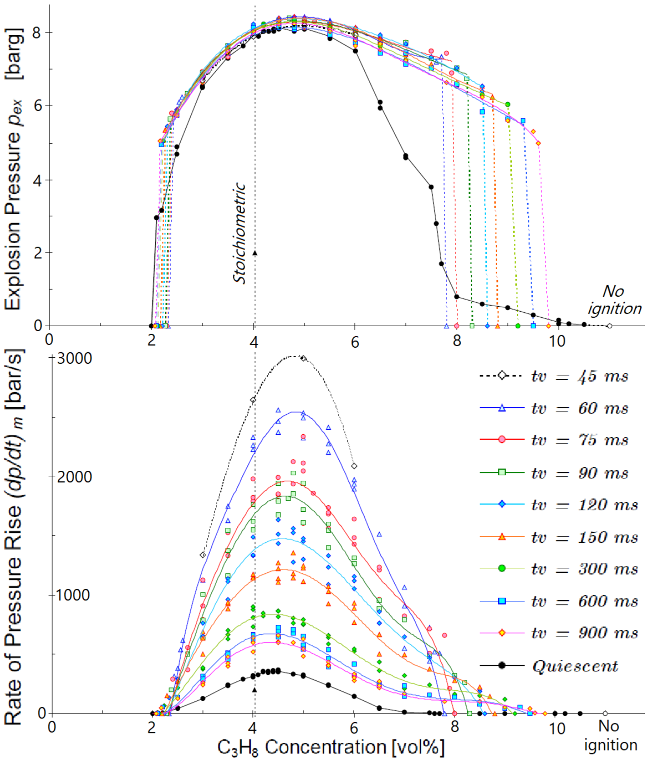

Figure 2.15.: Safety characteristics for propane-air mixtures, taken from [108]

The turbulence has also an influence on the minimum ignition energy. With higher turbulence intensity a higher ignition energy is required to ignite the gas-air mixture. Experiments showed that it depends on the pressure whether this rise is linear or exponential [126]. An explanation is given in Appendix E.4.

The correlations for turbulence on the safety characteristics of dusts were also described and summarized by Amyotte et. al. in a review article [127]. In general they are:

- (dp/dt) is linearily higher with higher turbulence
- p_{ex} is slightly higher with turbulence
- The minimum ignition energy rises with the turbulence. This effect is especially pronounced at the explosion limits.

- The explosion region (from LEL to UEL) is narrowed with higher turbulence if the ignition energy is not high enough

2.5. Limits of the methods and investigations

The methods that are presented in this thesis have several limits. Especially the test apparatus of the 20L-sphere and its procedure have the following disadvantages:

- With 20 liters it has a very small volume where upscaling might be difficult. This point has been investigated by researchers concluding both , that a testing volume above 16 liters is needed and with that upscaling from the 20L-sphere works [9] and that the values of the 20L-sphere are not comparable to the ones obtained in the 1m^{3}vessel [128]. Others stated, that it might be used choosing the experimental parameters carefully [129] or it is only useful under some conditions and not for all kinds of dusts [130].
- With an ignition energy of usually 2 kJ or 10 kJ it is a very conservative estimation of the ignition sources, that are normally prevalent in processes. Though this point only counts for the estimation of the explosibility and the explosion limits of dusts, it is often brought up by critics of the method.
- The calculation of the K$_{St}$-value (see section 2.1.2) is valid for 1) a point source of ignition that ignites the testing mixture in the center of the test vessel 2) under non-turbulent conditions and 3) the flame thickness should be negligible compared to the radius of the test vessel ([131], p. 347). All three requirements are not present with this method. Even though this was investigated before, and other methods were presented [132], simplicity outperformed the new findings so far.
- The method is sensitive to many experimental parameters and with that the comparison of the obtained values is difficult

On the other hand, the data, that is determined with the 20L-sphere, is a good start for the implementation of safety characteristics. The only other standardized test method for the determination of p$_{max}$ and (dp/dt)$_{max}$ respectively the K$_{St}$-value of dusts, the 1m^3 vessel, shares most of the disadvantages listed here, though less pronounced than in the 20L-sphere. The disadvantage is a higher effort cleaning the apparatus and the need for 50 times more dust than in the 20L-sphere which is not possible for many substances like pharmaceutical products because the costs are too high. Also the number of tests per day is three to four times lower for the 1m^3-vessel. For these reasons the 20L-sphere is more widespread today worldwide.

3. Experimental Methods

3.1. Ignition sources and experimental methods for their characterization

In this work the four types of ignition source mentioned in table 2.1 are characterized experimentally. The net ignition energy introduced into the system as well as the reproducibility was compared by calorimetric measurements. The burning duration and the igniting volume have been compared by high-speed recordings and schlieren-imaging. Finally, the influence of the orientation of the electrodes was studied for the exploding wire igniter. In the case of the exploding wire, the ignition energy was also determined directly by electrical measurements.

3.1.1. Ignition Sources

Induction spark

The induction spark as described in EN 1839 [42] was used. It has a secondary open circuit voltage of 15 kV (peak). In the setup used in this work the cables between the transformer and the electrodes had a length of 3,2 m, a cross-section of 4 mm ^{2}, an inductance of 4,7 μH, and a capacitance of 0,257 nF. The distance between the electrodes was kept constant with 5 ± 1 mm.

Surface gap spark

Two different surface gap spark devices were used. One had a loading voltage of 450 Volt and a capacitance of 220 μF, the other one had a capacitance of 600 μF and an adjustable voltage in steps of 50 Volts from 300 Volts to 450 Volts.
In the setup used in this work the cables between the capacitor and the electrodes had a length of 3,2 m, a cross-section of 4 mm^2, an inductance of 4,7 μH, and a capacitance of 0,257 nF (without pencil lead) or rather 0,991 nF (with pencil lead). For one test series to determine the influence of the cable length, cables with an overall length of 21 m were used. These were not checked on resistance, capacitance and inductance.

Chemical igniters

The chemical igniters as described in the EN 14034 series ([45], [59], [46], [47]) were used for most of the explosion tests with ignition energy of 1 kJ if not stated otherwise. In each explosion test in the 20L-sphere two igniters were used facing in opposite directions. For one comparing test series 5 kJ igniters were used and the calorimetric measurements were performed with (single) 100 J, 250 J, 500 J and 1 kJ igniters.

Exploding wire

The standardized exploding wire ignition device as described in EN 1839 [42] and EN 15967 [43] and described in section 2.2.4 was investigated.
Additionally a new exploding wire ignition device, differing from the standardized one, was built, also investigated and used for the explosion tests in this work for the following reasons:

- Higher ignition energies of up to 1000 J have to be applied
- Two igniters have to be triggered at the same time to compare the results with standard tests for dusts with the two chemical igniters
- The igniters have to be triggered very precisely and directly after the trigger-signal comes in

After being triggered externally the phase-fired controller always waits for the beginning of the next positive half-wave of the sine-shaped voltage from the power grid. So when the trigger-signal comes an additional delay of up to 20 ms arises with a lower level of turbulence and with that a lower value for (dp/dt). In figure 3.1 the trigger signal 1 would cause an additional delay of 18 ms, trigger signal 2 would cause an additional delay of 5 ms.

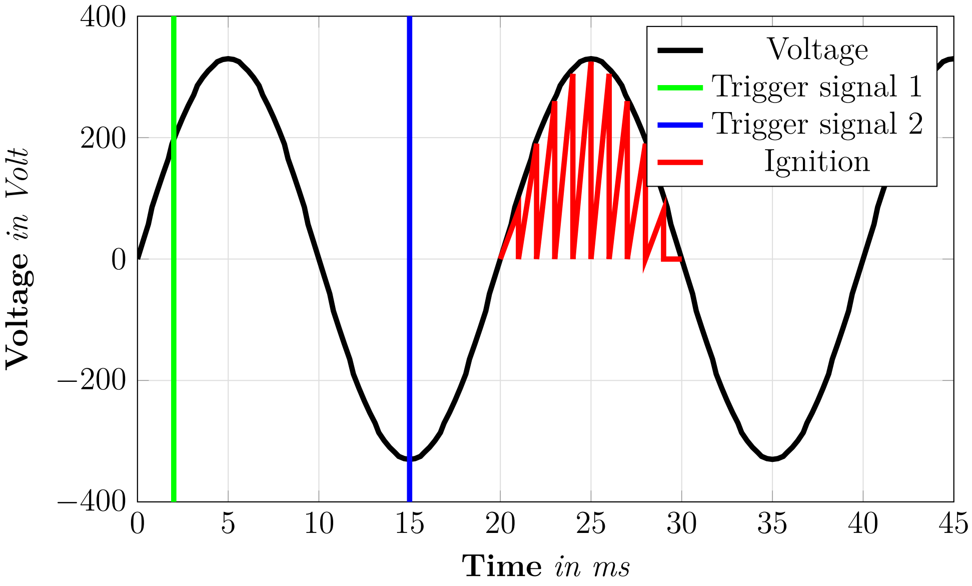

Figure 3.1.: Additional delay for the standard exploding wire device

That this additional delay causes different values, especially for the $(dp/dt)_{Ex}$-values of dusts was investigated with a constant concentration of 500 g/m^3 for corn starch, niacin and lycopodium while all other parameters were kept constant (see Appendix E.9 for values).

For the device that was used in this work capacitors with an operating voltage of 450 V and a capacity of up to 21 000 μF was used. To achieve a comparable burning duration of 4 ms to 10 ms an inductance was introduced to the circuit (see figure 3.2).

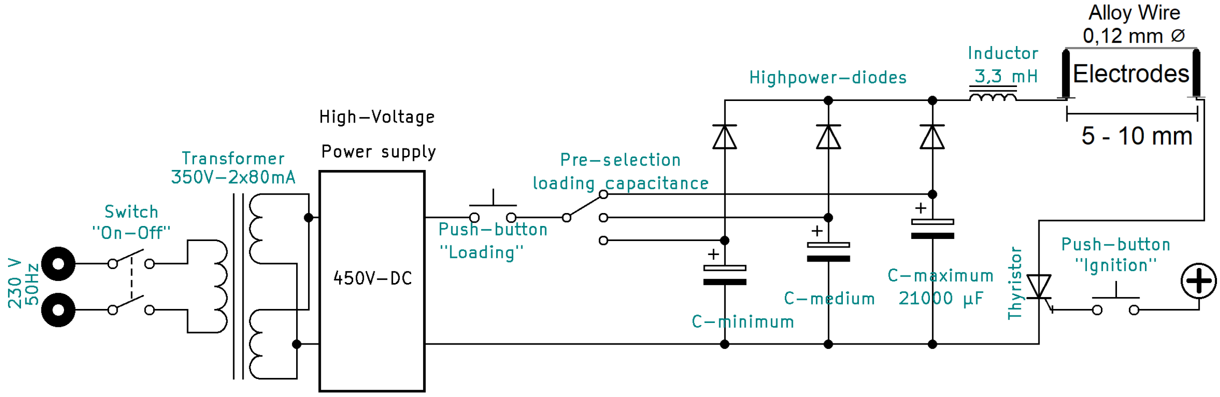

Figure 3.2.: Schematic of a high-energy exploding wire ignition source based on capacitors

The ignition devices for the exploding wire had built-in isolation amplifiers, which provided the voltage and current during the ignition process galvanically isolated with a defined factor as measuring voltage. The galvanic isolation and the factors were necessary to prevent voltages of 450 volts from being applied to the front panel, which would pose a significant hazard to the user.

By summing up the product of the measured ignition voltage and the measured ignition current for n samples in the given period of time and by dividing it by the number of samples. The ignition power $P_{ignition}$ and energy $E_{ignition}$ can be calculated according to the equations

$$P_{ignition} = U * I \tag{3.1}$$

$$E_{ignition} = \sum_{k=1}^{n} (\frac{U_k * I_k}{n}) \tag{3.2}$$

The voltage is measured with a voltage divider, the ignition current by means of a shunt resistor with a resistance of 0.5 mΩ. The voltage drop due to the resistance of the cable is subtracted from the measured voltage according to the following equation:

$$U_{res} = U_{meas.} - \frac{\rho_{copper} * l_{cable} * I_{meas.}}{A_{cable}} \tag{3.3}$$

Example plots of the voltage, the current and the ignition energy can be found in Appendix E.1. The ignition device for the explosion wire used in this work is described in detail in Appendix A.

3.1.2. Calorimetric measurements of the net energy of different ignition sources

For the measurement of the ignition energy, a bomb calorimeter was used. This method has the benefit, that the actual energy, that is normally introduced into the system, is measured and not the gross energy, that is stored in capacitors or in the chemical charge. Another benefit regarding the comparability is, that all ignition sources (electrical and chemical) were measured with the same apparatus.

The calorimeter was made of brass and had an inner diameter of 2 cm, an outer diameter of 6.5 cm and a total height of 7 cm (see figure 3.3, a CAD drawing is added in Appendix B). It was isolated by foamed polystyrene with a thickness of at least 90 mm (not shown in the figure). The temperature increase of the calorimeter was measured with a high-precision semiconductor thermistor, TS-NTC-203, Hygrosens Instruments GmbH, and a self-designed circuit board transforming the changing resistance into a changing voltage. The increase of the recorded voltage signal is proportional to the temperature increase and thus to the released energy. The calorimeter was calibrated with a 100 Watt lamp, a 12.5 V DC power source adjusted to an output of 8 A and a timed relay that was set to several switching times to get a calibration curve according to the equation

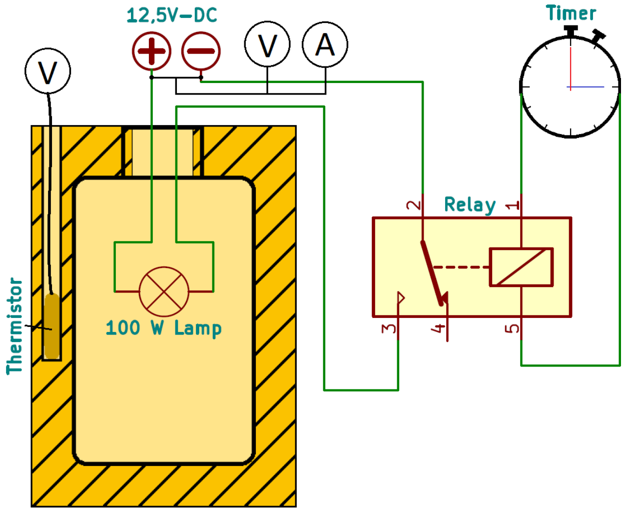

Figure 3.3.: Adiabatic brass calorimeter (left side) in the calibration set-up with a time controlled relay and a 100 W lamp

$$E = U * I * t \tag{3.4}$$

By means of the calibration a sensitivity of 69.8 mV/kJ and a mean deviation of 1.63 % (max. 4 %) was obtained. In figure 3.4 the calibration curve is shown together with the results of several validation tests.

With approximately 14 mΩ the energy loss of the connecting cables can be neglected. Compared to the resistance of the lamp (theoretical value: 1.5625Ω) the voltage drop across the cables is less than one percent and can be neglected, so most of the energy is introduced

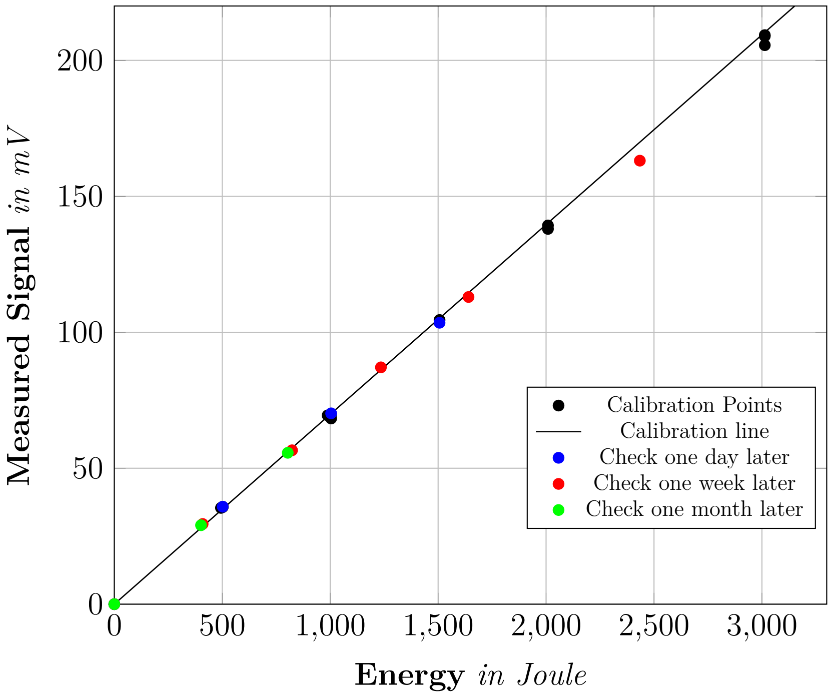

Figure 3.4.: Calibration line of the adiabatic calorimeter and three verification test series with a maximum deviation of 4 %, electric measuring signal of the thermistor against the electrical energy brought into the system

into the calorimeter.
The calculation of the energy is the difference between the voltage measured before triggering the ignition and when the values has stabilized again divided by the 0.0698 mV/J (see also Appendix B).
The exploding wire, the chemical igniters were single shots inside the calorimeter. Since the energy of the surface-gap spark and the induction spark is very low and with that harder to measure multiple shots were performed. The surface-gap spark was triggered several times and the measured energy then divided by the number of shots. The induction spark was triggered ten times in each test and the duration was varied with 200 ms, 500 ms and 1000 ms.

3.1.3. Determination of the burning duration of standardized ignition sources - Highspeed Recordings

Three different high-speed cameras (MotionCorder Analyzer Model SR-1000 from Kodak, FASTCAM APX RS from Photron and HPV-1 from Shimadzu) were used for filming the ignition sources with maximum framerates of 1 000, 20 000 and 1 000 000 frames per second. The last one can only take 100 pictures that are stored inside the pixel (so called “In-situ storage image sensor” or ISIS [133]). Therefore, it was only used for the fastest ignition source with the shortest burning duration after the other two cameras failed to record the process in detail. In table 3.1 the three cameras are listed with their characteristics.

Table 3.1.: Properties of the cameras used for determining the burning duration

Camera	Maximum framerate *in fps*	Color	Resolution
MotionCorder	1000	Color	400 x 248
Fastcam	20 000	B/W	512 x 512
HPV-1	1 000 000	B/W	936 x 780 only 100 frames

All the test setups consisted of the camera, the ignition source and a black paper in the background to reduce artifacts from shining and reflection (Figure 3.5).
After filming the pictures in which the ignition source was visible were simply counted and divided by the framerate. The burning duration of the induction spark is defined in the standards and set with a timed relay, hence it was not tested in this work.
The burning duration of the other three standardized ignition sources was determined using high-speed cameras. In each case, several ignitions were filmed and the images subsequently counted.

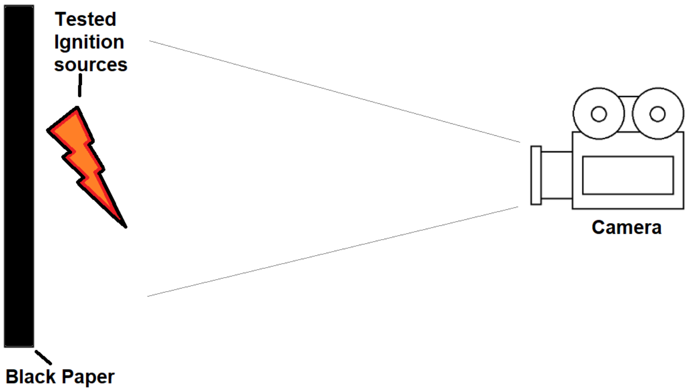

Figure 3.5.: Setup for the highspeed-imaging tests

As chemical igniters several tests with different ignition energies of 100 J, 250 J, 500 J, 1 kJ and 5 kJ were conducted.
The exploding wire had a loading voltage of 450 V, a capacitance of 21 000 μF, a cable length from the ignition device to the electrodes of 3.2 m with a cross-section of 4 mm^2 and an electrode distance of 6 mm.

3.1.4. Determination of the burning volume of standardized ignition sources

The optical inhomogenities caused by the density differences are called schlieren and there are different methods to visualize these differences that are called schlieren techniques [134]. For this study a set-up with one parabolic mirror, a knife-edge (razor blade) and a point source of light was used. The smaller and brighter the source of light, the better results could be seen. For this reason, an LED light was used in the experiments. The camera from Fastcam (described in section 3.1.3) was used to record a video during the execution of an experiment. The schematic of these individual components is shown in the following figure 3.6, for replications and optimization of the components see [134].

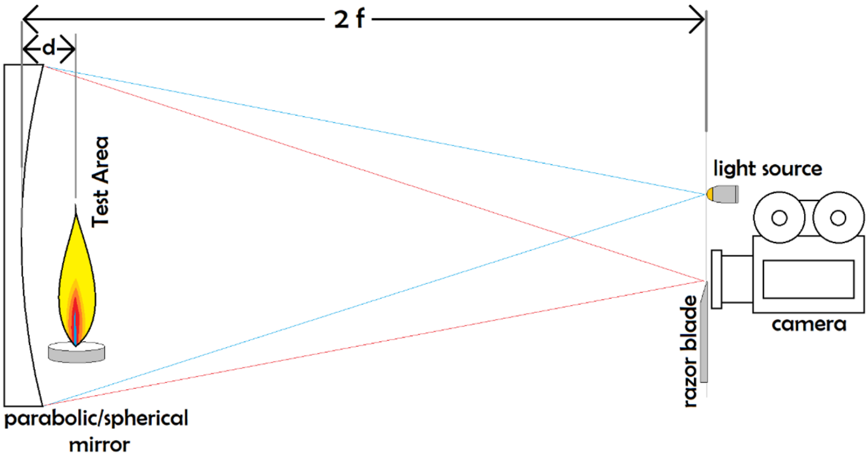

Figure 3.6.: Optical setup for the Schlieren-imaging tests

In this series of experiments the light source was positioned at a defined distance (2f) away from the parabolic mirror. The camera and the razor blade were placed right next to the light source. The light was focused on the double focal length (f) of the parabolic mirror[1]. This is given by Equation 3.5:

$$f \approx r/2 \tag{3.5}$$

At the end the camera was placed in the path of the light, behind the radius, respectively behind the razor blade. The razor blade then shields some of the reflected light from the mirror. If more light is blocked the schlieren-effect is more visible but the image gets darker. The testing area was as close as possible to the mirror otherwise the image would have gotten blurry. The basic theory of schlieren depends mostly on geometrical optics with additional consideration of diffraction affects. For the influence of the gases see Appendix E.3.
All four ignition sources stated in table 2.1 were put close ($0,05m < d < 0,15m$) to the

---

[1] “radius of curvature (r)”, that means the distance from the pole to the focal point. The author is aware of the fact, that a parabola has no radius and a spherical mirror has no focal point. For this set-up both types of mirrors work. For such a small part, a sphere and a parabola are pretty similar and the equation works as well

parabolic mirror and several ignitions were filmed with a high-speed camera (Photron FASTCAM) with 10 000 frames per second.

3.1.5. Distance and angle between the electrodes of the exploding wire

The influence of the distance and angle between the electrodes on the ignition energy and its scattering of the exploding wire was investigated using a U-shaped polypropylen rack. In this device the electrodes can be placed in different angles with 180 ° (A1 and A2, **A**djacent), 90 ° (R1 and R2, **R**ight-angled) and 0 ° (P1 and P2, **P**arallel) with a distance of 6 mm, see figure 3.7).

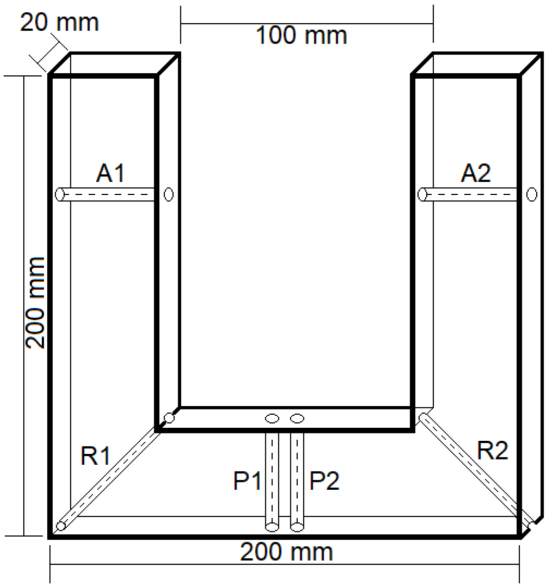

Figure 3.7.: Schematic of the electrode-rack, all holes with a diameter of 4 mm

The adjecent ones (A1 and A2) were also used for the tests with different distances between the electrodes. For the tests with distances above 100 mm one electrode was placed outside the device.

3.2. Preconditions for explosion tests - substance analysis and mixing procedures

The mixture preparation for the determination of safety characteristics of gases, the partial pressure method, is mostly used in the standards (see [42], [70] and [43]). The 20L-sphere is not designed to maintain a vacuum for a long period of time, one of the prerequisites for the partial pressure method. If the test vessel is air tight the concentration of the gas can still be flawed by imperfections of the pressure sensors, dead ends of the piping in which the

amount of gas gets pushed in or other uncertainties.
For these reasons a series of pre-tests was performed.

3.2.1. Mixing Procedures

For all the experiments a standard 20L-sphere with a rebound nozzle was used. Two piezoresistive pressure sensors (company: Keller, type: PA-10, linearity: better than 0.5 % full scale) were additionally installed for the tests, one with a resolution of 0.1 mbar and a range of 1 bara, the other with a resolution of 1 mbar and a range of 10 bara. The first one was just used for the filling process and had to be closed before initiating the ignition. An additional highly sensitive vacuum pressure sensor (pirani gauge) with a resolution of 0.1 mbar was installed to measure the absolute pressure during evacuation prior to each test.
For the determination of the leakage-rate the 20L-sphere was evacuated, then all valves were closed and the pressure was measured. Since the mixing process can take up to five minutes (depending on the type of connections and connecting lines) the pressure was recorded for at least ten minutes. With the time and pressure the leakage-rate was determined according to the equation

$$(dp/dt)_{Leakage} = \frac{p_{end} - p_{begin}}{t_{end} - t_{begin}} \tag{3.6}$$

If the leakage rate is less than 1 mbar/min it can be seen as within an acceptable range.

The mixture preparation was carried out optionally according to one of two different mixing procedures (Method I or Method II).

Method I

Prior to each test the mixture of flammable gas and air was prepared in a separate pressure resistant cylindrical 6L-mixing vessel that was connected to both the 20L-sphere and the dust chamber (see figure 3.8). The mixtures were prepared according to the partial pressure method in the mixing vessel, evacuating the mixing vessel to less than 5 mbara first and filling in the components of the mixture subsequently according to their partial pressures. The mixing vessel was equipped with a PC-fan for homogenizing the mixtures. The pressure in the mixing vessel was measured with a piezoresistive pressure sensor (company: Keller, type: PA-10, linearity: better than 0.5 % full scale) with a resolution of 5 mbar and a range of 50 bara (PIR 300 in figure 3.8). The mixtures were prepared at a final pressure of 26 bara for each test. For safety reasons, the set-up was installed in a safety room and operated by remote control. For the tests without dust the dust container was also evacuated prior to filling the gas mixture from the mixing vessel to the sphere and the dust container by opening the fast-acting valve between the dust container and the 20L-sphere several times, until the pressure in the 20L sphere did not rise anymore.

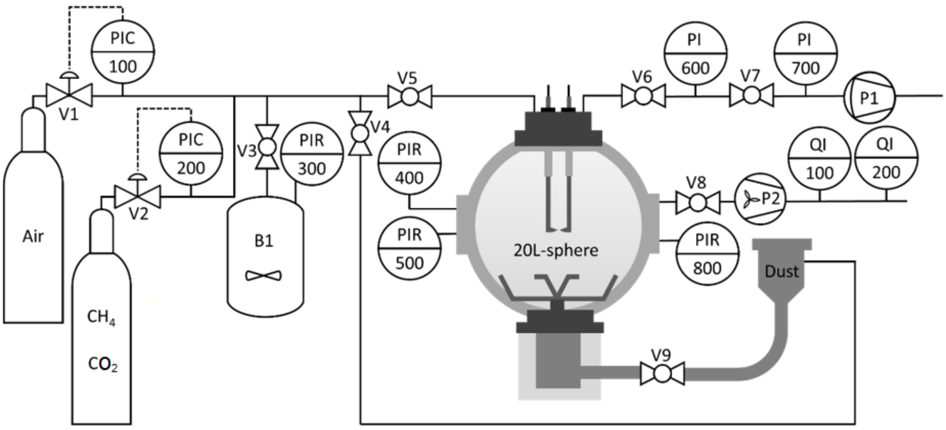

Figure 3.8.: Schematic of the standard 20L-sphere with adaptations for hybrid mixture testing (Method I), having premixtures inside a premixing vessel that can be filled to the 20L sphere and the dust container, valve V8 and the pump P2 are used for the gas analysis with QI-100 (O_2 measurement) and QI-200 (CO_2 measurement)

Method II

Filling the required amount of flammable gas for the mixture only into the 20L-sphere is safer, faster and needs less modifications than method I (see figure 3.9). After the evacuation the flammable gas was filled in the 20L-sphere up to the desired partial pressure and air was added afterwards to 400 mbara ± 2 mbar. With this method, mixtures with a flammable gas fraction of maximum 40 mol% can be tested. It is not appropriate for mixtures with air fractions of less than 60 mol% corresponding to an oxygen fraction of at least 12.6 mol%.

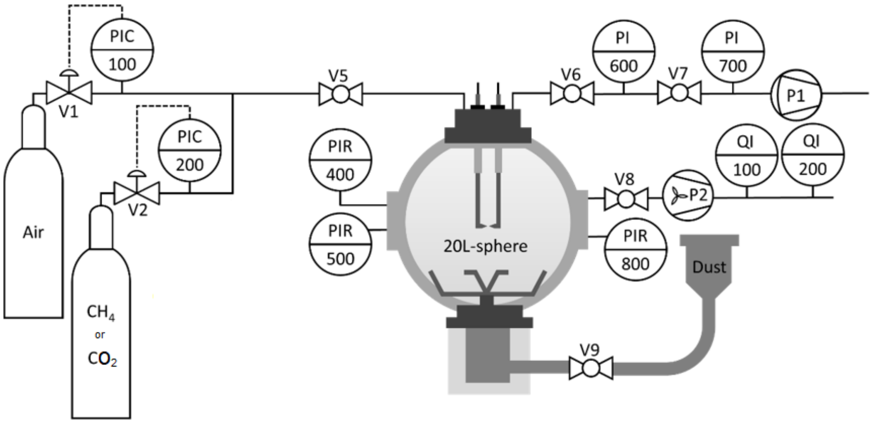

Figure 3.9.: Schematic of the standard 20L-sphere with adaptations for hybrid mixture testing (Method II, gas amount just inside the 20L sphere, valve V8 and the pump P2 are used for the gas analysis with QI-100 (O_2 measurement) and QI-200 (CO_2 measurement)

3.2.2. Pressure measurements

Since the mixing procedures in the standards for gases and dusts vary two things were investigated: The influence of the allowed range of the pressure increase when injecting the dust (pre-ignition pressure rise) and the pressure drop after injection of the dust due to compression and subsequent cooling of the air (post-injection pressure drop).

Variation of the pre-ignition pressure rise (PIPR)

For determining the influence of the PIPR on the safety characteristics of dusts in the 20L-sphere the allowed range according to the European dust standards of ± 100 mbar ([45], [59], [46], [47]) was tested. According to the standards the dust container is pressurized with air up to 21 bar a, which is theoretically necessary to achieve a pressure rise up to 1 bara. But this does not take into account that clogging or friction of the dust might slow the injection, so that the pressure in the dust container at the ignition moment is still elevated and in the 20L-sphere the pressure is lower than atmospheric pressure. For the tests the air pressure in the dust container was adjusted with a pressure reducer between 16 bara and 27 bara to achieve the variety of PIPRs on purpose and investigate their influence on the safety characteristics of dust clouds.

Determination of the post-injection pressure drop (PIPD)

The post-injection pressure drop is the difference between the 400 mbara plus the PIPR and the residual pressure after thermal equilibration. For determining the post-injection pressure drop in the 20L-sphere several tests without triggering the ignition source and without dust were carried out. The PIPR was varied from 0.5 bar to 0.7 bar. In additional tests the pressure in the 20L-sphere before injecting the dust was varied from 0.3 bara to 0.5 bara. In each test, it was waited for at least two minutes before injection of air to be sure, that the sphere and the air inside were fully thermally equilibrated. After the injection the pressure was recorded for three minutes with the 10 bara pressure sensor and additionally checked with the precise 1-bara pressure sensor. The recorded pressures were compared to the initial pressure before air injection plus the PIPR the manufacturer software stated.

3.2.3. Gas Analysis

The accuracy of the composition of the gas mixtures was determined by gas analysis in separate tests without triggering the ignition. For these tests the flammable gas methane was replaced by CO2, which is easier and safer to handle. A CO_2-measuring system (Infralyt Junkalor) with a range of 0 % to 20 % and a resolution of 0.01 % was connected to the 20L-sphere via a gas pump behind a valve (see figure 3.8 and 3.9). The measuring system was calibrated with a reference gas. An additional O_2-measuring system (Servomex MINI MP) with a range of 0 % to 100 %, a resolution of 0.1 %, a linearity of ± 0.1 % and an accuracy of ± 0.1 % was installed between the CO_2-measuring system and the pump (see figure 3.8 and 3.9).

For determining the accuracy of the gas preparation, mixtures with partial pressure fractions of 6%, 9% and 12% CO_2 in air were prepared with the two mixing methods described above. The injection of the gas from the dust chamber was carried out without dust and without igniters. Afterwards the fraction of CO_2 was measured with the analytic devices by taking samples directly from the 20L-sphere via the gas pump. Possible systematic deviations between the gas fraction calculated from the partial pressures and the measured gas fraction due to clearance volume, leakage, residual air or imprecise pressure sensors as well as the scattering were determined in this way. Considering the low pressures and being far away from boiling temperatures ideal gas behavior was assumed for all the mixture components.

3.2.4. Comparison of the safety characteristics for gases between Method I and Method II

Two of the three mixing procedures were compared by conducting explosion tests with the same fractions of methane and comparing the p_{ex} and K-value with otherwise constant parameters. The values were also compared to literature values.
The third method was not tested, because it is not very common and requires additional safety measures due to the compressed explosive atmosphere in the dust container.
For the comparison of the mixing methods hybrid tests with dust were not performed because the dust container could not have been evacuated resulting in an error of the gas amount for Method I.

3.2.5. Dust analysis

The particle size distribution was determined optically several times for the corn starch and at the beginning of the tests with the niacin, lycopodium and the quartz sand using a MALVERN Mastersizer 2000. It uses the diffraction of a laser beam and measures the scattering of the light. The samples were always tested three times and the results were averaged.
The moisture content of the corn starch was checked on a weekly basis while performing the tests using a Sartorius moisture analyzer (a picture is shown in Appendix D). It dries the dust sample for 15 minutes at a temperature of 115 °C and calculates the weight loss between the weights at the beginning and at the end of the drying process.

3.3. Experimental methods for the determination of safety characteristics of hybrid mixtures

Several explosion test series were conducted to determine different safety characteristics and to investigate other phenomena. In general they were all conducted the same way according to a newly developed standard operating procedure. This one was later also taken for the round robin test (see chapter 5) and is now part of the new standard for hybrid mixtures. If not stated otherwise all the tests were conducted according to the following steps.

3.3.1. Standard Operating Procedure

The sphere and all connecting lines were evacuated to a pressure lower than 2 mbara prior to each test. This was checked with a pirani gauge and the 1 bara and 10 bara pressure sensor were adjusted to the value of the pirani gauge (zero-point adjustment). Afterwards either the premixtures were filled from a mixing vessel to the 20L-sphere and the dust chamber (Method I) or air was filled in until 400 mbara minus the gas amount (for example 300 mbara for 10 mol%) with subsequent filling of the gas into the 20L-sphere and the dust chamber was filled with air (Method II). In each test the pressure in the 20L-sphere was 400 mbara ± 2 mbar before dust-injection. The pressure development was recorded with the two piezo-electric pressure sensors that are installed in the 20L-sphere in the default configuration of the manufacturer (internal resolution of 1 mbar, displayed in the software with 10 mbar and a measurement frequency of 5 kHz) and with the additional piezo-resistive sensor with a measuring range up to 10 bara. As igniters two 1 kJ chemical igniters or optionally two exploding wires with a net energy of 1 kJ each were used, pointing in opposite direction placed in the center of the sphere according to the standards for the determination of safety characteristics of dusts ([45], [59], [46], [47], [57]).
The ignition delay time was kept constant at 60 ms (except for the quiescent tests) and the pre-ignition pressure rise (PIPR or Pd) was narrowed to 0.64 bar ± 0.04 bar by adjusting the pressure in the dust container.
For the tests on the limiting oxygen concentration, the dust container was pressurized with nitrogen. Because of the dust it was not possible to evacuate the dust container before the tests. Oxygen, nitrogen and methane were filled into the sphere according to the partial pressure method. Before each test series the amount of flammable gas and of oxygen were validated with pre-tests (see 3.2.3). Again, for the pre-tests the methane was exchanged with carbon dioxide for safety reasons.
The amount of burning gas was calculated with the equation stated in section 4.2.3 and the oxygen fraction was calculated according to the following equation

$$x_{Oxygen} = p_{Oxygen}/(PV + PIPR - PIPD) * 100 - 0.68mol\% \tag{3.7}$$

*with p_{Oxygen} [bar] being the partial pressure of the oxygen, PV the **P**artial **V**acuum before injection of the dust (0.400 bar a ± 0.002 bar) and a **p**re-**i**gnition **p**ressure **r**ise (PIPR) of 0.64 bar ± 0.01 bar*

The residual air before filling the sphere with nitrogen was also considered for determining p_{Oxygen} but since the sphere was always evacuated to less than 2 mbara this increases the oxygen content by 0.045 mol% and may therefore be neglected. The value of 0.68 mol% is added because of the residual air inside the dust container and was determined experimentally. The PIPD was also determined experimentally and a constant value of 80 mbar was inserted into the equation.

3.3.2. The influence of the ignition energy and source on dusts

For the determination of p_{max} and $(dp/dt)_{max}$ of dusts in the 20L-sphere two 5 kJ chemical igniters are normally used according to the European Standards ([45], [59]), for the LEL and the LOC two 1 kJ igniters are normally used ([46], [47]). Since the high energies of 10 kJ were found to cause overdriving in the 20L-sphere while 2 kJ seemed to match the 1 m^3-results ([129], [135])[2] it was first checked, whether a decrease from 10 kJ to 2 kJ with chemical igniters would change the safety characteristics of the chosen dust. Afterwards the chemical igniter with 2 kJ was compared to the exploding wire with the same ignition energy. To further investigate the influence of the ignition energy on the explosion characteristics of dusts the energy of the exploding wire was reduced to 200 J and 20 J. For all these tests all other parameters like ignition delay time and pressures were kept constant.

3.3.3. Experimental method for the variation of the turbulence of gases

Since hybrid mixtures can not be tested in quiescent conditions, the influence of the turbulence, that is normally present in the dust testing conditions, on the gas component was checked. For this reason three test series were conducted varying the turbulence in the following way to have a proper A-B-comparison:

- **Turbulence:** The gas was added to the sphere and air was injected from the dust container. The mixture was ignited after 60 ms
- **Quiescence:** The gas was added to the sphere and air was injected from the dust container. The mixture was ignited after more than 3 minutes [3]

These tests were performed with hydrogen and methane at different fractions and methane was additionally checked on the limiting oxygen concentration. The ignition source and energy was also varied with two times 1 kJ chemical igniters and two exploding wires with 10 J, 100 J and 1000 J each (see table 3.2, for the results see chapter 4.3).

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[2] in both publications 2.5 kJ were used but since 1.25 kJ igniters are very uncommon we chose two 1 kJ igniters

[3] In the European standard for the determination of the maximum explosion pressure and the maximum rate of pressure rise of gases it is mandatory to wait two minutes after mixing to have quiescence [43]. Since the conditions here have a higher level of turbulence three minutes were assumed to be enough.

Table 3.2.: Conditions under which the turbulence was investigated with amounts stated

		p_{max} and $(dp/dt)_{max}$	LOC
Two each	**Hydrogen** *mol%*	**Methane** *mol%*	**Methane** *mol%*
1 kJ chemical igniters	1, 2, 3, 4, 5, 6, 7, 9	5.8, 8.8, 11.8	stoichiometric line
1 kJ exploding wires	1, 2, 3, 4, 5, 6, 7, 9	5.8, 8.8, 11.8	stoichiometric line
100 J exploding wires	1, 2, 3, 4, 5	-	stoichiometric line
10 J exploding wires	2, 3, 4, 5, 6	-	stoichiometric line

3.3.4. Test series evaluation

For the determination of safety characteristics several tests have to be conducted according to the standard operating procedure varying the amount of combustible substance - flammable gas and/or combustible dust. The step-sizes, ignition criteria and other variations are described in this chapter.

Ignition criteria

The ignition criteria for gases and dusts are defined in different ways (a full overview is in Appendix E.8):

In the gas standard "the criterion for an explosion (self-propagating combustion) is the occurrence of an explosion overpressure equal to or greater than the overpressure produced by the ignition source activated only in air, plus (5 ± 0.1) % of the initial pressure" [42]

In the standard for dusts an "ignition of the dust (dust explosion) shall be considered to have taken place, when the measured overpressure (influence of chemical igniters included) relative to the initial pressure p_i is greater or equal to 0.5 barg [$p_{ex} \geq (p_i + 0.5$ barg)]([46], [47]).

The different explosion criteria arise from the main two differences of the test methods, the turbulence and the ignition source. Since both cause a higher scattering of the measured values for dusts the criterion has to be higher[4].

Since the different ignition sources cause different overpressures, the dust criterion was used for the tests with two 1 kJ chemical igniters and lowered for the ignition sources causing a lower overpressure when activated only in air (see table 3.3).

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[4] The pressure sensors for dusts have a typical resolution of 10 mbar, while for gases the resolution is stated with ± 0.5 mbar

Table 3.3.: Pressure rise of different ignition sources and energies in air

Ignition source	total ignition energy	used value for the calculation	ignition criterion
	in J	*in bar g*	*in bar g*
two chemical igniters	2000	0.3	0.5
two exploding wires	2000	0.2	0.4
two exploding wires	200	0	0.2
two exploding wires	20	0	0.2

Lower explosion limit and limiting oxygen concentration

Since the scattering for the gas fraction is higher with the mixing method for hybrid mixtures than for gases alone a step-size of 1 mol% was chosen. All the stated values of gas fractions are calculated except for those where it was directly measured. Test series were performed with hydrogen and methane at different fractions and methane was additionally checked on the limiting oxygen concentration. The limiting oxygen concentration was determined along the stoichiometric line of methane and air with nitrogen. The step-size was on purpose varied by 1 mol% (in 10 mbar steps) but the calculated gas fractions are stated with one digit after the comma. The ignition energy and source were varied and the tests were conducted in quiescence and under turbulent conditions. The obtained values were compared to the literature value of methane of 10.7 mol%.

The ignition source and energy was also varied with two times 1 kJ chemical igniters and two exploding wires with 10 J, 100 J and 1000 J each (see table 3.2).

All fractions for gases, all concentrations for dusts and the combinations of gases with dust at which the tests did not exceed the ignition criterion were conducted at least three times for the LEL and LOC according to the European dust standards ([46], [47]).

Determination of the maximum explosion pressure and maximum rate of pressure rise of hybrid mixtures

Ignition tests involving three combustible dusts (corn starch, niacin and lycopodium) were carried out in the 20L-sphere based on the procedures of the EN 14034-series.

Additionally one inert dust, quartz sand, was checked with the same procedure to see, whether it is the combustion of the dust that causes a higher value of $(dp/dt)_{max}$ or not.

Two 1 kJ chemical igniters (Fa. Sobbe) were used as ignition source throughout all test series. At the concentrations with the highest values for (dp/dt) and around these concentrations the tests were repeated twice. The presented values for p_{max} were all corrected with the equations (2.1, 2.2) explained in 2.1.2.

The K_H-values (H is for hybrid) were calculated according to the cubic root relationship (see 2.3) in 2.1.2.

Niacin, lycopodium and corn starch were tested at the concentrations stated in table 3.4.

Table 3.4.: Tested combinations of methane and dust concentrations of niacin **N**, lycopodium **L** and corn starch **C**

	0	20	60	125	250	500	1000	1500	2000
$\mathbf{CH_4}$ *in mol%*	*in* $\frac{g}{m^3}$								
0	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**
1	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
2	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
3	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**
4	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
5	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
6	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
7	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
8	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
9	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**	**NLC**
10	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
12	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**
15	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**	**C**

The quartz sand was only tested around the stoichiometry of methane from 7 mol% to 11 mol% in steps of one percent and additionally at 9.5 mol% and low concentrations of dust at 0 $\frac{g}{m^3}$, 20 $\frac{g}{m^3}$, 40 $\frac{g}{m^3}$, 60 $\frac{g}{m^3}$ and 125 $\frac{g}{m^3}$.

Dust characterization

The 10^{th} percentile (d(0.1)), the median value (d(0.5)) and the 90^{th}th percentile (d(0.9)) are stated in table 3.5.

The corn starch had a stable moisture content between 6 weight% and 8 weight% (for details see Appendix D).

Table 3.5.: Particle size distribution of the three tested dusts

Dust	d(0.1)	d(0.5)	d(0.9)
	in μm	*in* μm	*in* μm
Corn Starch	9	13	21
Lycopodium	23	32	43
Niacin	4	17	54
Quartz sand	117	198	306

4. Results and Discussion

4.1. Comparative Study on standardized ignition sources

4.1.1. Results of the calorimetric measurements

Induction spark

Ten tests with ignition times of 10 x 200 ms, 10 x 500 ms and 10 x 1000 ms with an electronic induction spark device and an electrode distance of 6 mm showed a power of 11.9 W with a mean variance of 4.4 %. This matches the standard for the determination of the explosion limits of gases [42] as well as the standard for the determination of the maximum rate of pressure rise of gases [43] in which the power of this ignition source is specified with circa 10 W. In the standard gas explosion tests the burning duration is adjusted to 200 ms [42], 200 ms - 500 ms [43] or 200 – 400 ms [70] so the net energy released by the induction spark is between 2.2 J and 6.2 J (maximum deviation included). The energy can only be varied by the burning duration. A standard transformer (non-electronic, 30 mA short-circuit current and a peak-voltage of 15 kV) and one for standard tests from another testing laboratory were checked as well with similar results (see figure 4.1). Higher energies for dust explosions of at least a few hundred joules cannot be provided with the induction spark devices in a reasonable time span.

In practice, the mistake is often made of calculating the open-circuit voltage of the high-voltage transformer with the current intensity of the short-circuit current, which leads to an incorrect result ($\sim$ factor 45), since the internal resistance is neglected: In the standard for the determination of fire potential and oxidizing ability for the selection of cylinder valve outlets [69] the same transformer (15 kV, 30 mA) is specified with an energy of 10 J per spark, leading to an energy of 200 J to 240 J. Thus, in this standard, the energy specification is obviously an error (for a full overview see E.7).

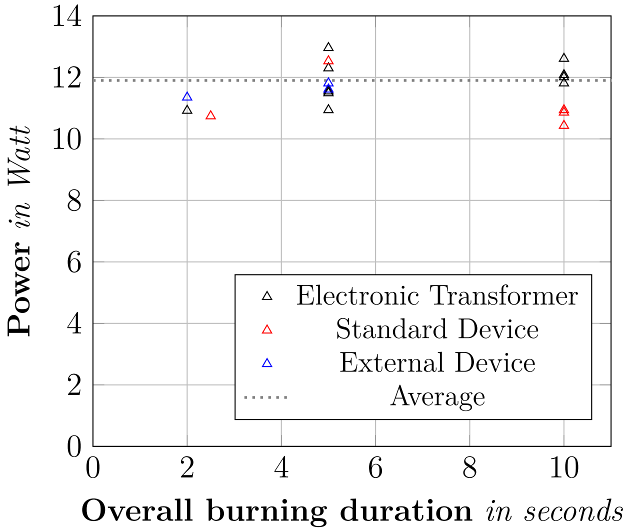

Figure 4.1.: Calorimetric measured power (energy divided by the overall burning duration) of three different induction sparks

Surface-gap Spark

Twenty-two tests with a surface-gap spark igniter were carried out. The energy was provided by capacitors with an operating voltage of 450 V and a capacitance of 220 μF. In the tests an average of the net ignition energy of 7.9 J with a maximum deviation of 4.5 % was measured. The efficiency in this set-up is 35 % related to the gross energy of 22.75 J. In order to obtain a better signal-to-noise ratio in calorimetry, several ignitions were performed in succession and the total energy was measured and then divided by the number of ignitions (see figure 4.2).

Another test with a capacitance of 600 μF and different loading voltages led to the results shown in the following diagram (see figure 4.3). The delivered energy increases while the efficiency was decreasing between 41 % and 29 % with higher voltages, which indicates that a simple calculation of the delivered energy using the stored net energy is imprecise without prior testing. Each test was performed twice.

The influence of the cable length was determined with two cables of the same cross section of 4 mm^2 and lengths of 3.2 m and 21.7 m. The inductance and capacitance of the longer cable was not measured, though it should be measured in future works. The efficiency decreased with the longer cable from 40 % on average to 32 % on average (maximum variation: 2 %, see figure 4.4). This may be caused by the higher resistance, the higher capacitance or the higher inductance of the cables.

The influence of the cable cross-section was not tested but should lead to a smaller resistance of the cable with increasing cross-section and thereby to a higher efficiency. The increase of the capacitance or inductance of the cables though not tested should lead to a lower efficiency. Another influencing factor is the number of the ignitions carried out with one pencil lead mainly consisting of graphite. In the first few ignitions the released energy is

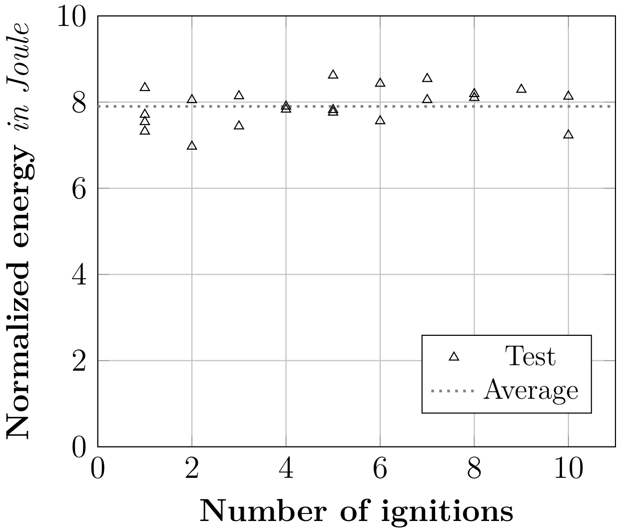

Figure 4.2.: Normalized energy (total energy/number of ignitions) as a function of the number of ignitions

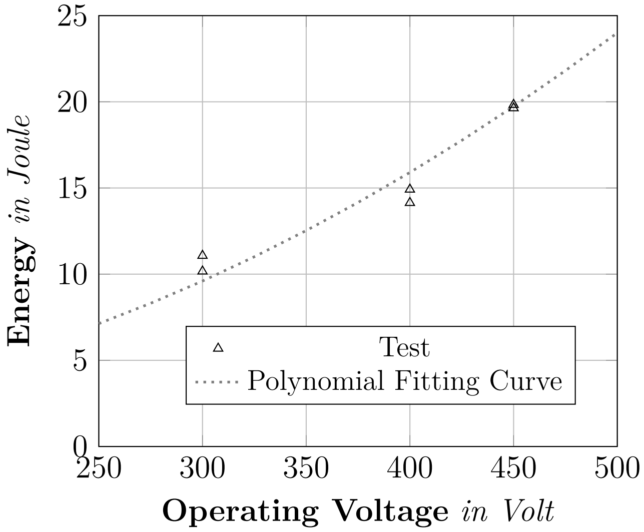

Figure 4.3.: Calorimetric measurements of a surface-gap spark with a capacitance of 600 μF, calorimetrically measured energy against operating voltage

decreasing from test to test, then after about 5 ignitions the released net energy is constant. This may be because of the lacquer or something else that is burned from the surface at the first ignitions. The resistance of the pencil lead was measured in an additional test showing the dropping resistance over the first three ignitions (see figure 4.5).

The surface-gap spark has many parameters influencing the energy and the efficiency. For every set-up, calorimetric tests should be made or the set-up conditions (cable length, cable cross- section, number of ignitions, resistance and length of pencil lead) should be described

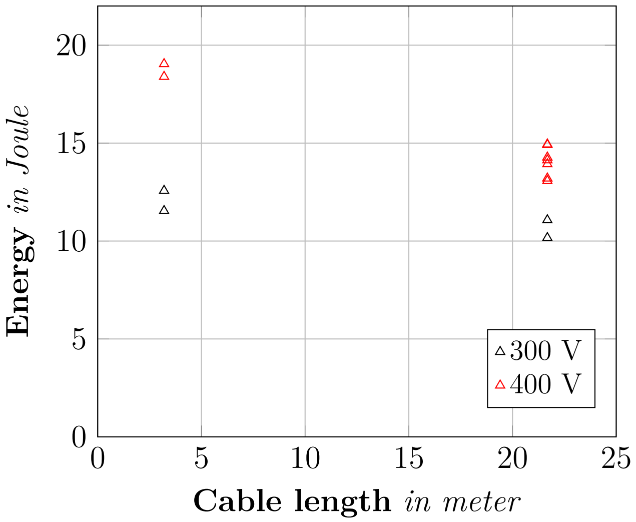

Figure 4.4.: Calorimetric measurements with a surface-gap spark with a capacitance of 600 μF at two different charging voltages and two different cable lengths

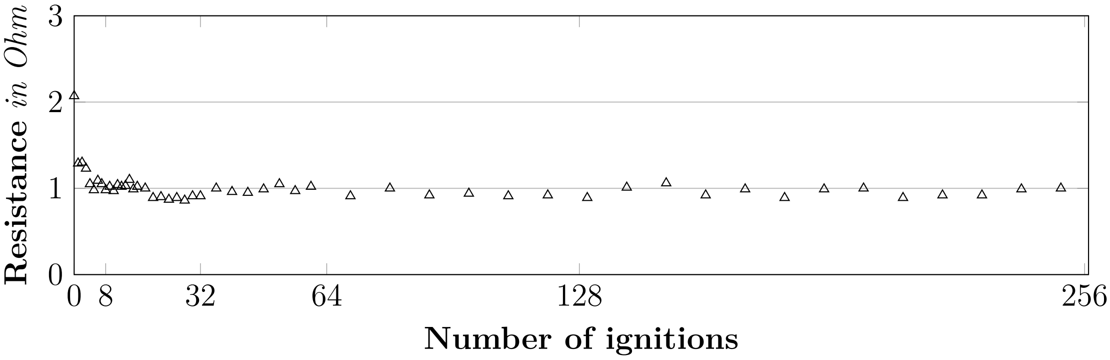

Figure 4.5.: Resistance of a 10 mm (length) * 2 mm (diameter) pencil lead against the number of ignitions

precisely to have a chance to determine the net energies in subsequent tests.

Chemical Igniters

Three tested chemical igniters with a specified energy of 1000 J had a calorimetric energy of 1090 J ± 24 J. For the igniters with smaller specified energies (three tests each) the difference between the the ignition energy stated by the manufacturer and the measured ignition energy was higher. The calorimetrically measured energies were 660 J ± 32 J instead of 500 J, 477 J ± 35 J instead of 250 J and 425 J ± 51 J instead of 100 J. The chemical igniters consist of an explosive mixture (40 weight% zirconium, 30 weight% barium nitrate and 30 weight% barium peroxide) and an electrical fuse head. It was assumed, that the weight of the explosive is adjusted by the manufacturer to produce igniters with different ignition

energies, and the energy of the electrical fuse head is disregarded. To prove this, chemical igniters of different specified energies were disassembled, and the explosive weight measured. Afterwards the ignition pills were ignited in the calorimeter without explosive.
The measured weights of the explosives are shown in table 4.1 and the calorimetric values are plotted in figure 4.6. The igniting pill with the explosive mixture removed was set equal to a specified ignition energy of 0 J in this graph, although the calorimetric measurements lead to values of 288 J ± 38 J, lying exactly around the extrapolated linear fit of the other tests.
Subsequent tests with a new batch of chemical igniters were performed one year later. The results are also displayed. The ignition pills were smaller in this second batch but the igniters still had an energy more than twice the value stated by the manufacturer.

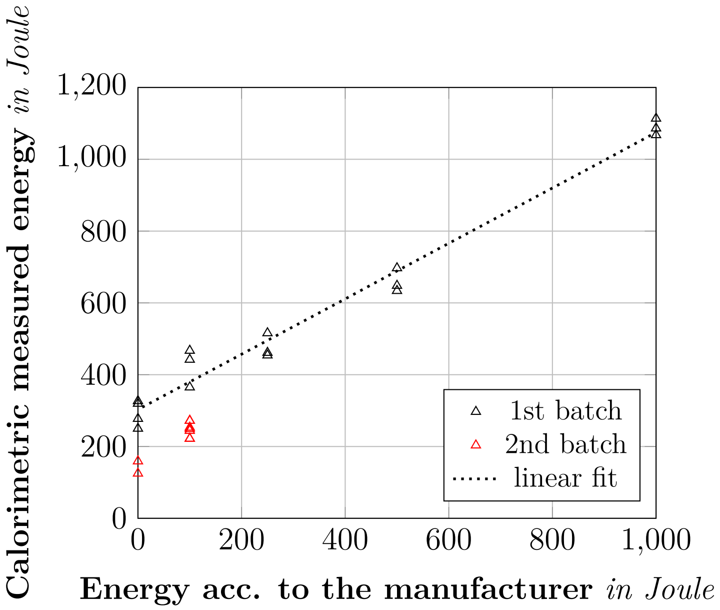

Figure 4.6.: Calorimetrically measured energy of chemical igniters against specified energy according to the manufacturer, three tests each except “0 J” (just the ignition pill, explosive removed) with four tests

Table 4.1.: Measured weights of the chemical igniters, with and without explosive and difference (mass of explosive without ignition pill)

Sample number	Specified energy *in J*	Gross weight filled *in g*	Gross weight empty *in g*	Difference - Mass of explosive mixture *in g*	Ratio of mass of the explosive mixture to the mass of the explosive mixture in the 1 kJ igniters -
1	1000	5,23	5,01	0,22	1
2	1000	5,28	5,05	0,23	1
3	1000	5,25	5,01	0,24	1
4	500	5,11	4,98	0,13	0.5
5	500	5,09	4,98	0,11	0.5
6	500	5,10	4,97	0,13	0.5
7	100	5,01	4,98	0,03	0.1
8	100	4,99	4,96	0,03	0.1
9	100	5,02	5,00	0,02	0.1

Exploding wire

The calorimetric tests with the exploding wire showed a low scattering and thus a good reproducibility. All the tests were carried out twice over a range from 6.6 J to 1 400 J varying the capacity and the loading voltage. The comparison between the calorimetric and the electrical measurements (voltage and current) showed that the ignition energy determined by calorimetric measurements was higher by 7% on average compared to the ignition energy determined by electric measurements (see figure 4.7). The exploding wire is the only ignition source allowing the determination of the ignition energy with two completely different methods.

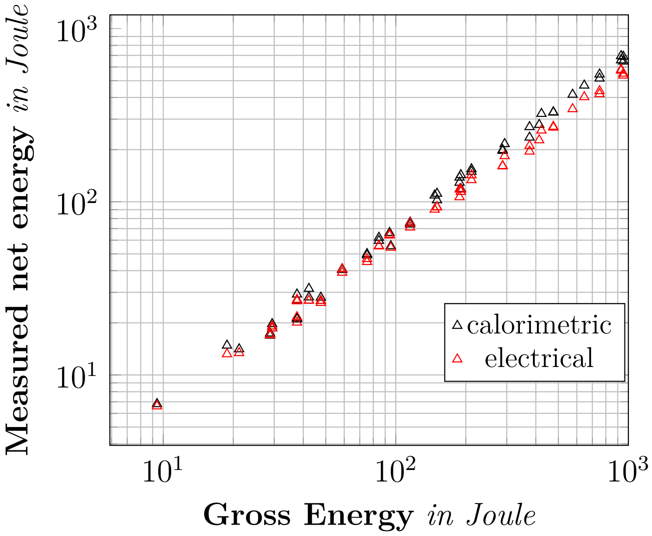

Figure 4.7.: Calorimetrically and electrically measured ignition energy against the gross energy of the loaded capacitors (double-logarithmic scale)

4.1.2. Determination of the burning duration

Induction spark

According to the standard, the burning time of the induction spark is set with a relay to 200 ms [42], between 200 ms and 400 ms [70] or 200 ms or 500 ms [43]. This makes it the only ignition source with a clearly defined and standardized burning duration. Also it is the one with the longest burning duration from the ignition sources studied in this work.

Surface-gap spark

To achieve an idea of the ignition procedure a camera with up to 1 000 000 fps was used. It turned out, that the whole burning duration is less than 170 μs long, with a core-time (where one can clearly see a light) of about 60 μs (see figure 4.8). In general the ignition duration for gases is shorter than for dusts ([136], [63]). A short burning duration would lead to the experimental determination of wrong safety characteristics for dusts .

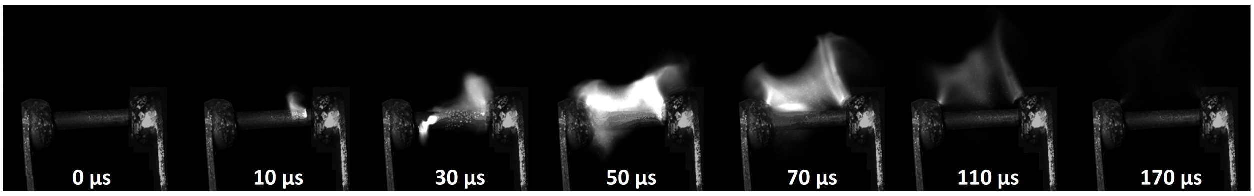

Figure 4.8.: Full ignition procedure of a surface-gap spark with a capacity of 220 μF and a loading voltage of 450 V, "main" burning duration of $\sim$ 60 μs

Chemical igniter

With chemical igniters, the determination of the burning time is more difficult, since individual particles sometimes continue to burn or glow for up to one second. Thus, when a 5kJ igniter was recorded, the fireball went out after 15-20 ms, individual particles still glowed after more than 300 ms after ignition (see figure 4.9).

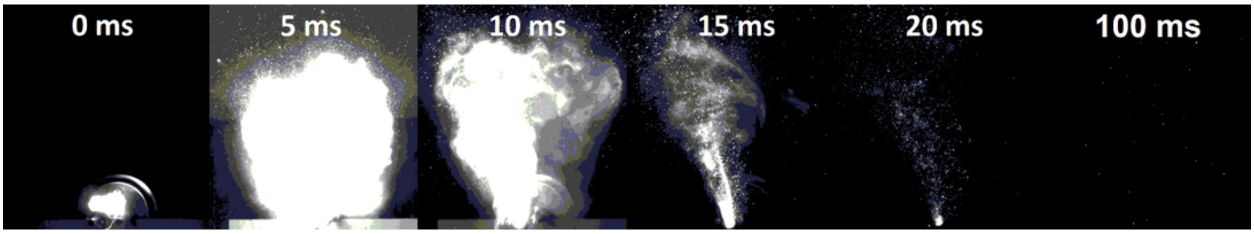

Figure 4.9.: Sequence of high-speed recordings of an ignition of a chemical igniter with a nominal ignition energy of 5 kJ, main burning time approx. 15 ms, single glowing particles visible from after 20 ms up to almost 350 ms after ignition

A total of eleven chemical igniters with stated energies from 100 J to 5 kJ were recorded. The values of the "main" burning duration (in which a clear flame is visible and not just sparks) range from 5 ms to 18 ms (see table E.1 in Appendix E.5).

Exploding wire

With the exploding wire, the burning time can be adjusted within a certain range, typical values are between 2 and 10 ms (see figure 4.10 and 4.13). The inductance and the capacitors of the exploding wire igniter are selected in a way, that the burning duration is with 8 ms to 12 ms comparable to the chemical igniters.

4.1.3. Influence of the angle between the electrodes of the exploding wire

Figure 4.10 is a series of images from high-speed recordings of ignitions with different angles of the electrodes. One can clearly see the well-controlled ignition with adjacent (180 °) electrodes with the lightning arc staying between the electrodes and lightning arcs pushed away from the electrodes if the angle is smaller.

This is especially visible, if the measured voltage is plotted against time for the ignition process of different angles (see figure 4.11).

This leads to a higher variation of the net energy with increasing angles (see figure 4.12).

The scattering of the ignition energy changes clearly with different angles. With parallel electrodes a mean variation of 11.2 % (max. 30.1 %) while with orthogonal electrodes a mean variation of 7.0 % (max. 28.8 %) and with adjacent electrodes a mean variation of 5.4 % (max. 23.1 %) was determined.

The above described correlation between increasing angle and decreasing variation does not

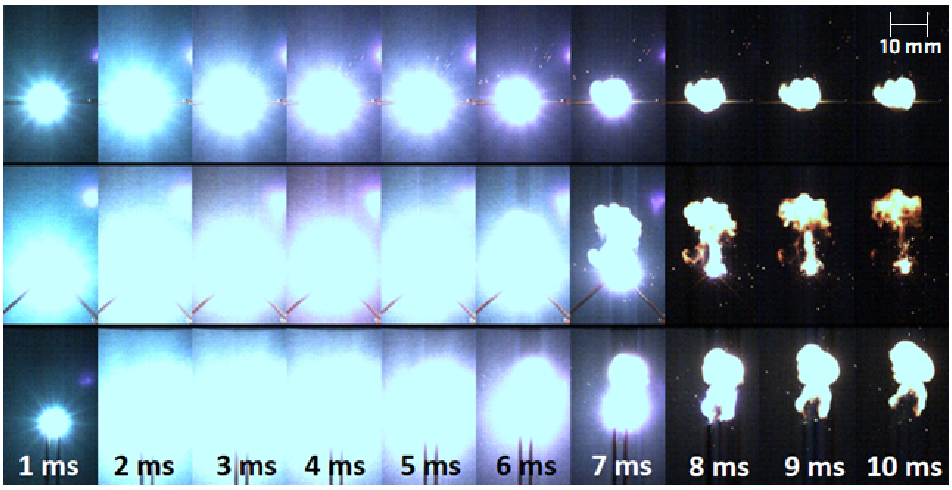

Figure 4.10.: Three different ignition procedures of the exploding wire with different electrode angles; 180° (adjacent) with 20.5 J in top row, 90° in the middle with 26.5 J and 0° (parallel) in the bottom row with 29.5 J

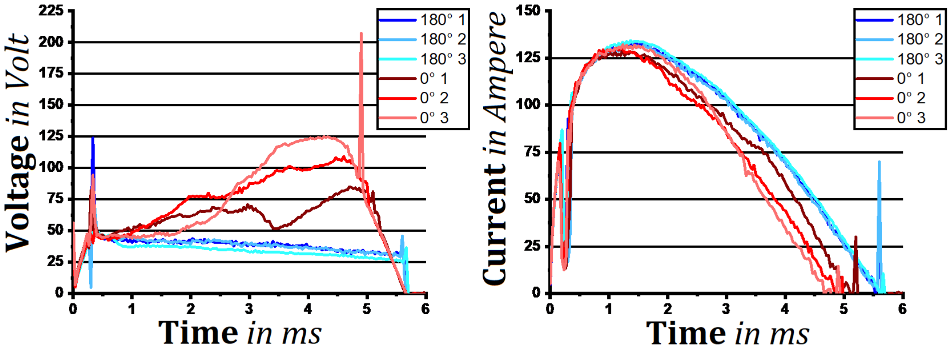

Figure 4.11.: Measured voltage and current against time from the exploding wire at angles of 180° (adjacent) and 0° (parallel)

apply for higher energies above ∼ 100 J. Parallel electrodes show a comparable mean variation of 3.0 % (max. 12.1 %) to orthogonal electrodes of 3.2 % (max. 13.9 %) and adjacent electrodes of 2.6 % (max. 11.5 %).

The reason for this may be that at high ignition energies the lightning arc is not staying between the electrodes with adjacent electrodes as it was observed for lower ignition energies and is pushed besides due to thermal and electromagnetic effects (see sequence in figure 4.13).

This causes a higher turbulence and therefore a higher scattering, comparable to the scattering of parallel electrodes. It was also observed, that parallel electrodes show higher net energies with otherwise identical set-ups of the ignition system, especially with higher energies (see figure 4.14).

The energy, that is needed to melt the wires of 4 mm to 8 mm of length, is with less than

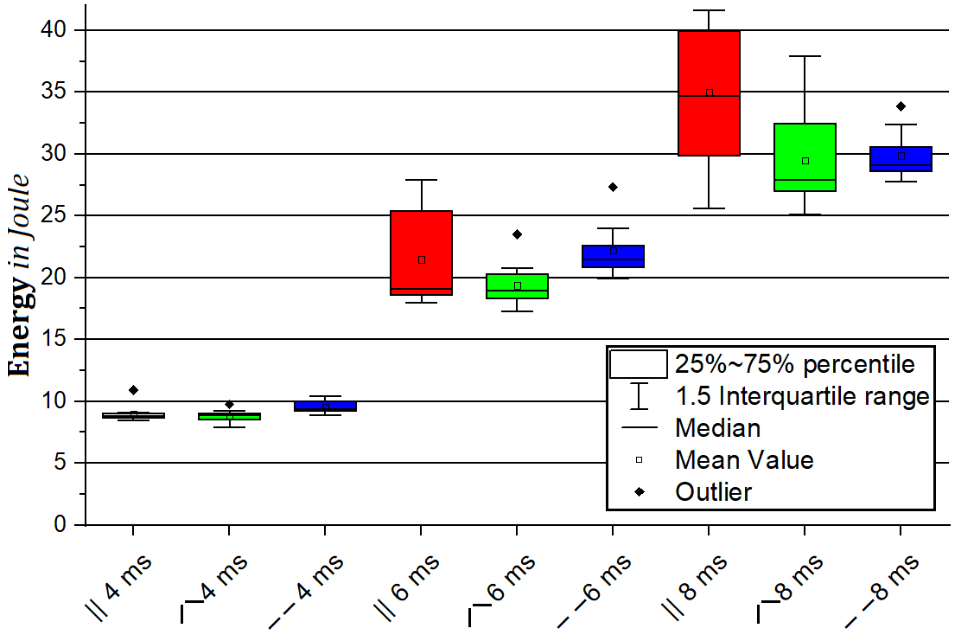

Figure 4.12.: Electrically measured ignition energy against ignition time and angle of the electrodes, ten tests were carried out for each set-up, || for parallel, |- for 90° and – – for adjacent electrodes

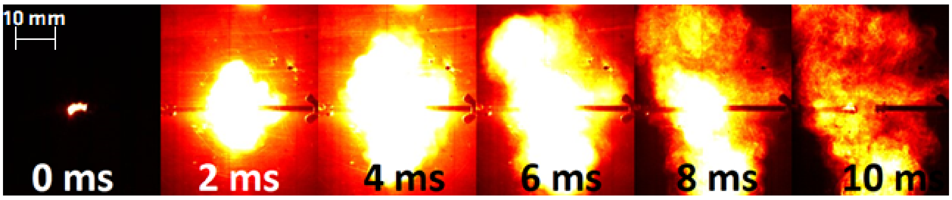

Figure 4.13.: Sequence of high speed recordings of the ignition with an exploding wire with 820 J and an electrode angle of 180° (adjacent)

0.5 J neglectable (see Appendix E.2).

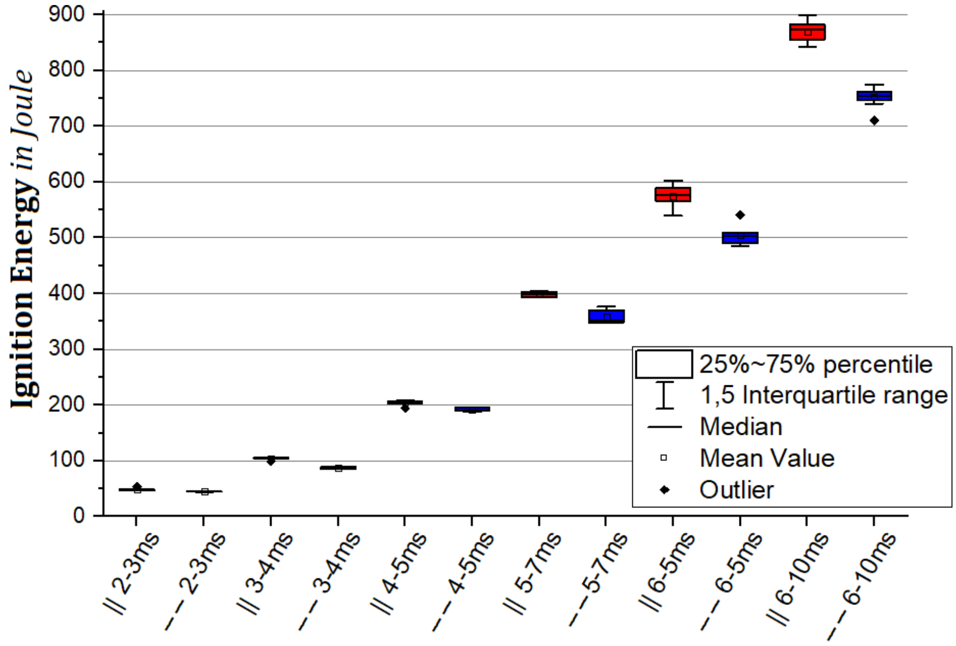

Figure 4.14.: Electrically measured ignition energy against angle of the electrodes, capacitance value (2 ≡ 940 μF, 3 ≡ 1880 μF, 4 ≡ 4700 μF, 5 ≡ 9400 μF, 6 ≡ 20 680 μF) and ignition time, unvaried loading voltage of 450 V, || for parallel and – – for adjacent electrodes

4.1.4. Determination of the burning volume of standardized ignition sources

Different types of phenomena were visible with the schlieren-technique. For the chemical igniters and the exploding wire the visible burning volume (flame) was not smaller than the heated volume, that was observed with the schlieren-imaging, in the first 10 milliseconds in which most of the energy is released. This is caused by the short burning duration and, with that, no convection can take place. In figure 4.15 it is displayed, when the exploding wire shows the first sign of ignition, after 5 ms, 10 ms, 15 ms and 50 ms.

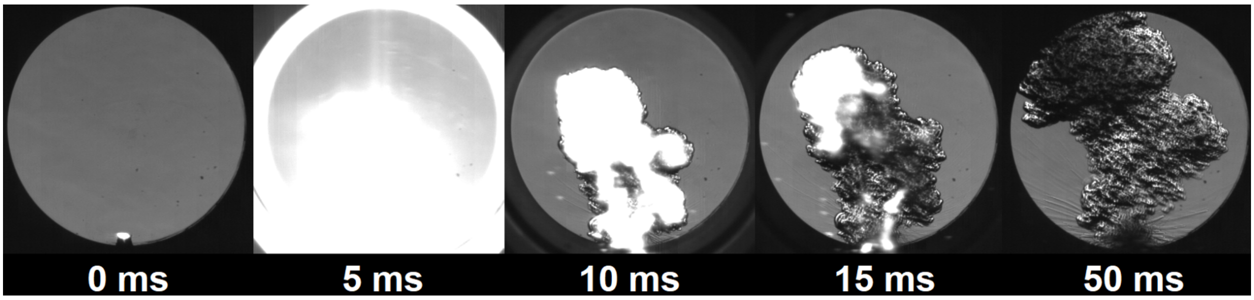

Figure 4.15.: Exploding Wire filmed with the Schlieren-Setup, 1kJ of net energy (2,2 kJ electrical (gross) energy)

In figure 4.16 it is displayed, when the chemical igniters show a first flame, when the shockwave front reaches the half diameter of the sphere, flame reaches half of the diameter of the sphere (normally it is placed in the middle), the full diameter and after 50 ms when the last sparks end to glow for one 1 kJ igniters and one 5 kJ igniter. One should keep in mind, that two ignition sources are used for the determination of safety characteristics.

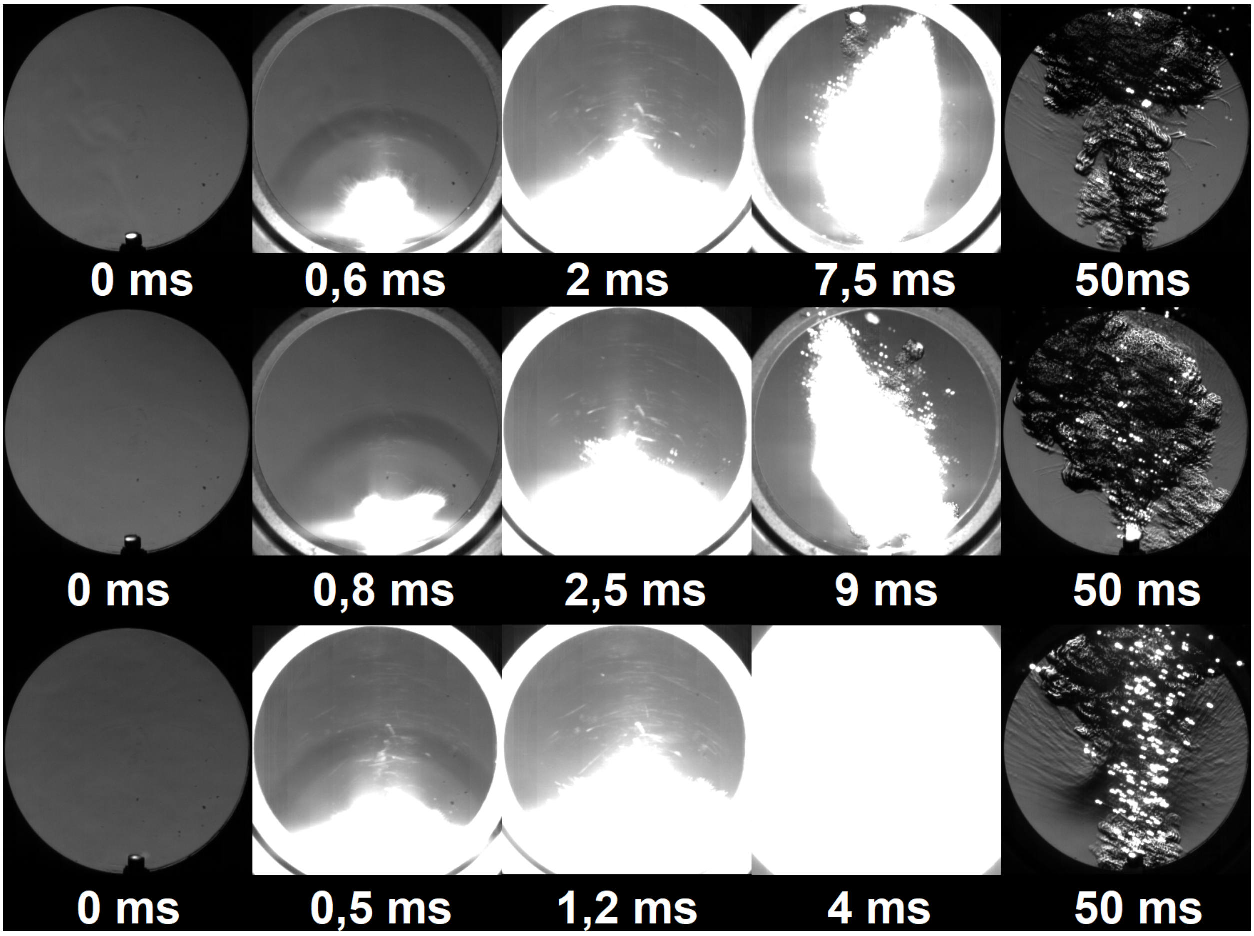

Figure 4.16.: Chemical Igniters filmed with the Schlieren-Setup, 1kJ (upper and middle row) and 5kJ (bottom row)

With that, the schlieren-images of the exploding wire and the chemical igniters were quite similar in volume and behaviour: During the first 10 ms no surrounding heated atmosphere was observed around the visible flame.
For the induction spark convection of the air in between the two electrodes was observed (see figure 4.17), that means the ignition energy does not stay in place but gets shifted away within 0,2 s and especially within 0,5 s. This is especially astonishing since in the European standard about the determination of maximum explosion pressure and the maximum rate of pressure rise of gases and vapors it is allowed to increase the burning duration from 0,2 s to 0,5 s, if the mixture is not ignitable [43]. If the energy is carried away because of convection from the electrodes, increasing the burning duration is increasing the number of sparks from

20 to 50 single sparks all having the same effect on the substance. A reason, why increasing the number of sparks donated to the mixture made a difference in the past may be an artifact of the gear used: Testing the induction spark of another laboratory it was observed, that the relay closing the circuit had an unwanted delay-time of about 30 ms when closing but none when opening. Some older gear might be even worse, so shifting the closing time of the relay from 0,2 s to 0,5 s might have resulted in an increase of the burning duration from some Milliseconds to at least over 0,3 s respectively from a few sparks to at least over 30, what leads to a real difference in probability of igniting the mixture.

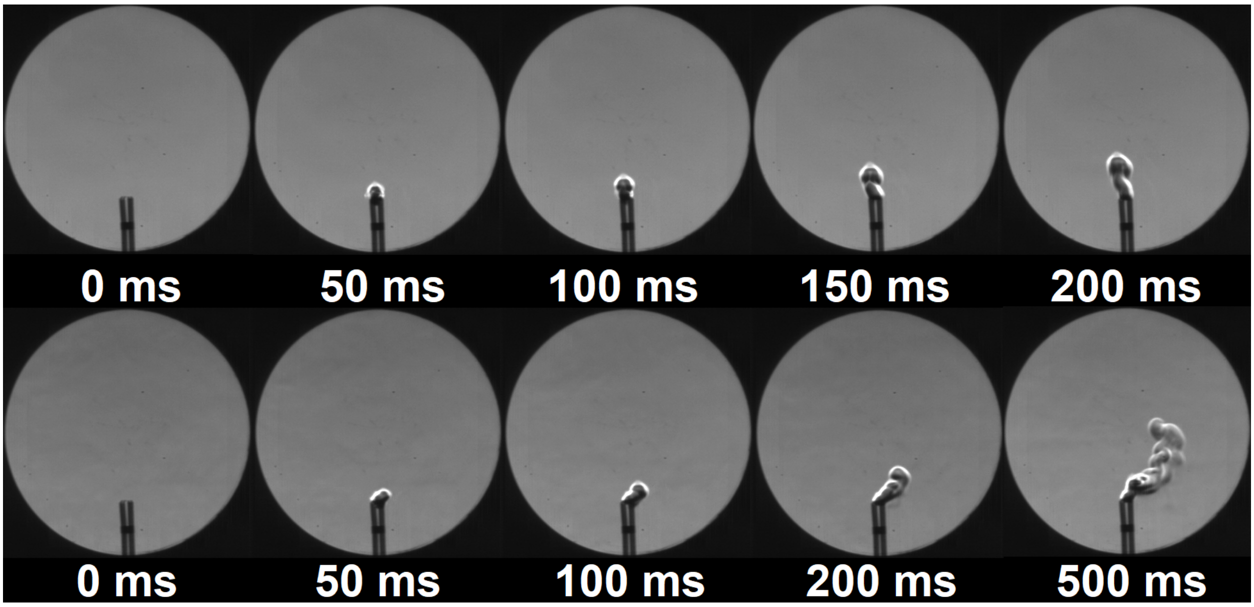

Figure 4.17.: Induction spark filmed with the schlieren-setup, 0,2 s (200 ms) of ignition duration (top) and 0,5 s (500 ms) ignition duration (bottom)

The schlieren images of the surface-gap spark showed a shockwave and an igniting volume about the same size as that produced by the induction spark (see Figure 4.18, filmed under quiescent conditions). Both, the shockwave pushing the dust away and the comparably small igniting volume may be the reason, why the surface-gap spark is considered unsuitable and is not used for dusts.

It shall be mentioned that for the ignition sources the heat, that was visible with the schlieren technique did not exceed the visible light except for the induction spark.
The height and width of the visible difference from the background was measured and with that the volume was approximated as a cylinder. The stated values in Table 4.2 for the ignition sources were determined at the following times:

- For the induction spark the volume was determined after 200 ms and after 500 ms since no extra energy is introduced into the system afterwards.
- For the exploding wire the volume after 10 ms was determined for the same reason.

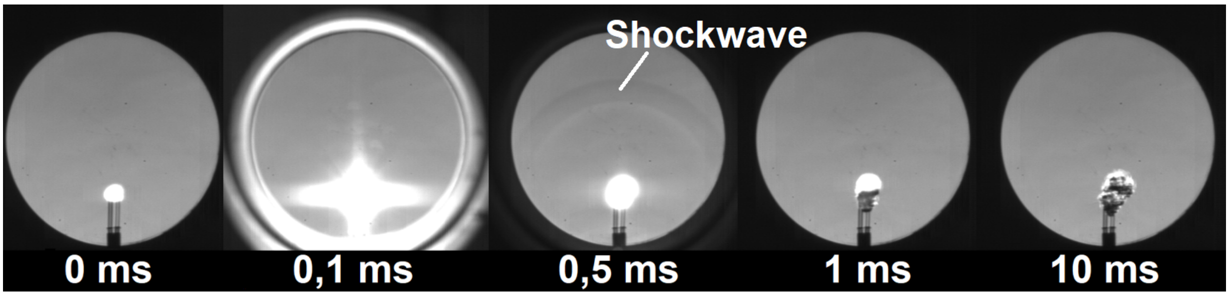

Figure 4.18.: Surface-gap spark filmed with the schlieren-setup, 7.9 J of net energy (22.3 J electrical (gross) energy)

- To compare the results (the focus was the comparison between exploding wires and chemical igniters), the volume of the chemical igniters was also taken after 10 ms even though the combustion of the firing charge might not have ended at this time.
- For the surface-gap spark the volume was determined after 1 ms since the visible light decreased afterwards.

This comparison also showed, that because of the turbulent conditions, that are normally present in dust testing conditions and the fast decay of this turbulence the induction spark and the surface-gap spark are not suitable, the first because it is burning too long, the latter because it is burning too fast. One should keep in mind, that the distance from the center of the 20L-sphere to the wall is 17 cm and the diameter of the mirror is 33,5 cm, so the full images resemble a 2D-impression of the whole sphere.

Table 4.2.: The initial ignition volume of the four investigated ignition sources (n.i.: not investigated)

	Chemical Igniter	Exploding Wire	Induction Spark	Surface-gap Spark
Burning duration Defined / Adjustable	No / No	No / Yes	Yes / Yes	No / No
Igniting volume (l)	8.56 (1 x 1 kJ) 6.74 (1 x 1 kJ) ~20 (1 x 5 kJ) ~17.8(1 x 5 kJ)	0.057 (15 J) 4.6 (1 kJ)	0.063 (200 ms)	0.088
Power (W)	n.i.	known	known	n.i.

The pictures from which the volumes in table 4.2 are determined are displayed in figure 4.19. For the chemical igniter with 5 kJ just one picture is shown since the other one was overexposed at 10 ms. In figure 4.19 a) and b) the different behavior of the chemical igniters can be observed since both were filmed under the same conditions.

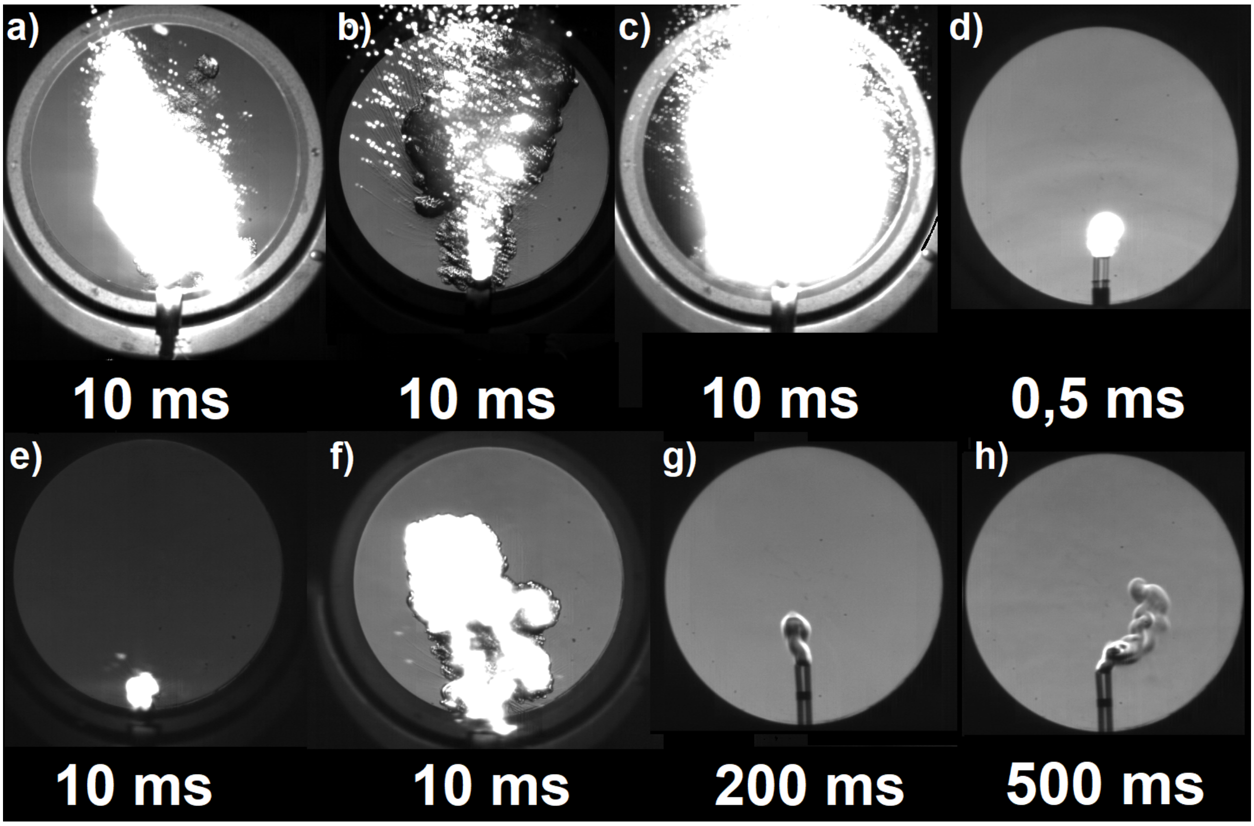

Figure 4.19.: All ignition sources filmed with the Schlieren-Setup; a) chemical igniter 1 kJ, b)chemical igniter 1 kJ, c) chemical igniter 5 kJ, d) surface-gap spark 7.9 J, e) exploding wire 15 J, f) exploding wire 1 kJ, g) induction spark 2 J, h) induction spark 5 J

4.2. Influence of the mixing procedure on the test results

4.2.1. Leakage-rate

The pressure rise with which the leakage-rate of the 20L-sphere used in this work was determined is presented in figure 4.20. With a typical time for mixture preparation of about three minutes, the influence of the leakage-rate that was measured in the sphere on the accuracy of the gas mixtures can be neglected. After three minutes the detected pressure rise was 0.3 mbar leading to an error of the gas fraction of 0.03 mol%.

Considering the great effort to achieve low leakage-rates in the 20L-sphere that was designed for dust-testing, the maximum permissible value of 1 mbar per minute was chosen for the standard operating procedure and the round robin test contributing to the overall uncertainty of the mixture composition by 0.5 mol%. If the tests are always conducted in the same way and in a comparable time this deviation is systematic and can therefore be adjusted.

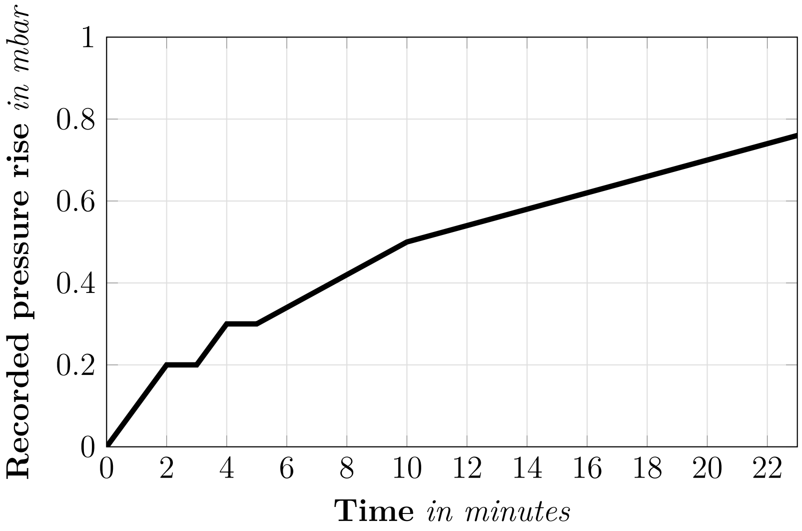

Figure 4.20.: Measured pressure inside the 20L-sphere, initial pressure set to 0. The division of the leakage by the time is the leakage-rate.

4.2.2. Influence of pre-ignition pressure rise (PIPR) and post-injection pressure drop

Influence of the PIPR on the explosion overpressure

In figure 4.21 the explosion overpressure measured for 500 g/m^3 corn starch is presented against the intentionally varied PIPR. The allowed ranges according to the European standards of ± 100 mbar ([45], [59], [46], [47]), the American standards of ± 60 mbar [57] and the manufacturer's software of -50 mbar to +100 mbar are also displayed.

The maximum explosion overpressure for the cornstarch sample was measured at 750 g/m^3 before, so it can be assumed that the oxygen was available in excess in each test. Thus, the result was not influenced by the stoichiometric ratio, an effect that could be observed on the oxygen-lean side at higher amounts of corn starch. All tests were performed with 2 kJ ignition energy. Chemical igniters and exploding wires were used but no difference was observed so they are presented with the same symbols.

One can clearly see the increasing explosion overpressure with increasing PIPR, which is mainly due to the higher initial pressure at the moment of ignition in the 20L-sphere. Increasing the PIPR within the permitted range according to the European standards from 0.5 bar to 0.7 bar, the measured average p_{Ex} will increase from 6.5 bar g to 8.5 bar g which is an increase of 30%. A similar tendency though tested in wider steps is stated as well in the literature [100]. To correct this very obvious error caused by different PIPRs and leading to different initial pressures at the moment of ignition, a normalized explosion pressure can be used according to equation 4.1, derived from the standards for the maximum explosion pressure of gases [43]. Pressures in the standards for gases are always stated as absolute pressures [43], in the ones for dusts as overpressures ([45], [59], [46], [47], [57]). Therefore the original equation used in the standard for gases using absolute pressures was adapted for dusts with the following equation.

$$p_{corr} = \frac{p_{ex} + p_0}{p_0}[bar] - p_0 \tag{4.1}$$

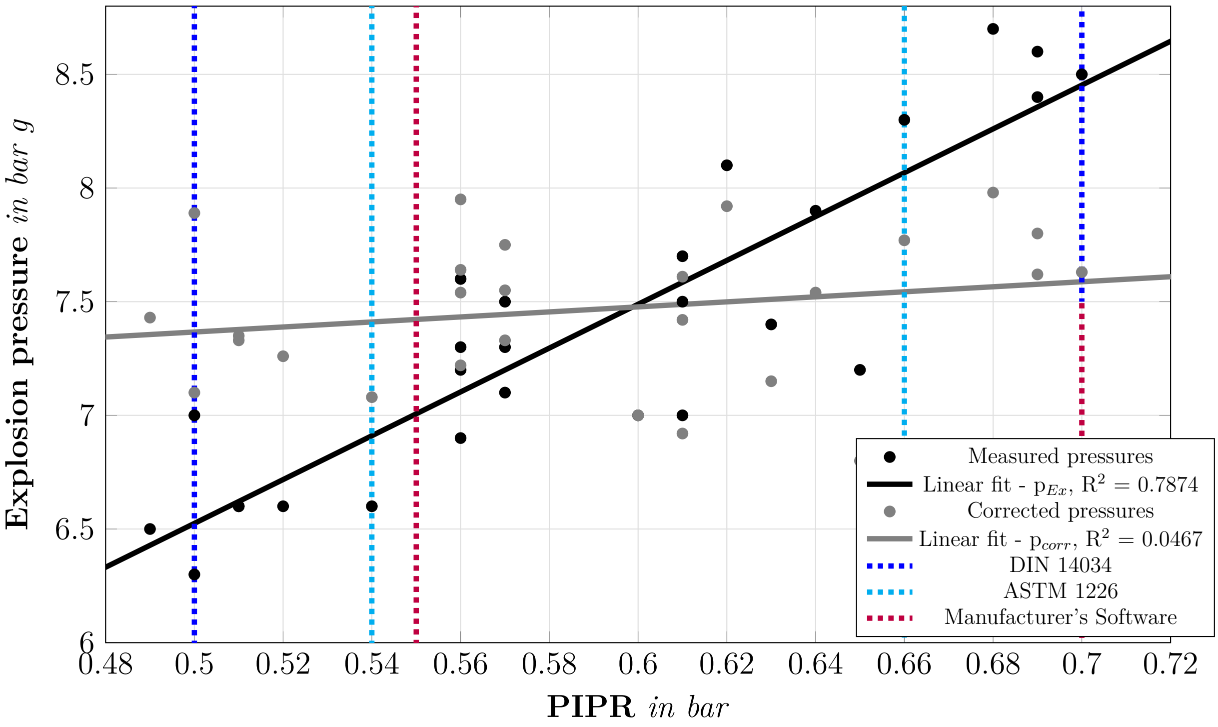

Figure 4.21.: Explosion overpressure of 500 g/m^3 cornstarch and calculated values of the normalized overpressures according to equation 4.1 as a function of the PIPR with allowed ranges according to different standards

With this correction, the maximum variation from the mean value of p_{Ex} decreases from ±18 % to ±8 % for PIPRs between 0.5 bar and 0.7 bar. Considering the corrected values of the explosion pressures, the uncertainty of only ±0.1 bar within the range of variation of the PIPR can be considered as insignificant. So, it can be concluded that p_{Ex} is only negligibly influenced by the PIPR, with a pressure average increase of only 3 % if the effect caused by different initial pressures is compensated. The allowed range of the PIPR should still be narrowed in future standards since the amount of oxygen changes as well and the different PIPRs also influence the (dp/dt)-values even though this is less obvious because of the higher scattering (see figure 4.22).

If hybrid mixtures are tested, variations of the PIPR additionally have a strong influence on the accuracy of the gas mixture, if the mixing is conducted by Method II or III (according to figure 2.10), what is usually the case. Therefore the allowed variations should be narrowed and the PIPR should be stated with all test results. Leaving the range for the PIPR at

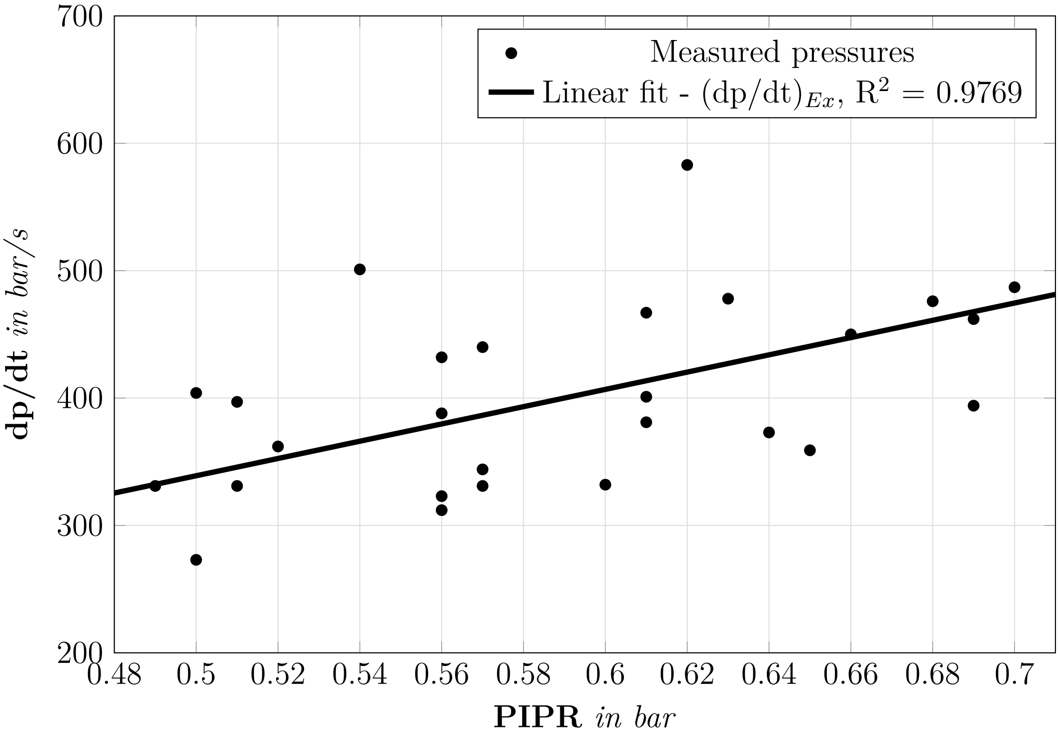

Figure 4.22.: Influence of the PIPR on the (dp/dt)-value of 500 g/m^3 corn starch

±100 mbar would lead to a wrongly calculated gas fraction of ±10 % rel.
With a dust container of 5.6 liters pressurized with 20 bar g, the PIPR in the 1 m^3 chamber with one pressurized dust container was with 115 mbar lower than the PIPRs in the 20L-sphere [80].
For tests with higher dust amounts two dust containers can be used in the standard 1 m^3 chamber so theoretically the PIPR may be around 200 mbar. For the reported values of p_{max} this means, the explosion pressures may be 10 % to 20 % higher than if they were measured under ambient pressure. In future standards, especially for hybrid mixtures, this should be taken into account and investigated further, since usually the tests are conducted with initial pressures of 1.1 bara or 1.2 bara in the 1 m^3 [60]. Only few test facilities conduct the tests in the 1 m^3 with initial pressures of 1 bara because it is not in accordance with the standards for tests in the 1 m^3 ([92], [137]).

Influence of the post-injection pressure drop

In figure 4.23 the pressure development in the 20L-sphere during and after injection of air is shown without the activation of the ignition source. The pressure increases directly up to the peak pressure. Afterwards the pressure decreases slightly and slowly because of dissipation of the heat that was induced previously by the fast compression. The end pressure after equilibration was measured after at least 180 s, even though after about 14 to 30 s the value did not change anymore.

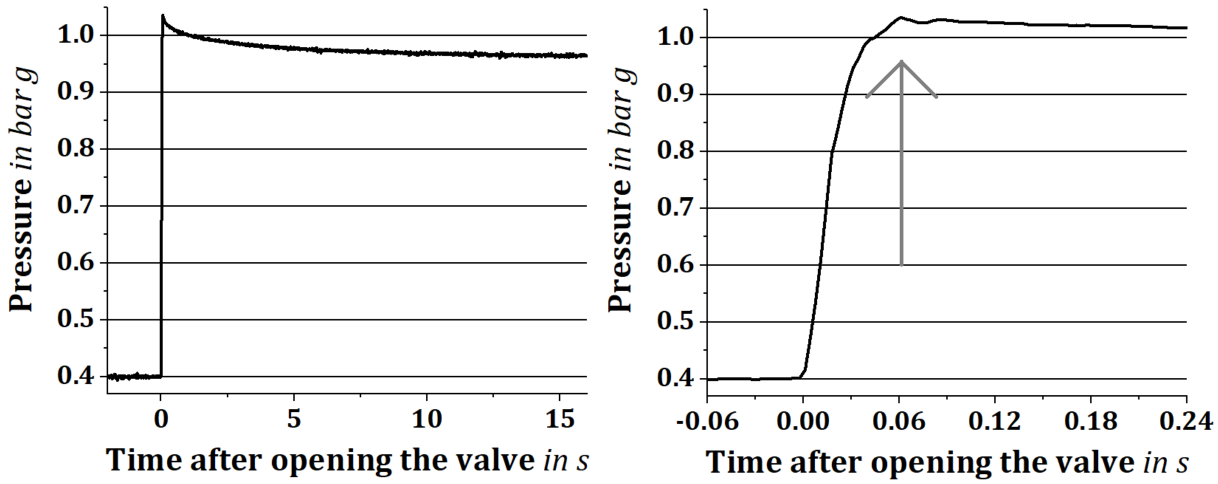

Figure 4.23.: Recorded pressure against time after opening the fast-acting valve without igniter and without dust (no explosion), close-up on the right side

Normally the ignition takes place at the peak pressure of the injection process. Due to the explosion this pressure after equilibration can not be recorded in regular tests (see figure 4.23).
The post-injection pressure drop is dependent on the PIPR and is slightly higher with higher initial pressures, even though this effect is less obvious (see figure 4.24).

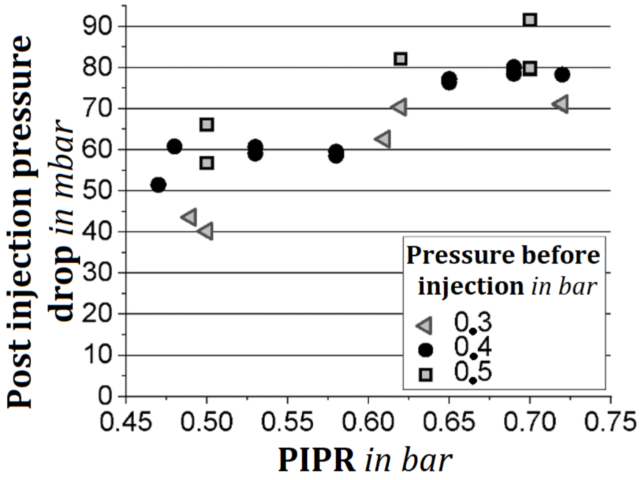

Figure 4.24.: Post-injection pressure drop against PIPR (acc. to the software) with 3 different initial pressures

With a constant pressure of 400 mbara before injection and a PIPR of 0.64 bar (acc. to the software) an average pressure drop of 80 mbar ± 10 mbar was measured. If this is neglected in the calculation it leads to an error of about 8% rel. for the calculation of the gas fraction. Calculating the fraction of flammable gas by partial pressures considering the post-injection pressure drop, the remaining variation of the final pressure (within ± 10 mbar) causes a

variation for the calculation of the gas component of about 1 % rel. For a methane fraction of 10 mol% this would be a mistake of 0.1 mol% and with that very small.
For determining the safety characteristics of hybrid mixtures greater variations in the concentration of the flammable gas have an influence on the test result, so it is necessary to reduce this variation to an acceptable level with the described techniques.

Estimation of the temperature rise due to compression

The initial temperature at the ignition moment can be estimated by the ideal gas law assuming homogeneous mixtures:

$$p * V = n * R * T \tag{4.2}$$

Because the number of moles of substance (n), the gas constant (R) and the volume (V) do not change after closing the fast-acting valve the equation can be converted into

$$T_2 = T_1 * \frac{p_2}{p_1} \tag{4.3}$$

Assuming that the pressure at the moment of ignition is p2 = 1.013 bara = 1013 mbar a and due to the PIPD of 80 mbar, the pressure after equilibrium is p1 = 933 mbara at a temperature after equilibrium of T1 = 293.15 K (water jacket temperature is set to 20° C), the temperature at the moment of ignition is determined at T2 = 318.3 K or 45.1° C. This temperature increase of 25 K is comparable to the results of Poletaev who measured a temperature increase of 14 K and estimated, because of the intertia of the thermocouple, that the real temperature increase is about 30 K [104]. Cashdollar [105] used different dimensions and volumina for the test vessel, the dust container and different beginning and injection pressures. So the values of his work can not be compared to this work.
The temperature increase should be considered because it could lead to an error in the determination of the safety characteristics. While most of the dusts react faster under higher temperatures others (for example the often-used niacin) are harder to ignite [138].
It shall be considered to use the equation 4.4 from EN 15967 [43] for conditions other than the standard (for gases this is 25 ° C and 1 bara) which leads to higher explosion pressures ([100], [101]).

$$p_{max}(T, p) = \frac{p_{max}(T_1, p_1) * T_1 * p}{T * p_1} \tag{4.4}$$

For all further tests the 0.64 bar ± 0.01 bar as PIPR were chosen, because with a pressure drop of 80 mbar it is the best compromise between being close to 1 bara at ignition and not too far away for the calculations and from comparison with literature values for dusts.

4.2.3. Verification of the gas amount

Several test series were carried out to compare the gas compositions determined according to the partial pressure method considering PIPR and PIPD with directly measured gas compositions using gas analysis. For safety reasons CO_2 was used as test gas instead of a fuel gas.

Figure 4.25 illustrates the deviations of the measured partial pressure fractions from the mole fractions measured directly with the gas analyzer. The CO_2-fractions determined from the partial pressures were always slightly higher than the directly measured fractions, no matter if the gas mixtures were prepared in a separate vessel or directly in the 20L-sphere. This may be caused by residual air in the connecting tubes or a systematic error by the linearity of the pressure sensor. When the mixtures were prepared in a separate mixing vessel (Method I), a mean deviation of 0.24 mol% was determined that was subsequently substracted from the test gas fractions determined from to the partial pressuress resulting in a scattering of ± 0.11 mol% (see figure 4.25). When the gas mixtures were prepared directly in the 20L-sphere (Method II) the fraction of the added gas measured with the gas analyzer was also lower than the fraction calculated from the partial pressures. The scattering was higher than the scattering obtained for the mixtures prepared in the separate mixing vessel (see figure 4.25). The mean deviation was subtracted from the calculated partial pressure fractions in the following tests as well. This results in a decreasing scattering of maximum ± 0.15 mol%, so still comparable to the the scattering of the other method.

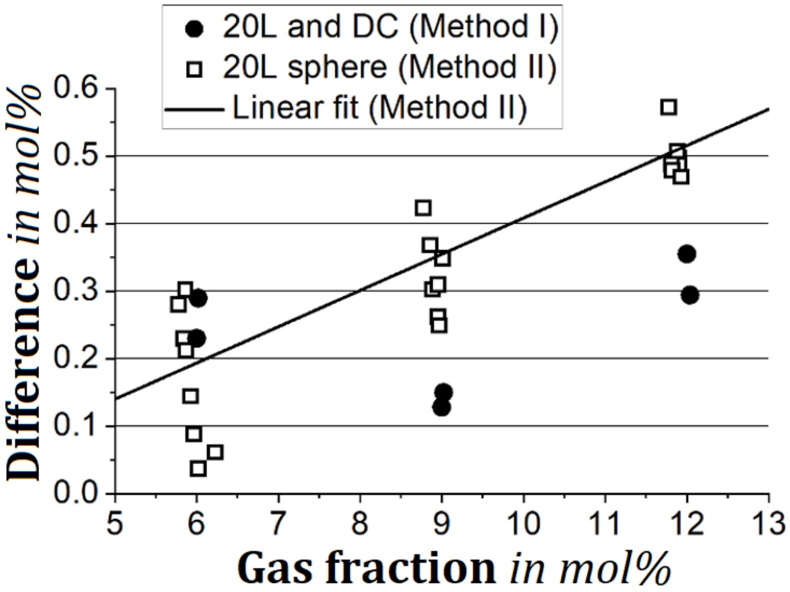

Figure 4.25.: Difference between the calculated fraction after correction considering systematic deviations and the directly measured fraction of gas against the calculated fraction

Subsequently, the test gas fractions were calculated according to following equation, if the mixtures were prepared directly in the 20L-sphere (Method II):

$$c_{Gas} = p_{Gas}/(PV + PIPR - PIPD) - Deviation_{Average} \tag{4.5}$$

with p_{Gas} [bar] being the partial pressure of the flammable gas, PV the ***P****artial* ***V****acuum before injection of the dust (0.400 bara ± 0.002 bar) and a* ***p****re-****i****gnition* ***p****ressure* ***r****ise (PIPR) of 0.64 bar ± 0.01 bar*

If the mixtures were prepared in a separate vessel (Method I) the average systematic deviation of 0.24 mol% was always substracted from the calculated test gas fractions subsequently. For Method II the values were fraction dependent and therefore different values of 0.2 mol%, 0.35 mol% and 0.5 mol% were subtracted (see figure 4.25)[1].
Considering a standardized test procedure, pre-test with a gas analysis should be mandatory for testing hybrid mixtures since the accuracy of the gas mixture seems to be an important source of error.

4.2.4. Influence of the mixing method on the safety characteristics

The explosion characteristics p_{ex} and K_G-value were measured preparing the gas mixtures with two different mixing methods (Method I and Method II, see section 3.2.1) and with two standard chemical igniters with 1 kJ each. The values for p_{ex} are comparable with the two mixing procedures. The average of the explosion overpressure values at methane concentrations with the highest values is only slightly higher for the mixing procedure according to Method II (with 7.4 barg ± 0.2 bar scattering), compared to the other mixing procedure (7.3 barg ± 0.2 bar scattering). This difference is not significant according to EN 15967 [43] which states 10 % as deviation being inside the allowed range for verification of the test apparatus. When the data is compared to the explosion pressures measured according to EN 15967 at quiescent conditions from a reference database [40] the values from the 20L-sphere in this work are slightly higher close to the stoichiometry (see figure 4.26). The difference increases at the methane lean side. This is presumably caused by the turbulence, that lowers the heat losses on the walls of the test vessels due to a faster combustion and is and with that increases the determined values for p_{Ex}, especially for non-stoichiometric mixtures ([111], [139], [110]).

The average K-values are also comparable for both mixing methods as shown in figure 4.27, but the variation is higher when the mixtures are prepared according to Method II. A comparison with the reference database is not possible, because gases are usually tested under quiescent conditions and in contrast to p_{ex} the K-values are highly affected by turbulence. The literature values for the three tested fractions are 10 bar/s, 240 bar/s and 140 bar/s and thus lower by a factor of 40, 6 and 6 compared to the values presented.
The highest K-value for the mixing procedure with separate mixing vessel (Method I) is

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[1] It shall also be mentioned, that other facilities had deviations of more than 2 mol%, which led to the determination of false safety characteristics

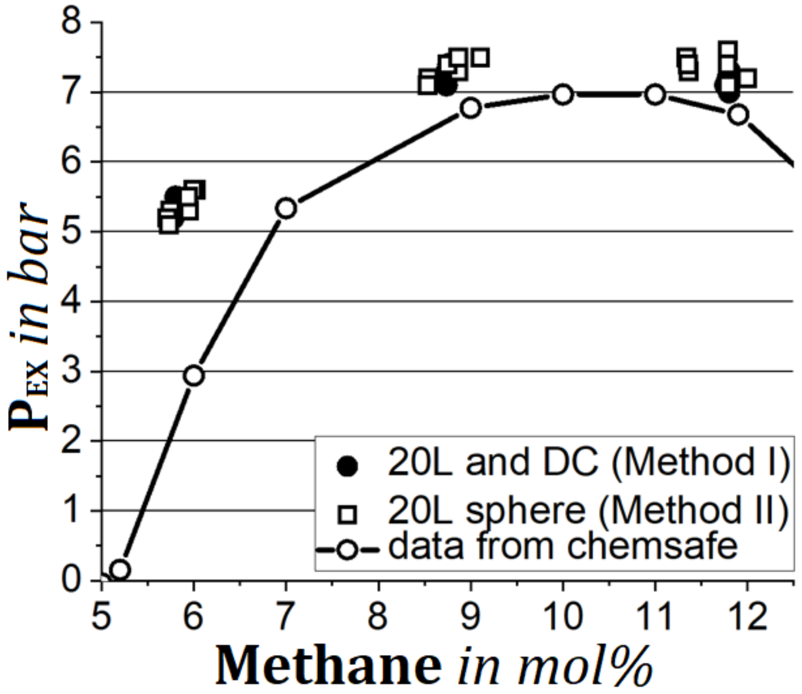

Figure 4.26.: Explosion overpressure of methane; two different mixing procedures mixing of the gases directly in the 20L-sphere and with pre-mixtures filled in the 20L-sphere and in the dust container (DC) and data from reference database [40]

381 bar/s (± 9 %) and thus slightly lower, than for the other mixing procedure (Method II) with 390 bar/s (± 14 %), but the values are within the scattering of each other and can thereby be seen as comparable (Fig. 4.27). Following the standard procedure DIN EN 15967 [43] for determination of the maximum rate of pressure rise of gases a deviation of less than 10 % (which was observed) between the two mixing methods is not considered as significant. Consequently, it can be concluded that the mixing method has no influence on the explosion characteristics $p_e x$ and K-value measured in the 20L-sphere. Obviously, homogenization of the gas mixtures can be obtained sufficiently by the turbulence that is caused by the injection from the dust container within the 60 ms between injection of the dust and triggering the ignition source.

The outcome of the investigated influence of the different mixing methods can be summarized with the following two main conclusions:

- The three different mixing methods for hybrid mixtures can be expected to be interchangeable. A full mixing has taken place after the standard ignition delay time of 60 ms.
- The accuracy of the gas fraction has to be measured and calibrated considering systematic deviations before starting the explosion tests. Inaccuracies in the gas composition cannot be quantified without gas analysis and they can influence the test results strongly.

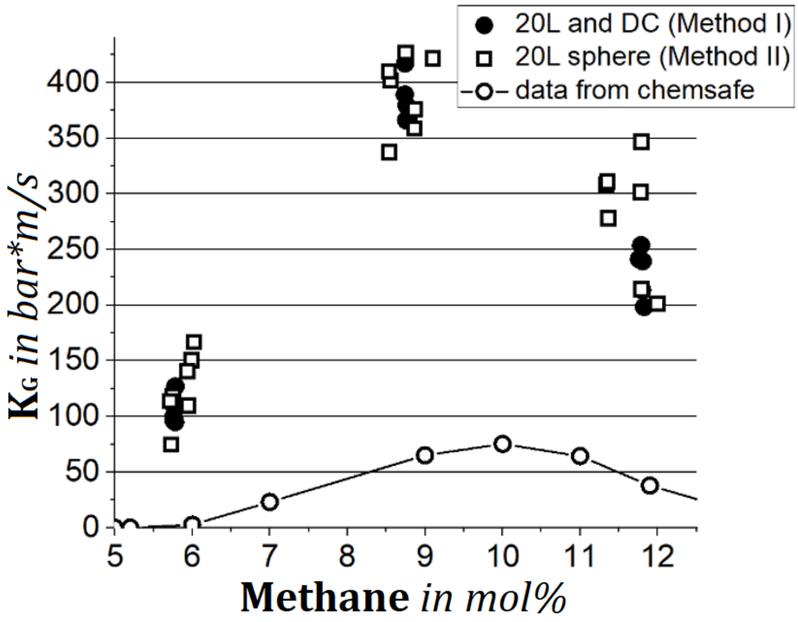

Figure 4.27.: K-values of methane; two different mixing methods: flammable gas inside the 20L-sphere only and premixture in the 20L sphere and the dust container (DC) and data from reference database (chemsafe (2021))

For testing hybrid mixtures, preparation of the gas mixtures is much easier directly in the 20L-sphere, but the gas fraction should be validated before conducting explosion tests. Moreover, the accuracy of the pressure sensors that are usually installed in the 20L-sphere for dust explosion testing is too low for preparing gas mixtures. Consequently, for testing hybrid mixtures, the standardized 20L-sphere must be modified by installing a pressure sensor with a higher accuracy that can be blocked before triggering the ignition to avoid destruction. Also, a gas measuring system must be used and the tightness of the 20L-sphere should be ensured by leakage tests before conducting the explosion tests. For tests with flammable gas fractions of more than 40 mol% Method I has to be applied for preparing the gas mixtures.

4.3. Influence of turbulence, ignition energy and type of ignition source on the safety characteristics of gases

4.3.1. The influence of turbulence on the lower explosion limit of hydrogen

Because of its high sensitivity (the MIE is with 0.017 mJ [140] lower by a factor of 17 compared to methane with an MIE of 0.29 mJ [141]) for the test series on the lower explosion limit hydrogen was chosen. For all other investigations in the laboratory and the round robin test methane was chosen.

The ignition source did not affect the explosibility of hydrogen but the energy did: The determined lower explosion limit was always determined at 4 mol% with a clear explosion at 5 mol% using the exploding wire with 200 J and 2 kJ and with two 1 kJ chemical igniters, both with turbulence and without turbulence. An ignition energy of 20 J seemed to be insufficient to ignite the mixture with 5 mol% under turbulent condtitions. Just two out of five tests had a significant pressure rise in the tests (figure 4.28). In all tests under quiescent conditions no ignition was observed with 4 mol% and in all tests with 5 mol% an ignition was observed with the same ignition energy.

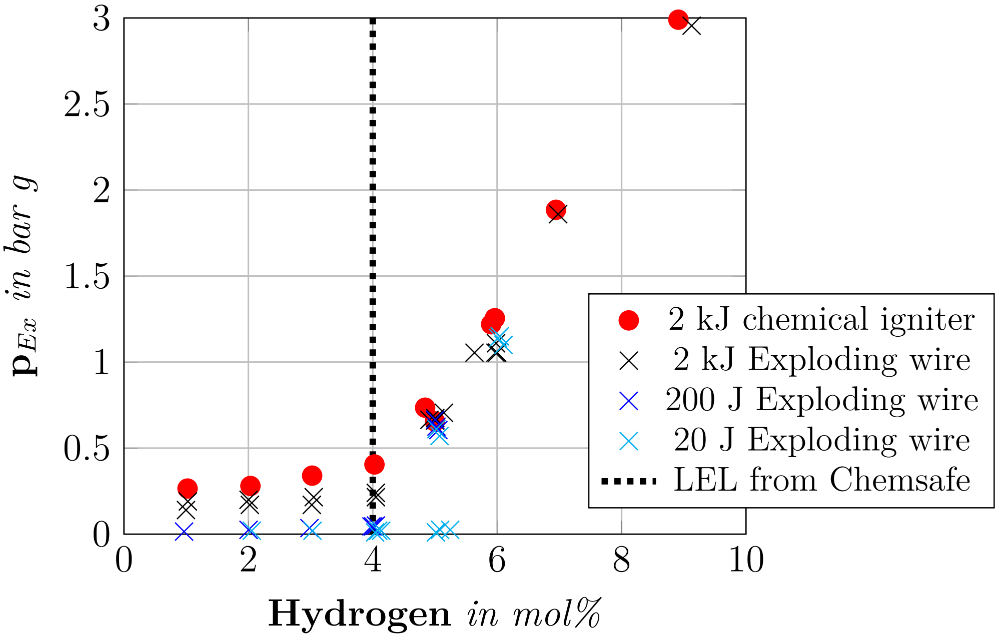

Figure 4.28.: Explosion overpressure of hydrogen air mixture with different ignition energies and sources under turbulence

This is especially remarkable since hydrogen has a minimum ignition energy of 0.017 mJ and even the lowest tested ignition energy of 20 J is higher by a factor of one million. But the fact, that the minimum ignition energy rises at the ends of the explosive region and the high level of turbulence seem to be enough to lower the explosion probability to 40 mol%. Askar and Schröder also saw, that the lower explosion limit of methane does not vary with higher ignition energies tested under quiescent conditions.[53]
These findings lead to the conclusion, that hybrid mixtures shall not be tested with ignition energies that are normally used for gases. Especially with turbulence the ignition energy gets distributed so that no ignition can be observed anymore with lower ignition energies. An overdriving effect was also not observed since both, the exploding wire and the chemical igniters did not exceed the ignition criteria at 4 mol%.

4.3.2. The influence of turbulence on the limiting oxygen concentration of methane

The ignition source and energy did not affect the determined limiting oxygen concentration of methane when tested under quiescent conditions. However, under turbulent conditions that are normally present when hybrid mixtures are tested, the measured LOC-value increased from 11 mol% determined at quiescent conditions to 13 mol% with an ignition energy of 20 J (4.29, left side). The determined LOC might lead to unsafe safety measures since inerting is typically applied with the LOC minus a safety distance of three mol% [25].
Increasing the ignition energy from 20 J to 200 J, the determined value of the LOC decreased from 14 mol% to about 12 mol% under turbulence. This is closer to the literature value of 10.7 mol% but the deviation is still on the unsafe side (4.29, right side).

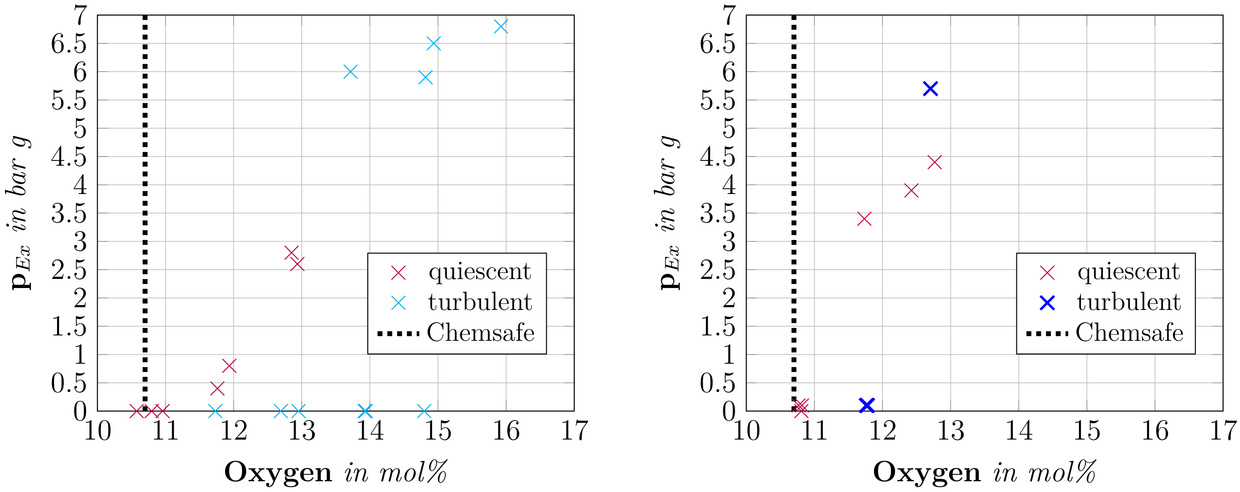

Figure 4.29.: Explosion overpressure for stoichiometric methane - mixtures with different oxygen fractions with 20 J (left) and 200 J (right) ignition energy

A further increase of the ignition energy to 2 kJ led to the same value for the LOC under turbulent conditions of 10.7 mol% (or with 11 mol% close to that) as found in the literature determined according to the standard procedure for gases [42] under quiescent conditions and with an ignition energy of 20 J (see 4.30, left side). Under quiescent conditions the ignition criterion (pressure rise) was just reached at an oxygen fraction of 10.8 mol% and clearly exceeded when the oxygen fraction was further increased by 1 mol%. Using the exploding wire with 2 kJ the explosion pressure was clearly increased, if the oxygen fraction was increased from 11 mol% to 12 mol% allowing a clear distinction between "ignition" and "non-ignition" for both quiescent and turbulent conditions.
With the chemical igniters the LOC was as well 11 mol% with a pressure rise exceeding the ignition criterion at 12 mol% for turbulent conditions.
However, the increase of the explosion pressure with increasing oxygen fraction is so flat that the distinction between "ignition" and "non-ignition" is difficult and that small changes in

the experimental parameters might have resulted in unsafe values. A clear ignition with an explosion pressure clearly exceeding the ignition criterion of 0.5 barg was not detected under turbulent conditions until 14 mol% (4.30, right side). In the upcoming figures the methane fraction is half the oxygen fraction (stoichiometric mixture) and the plotted value of 10.7% is taken from the Chemsafe database [40].

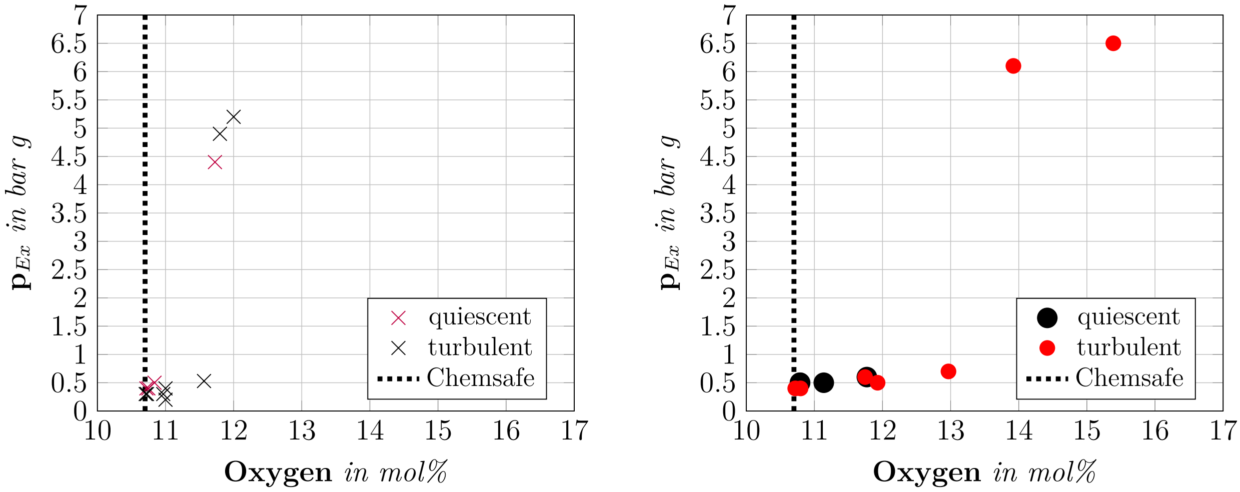

Figure 4.30.: Explosion overpressure for stoichiometric methane - mixtures with different oxygen fractions with 2 kJ ignition energy and exploding wires (left) and chemical igniters (right) as ignition source

This might be a result of the fact, that the chemical igniters consume oxygen or might be influenced if the oxygen amount is decreased.

4.3.3. The influence the ignition energy on the explosion pressure and the rate of pressure rise of methane

The variation of the ignition energy from 200 J to 2 kJ does not affect the explosion pressure of methane with fractions, that were clearly within the explosion region (see figure 4.31, left side). This is in accordance to earlier findings from other researchers, that the explosion limits can be influenced by the ignition energy but the explosion pressures measured at fractions that are further away from the limits are unaffected ([99], [32], [53]). The variation of the ignition energy from two times 100 J to two times 1 kJ did not affect the maximum rate of pressure rise at the near stoichiometric fraction of 8.8 mol% and for the lean mixture with 5.8 mol% of methane as well. However, it did affect the values for the rich mixture with 11.8 mol% with lower values for 2 kJ (1010 ± 71 bar/s) than for 200 J (1205 ± 98 bar/s) (see figure 4.31, right side).

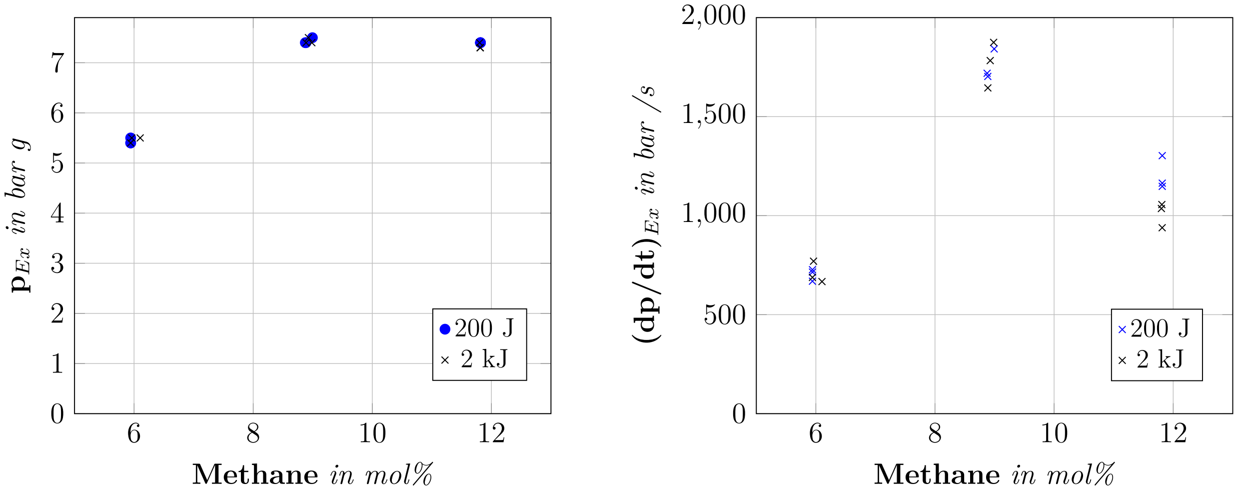

Figure 4.31.: Explosion pressure (left) and maximum rate of pressure rise (right) of methane with the exploding wire as ignition source with different ignition energies

Changing the ignition source from exploding wires to chemical igniters with the same ignition energy of two times 1 kJ the maximum explosion pressure stayed the same (see figure 4.32, left side).

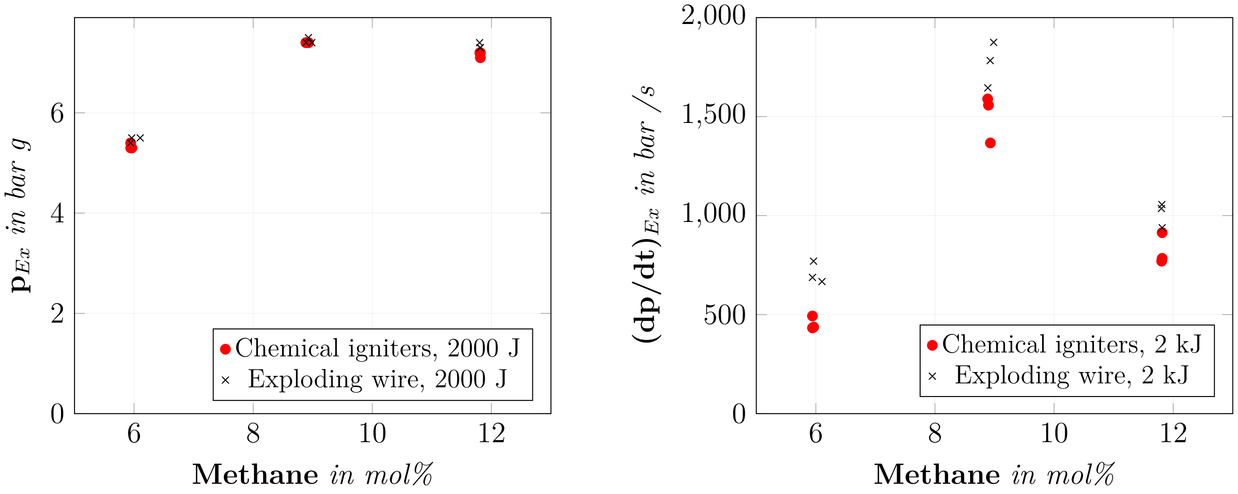

Figure 4.32.: Explosion pressure (left) and maximum rate of pressure rise (right) of methane with exploding wires and chemical igniters as ignition source

However, the maximum rate of pressure rise determined at a fraction of 9 mol% was lower for the chemical igniters by 10 % on average (see figure 4.32, right side). This may be caused by the shape of the ignition volume. While investigating ignition source requirements for gases Hertzberg. et. al. found, that spark ignitions cause a higher dp/dt-value than chemical igniters. They conclude, that "the result is an artifact of the differences in the source geometries: the spark is a point-source, whereas the chemical igniter approximates a line source.

The spark generates a spherical wave front that contacts the wall almost simultaneously everywhere along the flame front surface at the instant combustion is complete. For the line source chemical igniters, the wave front is not spherical and the wave surfaces initiated near ends of the line contact the wall before other volume elements are consumed. As a result, combustion from the line source is less adiabatic, resulting in slightly lower K_G-values." [99] Here it might be another explanation, because the exploding wire and the chemical igniters were found to be quite similar in the shape of the igniting volume: The chemical igniters have an additional time delay because the energy source that ignites them can take up to 10 ms for that. So the exploding wire ignites the mixture at an earlier time when the level of turbulence is higher.
Chatrathi et. al. [32] measured the exploding characteristics of propane in a $1m^3$ comparing exploding wires and chemical igniters. There, no difference was measured between the two ignition sources.

4.3.4. The influence of turbulence on the explosion pressure and the rate of pressure rise of methane

The influence of turbulence on the explosion characteristics of methane was investigated with chemical igniters and the exploding wire, both with an overall energy of 2 kJ.
The maximum explosion pressure was slightly higher, when tested under turbulence for both, the chemical igniters. However, no difference was observed between the two ignition sources in quiescence (see 4.33, left side) and under turbulent conditions (see 4.33, right side).

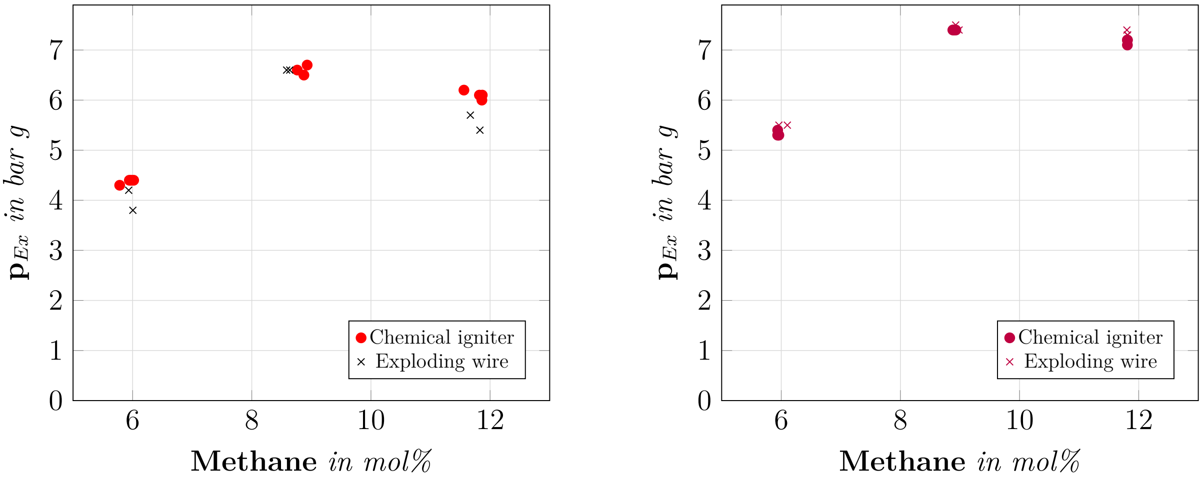

Figure 4.33.: The explosion pressure of methane with exploding wires and chemical igniters of two times 1 kJ under quiescence (left) and under turbulent conditions (right)

The rate of pressure rise is highly affected by the turbulence level. At the near stoichiometric mixtures (8.8 mol% methane) the values were twelve times higher at turbulent conditions

(1768 ± 123 bar/s compared to 152 ± 23 bar/s). For the lean and the rich mixture the effect was even higher with factors of 17 (708 ± 62 bar/s compared to 42 ± 9 bar/s for 5.8 mol% methane) and 13 (1010 ± 71 bar/s compared to 76 ± 26 bar/s, see figure 4.34, left side). Exchanging the chemical igniters with exploding wires having the same ignition energy did not change the results by more than 10 % as described in the section before for the turbulent conditions (see figure 4.34, right side).

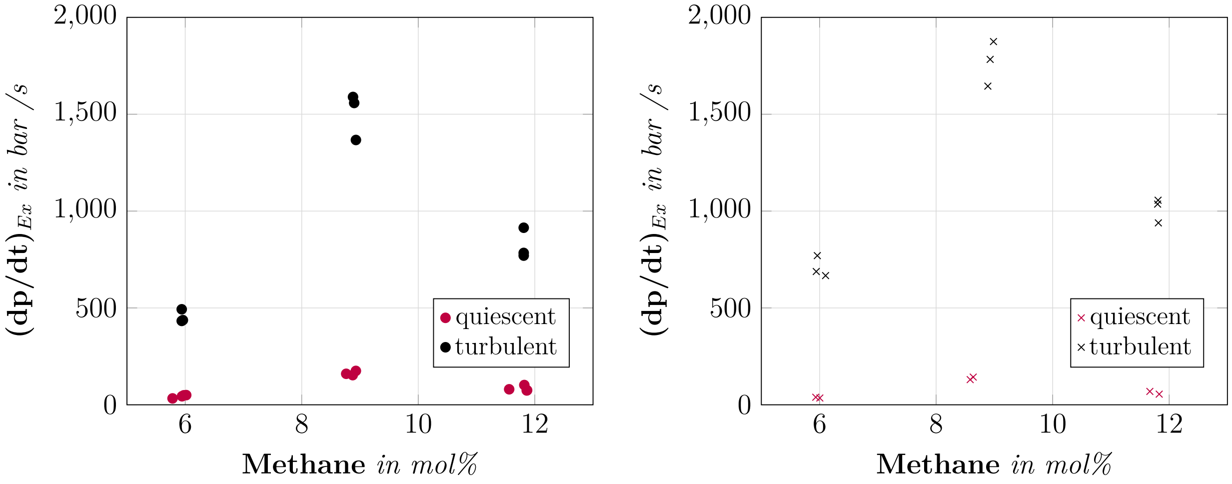

Figure 4.34.: Turbulence effect on the maximum rate of pressure rise of methane with chemical igniters of two times 1 kJ (left) and exploding wires of two times 1 kJ(right)

This matches the findings by Skjold [108] and Chatrathi et. al. [32] for propane and also the conclusions from Wheeler [110], that the combustion is faster with turbulence and that this is not a fixed factor but more prone to mixtures with a lower laminar burning velocity. Because of the limits discussed in section 2.5 the connection between the laminar burning velocity and $(dp/dt)_{max}$ was not further investigated.

These findings lead to the conclusion, that hybrid mixtures can be tested with ignition energies higher than the ones that are usually taken for gases. Also they should not be tested with lower ignition energies since under turbulent conditions no ignition can be observed at fractions near the explosion limits or limiting oxygen concentrations where an explosion would take place under quiescent conditions. An overdriving effect was also not observed since the LOC and the LEL did not change to lower values than those stated in the literature. At near stoichiometric mixtures and lean or rich mixtures, that are further away from the explosion limits the ignition energy did not have an effect on both, p_{max} and $(dp/dt)_{max}$. The exploding wire and the chemical igniters with two times 1 kJ seem to produce comparable results when explosion limits, the maximum rate of pressure rise or the maximum explosion pressure are determined. For the limiting oxygen concentration only the exploding wire produces satisfying results.

4.4. The influence of the ignition energy and type of ignition source on the safety characteristics of dusts

4.4.1. Influence of the ignition energy on the explosion characteristics of dusts

Chemical igniters: 2 kJ vs. 10 kJ

Explosion tests with the 20L-sphere and corn starch as dust sample were performed over a wide range of concentrations. All parameters, other than the ignition energy were kept in a narrow range according to chapter 3.3.1. The first test series was aimed at the reduction of the ignition energy of the chemical igniters from two times 5 kJ to two times 1 kJ. One can clearly see the differences in the explosion pressures for small amounts of dust below 250 g/m^3 (see figure 4.35, left side). At higher amounts of dust no significant difference can be found with different ignition energies. At the dust amounts of 750 g/m^3 the explosion pressures determined with lower ignition energy are even slightly higher. However, this effect is with less than 9 % (8.5 barg for 2 kJ against 7.8 barg for 10 kJ at 1000 g/m^3) lower than the range of scattering for the same testing parameters. With that the explosion pressure is hardly influenced by the reduction of the overall ignition energy from 10 kJ to 2 kJ.
The maximum rate of pressure rise also shows a significant influence of the ignition energy at low concentrations of dust but small variations for higher dust concentrations. At concentrations of 1000 g/m^3 the difference of the average values is with less than 2 % neglectable (540 bar/s for 2 kJ vs. 533 bar/s for 10 kJ, see figure 4.35, right side).

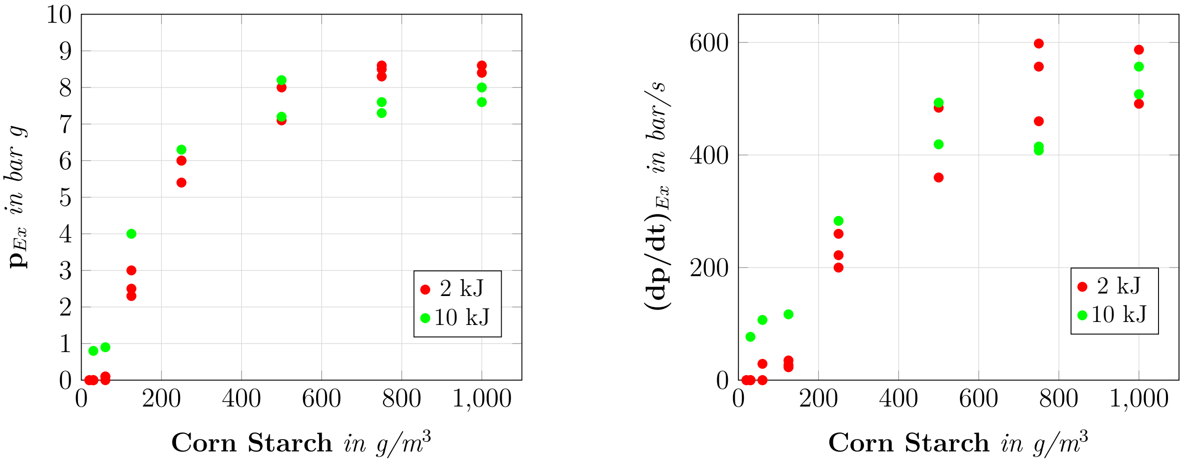

Figure 4.35.: Influence of the ignition energy on p_{Ex} and $(dp/dt)_{Ex}$ of corn starch

Exploding wire: 20 J vs. 200 J vs 2 000 J

The energy was further reduced with the exploding wire. Every reduction of the ignition energy by a factor of ten increased the lower explosion limit by one step: From 60 g/m^3 with 2 kJ over 125 g/m^3 with 200 J to 250 g/m^3 with 20 J. However, once the explosion region was entered no difference could be observed anymore (see figure 4.36, left).

The values for the maximum rate of pressure rise did not change either with varying ignition energy (see figure 4.36, right). Again, the scattering seems to be lower with the highest ignition energy of 2 kJ but more experiments are necessary to prove this.

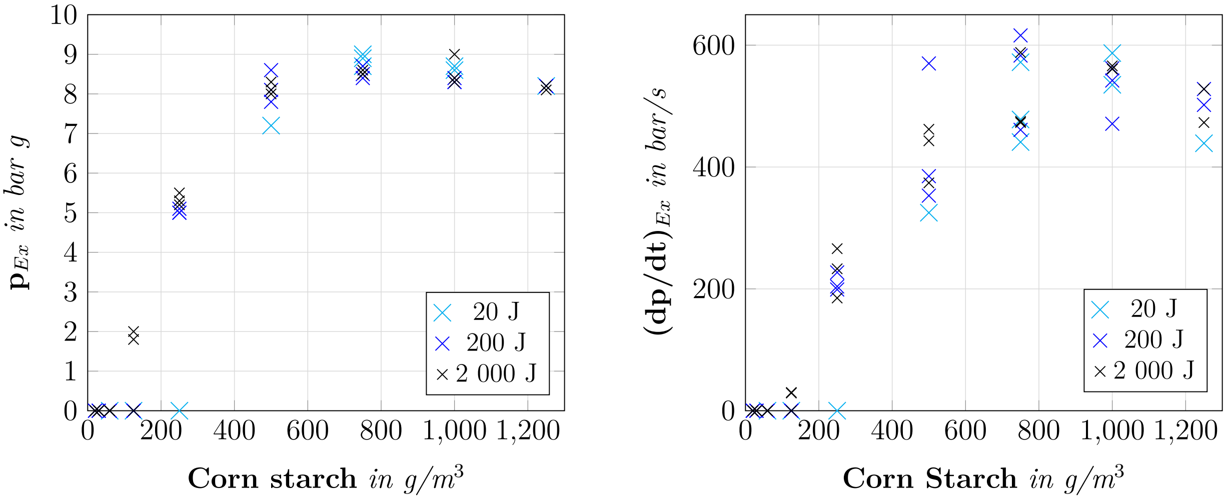

Figure 4.36.: Influence of the ignition energy on the explosion pressure (left) and the maximum rate of pressure rise (right) of corn starch

Both, the maximum explosion pressure and the maximum rate of pressure rise, seem to be unaffected by the reduction of the ignition energy. However, this should be tested for more dust samples. If coarse dusts are tested they might be so hard to ignite, that the ignition energy does affect the determined safety characteristics[2]: A test series with coarse soy flour with a median value for the particle size distribution of over 125 μm showed the following values for p$_{Ex}$ that were determined with different ignition energies of chemical igniters (see

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[2] According to the European standard for the determination of safety characteristic of dusts, the EN14034-series and the international ISO80079-2, solid particles with a diameter below 500 μm are called dusts ([45], [59], [46], [47], [58]). According to the American standard ASTM1226e particles above 75 μm shall be ground and sieved before testing [57]. The German compulsive regulatory VDI2263-Part1 differentiates between dust layers and elevated dusts: "If a representative sample cannot be taken, e.g., in the case of plants at the planning stage or with frequent changes in process variables, the sample material delivered can/should be appropriately prepared in the laboratory. As a rule, this includes drying the sample material in a way that is gentle on the product (e.g., approx. 50 ° C in a vacuum) and producing a defined particle size fraction (<250 μm for dust layers and <63 μm for dust clouds). This procedure leads to characteristics which also ensure a high degree of safety" [142]. However, the superordinate VDI2263 defines everything below 500 μm as dust.[143]

figure 4.37).

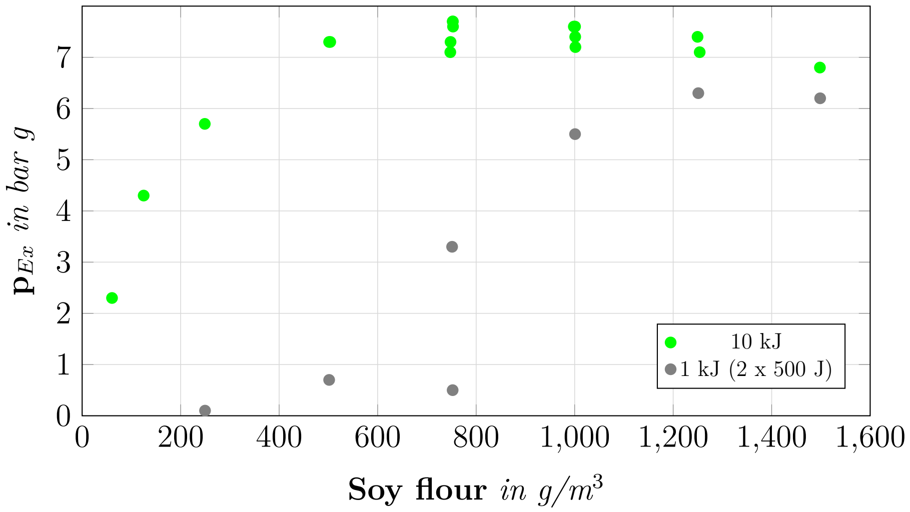

Figure 4.37.: Explosion pressure of coarse soy flour tested with chemical igniters of different ignition energies

Since the explosibility is tested with an ignition energy of 2 kJ according to ISO 80079 [58] it does not make sense to increase the ignition energy afterwards to 10 kJ for the determination of p_{max} and $(dp/dt)_{max}$. Also, it does not seem to affect the values inside the explosion region for dusts with typical particle size distributions below 100 μm. Whether the combustion of the coarse soy flour was forced and would normally not take place under normal circumstances as described by Going et. al. [129] with these high ignition energies was not investigated because no 1m^3 was available. Since Addo et. al. also recommend the investigation of marginally explosive dusts in the 1m^3 instead of the 20L-sphere [130] they might be excluded from the standard on hybrid mixtures.
For these reasons the overall ignition energy of 2 kJ was chosen for the SOP in this work.

4.4.2. Influence of the type of ignition source on the explosion characteristics of dusts

No difference was observed between the explosion pressures determined with chemical igniters and with exploding wires of the same ignition energy. (see figure 4.38, left side). The points are overlapping for all concentrations and the value for the lower explosion limit was also the same with 60 g/m^3. With that it can be said, that the exchange of the ignition sources does not influence the safety characteristics maximum rate of pressure rise and maximum explosion pressure. The measured values for the maximum rate of pressure rise are also overlapping when the ignition source is changed from chemical igniters to exploding wires for all concentrations of corn starch. The scattering seems to be slightly lower for the

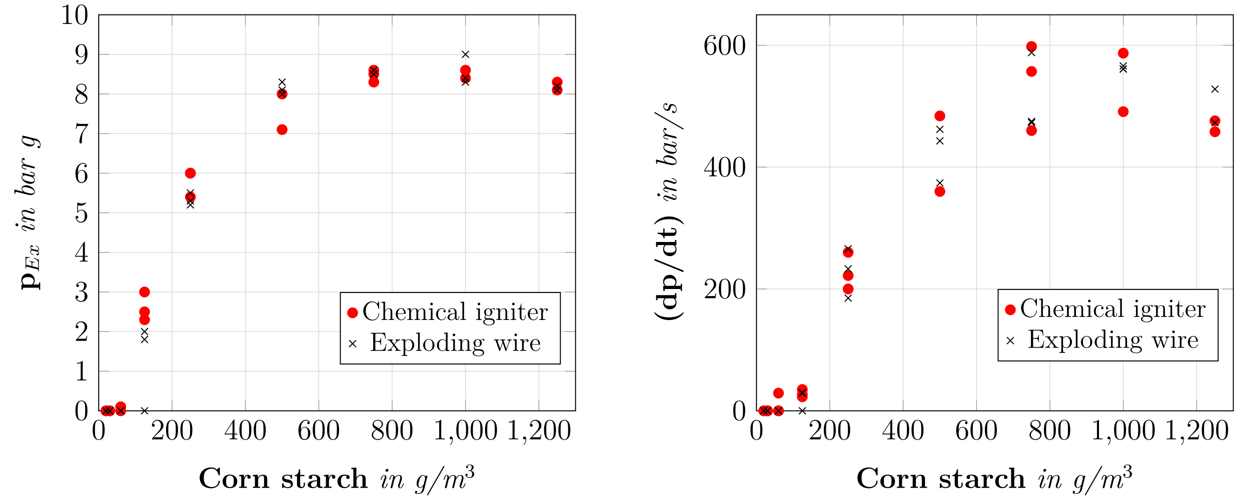

Figure 4.38.: Influence of the ignition source on the explosion pressure (left) and the maximum rate of pressure rise (right) of corn starch, Exploding wire and chemical igniters with the same ignition energy of 2 x 1 kJ

exploding wires but this effect might be an artifact of the small number of tests (see figure 4.38, right side)[3].

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[3] With the typical number of three tests for dust explosions it is always hard to tell the difference between a "signal" and "noise" if the parameter of interest influences the measured value only slightly (see Appendix E.10)

4.5. Safety characteristics of hybrid mixtures

4.5.1. Influence of the type of ignition source on the explosion characteristics of hybrid mixtures

Corn starch was tested with the addition of methane with 3 mol%, 6 mol% and 9 mol% with chemical igniters and exploding wires, with an overall ignition energy of 2 kJ. All tests were conducted twice. The results are comparable for the measured explosion pressures for all three gas fractions (see figures 4.39 to 4.41, left side).
The rate of pressure rise showed comparable results for 3 mol% of methane (see figure 4.39, right side) and slightly higher values for the exploding wire for 6 mol% and 9 mol% (see figures 4.40 and 4.41, right side). The reasons for that are presumably the same than the ones that were identified for the rate of pressure rises of gases without dust (see 4.3.4). With about 20 % the values are still within the scattering of each other and with that within an acceptable range.

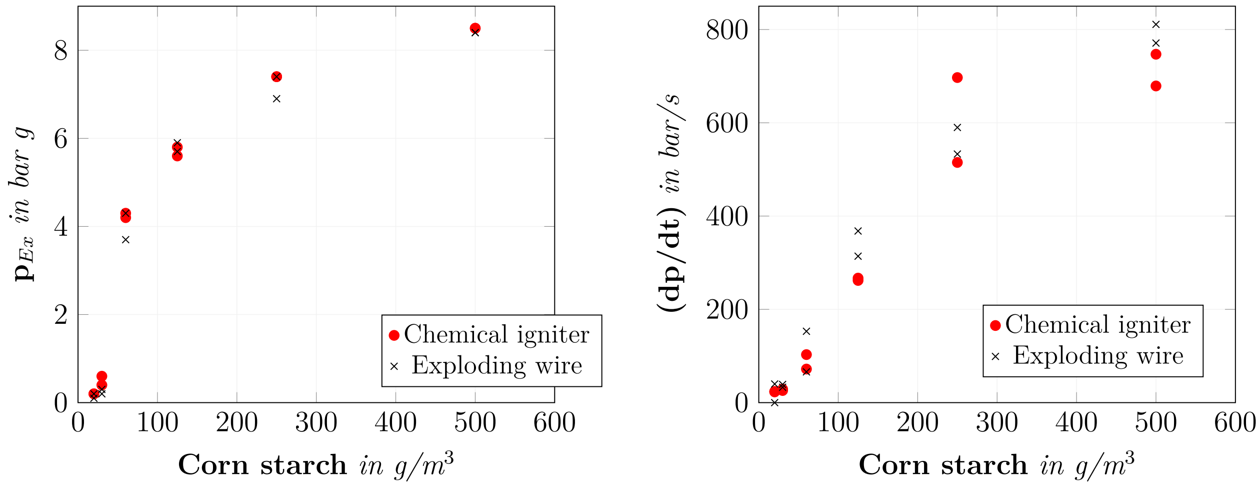

Figure 4.39.: Influence of the ignition source on the explosion pressure and the maximum rate of pressure rise of corn starch with 3 mol% methane

Figure 4.41 also shows, that the addition of corn starch to the (near) stoichiometric mixture of 9 mol% of methane in air leads to a decrease of the determined values of p_{max} and $(dp/dt)_{max}$, presumably because the dust acts as a heat sink and by that lowers the flame temperature. Also some of the dust might be forced to combust and with that consumes oxygen that is not available anymore for the combustion of the methane.

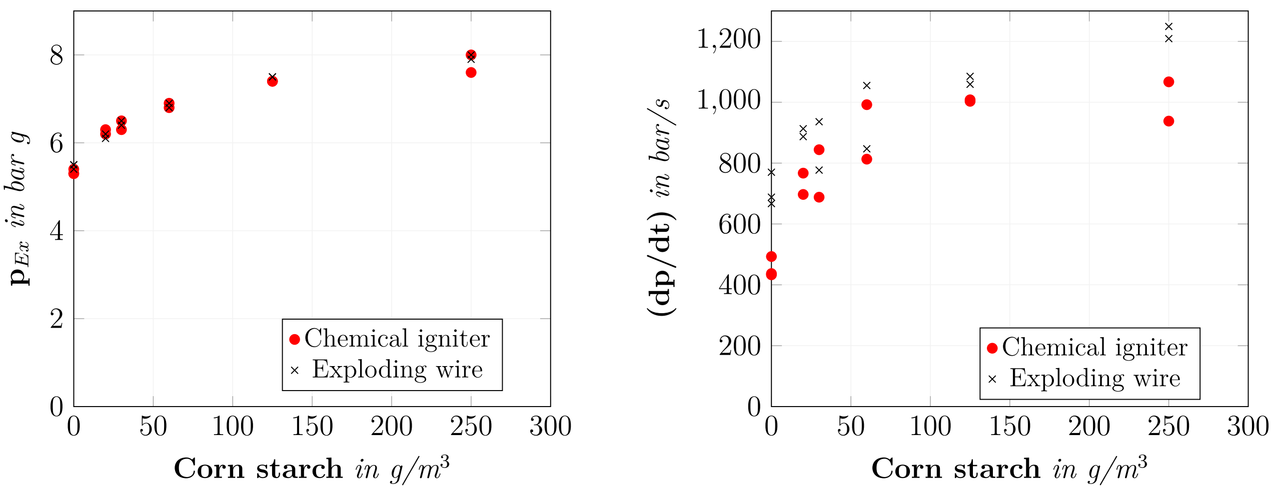

Figure 4.40.: Influence of the ignition source on the explosion pressure and the maximum rate of pressure rise of corn starch with 6 mol% methane

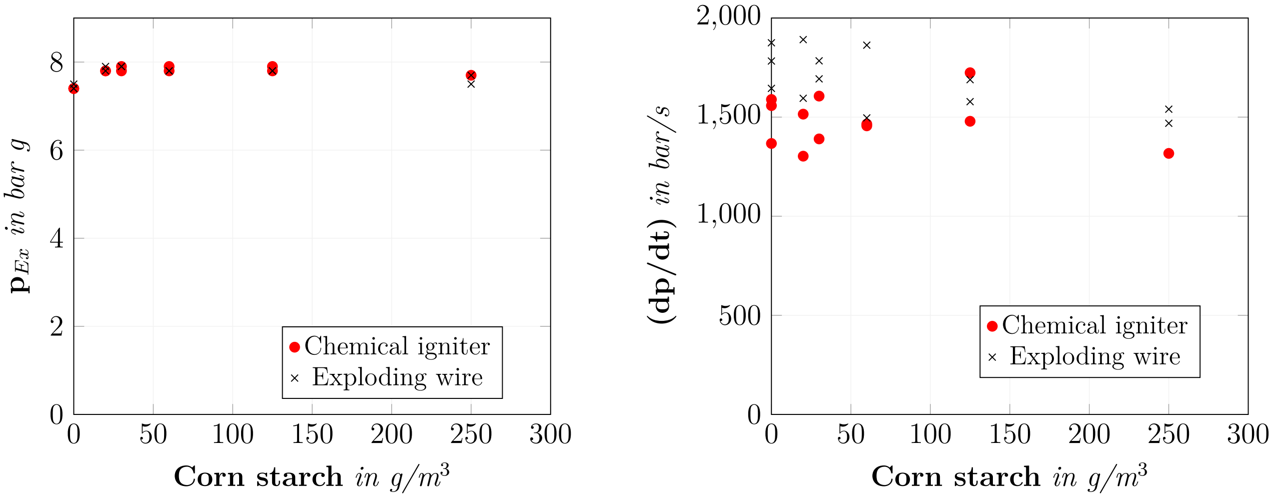

Figure 4.41.: Influence of the ignition source on the explosion pressure and the maximum rate of pressure rise of corn starch with 9 mol% methane

4.5.2. Influence of the ignition energy on the explosion characteristics of hybrid mixtures

Corn starch was tested with the addition of methane with 3 mol%, 6 mol% and 9 mol% with two exploding wires, with an overall ignition energy of 200 J and 2 kJ. All tests were conducted twice.

The results of the maximum values are comparable for the measured explosion pressures for all three fractions. The lower explosion limit was again one concentration step higher for the lower ignition energy with 3 mol% of methane (see figure 4.42), because methane fractions of 6 mol% and 9 mol% are inside the explosion region of methane even without dusts. No difference was observed here (see figure 4.43 a and b).

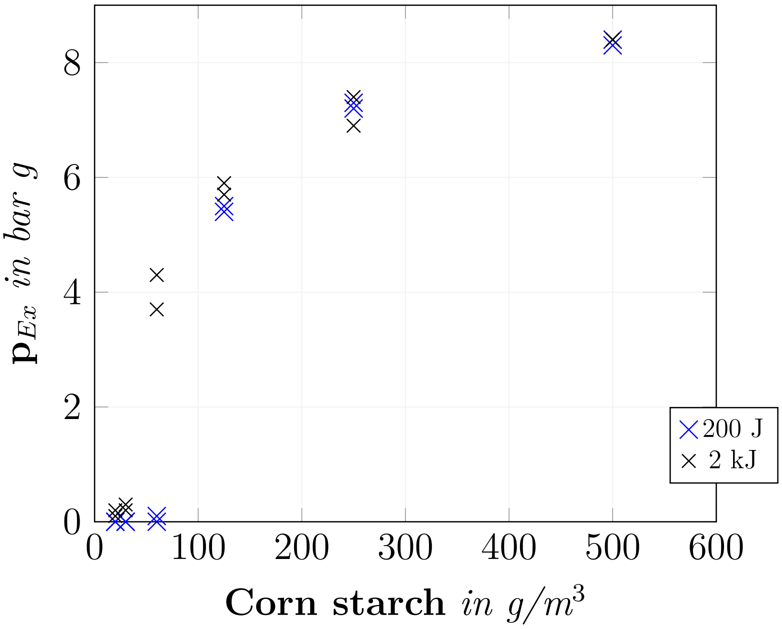

Figure 4.42.: Influence of the ignition energy on the explosion pressure of corn starch with 3 mol% methane

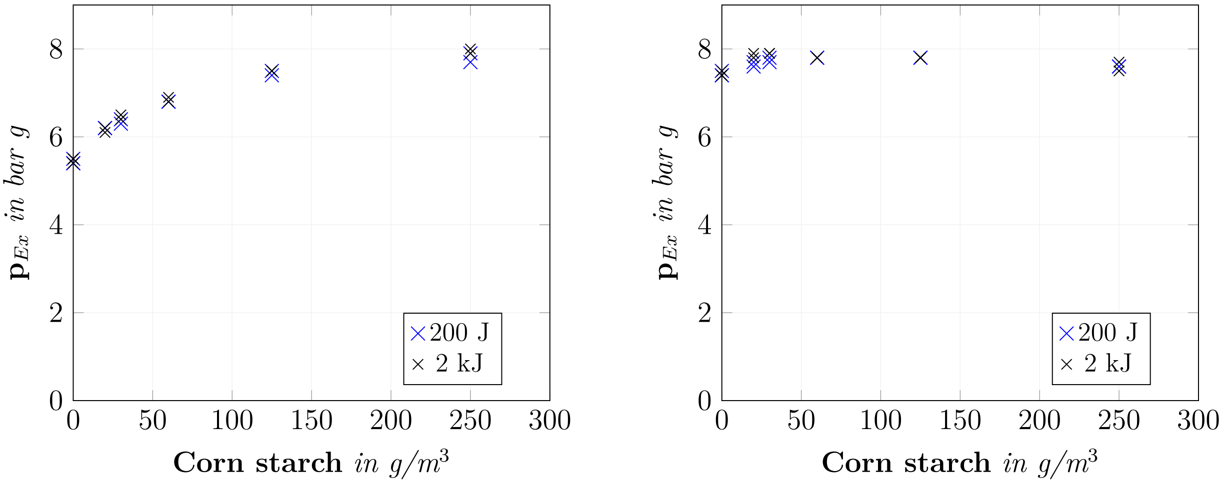

Figure 4.43.: Influence of the ignition energy on the explosion pressure of corn starch with 6 mol% (left) and 9 mol% (right) methane

The rate of pressure rise showed comparable results for all three tested fractions of methane (see figures 4.44 and 4.45).
This was expected since - as discussed above - the reduction of the ignition energy did neither

affect the values of the dust nor the values of the gas.

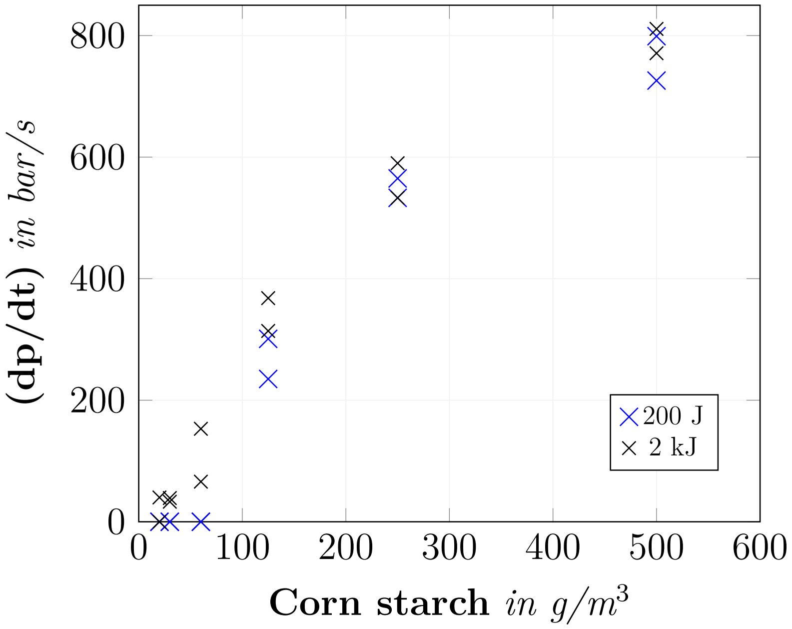

Figure 4.44.: Influence of the ignition energy on the maximum rate of pressure rise of corn starch with 3 mol% methane

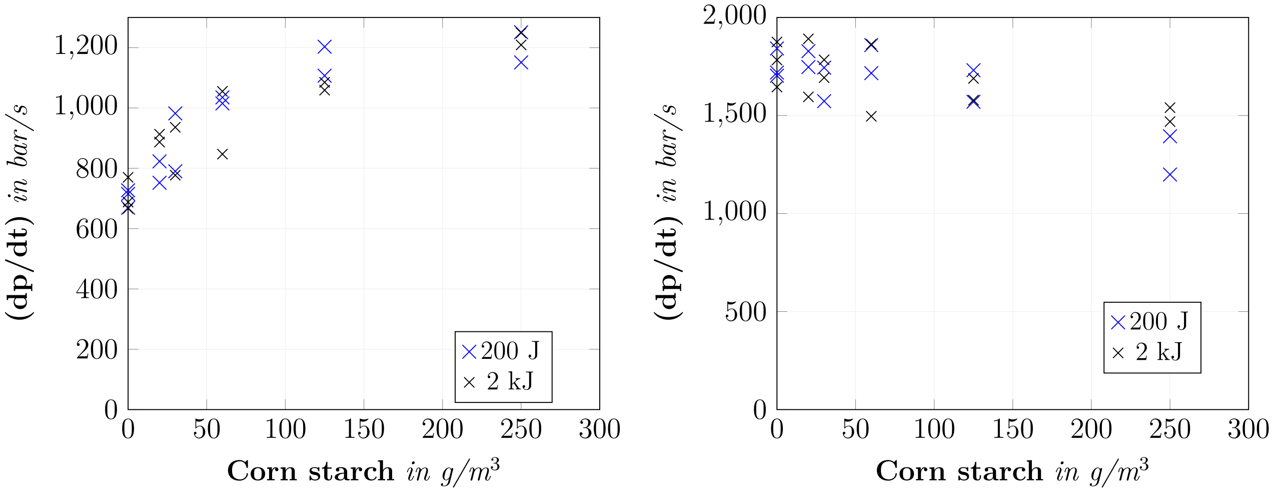

Figure 4.45.: Influence of the ignition energy on the maximum rate of pressure rise of corn starch with 6 mol% (left) 9 mol% (right) methane

4.5.3. Influence of the ignition energy on the limiting oxygen concentration of hybrid mixtures

The limiting oxygen concentration of the corn starch was determined according to the European standard [47] with different ignition sources and energies. The dust concentrations, that were tested were 125 g/m^3, 250 g/m^3, 500 g/m^3 and 750 g/m^3. The results are presented in table 4.3. It can be seen clearly, that the ignition energy should not be reduced below 2000 J for dusts when determining the limiting oxygen concentration since this would lead to conclusions on the unsafe side. However, the influence of the addition of 1 mol% and 3 mol% of methane was checked with the result, that the lowest ignition energy of 20 J did ignite at a closer value to the ones determined with high ignition energies, still being unsafe and not applicable. The determined value for 200 J and 2 kJ for the exploding wire did not change for all tested dust concentrations. The determined value for the chemical igniters was slightly lower and at the same level as the exploding wire with 2 kJ.

Table 4.3.: Limiting oxygen concentration of corn starch with different ignition sources and energies

Ignition source	Ignition energy	LOC	LOC with 1 % CH4	LOC with 3 % CH4
-	*in Joule*	*in mol%*	*in mol%*	*in mol%*
Chemical Igniter	2000	12	12	11
Exploding wire	2000	11	11	11
Exploding wire	200	13	13	13
Exploding wire	20	17	16	14

With that it can be said, that the SOP works for hybrid mixtures and produces reproducible results. The connection to the single phase substances is given as well (see also chapter 4.3.2). The ignition energy should be higher than the ones that are used for gases under quiescent conditions. An ignition energy of two times 1 kJ delivered the best results and especially for the LOC the exploding wire had the advantage of a clearly detectable pressure rise inside the explosion region (see figure 4.30).

4.6. The explosion characteristics of hybrid mixtures determined according to the SOP

The p$_{max}$ and (dp/dt)$_{max}$ respectively the K$_H$-values that were determined for all substances and combinations are listed in table 4.4. Detailed information about the dust samples can be found in Appendix D.

The results for the hybrid maximum explosion overpressure values were as expected. Since the p$_{max}$ of corn starch and niacin is higher than the p$_{max}$ for methane this value was the same as for the dust component alone and occurred when no gas was added to the system (see figure 4.46). For lycopodium the p$_{max}$ is slightly lower than the one for methane and

Table 4.4.: Tested single materials and hybrid mixtures and their maximum values. *Values in italic are the same than those of the single substances. They are either on the x-axis in the hybrid field of figure 4.46 and on the y-axis of figure 4.48 and no additional effect was observed*

Hybrid mixture	p_{max} *in bar g*	$(dp/dt)_{max}$ *in bar/s*	K_H-value *in bar*m/s*
Corn starch	9.2	629	171
Corn starch - CH_4	*9.2*	1556	422
Niacin	8.5	865	235
Niacin - CH_4	*8.5*	1515	411
Lycopodium	7.8	606	164
Lycopodium - CH_4	*7.9*	1506	409
CH_4	7.9	1471	399
Quartz sand			
Quartz sand - CH_4	*7.9*	1518	412

hence was the p_{max} for the hybrid mixture the same than for methane alone (see figure 4.47).

For the investigated system of the non-combustible quartz sand and methane, the highest values were observed with methane only or with very small quantities of dust where the heat capacity of the inert particles additionally injected into the explosion chamber did not result in lower explosion pressures (see figure 4.48).

The values for $(dp/dt)_{max}$ however where doubling for all the hybrid mixtures compared to the combustible dusts alone. The values for $(dp/dt)_{max}$ of the hybrid mixtures were all even slightly higher than the $(dp/dt)_{max}$-value of turbulent methane alone, though the effect was with three to twelve percent relatively small. It seemed not to matter, which one of the four dusts were added. The methane fraction with the highest (dp/dt)-value was always found at 9 mol% to 10 mol% of methane (stoichiometric) and at 20 $\frac{g}{m^3}$ to 125 $\frac{g}{m^3}$ ((0.4 g to 2.5 g) of combustible dust in the 20L-sphere (see figure 4.49, 4.50 and 4.51). It shall be mentioned, that especially for figure 4.49 the scale had to be adjusted, otherwise the difference would have been too small to be seen.

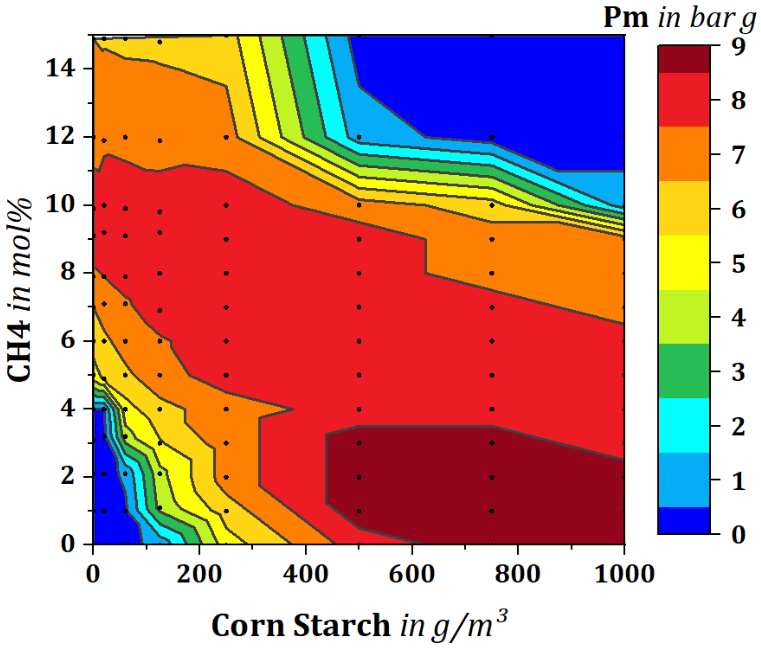

Figure 4.46.: Explosion overpressure for hybrid mixtures of methane and corn starch, black dots indicate the measuring points or their average

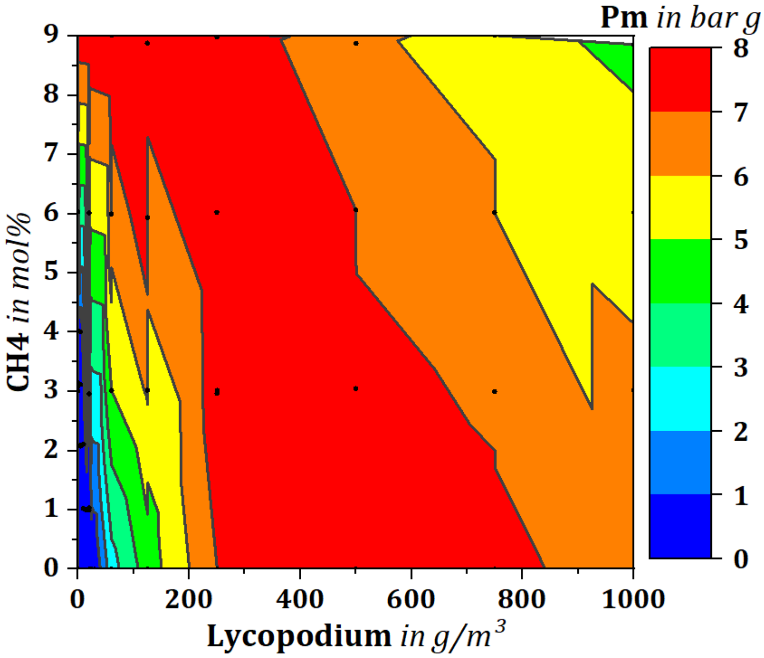

Figure 4.47.: Explosion overpressure for hybrid mixtures of methane and lycopodium, black dots indicate the measuring points or their average

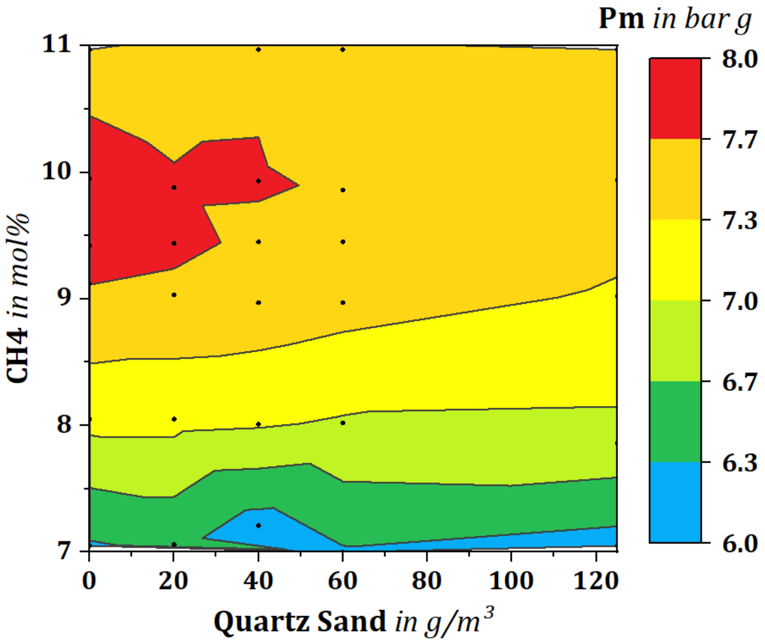

Figure 4.48.: Explosion overpressure for methane and quartz sand, black dots indicate the measuring points or their average

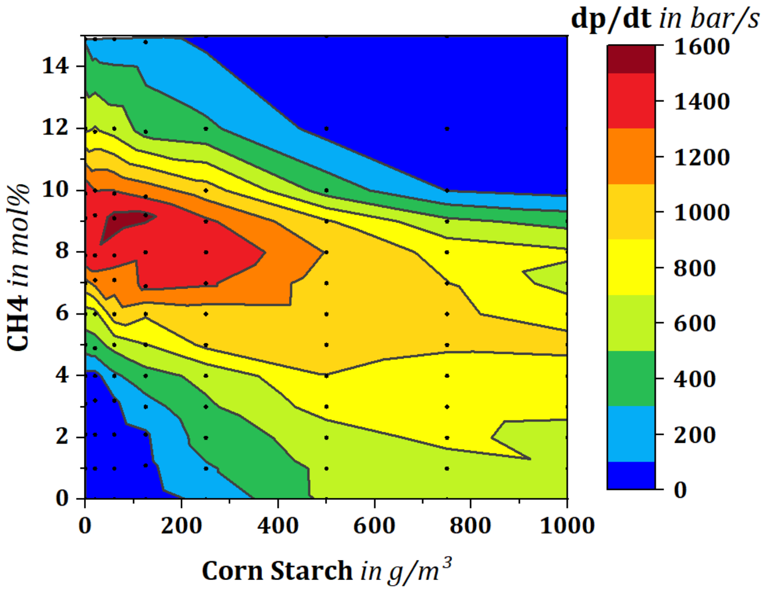

Figure 4.49.: (dp/dt) for methane and corn starch, black dots indicate the measuring points or their average

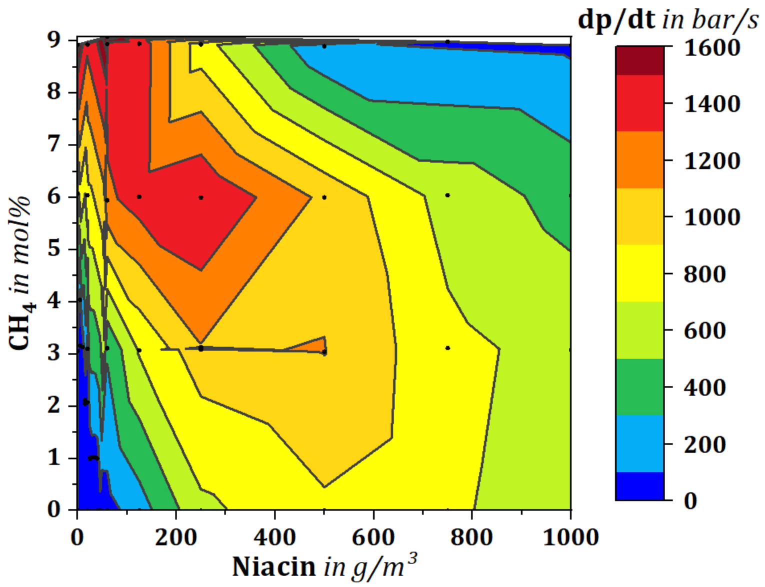

Figure 4.50.: (dp/dt) for methane and niacin, black dots indicate the measuring points or their average

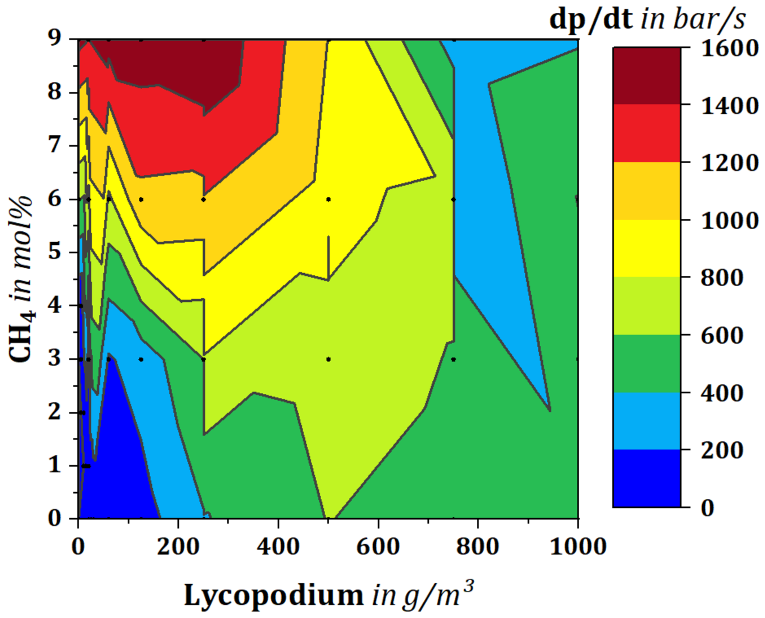

Figure 4.51.: (dp/dt) for methane and lycopodium, black dots indicate the measuring points or their average

It shall be mentioned that all values were obtained having the same level of turbulence and that especially the values of methane alone cannot be compared to literature values that are usually obtained under quiescent conditions [67]. This is especially highlighted because the $(dp/dt)_{max}$ of methane under quiescent conditions is with 239.8 bar/s for 9 mol% or 277.4 bar/s for 10 mol% smaller by a factor of about six.
The determined value for the explosion pressure of methane was wih 7.9 barg slightly higher than the literature value of 7.3 barg. This is presumably caused by the faster combustion due to the higher level of turbulence and with that the lower heat losses on the walls of the test vessel (see also chapter 4.2.4, all values from CHEMSAFE [40]).

The fact, that three different combustible dusts with different safety characteristics all resulted in slightly increased values for $(dp/dt)_{max}$ when added to stoichiometric methane-air-mixtures, although the $(dp/dt)_{max}$-values for all three dusts alone were clearly lower than the $(dp/dt)_{max}$ of methane alone, proves the idea, that it is not necessarily the combustion behaviour of the dust, that enhances the combustion rate. This effect was with 10 % to 20 % rather small and by further increasing the dust concentration the values decreased.
However, to further investigate the presumption that its not the combustion of the dust, tests with an inert dust (quartz sand) were performed around the stoichiometry of methane and with very little amounts of dust only (see figure 4.52). It was observed that the highest value of this hybrid system was as well at the stoichiometric fraction of the gas and the smallest tested concentration of dust. If the dust concentration was further increased it acted as a heat sink and thereby decreased the values for (dp/dt).

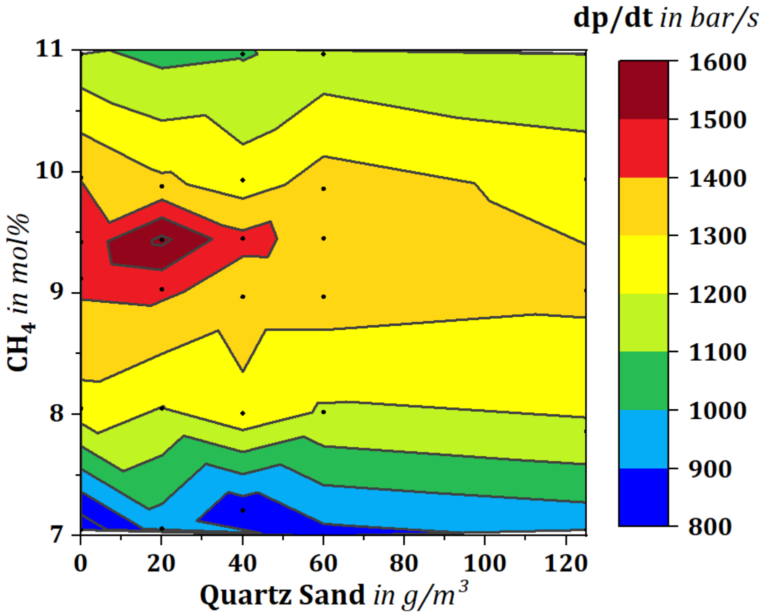

Figure 4.52.: (dp/dt) for methane and quartz sand as inert dust, black dots indicate the measuring points or their average

This phenomenon of slightly higher values for (dp/dt) at stoichiometric gas mixtures with very small amounts of dust was observed by other researchers in the 20L-sphere ([144], [145] [146]), in the standard 1m^3 ([26], [32]) and in larger vessels with a volume of 8 m^3 [147] and also simulated [148].
The observation, that even inert dust leads to a higher rate of the explosion pressure rise at very little amounts was also mentioned in a research paper published in 1983 [149] in which the authors concluded this is caused by the higher turbulence. They chose a very fine step-size for the dust and the gas on the lower end and a large one with higher concentrations, presenting their data in a logarithmic scale for the dust component. This unusual choice for the step-size and the presentation of the data also showed an optimum in the explosion region around the stoichiometry of the gas component and very low dust concentrations, though it cannot be seen in their research paper, that the value actually increased but that the concentration, where the maximum value occurs, widens (see figure 4.53). Unfortunately, for the explosion intensity they defined an own unit and called it "k$-ex$", not to be confused with the K-value. This k$_{ex}$-value is the square-root of the (dp/dt) multiplied with the highest occurring pressure for the chosen concentration (p$_{ex}$) divided by the time from ignition to the highest pressure (Δt), so a comparison to new data is difficult.

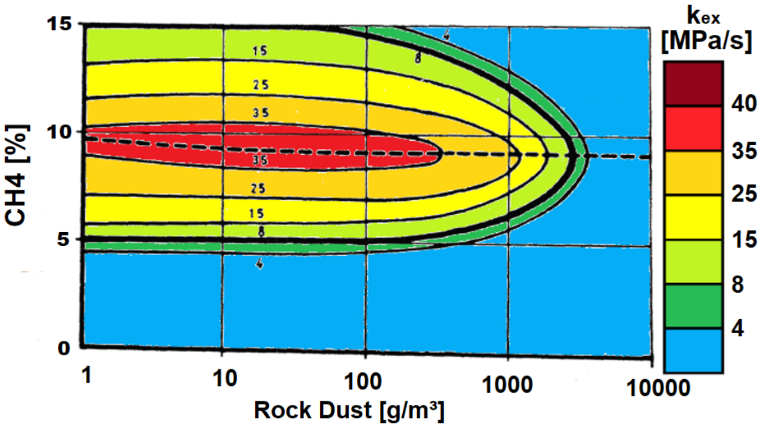

Figure 4.53.: Explosion intensity of methane with inert rock dust, taken from [149], p. 11, colors and legend added by the author

Another explanation, why small amounts of any dust enhance the flame propagation and thereby the (dp/dt) is given by Ivanov et. al. [150] who simulated the ignition of gas mixtures ahead of the flame front and identified a radiative preheating of suspended inert particles as a cause for this behavior: Because the gas is transparent the infrared radiation does not heat up the atmosphere around the ignition point. The solid particles are nontransparent, heat up and act as distant distributed ignition sources. Torrado et. al. come to the same conclusion with a numerical study of the combustion process of turbulent gas flames with nano-particles and both, combustible and non-combustible dusts [151]. That sole radiation may really be igniting distant dust clouds (though tested in slower time scales) has been investigated experimentally before [152].

The assumption also occured, that the dust simply slowes the injection process down. Since normally the injection process is finished after about 50 ms and the turbulence decays from this moment on, this prolonged injection process causes an ignition at a higher level of turbulence. This assumption was disproved by taking a closer look on the injection curves that did not show any differences for stoichiometric mixtures of 9.5 mol% methane with air and 0 g, 0.4 g, 0.8 g and 1.2 g of quartz sand (see figure 4.54).

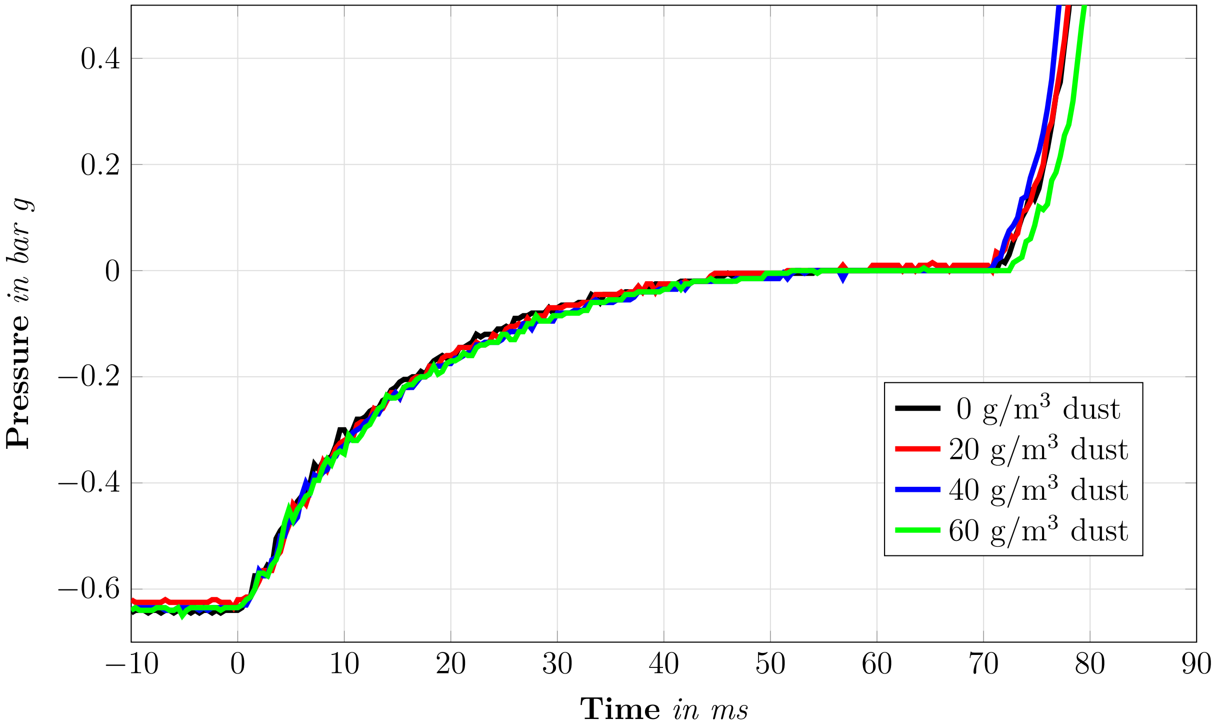

Figure 4.54.: Measured pressure of the injection process in ms after the first detectable pressure rise for different quartz sand dust concentrations

One other theory is, that the dust, being inert or not, causes the gas phase to react via different reaction mechanisms by catalytic effects or by playing the role of condensation kernel during soot formation. This was investigated by Torrado et. al. [153] for the hybrid dust gas mixtures of methane and carbon black by analyzing the combustion products.

Another explanation for this phenomenon could be, that the dispersed particles are spiking through the flame front and by further mixing and wrinkling of it cause a faster combustion. This theory was not investigated yet.

The whole effect of increasing the value of $(\mathrm{dp/dt})_{max}$ is often hidden by the scattering of the values, that is of the same magnitude and thus it takes several tests and averaging to clearly see this effect [128].
Lower values in research were obtained presumably because this maximum point is usually

at very low concentrations of the dust and the usual step-sizes are too coarse [27].
Higher values in research were obtained presumably because the hybrid mixture was compared to the non-turbulent gas mixture [14], different ignition sources were used or other experimental parameters were changed.

Furthermore, it was shown, that it is presumably not the combustion of the dust leading to higher values by conducting tests with a flammable gas and an inert dust, which showed the same effect. There are several assumptions why this is the case but for the implementation of safety measures, it does not matter, which of them is right.

5. International Round Robin Test

5.1. Approach and Objectives

An international round robin test on the determination of the explosion pressure and the rate of pressure rise for hybrid mixtures based on the SOP described in chapter 3.3.1 was organized. A mixture of methane and corn starch was used as reference system. Altogether eleven institutions participated in the round robin test (see also figure 5.1):

- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin, Germany
- Physikalisch Technische Bundesanstalt (PTB), Braunschweig, Germany
- Otto von Guericke University, Magdeburg, Germany
- INERIS, Verneuil-en-Halatte, France
- Université de Lorraine, Nancy, France
- Adinex NV, Herentals, Belgium
- Technicka Univerzita, Ostrava, Czech Republic
- GIG Research Institute, Mikołów, Poland
- Simtars Sponcom, Redbank, Australia
- Northeastern University, Shenyang, P. R. China
- EnvSafe Test, Suzhou, P. R. China

Figure 5.1.: Map with the facilities involved in the round robin test (CC BY-SA 3.0 `https://commons.wikimedia.org/wiki/User:Alexrk2`, image cut and marked by the author)

The objectives of this round robin test were to identify the international interest on such a new standardized procedure and to determine the reproducibilty of the test procedure by comparing the results of the different test facilities.
For gases a scattering of less than 10 % for p_{max} and $(dp/dt)_{max}$ is valid according to the European standard [43]. The scattering of the reference values given in this standard is in the range between 2.3 % and 20 % for p_{max} and 3.1 % and 6.8 % for $(dp/dt)_{max}$ [43].
For dusts no statements about the scattering were found. A deviation of 10 % for p_{max} is allowed in the European standard [45]. The allowed deviation for the $(dp/dt)_{max}$-values of dusts is decreasing with higher values in the European standard (see figure 5.2). In the

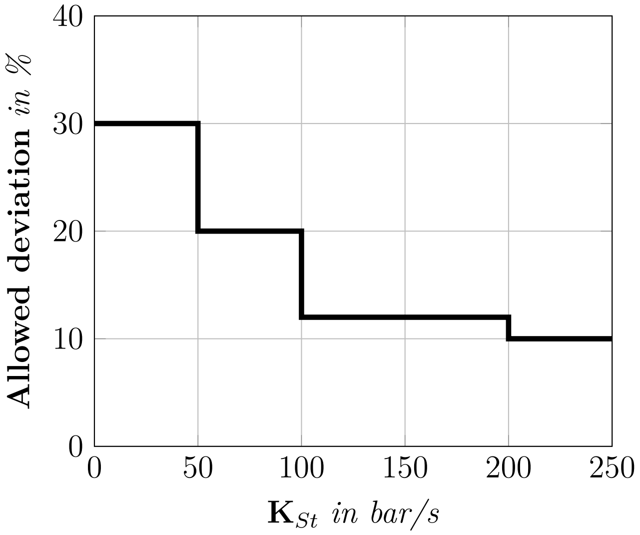

Figure 5.2.: Allowed deviation of $(dp/dt)_{max}$ for dusts according to the European standard [46]

American standard for dusts a deviation is allowed up to 10 % for the value of p_{pax} and 20 % for $(dp/dt)_{max}$ [57].

5.2. Test procedure and specifications

Shortly before the dispatch of the dust samples the moisture content was measured. Afterwards the dust was filled in bottles and sealed. The receiving facilities were asked to open the dust samples shortly before conducting the hybrid explosion tests and to check for the moisture content again. The moisture content tested at BAM over the whole time of the round robin was between 7 weight% and 8 weight% (for details see Appendix D). Methane with a purity of higher than 99.9 mol% had to be procured by the participating facilities.
All facilities participating in the round-robin test were asked to determine the leakage-rate as well as the Post-injection pressure drop (PIPD, see chapter 3.2.2) and to confirm the accuracy of the gas mixtures by gas analysis prior to the tests. The leakage rate of three facilities is displayed in figure 5.3, one handed in first results and had to adjust the sphere and the connections until it was tight.
The leakage-rate was determined by evacuating the 20L-sphere to 100 mbara. Afterwards all valves were closed and the pressure was recorded for at least 10 minutes. A maximum leakage-rate of 1 mbar/min was allowed. If the leakage-rate was higher, the test vessel had to be tightened before starting the tests (see 4.2.1).

Altogether three tests had to be carried out to determine the PIPD and to carry out gas analysis. In the tests the gas mixtures were prepared in the test vessel without dust injection

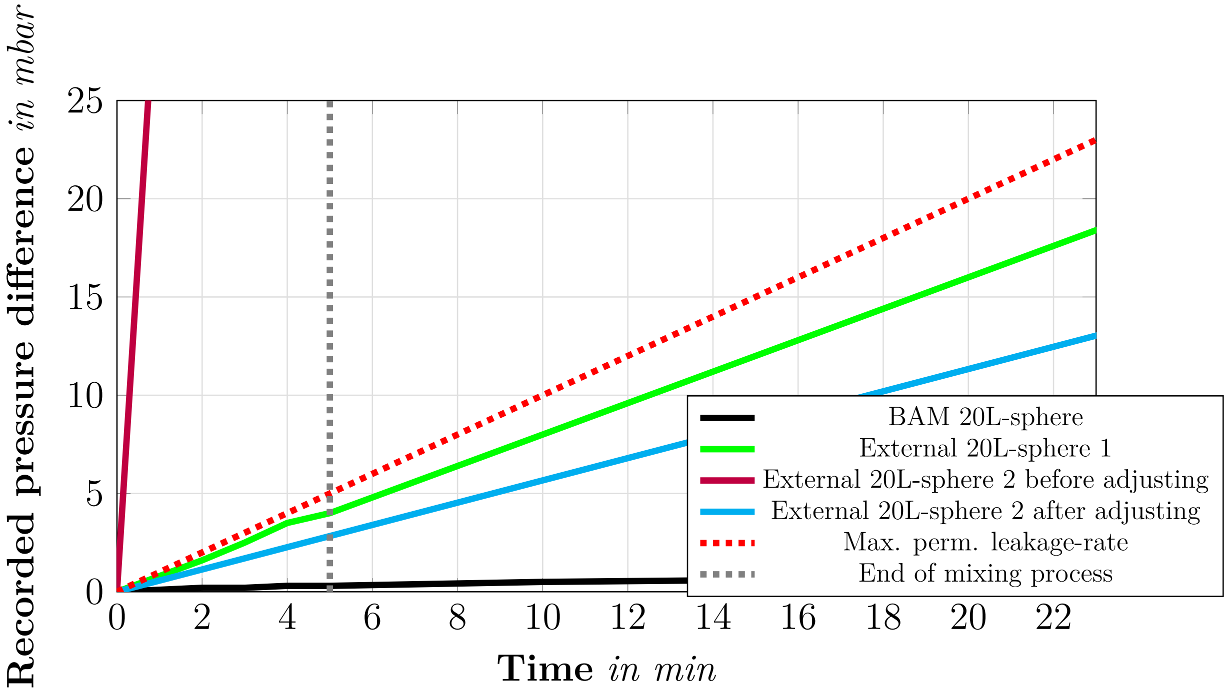

Figure 5.3.: Measured pressures inside three 20L-spheres, beginning pressures all set to 0 for a better comparison

and without ignition source. The pressure was recorded for at least three minutes after the injection process to determine the post-injection pressure drop. Then, the gas was pumped from the test vessel to a gas analyzer and the difference between the aimed fraction of gas and the obtained fraction was calculated. If the mean deviation was less than 0.2 mol% the round robin tests could start. If not, the calculation of the gas fraction had to be adjusted with that value and three more tests had to be conducted.

The explosion tests were conducted according to the standard operating procedure described in 3.3.1. The starting pressure in the test vessel before injection of the dust sample had to be 400 mbara ± 2 mbar, the pre-ignition pressure rise had to be kept constant at 0.64 bar ± 0.02 bar and the ignition source was two 1kJ chemical igniters. The tested gas fractions were 0 mol% (pure dust), 3 mol% and 9 mol%. The dust concentrations tested for each of these gas fractions were 0 g/m^3, 20 g/m^3, 60 g/m^3, 125 g/m^3, 250 g/m^3, 500 g/m^3, 750 g/m^3 and 1 000 g/m^3. The ignition delay time was constant with 60 ms for the 20L-sphere and 600 ms for the 1 m^3 vessel.

The type of gas-analyzer, the type and number of pressure sensors, the quality of the air (pressurized or synthetic air) and the type of nozzle were not specified.

5.3. Results and Discussion

The presented values for the explosion pressures were corrected with the equations 2.1 and 2.2 according to EN 14034-1 [45] and ASTM 1226 [57].

The results from all the test facilities were averaged, if several results were sent for one point according to the dust standards. For all the test points the results from all the facilities were averaged and the highest deviation was calculated. No outliers were excluded.

The results for p_{max} for 3 mol% of methane from the different facilities are shown in figure 5.4. The deviation between the different facilities is small for the highest values but for the determination of the LEL (respectively the MEC) this procedure seems to have too many degrees of freedom: For 3 mol% of methane and 20 g/m^3 corn starch half of the institutions detected an explosion, one with an explosion pressure of 5 barg, while the other half could not measure explosions (p_{ex} being under 0.3 barg). One facility even detected a very slight explosion with a p_{ex} of 0.5 barg with no dust at all.
However, for the aimed characteristic p_{max} this method showed comparable results with a deviation of less than 10 %.

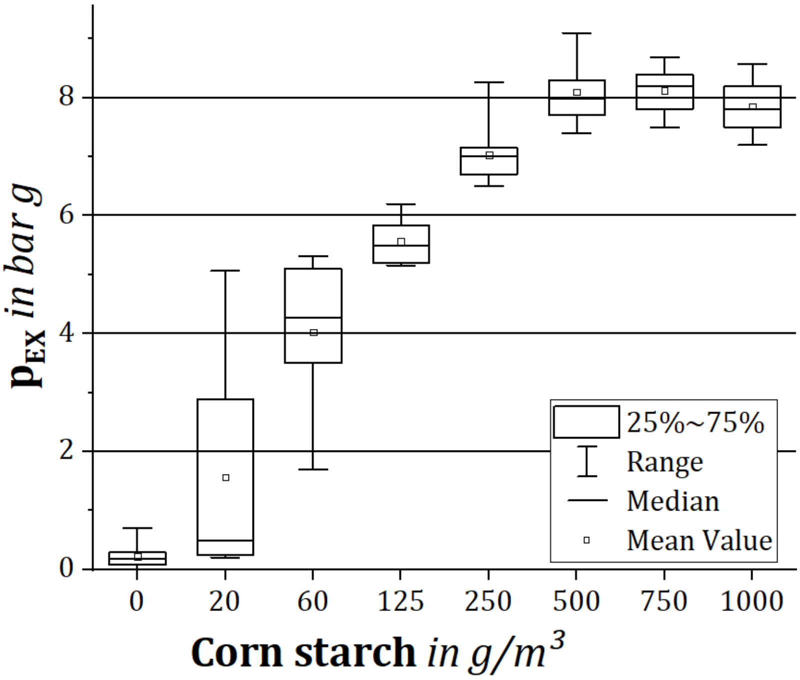

Figure 5.4.: Explosion pressures of corn starch with 3 mol% methane

The results for (dp/dt) for 3 mol% of methane from the different facilities are shown in figure 5.5. The maximum deviation from the mean value between the different facilities is less than 20 % for the highest values. The highest values were also obtained by all facilities at the same concentration of 750 g/m^3 or one step up or down. This could be an effect of different distribution systems, that were not specified in the operating procedure.

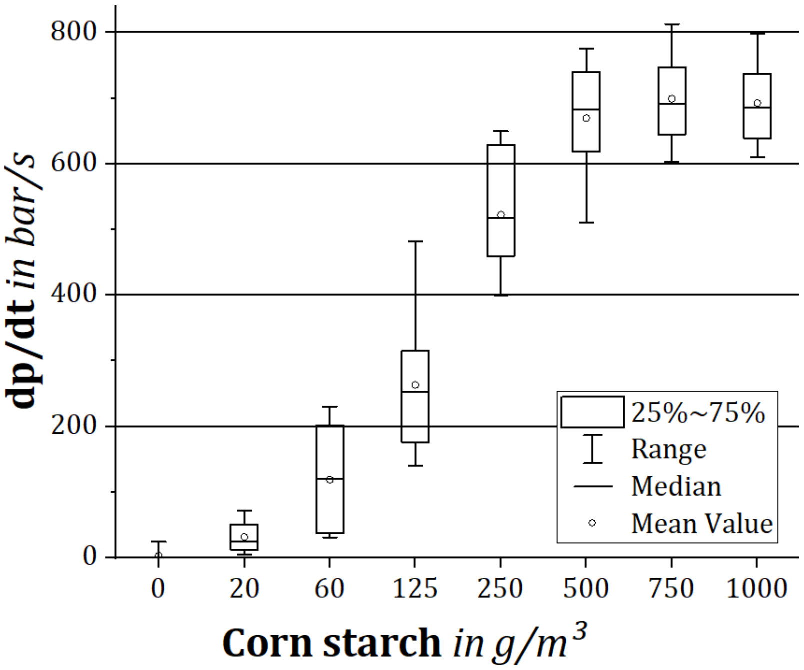

Figure 5.5.: Rate of pressure rise of corn starch with 3 mol% methane

The results for p_{ex} for 9 mol% of methane from the different facilities are shown in figure 5.6. The maximum deviation from the mean value for all tested concentrations was less than 11 % and thus lower than for p_{ex} tested at 3 mol% methane with an increasing tendency with increasing dust concentration (below 5 % with no dust, 9 mol% with 60 g/m^3 and 11 % with 1000 g/m^3). It should also be mentioned, that the values for p_{max} determined by all test facilities are below the values of the dust tested alone.

The results for (dp/dt) for 9 mol% of methane from the different facilities are shown in figure 5.7. Except for one facility all measured the highest value of (dp/dt) with small amounts of dust added. This exception occurred at a facility with a self-written testing program and could be caused by one or more of the following reasons:

- This facility took synthetic air with 20 mol% oxygen and 80 mol% nitrogen
- The effect is with 10 % about the same magnitude as the scattering and thereby hard to spot anyways
- The ignition delay time is defined on an event-basis in the different standards and could have an impact, if it is implemented otherwise [1]

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[1] The ignition delay time is defined as the time between the first measurable pressure rise inside the sphere until activation of the ignition source (ASTM 1226, EN 14034-series). This event-based definition is often misunderstood as the time between activation of the fast-acting valve and activation of the ignition source (descriptive definition). Since the ignition source takes 0-10 ms to ignite and the fast-acting valve takes 20-50 ms to open this is the main source of error if equipment is self-built.

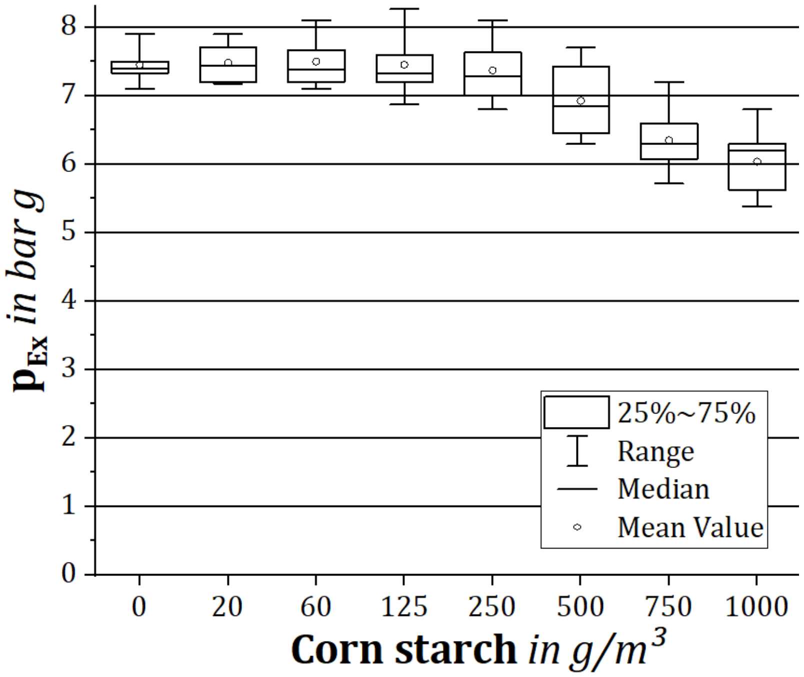

Figure 5.6.: Explosion pressures of corn starch with 9 mol% methane

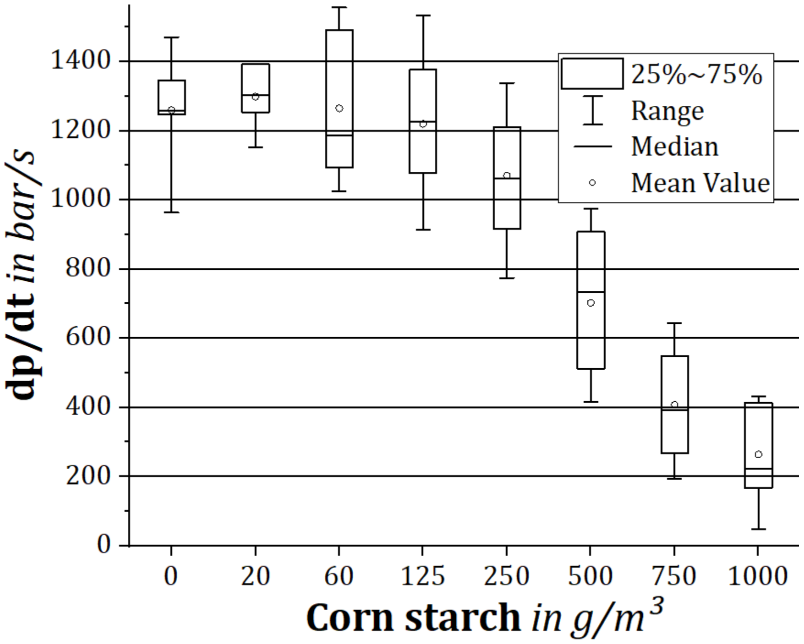

Figure 5.7.: Highest rate of pressure rise of corn starch with 9 mol% methane

However, the highest points were still within two steps apart from each other at the very fine scale (it shall be pointed out, that the x-Axes in figure 5.4 to 5.7 are not linear). The decreasing value for p_{Ex} with increasing fuel gas fraction may be an effect of the decreasing amount of oxygen in the vessel.

All results are summarized in table 5.1. All in all it was found that the maximum deviation from the average values of p_{max} and $(dp/dt)_{max}$ were not higher for the hybrid mixtures than for the dust alone with 0 mol% of methane. Thus it was concluded that the applied test procedure is appropriate for determining the explosion characteristics of hybrid mixtures.

Table 5.1.: Overall results for the different concentrations of methane and corn starch

	$(dp/dt)_{max}$ *in bar/s*		**p_{max}** *in bar g*	
0 mol% methane	540 ± 120	± 22 %	8.5 ± 0.7	± 8 %
3 mol% methane	693 ± 105	± 15 %	8.2 ± 0.7	± 9 %
9 mol% methane	1380 ± 240	± 17 %	7.6 ± 0.7	± 9 %

5.4. Remarks and conclusions for the round robin test

This round robin test is a first step to a standard for the determination of the safety characteristics of hybrid dust gas mixtures. Since there has never been a comparison between different facilities on the same mixtures it was proven for the first time, that it is possible to obtain comparable results, if many of the test parameters are narrowed. For example the type of the ignition source and the ignition energy were the same for all test facilities and with that this influencing parameter was excluded.

This round robin test also showed, that the measurement of the gas fraction is a crucial step, when testing hybrid mixtures: Some facilities had deviations of more than 2 mol% performing the pre-tests what would lead to the determination of highly flawed safety characteristics. The calculation of the gas fraction by the partial pressure of the gas, especially when the beginning pressure is estimated to be 1 bara leads to deviations of more than 1 mol%. This step has not been undertaken by any research facility so far and might be the decisive factor for the reproducibility of the results.

Some of the following parameters that were not specified yet might be narrowed or stated at all in the upcoming standard:

- Pressurized air and no synthetic air (or describing it further with the amount of oxygen and oil-free)
- Distribution system and nozzle type
- Vessel temperature
- Length and thickness of the connecting pipes for the admixture of gas
- Leakage-rate
- Gas analyzing system

However, taking into account that all the parameters for the determination of the safety characteristics of hybrid mixtures of gases and dusts have an impact, the deviation observed in the tests is reasonable being of the same magnitude as the variation that is stated in the standards for dusts. This round robin proved, that the operating procedure is feasible and accurate enough to obtain reproducible results.

6. Conclusions

6.1. Key Findings

The influence of the ignition source on the safety chararcteristics of hybrid mixtures was investigated systematically in this thesis. The key findings are presented in this section.

The chemical igniters and the exploding wire are suitable ignition sources for the determination of safety characteristics of hybrid mixtures. Their ignition energy is high enough to ignite dusts with higher minimum ignition energies and they can be triggered quick enough to avoid sedimentation of the injected dusts before ignition.
As a first step four different ignition sources, chemical igniter, surface-gap spark, induction spark and exploding wire, were compared and their main features evaluated on suitability for the determination of safety characteristics of hybrid mixtures. Special focus was on the ignition energy, the burning duration and their combination, the power. Because of its low ignition energy and since the timing of the activation of the ignition source influences the safety characteristics significantly the induction spark was dismissed for further tests. The surface gap-spark was also not further investigated because of its low ignition energy and because of its burning duration, that might be too short to ignite dusts.

The partial pressure method works for mixing hybrid mixtures but the pressures should be measured very accurately and the amount of gas should be validated by gas analysis.
There are three different ways of mixing hybrid mixtures in the 20L-sphere: With premixtures having the same gas amount in the 20L-sphere and in the dust container, with a higher amount of gas inside the 20L-sphere and only air in the dust container or with air inside the 20L-sphere and a higher amount of gas inside the dust container before the injection process. So far they were used interchangeably in other works and it was not proven, if the mixing has been complete after the injection. The amount of gas was not validated for any method with the 20L-sphere before.
It was shown, that the mixing method has no influence on the test results concluding that homogeneous mixtures are present after the short time of 60 ms between injection of the dust and ignition. But the gas amount has to be calculated with a more sophisticated equation than using only the ratios of the partial pressures measured with the default equipment of the 20L-sphere. The heating and cooling that is caused by the compression while injecting the dust must be taken into account. Moreover it was shown that the accuracy of the gas composition can be increased clearly by a correction based on gas analysis tests.

The pre-ignition pressure rise must be kept constant by variation of the pressure in the dust chamber and used for the calculation of the gas amount.
For obtaining reproducible test results the injecting pressure has to be adjusted depending on the type and amount of dust injected and the pressure rise has to be kept constant throughout all tests. If not kept constant it influences the gas fraction, the maximum explosion pressure, the (dp/dt)-value and the dust concentration.

The chemical igniters and exploding wires produce comparable results for the determination of maximum explosion pressure, lower explosion limit and maximum rate of pressure rise of gases under turbulence. For lower oxygen concentration only exploding wires with two times 1 kJ work.
Only a very slight influence of the type of ignition source on the p_{Max} and $(dp/dt)_{max}$ was found. Both safety characteristics for methane were investigated with chemical igniters of two times 1 kJ and exploding wires of two times 100 J and two times 1 kJ. The differences were neglectable.
The exploding wire and the chemical igniters were further investigated and the results of ignitions of gases under turbulence were compared.
It was possible to determine the lower explosion limit of hydrogen under turbulence with chemical igniters of two times 1 kJ and with exploding wires with two times 1 kJ and two times 100 J. When the energy was lowered to two times 10 J only 2 of 5 tests showed an ignition. So this low energy might produce unsafe results.
The limiting oxygen concentration of methane under turbulence was only clearly detectable with exploding wires of two times 1 kJ obtaining similar results to the literature values measured at quiescent conditions. With chemical igniters the ignition criterion was slightly exceeded but small variations of the experimental parameters might have resulted in "false negatives" and with that to unsafe safety characteristics. A clear pressure increase was not detected until the literature value was exceeded by 3 mol%. Lower ignition energies of the exploding wire also resulted in higher and and thus more critical values compared to the literature value determined under quiescent conditions.

The maximum explosion pressure of hybrid mixtures usually corresponds with the highest maximum explosion pressure of the single substances.
Three different combustible dusts and an inert dust were tested with methane over a wide range of concentrations. If the p_{max} of the combustible dust exceeded the one from methane this was also the maximum obtained value for the hybrid system, if it was lower the value for methane was the highest one. With the inert dust the highest value was also the same as for methane alone. For hybrid systems with components that are able to react with each other deviations might occur.

The chemical igniters and exploding wires produce comparable results for the determination of maximum explosion pressure and maximum rate of pressure rise of dusts if the ignition energy is kept constant. Decreasing the ignition

energy does not affect the maximum explosion pressure and maximum rate of pressure rise.
The maximum rate of pressure rise and the maximum explosion pressure of corn starch were investigated with chemical igniters of two times 1 kJ and two times 5 kJ and exploding wires of two times 10 J, two times 100 J and two times 2 kJ. The differences on the maximum rate of pressure rise and the maximum explosion pressure were neglectable[1].

The exploding wires with an overall energy of 2 kJ produces values, that match literature values for the limiting oxygen concentrations of hybrid mixtures.
The limiting oxygen concentration was determined for methane gas and for corn starch with different ignition energies of the exploding wire and with chemical igniters. The clearest pressure rise above the ignition criterion inside the explosion region was obtained with the exploding wires with two times 1 kJ. The chemical igniters however produced comparable results and were 1 mol% higher or the same when tested on hybrid mixtures. The weak rise inside the explosion region and the slightly higher values may arise from the fact, that the chemical igniters need oxygen themself to burn.
The reduction of the ignition energy produced LOC-values that were 2 mol% to 6 mol% higher and with that unsafe. A reduction is not recommended.

The maximum rate of pressure rise of hybrid mixtures is about 10 % to 25 % higher than the value of the stoichiometric gas mixture under turbulence. The maximum rate of pressure rise of the hybrid system is usually found at the stoichiometric gas fraction with very little amounts of dust.
For all tested dusts including the inert gas the maximum rate of pressure rise was found around 9 mol% of methane with dust concentrations of 20 g/m^3 or 30 g/m^3. These concentrations are lower than the concentrations that are tested usually according to the standard procedures for dusts ([45], [46], [57], [47], [59]). This corresponds with the findings from other researchers who tested hybrid mixtures at these concentrations.

A standardized test method for the determination of safety characteristics of hybrid mixtures was developed and internationally tested in 11 facilities in 7 countries. The results were comparable within a reasonable range concluding that the applied standard operating procedure delivers reproducible test results for the determination of explosion characteristics of hybrid mixtures.
An operating procedure was developed and dust samples were sent to test facilities in Germany, France, Belgium, Czech Republic, Poland, Australia and China. This round robin test proved the test procedure that will now be implemented in the standard. It also showed the reliability and reproducibility of safety characteristics of hybrid mixtures.

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[1] The lower explosion limit changed from 60 g/m^3 using 2 kJ as overall energy (for both, exploding wires and chemical igniters) over 125 g/m^3 using 200 J to 250 g/m^3 with 20 J. With chemical igniters of two times 5 kJ it would depend on the ignition criterion whether the lower explosion limit is 20 g/m^3 or 125 g/m^3: According to the German criterion it would be counted as ignition, according to the American standard not (see Appendix E.8)

6.2. Alternative ignition source for the determination of explosion characteristics

The exploding wire is a suitable ignition source for hybrid dust gas mixtures. It has an adjustable energy output and a defined burning duration with a precisely triggerable start. This makes it the perfect ignition source concerning the decay of turbulence in the 20L-sphere.
Comparable tests with dusts and gases were performed and showed, that no difference was observed between two 1 kJ chemical igniters and two 1 kJ exploding wires.
It is possible to use it for many kinds of dusts except for metal dusts since the conductivity of these dusts influence the resistivity of the arc.

Two features that have not been discussed before, because they are not technical but financial and legal, are worth mentioning: Once the exploding wire ignition device is built it has almost no costs what might help poorer countries to found their own safety companies and perform tests to determine the safety characteristics of dusts and hybrid mixtures. With the standard chemical igniters, in the moment the determination is rather expensive, even for German or American companies.
Another aspect is, that the igniters stated in the dust standard are not allowed at all in some countries including China and India or very hard to obtain. In Brazil the military has to deliver them making one facility in Sao Paulo the only one in whole South America determining safety characteristics of dusts in the 20L-sphere. In Australia the delivery is comparably complicated with changing policies. With the exploding wire these problems don't occur. It is also rather simple (see figure 6.1) to built if the components are all tested (which they have been now).

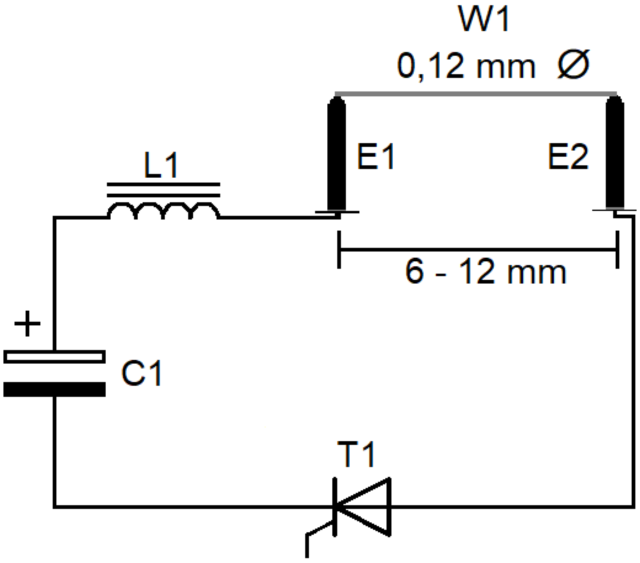

Figure 6.1.: Schematic of a precisely triggerable exploding wire device

6.3. Outlook

Many problems of the single-substance standards had to be investigated before going on with the hybrid mixtures. The following topics may give an overview of what has been initiated as an outcome of this thesis:

- A standard on the determination of the maximum explosion pressure and the maximum rate of pressure rise of hybrid dust gas mixtures has been developed and will soon be published
- Narrowing the values for the PIPR in the European and in the American standards for the determination of safety characteristics of dusts has been initiated
- A recurring international round robin test on hybrid dust gas mixtures

Additionally several topics have been identified that should be investigated further. Some are already being investigated as a result of this work, some myths still have to be enlightened and other joint research projects have been initiated:

- A standardized procedure for the determination of safety characteristics of hybrid vapor dust mixtures is initiated with an international round robin test
- A criterion for the applicability of the exploding wire igniter for dusts with low electrical resistance (especially metals) will soon be developed
- The implementation of the exploding wire in the dust standard has been taken into account
- A round robin test with the exploding wire as ignition source will be initiated
- An international joint research on the newly implemented mushroom-cup-nozzle in the European standard for dusts respectively on new methods to inject higher amounts of dust than usual or dusts, that can not be injected because of their poor conveying properties (long, edgy) has been initiated
- An investigation on the correction equation 6.1 for the maximum explosion overpressure of dusts has been initiated with the PTB (Germany), BAM (Germany), the University of Bratislava (Slovakia) and the University of Ostrava (Czech Republic)

  $$p_{Ex}[barg] = 0.775 * p_{Ex,20L}^{1.15}[barg] \tag{6.1}$$

  It seems, that if the beginning pressures at the moment of ignition in the 20L-sphere and the 1m^3 chamber are the same, the explosion pressures are also the same and that the lower explosion pressures, that were measured in the past in the 20L-sphere were casued by these differing pressures and not by heat losses.

References

[1] ISO. ISO 6184-3: Explosion Proteciton Systems - Determination of explosion indices of fuel-air mixtures other than dust-air and gas-air mixtures. International Qrganization for Standardization, 1985.

[2] Faraday, M. and Lyell, C. Explosions in Coal Mines. *Philosophical Magazine and Journal of Science*, 1844.

[3] Galloway, W. On the Influence of Coal-Dust in Colliery Explosions. *Proceedings of the Royal Society of London*, 24(164-170), 1876. DOI: 10.1098/rspl.1875.0047.

[4] Engler, C. Einfacher Versuch zur Demonstration der gemischten Kohlenstaub- und Gasexplosionen. *Chemiker-Zeitung*, 1907.

[5] Engler, C. Beiträge zur Kenntnis der Staubexplosionen. *Chemische Industrie*, pages 171–173, 1885.

[6] Abel, F. A. Some of the Dangerous Properties of Dusts. *Nature*, 1882.

[7] Rice, G. S. Notes on the prevention of dust and gas explosions in coal mines. Bureau of Mines, 1913.

[8] Walter, T. *Die Kohlenstaubfrage bei Schlagwetter-Explosionen.* Walther & Apolant, 1887.

[9] Siwek, R. 20-L-Laborapparatur für die Bestimmung von Explosionskenngrößen brennbarer Stäube. Master's thesis, Technikum Winterthur Ingenieurschule, 1977.

[10] Singer, J. M. Ignition of coal dust-methane-air mixtures by hot-turbulent-gas jets. Bureau of Mines, 1964.

[11] Pellmont, G. *Explosions- und Zündverhalten von hybriden Gemischen aus brennbaren Stäuben und Brenngasen.* PhD thesis, Eidgenössische Technische Hochschule Zürich, 1979.

[12] Ishihama, W., Takagi, H., and Enomoto, H. Explosion characteristics of coal dust-methane-air mixture. *international conference on scientific research in the field of safety at work in mining industry*, 1979.

[13] Schuber, G. M. *Zünddurchschlagverhalten von Staub/Luft- und hybriden Gemischen durch enge Spalte.* PhD thesis, ETH Zürich, 1987.

[14] Khalil, Y. F. Experimental investigation of the complex deflagration phenomena of hybrid mixtures of activated carbon dust/hydrogen/air. *Journal of Loss Prevention in the Process Industries*, 26(6):1027–1038, 2013. DOI: 10.1016/j.jlp.2013.03.006.

[15] Jiang, J., Liu, Y., and Mannan, M. S. A correlation of the lower flammability limit for hybrid mixtures. *Journal of Loss Prevention in The Process Industries*, 2014. DOI: 10.1016/j.jlp.2014.07.014.

[16] Bartknecht, W. Explosionsablauf und Bekämpfungsmaßnahmen bei Staub- und Gasexplosionen in Behältern und Rohren. *Chemieingenieur Technik*, 1975.

[17] Denkevits, A. Explosibility of hydrogen–graphite dust hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 20(4):698–707, 2007. DOI: 10.1016/j.jlp.2007.04.033.

[18] Denkevits, A. and Hoess, B. Hybrid H2/Al dust explosions in Siwek sphere. *Journal of Loss Prevention in the Process Industries*, 36:509–521, 2015. DOI: 10.1016/j.jlp.2015.03.024.

[19] Cheng, M.-H. and Rosentrater, K. A. Economic feasibility analysis of soybean oil production by hexane extraction. *Industrial Crops & Products*, 2017. DOI: 10.1016/j.indcrop.2017.07.036.

[20] Cheng, Y.-F., Song, S.-X., Ma, H.-H., Su, J., Han, T.-F., Shen, Z.-W., and Meng, X.-R. Hybrid H2/Ti dust explosion hazards during the production of metal hydride TiH2 in a closed vessel. *International Journal of Hydrogen Energy*, 2019. DOI: 10.1016/j.ijhydene.2019.02.189.

[21] Pilao, R., Ramalho, E., and Pinho, C. Explosibility of cork dust in methane/air mixtures. *Journal of Loss Prevention in the Process Industries*, 19(1):17–23, 2006. DOI: 10.1016/j.jlp.2005.05.001.

[22] Bergthorson, J. M. Recyclable metal fuels for clean and compact zero-carbon power. *Progress in Energy and Combustion Science*, 2018. DOI: 10.1016/j.pecs.2018.05.001.

[23] Spreitzer, D. and Schenk, J. Reduction of Iron Oxides with Hydrogen. *steel research international*, 2019. DOI: 10.1002/srin.201900108.

[24] ZEMA. 1994-07-09 Explosion eines Staub- / Luftgemisches mit Folgebrand. Resopal, 1994.

[25] Ausschuss für Gefahrstoffe (AGS). TRGS 722 - Vermeidung oder Einschränkung gefährlicher explosionsfähiger Gemische, 2021.

[26] Bartknecht, W. *Untersuchung des Explosions- und Zündverhaltens brennbarer Stäube und hybrider Gemische.* Ciba-Geigy AG, 1985.

[27] Wang, Y., Qi, Y., Gan, X., Pei, B., Wen, X., and Ji, W. Influences of coal dust components on the explosibility of hybrid mixtures of methane and coal dust. *Journal of Loss Prevention in the Process Industries*, 67, 2020. DOI: 10.1016/j.jlp.2020.104222.

[28] Dufaud, O., Perrin, L., and Traoré, M. Dust/vapour explosions: Hybrid behaviours? *Journal of Loss Prevention in the Process Industries*, 21(4):481–484, 2008. DOI: 10.1016/j.jlp.2007.11.005.

[29] Krause, U., Addai, E. K., and Gabel, D. Determination of the limiting oxygen concentration of dust / air and hybrid mixtures based on thermochemical ... Determination of the limiting oxygen concentration of dust / air and hybrid mixtures based on thermochemical properties. In *11th ISHPMIE*, 2016.

[30] Addai, E., Clouthier, M., Amyotte, P., and Krause, U. Limiting oxygen concentration of hybrid mixtures. In *Global Congress on Process Safety 2017 - Topical Conference at the 2017 AIChE Spring Meeting and 13th Global Congress on Process Safety*, volume 3, 2017.

[31] Ji, W.-t., Gan, X.-y., and Li, L. Prediction of the explosion severity of hybrid mixtures. *Powder Technology*, 2022. DOI: 10.1016/j.powtec.2022.117273.

[32] Chatrathi, K. Dust and hybrid explosibility in a 1 m3 spherical chamber. *Process Safety Progress*, 1994. DOI: 10.1002/prs.680130403.

[33] Kuracina, R., Szabová, Z., and Škvarka, M. Study into parameters of the dust explosion ignited by an improvised explosion device filled with organic peroxide. *Process Safety and Environmental Protection*, 2021. DOI: 10.1016/j.psep.2021.09.011.

[34] Kuracina, R., Szabova, Z., Kosar, L., and Sahul, M. Study into influence of different types of igniters on the explosion parameters of dispersed nitrocellulose powder. *Journal of Loss Prevention in the Process Industries*, 83, 2023. DOI: 10.1016/j.jlp.2023.105017.

[35] Kuna, P., Pelikan, V., and Janovsky, B. Igniter burning time in dust explosion measurements. In *Work in Progress Poster - 14th International Symposium on Hazards, Prevention and Mitigation of Industrial Explosions*, 2022.

[36] Bernard, S., Lebecki, K., Gillard, P., Youinou, L., and Baudry, G. Statistical method for the determination of the ignition energy of dust cloud-experimental validation. *Journal of Loss Prevention in the Process Industries*, 2010. DOI: 10.1016/j.jlp.2010.01.006.

[37] Bernard, S., Gillard, P., Foucher, F., and Mounaïm-Rousselle, C. MIE and flame velocity of partially oxidised aluminium dust. *Journal of Loss Prevention in the Process Industries*, 2012. DOI: 10.1016/j.jlp.2011.11.013.

[38] Bernard, S., Gillard, P., and Frascati, F. Ignition and explosibility of aluminium alloys used in Additive Layer Manufacturing. *Journal of Loss Prevention in the Process Industries*, 2017. DOI: 10.1016/j.jlp.2017.04.014.

[39] El-Zahlanieh, S., Sivabalan, S., Tribouilloy, B., Benoit, T., Brunello, D., Vignes, A., and Dufaud, O. Lifting the Fog Off Hydrocarbon Mist Explosions. In *AIChE Spring Meeting - Global Congress on Process Safety (GCPS)*, 2021.

[40] PTB. chemsafe.ptb.de. Slightly differing values for pmax of methane because of different sources, checked on 22nd of February 2022.

[41] GESTIS-Stoffdatenbank. Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (DGUV). Online-Database, 2022. https://gestis.dguv.de/.

[42] EN 1839:2017. Bestimmung der Explosionsgrenzen von Gasen und Dämpfen und Bestimmung der Sauerstoffgrenzkonzentration (SGK) für brennbare Gase und Dämpfe. CEN, April 2017.

[43] EN 15967:2011. Verfahren zur Bestimmung des maximalen Explosionsdruckes und des maximalen zeitlichen Druckanstieges für Gase und Dämpfe. CEN, October 2011.

[44] ASTM. 2079 Standard Test Methods for Limiting Oxygen (Oxidant) Concentration in Gases and Vapors. American Society for Testing and Materials, 2000.

[45] EN 14034 - 1. Determination of explosion characteristics of dust clouds - part 1: Determination of the maximum explosion pressure pmax of dust clouds. CEN, 2011.

[46] EN 14034 - 3. Determination of explosion characteristics of dust clouds - part 3: Determination of the lower explosion limit lel of dust clouds. CEN, 2011.

[47] EN 14034 - 4. Determination of explosion characteristics of dust clouds - part 4: Determination of the limiting oxygen concentration loc of dust clouds. CEN, 2011.

[48] Wagner, H. G. and Steen, H. *Handbuch des Explosionsschutzes.* WILEY-VCH Verlag, 2000.

[49] Hüttenbrenner, K., Kern, H., and Raupenstrauch, H. Erarbeitung der Grundlagen für eine Prüfapparatur zur Bestimmung der Flammengeschwindigkeit in Staub-Luft-Gemischen. *BHM Berg- und Hüttenmännische Monatshefte*, 165:329–333, 2020. DOI: 10.1007/s00501-020-00954-7.

[50] Hüttenbrenner, K. U. *Flammenausbreitung in Großbehälterninnerhalb von Staub-Luft-Gemischen mitgeringer Anfangsturbulenz.* PhD thesis, Montanuniversität Leoben, 2020.

[51] ASTM 1515. Standard Test Method for Minimum Explosible Concentration of Combustible Dusts. American Society for Testing and Materials, 2007.

[52] ASTM. E2931: Standard Test Method for Limiting Oxygen (Oxidant) Concentration of Combustible Dust Clouds. American Society for Testing and Materials, 2013.

[53] Askar, E. and Schröder, V. The influence of strong ignition sources on the explosion and decomposition limits of gases. *Chemical Engineering Transactions*, 75, 2019. DOI: 10.3303/CET1977022.

[54] Mynarz, M., Lepík, P., and Melecha, J. Behaviour of selected flammable gas mixtures. In *Proceedings of the 2nd Czech-China Scientific Conference*, 2016.

[55] Holtappels, K. SAFEKINEX Del. No 2. Bundesanstalt für Materialforschung und -prüfung, 2002.

[56] Kuai, N., Huang, W., Du, B., Yuan, J., Li, Z., Gan, Y., and Tan, J. Experiment-based investigations on the effect of ignition energy on dust explosion behaviors. *Journal of Loss Prevention in the Process Industries*, 2013. DOI: 10.1016/j.jlp.2013.03.005.

[57] ASTM. 1226 – 12a - Standard Test Method for Explosibility of Dust Clouds. American Society for Testing and Materials, 2012.

[58] DIN EN ISO/IEC 80079-20-2:2016-12. Explosive atmospheres – Part 20-2: Material characteristics – Combustible dusts test methods. International Standardization Organisation, 2016.

[59] EN 14034 - 2. Determination of explosion characteristics of dust clouds - part 2: Determination of the maximum rate of explosion pressure rise (dp/dt)max of dust clouds. CEN, 2011.

[60] Bartknecht, W. *Dust explosions, course, prevention, protection.* Berlin: Springer-Verlag, 1989.

[61] Bartknecht, W. Brenngas-und Staubexplosionen. Bundesinstitut für Arbeitsschutz, 1971.

[62] Bartknecht, W. *Explosionen, Ablauf und Schutzmassnahmen.* Berlin, Springer-Verlag, 1978.

[63] Franke, H. Bestimmung der Mindestzuendenergie von Kohlenstaub/Methan/Luft Gemischen (hybride Gemische). *VDI-Berichte*, 1978.

[64] Rose, H. E. and Priede, T. Ignition Phenomena in Hydrogen-Air Mixtures. *7th Symposium (International) on Combustion*, 1958. DOI: 10.1016/S0082-0784(58)80076-4.

[65] Bane, S. P. M. *Spark Ignition: Experimental and Numerical Investigation with Application to Aviation Safety.* PhD thesis, California Institute of Technology, 2010.

[66] Shepherd, J. E., Krok, J. C., and Lee, J. J. Spark Ignition Energy Measurements in Jet A, Explosion Dynamics Laboratory Report FM97-9. National Transportation Safety Board, 2000.

[67] Cashdollar, K., Zlochower, I. A., Green, G. M., and Thomas, R. A. Flammability of methane, propane, and hydrogen gases. *Journal of Loss Prevention in the Process Industries*, 13, 2000. DOI: 10.1016/S0950-4230(99)00037-6.

[68] ASTM. ASTM E 918-19 - Standard Practice for Determining Limits of Flammability of Chemicals at Elevated Temperature and Pressure. American Society for Testing and Materials, 2019.

[69] ISO. EN 10156 - Gas cylinders – Gases and gas mixtures – Determination of fire potential and oxidizing ability for the selection of cylinder valve outlets. International Standardization Organisation, Beuth Verlag GmbH, 10772 Berlin, 2017.

[70] ASTM. ASTM E681 - 09(2015) Standard Test Method for Concentration Limits of Flammability of Chemicals (Vapors and Gases). American Society for Testing and Materials, 2009.

[71] EN 17624. Determination of explosion limits of gases and vapours at elevated pressures, elevated temperatures or with oxidizers other than air. CEN, 2021.

[72] Pellmont, G. Minimum ignition energy of combustible dusts and explosion behaviour of hybrid mixtures. In *3rd International Symposium on Loss Prevention and Safety Promotion in the Process Industries*, 1980.

[73] ISO. ISO 6184-1: Explosion Proteciton Systems - Determination of explosion indices of combustible dusts in air. International Standardization Organisation, 1991.

[74] Eisenhuth, H. Personal message from Hardy Eisenhuth. – with a fifth of the Energy the ignitors have a fifth of the firing charge, 2022.

[75] ASTM. E 789–95 (Reapproved 2001) Standard Test Method for Dust Explosions in a 1.2-Litre Closed Cylindrical Vessel. American Society for Testing and Materials, 2001.

[76] Filip, A. Elektrische Funken und explodierende Drähte als Zündquellen brennbarer Methan-Luftgemische. EMPA Bericht, 1982.

[77] Scheid, M., Kusche, C., Schröder, V., and Barth, U. Tests on Suitability of the Ignition Source “Exploding Wire” for the Determination of Explosion Characteristics of Combustible Dusts in the 20-L-Sphere. *chemical engineering transactions*, 31:703–708, 2013. DOI: 10.3303/CET1331118.

[78] Scheid, M., Kusche, C., Schröder, V., and Barth, U. Suitability of ignition source “Exploding Wire” for the determination of dust explosion characteristics in the 20-L-Sphere. *Journal of Loss Prevention in the Process Industries*, 26(6), 2013. DOI: 10.1016/j.jlp.2013.08.017.

[79] Cesana, C. and Siwek, R. *Manual for 20-l-Apparatus.* Cesana AG, Baiergasse 56, CH-4126 Bettingen, Switzerland, 7.1 edition, November 2020.

[80] Spitzer, S. H., Askar, E., Benke, A., Janovsky, B., Krause, U., and Krietsch, A. Influence of pre-ignition pressure rise on safety characteristics of dusts and hybrid mixtures. *FUEL*, 2022. DOI: 10.1016/j.fuel.2021.122495.

[81] Kalkert, N. Theoretische und experimentelle Untersuchungen der Explosionskenndaten von Mischungen aus mehreren gas- und staubförmigen Brennstoffkomponenten und Luft. Verein Deutscher Ingenieure, 1982.

[82] Amyotte, P. R., Mintz, K. J., Pegg, M. J., Sun, Y.-H., and Wilkie, K. I. Effects of methane admixture, particle size and volatile content on the dolomite inerting requirements of coal dust. *Journal of Hazardous Materials*, 27(2):187–203, 1991. DOI: 10.1016/0304-3894(91)80029-N.

[83] Amyotte, P. Personal message from Paul Amyotte on 13th of May 2021. – this method has not been used there since the mid-90s, 2021.

[84] Li, G., Yuan, C. M., Fu, Y., Zhong, Y. P., and B.Z.Chen. Inerting of magnesium dust cloud with Ar, N2 and CO2. *Journal of Hazardous Materials*, 2009. DOI: 10.1016/j.jhazmat.2009.04.121.

[85] Addai, E. K., Gabel, D., and Krause, U. Explosion characteristics of three component hybrid mixtures. *Process Safety and Environmental Protection*, 98:72–81, 2015. DOI: 10.1016/j.psep.2015.06.013.

[86] Amyotte, P., Lindsay, M., Domaratzki, R., Marchand, N., Di Benedetto, A., and Russo, P. Prevention and mitigation of dust and hybrid mixture explosions. *Process Safety Progress*, pages 17–21, 2009. DOI: 10.1002/prs.10333.

[87] Su, J., Cheng, Y., Song, S., Ma, H., Wang, W., Wang, Y., and Zhang, S. Explosion Characteristics and Influential Factors of Coal dust/sodium Chlorate Mixture on Basis of an Explosion Accident in China. *Combustion Science and Technology*, 193(8):1313–1325, 2019. DOI: 10.1080/00102202.2019.1689965.

[88] Garcia-Agreda, A., Di Benedetto, A., Russo, P., Salzano, E., and Sanchirico, R. Dust/gas mixtures explosion regimes. *Powder Technology*, 205(1):81–86, 2011. DOI: 10.1016/j.powtec.2010.08.069.

[89] Landman, G. V. R. *Ignition and initiation of coal mine explosions*. Dissertation, University of the Witwatersrand, 1992.

[90] Di Benedetto, A., Garcia-Agreda, A., Russo, P., and Sanchirico, R. Combined Effect of Ignition Energy and Initial Turbulence on the Explosion Behavior of Lean Gas/Dust-Air Mixtures. *Industrial & Engineering Chemistry Research*, 51(22):7663–7670, jun 2012.

[91] Li, H., Deng, J., Chen, X., Shu, C.-M., Kuo, C.-H., and XiangyuHu. Influence of ignition delay on explosion severities of the methane–coal particle hybrid mixture at elevated injection pressures. *Powder Technology*, 2020. DOI: 10.1016/j.powtec.2020.04.034.

[92] Janovsky, B., Skrinsky, J., Cupak, J., and Veres, J. Coal dust, Lycopodium and niacin used in hybrid mixtures with methane and hydrogen in 1 m and 20l chambers. *Journal of Loss Prevention in the Process Industries*, 62, 2019. DOI: 10.1016/j.jlp.2019.103945.

[93] Kundu, S. K., Zanganeh, J., Eschebach, D., and Moghtaderi, B. Confined explosion of methane-air mixtures under turbulence. *FUEL*, 323:95–102, 2018. DOI: 10.1016/j.powtec.2017.09.041.

[94] Ji, W., Yu, J., Yu, X., and Yan, X. Experimental investigation into the vented hybrid mixture explosions of lycopodium dust and methane. *Journal of Loss Prevention in the Process Industries*, 2018. DOI: 10.1016/j.jlp.2017.12.002.

[95] Cao, W., Qin, Q., Cao, W., Lan, Y., Chen, T., Xu, S., and Cao, X. Experimental and numerical studies on the explosion severities of coal dust/air mixtures in a 20-L spherical vessel. *Powder Technology*, 2017. DOI: 10.1016/j.powtec.2017.01.019.

[96] Zhao, P., Tan, X., Schmidt, M., Wei, A., Huang, W., Qian, X., and DejianWu. Minimum explosion concentration of coal dusts in air with small amount of CH4/H2/CO under 10-kJ ignition energy conditions. *FUEL*, 2020. DOI: 10.1016/j.fuel.2019.116401.

[97] Spitzer, S. 2020 - several personal E-mails. The authors from various articles, where the method wasn't mentioned or just referred to as "the partial pressure" method were contacted by the author. Three of them answered, stating that they used Method II, assuming that this was obvious, 2022.

[98] Pilao, R., Ramalho, E., and Pinho, C. Overall characterization of cork dust explosion. *Journal of Hazardous Materials*, 2006. DOI: 10.1016/j.jhazmat.2005.10.015.

[99] Hertzberg, M., Cashdollar, K. L., and Zlochower, I. A. Flammability limit measurements for dusts and gases: ignition energy requirements and pressure dependences. *Symposium (international) on Combustion*, 1988. DOI: 10.1016/S0082-0784(88)80258-3.

[100] Glarner, T. *Temperatureinfluss auf das Explosions- und Zündverhalten brennbarer Stäube.* PhD thesis, ETH Zürich, 1983.

[101] Holtappels, K. SAFEKINEX Del. No 8. Bundesanstalt für Materialforschung und -prüfung, 2002.

[102] Lazaro, E. C. and Torrent, J. G. Experimental research on explosibility at high initial pressures of combustible dusts. *Journal of Loss Prevention in the Process Industries*, 2000. DOI: 10.1016/S0950-4230(99)00047-9.

[103] Pascaud, J. M. and Gillard, P. Study of the propagation of kerosene explosions inside a partitioned vessel. *Journal of Loss Prevention in the Process Industries*, 2006. DOI: 10.1016/j.jlp.2005.05.005.

[104] Poletaev, N. L. A change in the air temperature inside a 20-liter chamber when air is added from the receiver. *Pozharovzryvobezopasnost/Fire and Explosion Safety*, 2021.

[105] Cashdollar, K. L. Coal dust explosibility. *Journal of Loss Prevention in the Process Industries*, 1996. DOI: 10.1016/0950-4230(95)00050-X.

[106] Skrbek, L. and Stalp, S. R. On the decay of homogeneous isotropic turbulence. *Physics of Fluids*, 2000. DOI: 10.1063/1.870447.

[107] Dahoe, A. E., Cant, R. S., and Scarlett, B. On the decay of turbulence in the 20-liter explosion sphere. *Flow, Turbulence and Combustion*, 2001. DOI: 10.1023/A:1015099110942.

[108] Skjold, T. Selected aspects of turbulence and combustion in 20-litre explosion vessels. Master's thesis, University of Bergen, 2003. URL: https://hdl.handle.net/1956/1631.

[109] Pu, Y. K., Jarosinski, J., Johnson, V. G., and Kauffman, C. W. Turbulence effects on dust explosions in the 20-liter spherical vessel. *23rd Symposium (International) on Combustion*, 1990. DOI: 10.1016/S0082-0784(06)80338-3.

[110] Wheeler, R. V. VIII. - The Inflammation of Mixtures of Ethane and Air in a Closed Vessel: The Effects of Turbulence. *Journal of the Chemical Society*, 115:81–94, 1919.

[111] Harris, G. F. P. The effect of vessel size and degree of turbulence on gas phase explosion pressures in closed vessels. *Combustion and Flame*, 1967. DOI: 10.1016/0010-2180(67)90005-3.

[112] Chang, X., Bai, C., Zhang, B., and Sun, B. The effect of ignition delay time on the explosion behavior in non-uniform hydrogen-air mixtures. *International Journal of Hydrogen Energy*, 2022. DOI: 10.1016/j.ijhydene.2022.01.026.

[113] Chen, J. and Zhang, Q. Flow characteristics of dusts dispersed by high-pressure air blast in 20 L chamber. *Engineering Computations*, 2015. DOI: 10.1108/EC-12-2013-0298.

[114] Garcia Agreda, A., Di Benedetto, A., Russo, P., Salzano, E., and Sanchirico, R. The role of ignition delay time on the deflagration index in a 20l bomb. *6th International Seminar on Fire and Explosion Hazard (ISFEH6)*, 2010.

[115] Di Benedetto, A. and Russo, P. Thermo-kinetic modelling of dust explosions. *Journal of Loss Prevention in the Process Industries*, 20(4-6):303–309, 2007. DOI: 10.1016/j.jlp.2007.04.001.

[116] Zhang, Q. and BoZhang. Effect of ignition delay on explosion parameters of corn dust/air in confined chamber. *Journal of Loss Prevention in the Process Industries*, 33:23–28, 2015. DOI: 10.1016/j.jlp.2014.11.009.

[117] Dahoe, A. E., van der Nat, K., Braithwaite, M., and Scarlett, B. On the sensitivity of the maximum explosion pressure of a dust deflagration to turbulence. *KONA Powder and Particle*, 2001. DOI: 10.14356/kona.2001021.

[118] Zhen, G. and Leuckel, W. Effects of ignitors and turbulence on dust explosions. *Journal of Loss Prevention in the Process Industries*, 10(5-6):317–324, 1997. DOI: 10.1016/S0950-4230(97)00021-1.

[119] Cuervo, R. *Influences of turbulence and combustion regimes on explosions of gas-dust hydrid mixtures*. Dissertation, University of Lorraine, 2015.

[120] Ren, J., Chang, C., Rao, G., Bai, C., Jing, Q., Peng, X., and Xiao, Q. Experimental and numerical simulation study on the effect of ignition delay time on dust explosion in the 1 m3 vessel. *Journal of Loss Prevention in the Process Industries*, 2022. DOI: 10.1016/j.jlp.2022.104801.

[121] Kuracina, R. and Szabova, Z. Determination of timing parameters of dust clouds explosion in dependence on the size of the vessel volume. *RESEARCH PAPERS FACULTY OF MATERIALS SCIENCE AND TECHNOLOGY IN TRNAVA*, 2021. DOI: 10.2478/rput-2021-0005.

[122] Sun, Z. Turbulent explosion characteristics of stoichiometric syngas. *International Journal of Energy Research*, 42(3):1225–1236, 2017. DOI: 10.1002/er.3922.

[123] Du, B., Huang, W., Liu, L., Zhang, T., Li, H., Ren, Y., and Wang, H. Visualization and analysis of dispersion process of combustible dust in a transparent Siwek 20-L chamber. *Journal of Loss Prevention in the Process Industries*, 33:213–221, 2015. DOI: 10.1016/j.jlp.2014.12.017.

[124] de Heij, W. B. C. On the application of lase doppler anemometry to the transient flow inside the standard 20-litre explosion sphere. Master's thesis, Delft University of Technology, 1998.

[125] van der Wel, P. G. J., van Veen, J. P. W., Lemkowitz, S. M., Scarlett, B., and van Wingerden, C. J. M. An interpretation of dust explosion phenomena on the basis of time scales. *Powder Technology*, 1992. DOI: 10.1016/0032-5910(92)80010-T.

[126] Sweet, C. C. Effect of gas stream parameters on the energy and power dissipated in a spark and on ignition. *Third Symposium on Combustion, Flame and Explosion Phenomena*, 3(1):353–361, 1949. DOI: 10.1016/S1062-2896(49)80042-0.

[127] Amyotte, P., Chippett, S., and Pegg, M. J. Effects of Turbulence on Dust Explosions. *Progress in Energy and Combustion Science*, 1988. DOI: 10.1016/0360-1285(88)90016-0.

[128] Proust, C., Accorsi, A., and Dupont, L. Measuring the violence of dust explosions with the “20 l sphere” and with the standard “ISO 1m3 vessel ” Systematic comparison and analysis of the discrepancies. *Journal of Loss Prevention in the Process Industries*, 20:599–606, 2007.

[129] Going, J. E., Chatrathi, K., and Cashdollar, K. L. Flammability limit measurements for dusts in 20-L and 1-m3 vessels. *Journal of Loss Prevention in the Process Industries*, 13(3-5):209–219, 2000. DOI: 10.1016/S0950-4230(99)00043-1.

[130] Addo, A., Dastidar, A., Taveau, J., Morrison, L., Khan, F., and Amyotte, P. Niacin, lycopodium and polyethylene powder explosibility in 20-L and 1-m3 test chambers. *Journal of Loss Prevention in the Process Industries*, 2019. DOI: 10.1016/j.jlp.2019.103937.

[131] Eckhoff, R. K. *Dust explosions in the process industries.* Butterworth and Heinemann, Oxford, 1991.

[132] Dahoe, A. E., Zevenbergen, J. F., Lemkowitz, S. M., and Scarlett, B. Dust explosions in spherical vessels: The role of flame thickness in the validity of the ‘tube-root law’. *Journal of Loss Prevention in the Process Industries*, 9:33–44, 1996. DOI: 10.1016/0950-4230(95)00054-2.

[133] Etoh, T. G., Poggemann, D., Kreifer, G., Mutoh, H., Theuwissen, A. J. P., Ruckelshausen, A., Kondo, Y., Maruno, H., Takubo, K., Soya, H., Takehara, K., Okinaka, T., and Takano, Y. An image sensor which captures 100 Consecutive Frames at 1 000 000 frames/s. *IEEE Transactions on Electron Devices*, 2003. DOI: 10.1109/TED.2002.806474.

[134] Bunjong, D., Pussadee, N., and Wattanakasiwich, P. Optimized conditions of Schlieren photography. *Journal of Physics*, 1144, 2018. DOI: 10.1088/1742-6596/1144/1/012097.

[135] Chawla, N., Amyotte, P. R., and Pegg, M. J. A comparison of experimental methods to determine the minimum explosible concentration of dusts. *FUEL*, 75(6):654–658, 1996. DOI: 10.1016/0016-2361(96)00006-3.

[136] Ono, R., Nifuku, M., Fujiwara, S., Horiguchi, S., and Oda, T. Minimum ignition energy of hydrogen-air mixture Effects of humidity and spark duration. *Journal of Electrostatics*, 65(2):87–93, 2007. DOI: 10.1016/j.elstat.2006.07.004.

[137] Skrinsky, J. and Ochodek, T. Influence of Initial Temperature on Explosion Severity Parameters of Methanol/Air Hybrid Mixture measured in 1-m3 Vessel. *Chemical Engineering Transactions*, 67:175–180, 2018. DOI: 10.3303/CET1867030.

[138] Pellmont, G. Einfluss der Temperatur auf das Zünd- und Explosionsverhalten von Nikotinsäure. Pellmont Explosionsschutz, 1997.

[139] Bartknecht, W. *Explosions – Course, Prevention, Protection.* Springer Verlag, 1981.

[140] Calcote, H. F., Gregory, C. A., Barnett, C. M., and Gilmer, R. B. Spark Ignition Effects of Molecular Structure. *Industrial and Engineering Chemistry*, 44(11):2656–2662, 1952. DOI: 10.1021/ie50515a048.

[141] Blanc, M. V., Guest, P. G., Von Elbe, G., and Lewis, B. Ignition of Explosive Gas Mixtures by Electric Sparks III. Minimum Ignition Energies and Quenching Distances of Mixtures of Hydrocarbons and Ether with Oxygen and Inert Gases. *Third Symposium on Combustion, Flame, and Explosion Phenomena*, 3(1):363–367, 1949. DOI: 10.1016/S1062-2896(49)80044-4.

[142] VDI 2263 Blatt 1. Dust fires and dust explosions Hazards – assessment – safety measures Safety-related parameters of bulk goods. VEREIN DEUTSCHER INGENIEURE, 2022.

[143] VDI 2263. Dust fires and dust explosions Hazards – assessment – safety measures. VEREIN DEUTSCHER INGENIEURE, 2018.

[144] Dufaud, O., Perrin, L., Traore, M., Chazelet, S., and Thomas, D. Explosions of vapour/dust hybrid mixtures: A particular class. *Powder Technology*, 190(1):269–273, 2009. DOI: 10.1016/j.powtec.2008.04.046.

[145] Sanchirico, R., Di Benedetto, A., Garcia-Agreda, A., and Russo, P. Study of the severity of hybrid mixture explosions and comparison to pure dust-air and vapour-air explosions. *Journal of Loss Prevention in the Process Industries*, 24(5):648–655, 2011. DOI: 10.1016/j.jlp.2011.05.005.

[146] Kosinski, P., Nyheim, R., Asokan, V., and Skjold, T. Explosions of carbon black and propane hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 26(1):45–51, jan 2013. DOI: 10.1016/j.jlp.2012.09.004.

[147] Boeck, L. R., Bauwens, C. R. L., and Dorofeev, S. B. Hybrid-Mixture Explosions: Large-Scale Testing and Estimation of Reactivity Parameters. In *10th International Seminar on Fire and Explosion Hazards*, 2022. URL: https://hdl.handle.net/11250/3030345.

[148] Torrado, D., Pinilla, A., Amin, M., Murillo, C., Munoz, F., Glaude, P.-A., and Dufaud, O. Numerical study of the influence of particle reaction and radiative heat transfer on the flame velocity of gas/nanoparticles hybrid mixtures. *Process Safety and Environmental Protection*, 118:211–226, 2018. DOI: 10.1016/j.psep.2018.06.042.

[149] Banhegyi, M. and Egyedi, J. Method for determining the explosive limits of a mixture of coal dust, methane and inert matter. *Paper presented at the International Conference of Safety in Mines Research Institutes*, 1983.

[150] Ivanov, M., Kiverin, A., and Liberman, M. Ignition of Deflagration and Detonation Ahead of the Flame due to Radiative Preheating of Suspended

Micro Particles. *Combustion and Flame*, 162(10):3612–3621, 2015. DOI: 10.1016/j.combustflame.2015.06.018.

[151] Torrado, D., Buitrago, V., Glaude, P. A., and Dufaud, O. Explosions of methane/air/nanoparticles mixtures: Comparison between carbon black and inert particles. *Process Safety and Environmental Protection*, 110:77–88, 2017. DOI: 10.1016/j.psep.2017.04.014.

[152] Leuschke, G. Beiträge zur Erforschung des Mechanismus der Flammenausbreitung in Staubwolken. *Sonderdruck aus "Staub" Band 25*, 1965.

[153] Torrado, D., Glaude, P.-A., and Dufaud, O. Effect of carbon black nanoparticles on methane/air explosions: Influence at low initial turbulence. *Journal of Physics*, 838(012022), 2017. DOI: 10.1088/1742-6596/838/1/012022.

[154] Galloway, W. On the Influence of Coal-Dust in Colliery Explosions ||. *Proceedings of the Royal Society of London*, 28(190-195), 1879. DOI: 10.1098/rspl.1878.0147.

[155] Galloway, W. On the Influence of Coal-Dust in Colliery Explosions |||. *Proceedings of the Royal Society of London*, 33(216-219), 1881. DOI: 10.1098/rspl.1881.0136.

[156] Galloway, W. On the Influence of Coal-Dust in Colliery Explosions IV. *Proceedings of the Royal Society of London*, 33(216-219), 1881. DOI: 10.1098/rspl.1881.0129.

[157] Galloway, W. On the Influence of Coal-Dust in Colliery Explosions V. *Proceedings of the Royal Society of London*, 37(232-234), 1884. DOI: 10.1098/rspl.1884.0010.

[158] Galloway, W. The Coal-Dust Question. *Nature*, 33(197-198), 1886. DOI: 10.1038/033197a0.

[159] Franke, B. Untersuchungen über Schlagwetter. *Journal Fur Praktische Chemie-chemiker-zeitung*, 1887.

[160] Gilpin, E. Notes on some explosions in Nova Scotia coal mines. In *Proceedings and Transactions of the Nova Scotian Institute of Science*, volume 8, pages 58–70, 1891.

[161] Thorpe, T. E. A lecture experiment to illustrate the phenomena of coal dust explosions. *Journal of the Chemical Society, Transactions*, 61(414-420), 1892. DOI: 10.1039/CT8926100414.

[162] Rice, G. S., Frazer, J. C. W., Larsen, A., and Haas, F. *The Exposibility of Coal Dust*. DEPARTMENT OF THE INTERIOR UNITED STATES GEOLOGICAL SURVEY, 1910.

[163] Taffanel, J. L. J. Experiences sur les poussieres de houille et sur les moyens de combattre leurs dangers. *Annales des Mines*, XVIII(10):73–187, 1910.

[164] Rice, G. S. Coal-Dust Explosions. Bureau of Mines, 1911.

[165] Galloway, W. The Coal-Dust Question in the United States and in Austria. *Nature*, 86(2174):595–598, 1911.

[166] Galloway, W. and Harger, J. Colliery Warnings. *Nature*, 86(2157):12, 1911.

[167] Greenwald, H. P. Explosibility of coal dust from four mines in Utah. United States Department of the Interior - Bureau of Mines, 1927.

[168] Rice, G. S., Greenwald, H. P., and Howarth, H. C. Coal dust explosion tests in the experimental mine 1919 to 1924, inclusive. United States Department of the Interior - Bureau of Mines, 1927.

[169] Rice, G. S., Greenwald, H. P., and Howarth, H. C. Coal dust explosions in mines, causes, effects and recommendations for prevention. United States Department of the Interior - Bureau of Mines, 1929.

[170] Rice, G. S., Greenwald, H. P., and Howarth, H. C. Some experiments on the initiation of coal-dust explosions by gas explosions. United States Department of the Interior - Bureau of Mines, 1930.

[171] Rice, G. S., Greenwald, H. P., and Howarth, H. C. Explosibility tests of Pittsburgh coal dust in the experimental mine 1925 to 1932, inclusive. United States Department of the Interior - Bureau of Mines, 1933.

[172] Greenwald, H. P. Explosibility of semianthracite, low-volatile bituminous coal, and medium-volatile bituminous-coal dusts. United States Department of the Interior - Bureau of Mines, 1940.

[173] Owings, C. W. Some preliminary data on methods for controlling the dust hazards in mechanical mining. United States Department of the Interior - Bureau of Mines, 1941.

[174] Hartmann, I., Nagy, J., Rauschenberger, J. K., and Mitchell, D. W. Coal-mine-explosion Research by the Bureau of Mines, 1954-55. United States Department of the Interior - Bureau of Mines, 1956.

[175] Hartmann, I. Studies on the Development and Control of Coal-dust Explosions in Mines. United States Department of the Interior - Bureau of Mines, 1957.

[176] Roychowdhury, S. N. Coal dust explosions and their prevention. Master's thesis, SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI, 1960.

[177] Nagy, J. and Portman, W. Explosibility of coal dust in an atmosphere containing a low percentage of methane. Bureau of Mines, 1961.

[178] Singer, J. M. Ignition of mixtures of coal dust, methane, and air by hot laminar nitrogen jets. *Symposium (International) on Combustion*, 1963. DOI: 10.1016/S0082-0784(63)80049-1.

[179] Anthony, E. J. The determination of the minimum explosible conentration of polyvinyl chloride powder in the presence of methane and air. Fire Research Station, Hertfordshire, 1977.

[180] Cardillo, P. and Anthony, E. J. The flammability limits of hybrid gas dust systems. *La Rivista dei combustibili*, 1978.

[181] Nindelt, G. Untersuchungsergebnisse zur Explosionsneigung hybrider Gemische beim Elektroabscheiderbetrieb. *Staub-Reinhaltung Luft*, 1981.

[182] Foniok, R. Hybrid dispersive mixtures and inertized mixtures of coal dust-explosiveness and ignitability. *Staub Reinhaltung der Luft*, 45:151–154, 1985.

[183] Cashdollar, K. L., Sapko, M. J., Weiss, E. S., and Hertzberg, M. Laboratory and Mine Dust Explosion Research at the Bureau of Mines. *ASTM Special Technical Publication (STP)*, 958:107–123, 1987. DOI: 10.1520/STP28169S.

[184] Napier and Roopchand. *Ignition Probability of Hybrid Mixtures.* ASTM International, 1987.

[185] Franke, H. Zündung hybrider Gemische aus Kohlenstaub und Methan durch schwache Zündquellen. DMT Publik, 1990.

[186] Amyotte, P., Mintz, K. J., Pegg, M. J., and Wilkie, K. Laboratory investigation of the dust explosibility characteristics of three Nova Scotia coals. *Journal of loss prevention in the process industries*, 1991. DOI: 10.1016/0950-4230(91)80014-L.

[187] Amyotte, P. R., Mintz, K. J., Pegg, M. J., and Sun, Y. H. The ignitability of coal dust-air and methane-coal dust-air mixtures. *FUEL*, 72(5):671–679, 1993. DOI: 10.1016/0016-2361(93)90580-U.

[188] Amyotte, P. R. and Pegg, M. J. Explosion hazards in underground coal mines. *Toxicological and Environmental Chemistry*, 40(1):189–199, 1993. DOI: 10.1080/02772249309357943.

[189] Siwek, R. and Cesana, C. Ignition Behavior of Dusts: Meaning and Interpretation. *Process Safety Progress*, 14(2):107–119, 1995. DOI: 10.1002/prs.680140205.

[190] Landman, G. V. R. Ignition behaviour of hybrid mixtures of coal dust, methane, and air. *Fuel and Energy Abstracts*, 37(1):45–50, 1996. DOI: 10.1016/0140-6701(96)87078-0.

[191] Khasainov, B. A. and Veyssiere, B. Initiation of detonation regimes in hybrid two-phase mixtures. *Shock Waves*, 6:9–15, 1996. DOI: 10.1007/BF02511399.

[192] Siwek, R. Determination of technical safety indices and factors influencing hazard evaluation of dusts. *Journal of Loss Prevention in the Process Industries*, 9(1):21–31, 1996. DOI: 10.1016/0950-4230(95)00057-7.

[193] Siwek, R. Explosion venting technology. *Journal of Loss Prevention in the Process Industries*, 9(1):81–90, 1996. DOI: 10.1016/0950-4230(95)00058-5.

[194] Bowen, P. J., Bull, D. C., Prothero, A., and Rowson, J. J. Deflagration of Hydrocarbon Aerosol Fuels. *Combustion Science and Technology*, 130:25–47, 1997. DOI: 10.1080/00102209708935736.

[195] Gillies, A. D. S. and Jackson, S. Some investigations into the explosibility of mine dust laden atmospheres. In *Proceedings of the 1998 Coal Operators' Conference*, 1998.

[196] Britton, L. G. Estimating the Minimum Ignition Energy of Hybrid Mixtures. *Process Safety Progress*, 17(2):124–126, 1998. DOI: 10.1002/prs.680170208.

[197] Jaeger, N. and Siwek, R. Prevent Explosions of Combustible Dusts. *Chemical Engineering Progress*, 95:25–37, 1999.

[198] Veyssiere, B., Arfi, P., and Khasainov, B. A. Detonations of starch suspensions in gaseous O2-N2 and stoichiometric H2-O2 mixtures. *Combustion and Flame*, 117(3):477–492, 1999. DOI: 10.1016/S0010-2180(98)00091-1.

[199] Cashdollar, K. L. Overview of dust explosibility characteristics. *Journal of Loss Prevention in the Process Industries*, 13:183–199, 2000. DOI: 10.1016/S0950-4230(99)00039-X.

[200] Dahn, C. J., Reyes, B., and Kusmierz, A. A methodology to evaluate industrial vapor and dust explosion hazards. *Process Safety Progress*, 19:86–90, 2000. DOI: 10.1002/prs.680190207.

[201] Burghammer, P., Wiemann, W., and Woersdoerfer, K. Applicability of modified inert materials for inertisation of coal dust deposits in the T-junction - Untersuchung der Anwendungsmoeglichkeit modifizierter Inertstoffe zur Inertisierung von Kohlenstaubablagerungen im Uebergangsbereich Streb-Strecke. DMT-Berichte aus Forschung und Entwicklung, 2001.

[202] Siwek, R. Explosionsschutz an Wirbelschichtanlagen. *Technische Überwachung*, 43(9):52–56, 2002.

[203] Nettleton, M. A. Recent work on gaseous detonations. *SHock Waves*, 12:3–12, 2002. DOI: 10.1007/s001930200134.

[204] Zhang, F., Murray, S. B., and Gerrard, K. B. Hybrid Detonations in Aluminum Dust-Gas Mixtures. In *Proceedings of the 19th International Colloquium on the Dynamics of Explosions and Reactive Systems (ICDERS)*, 2003.

[205] Glor, M. Ignition hazard due to static electricity in particulate processes. *Powder Technology*, 135:223–233, 2003. DOI: 10.1016/j.powtec.2003.08.017.

[206] Arntzen, B. J., Salvesen, H. C., Nordhaug, H. F., Storvik, I., and Hansen, O. CFD-modelling of oil mist and dust explosion experiments. In *Proceedings of the 4th International Seminar on Fire and Explosion Hazards*, 2003.

[207] Puttick, S. and Gibbon, H. Solvents in powders. *IChemE Symposium Series No. 150*, 2004.

[208] Dastidar, A. G., Nalda-Reyes, B., and Dahn, C. J. Evaluation of Dust and Hybrid Mixture Explosion Potential in Process Plants. *Process Safety Progress*, 24(4):294–298, 2005. DOI: 10.1002/prs.10097.

[209] Glor, M. Electrostatic ignition hazards in the process industry. *Journal of Electrostatics*, 63(6):447–453, 2005. DOI: 10.1016/j.elstat.2005.03.001.

[210] Chuyanov, V. and Topilski, L. Prevention of hydrogen and dust explosion in ITER. *Fusion Engineering and Design*, 81(8):1313–1319, 2006. DOI: 10.1016/j.fusengdes.2005.05.009.

[211] Liu, Y., Sun, J., and Chen, D. Flame propagation in hybrid mixture of coal dust and methane. *Journal of Loss Prevention in the Process Industries*, 20(4-6):691–697, 2007. DOI: 10.1016/j.jlp.2007.04.029.

[212] Dufaud, O., Perrin, L., Traore, S., Chazelet, S., and Thomas, D. Hybrid Mixtures Explosions : When Vapours Met Dusts. In *IChemE Symposium*, volume 12, pages 1–6, 2007.

[213] Liu, Q., Bai, C., Jiang, L., and Dai, W. Deflagration-to-detonation transition in nitromethane mist-aluminum dust-air mixtures. *Combustion and Flame*, 157(1):106–117, 2010. DOI: 10.1016/j.combustflame.2009.06.026.

[214] Denkevits, A. Hydrogen-dust explosion hazard in ITER - Effect of nitrogen dilution on explosion behavior of hydrogen-tungsten dust-air mixtures. *Fusion Engineering and Design*, 85(7):1053–1063, 2010. DOI: 10.1016/j.fusengdes.2010.01.009.

[215] Bai, C., Gong, G., Liu, Q., Chen, Y., and Niu, G. The explosion overpressure field and flame propagation of methane-air and methane-coal dust-air mixtures. *Safety Science*, 49(10):1349–1354, 2011. DOI: 10.1016/j.ssci.2011.05.005.

[216] Man, C. K. and Gibbins, J. R. Factors affecting coal particle ignition under oxyfuel combustion atmospheres. *FUEL*, 90(1):294–304, 2011. DOI: 10.1016/j.fuel.2010.09.006.

[217] Benedetto, A. D., Garcia-Agreda, A., Dufaud, O., Khalili, I., Sanchirico, R., Cuervo, N., Perrin, L., and Russo, P. Flame Propagation of Dust and Gas-Air Mixtures in a Tube. In *MCS 7 Seventh Mediterranean Combustion Symposium*, pages 11–13, 2011.

[218] Serafín, J. and Damec, J. Influence of inerts on explosion limits of hybrid mixtures. *Safety and Security Engineering*, IV(117):479–484, 2011. DOI: 10.2495/SAFE110411.

[219] Li, Q., Lin, B., Dai, H., and Zhao, S. Explosion characteristics of H2-CH4-air and CH4-coal dust-air mixtures. *Powder Technology*, 229:222–228, 2012. DOI: 10.1016/j.powtec.2012.06.036.

[220] Dufaud, O., Poupeau, M., Khalili, I., Cuervo, N., Christodoulou, M., Olcese, R., Dufour, A., and Perrin, L. Comparing Pyrolysis Gases and Dusts Explosivities - A Clue to Understanding Hybrid Mixtures Explosions. *Industrial & Engineering Chemistry Research*, 51(22):7656–7662, 2012. DOI: 10.1021/IE201646S.

[221] Khalili, I., Dufaud, O., Poupeau, M., Cuervo-Rodriguez, N., and Perrin, L. Ignition sensitivity of gas-vapor/dust hybrid mixtures. *Powder Technology*, 217:199–206, 2012. DOI: 10.1016/j.powtec.2011.10.027.

[222] Russo, P., Di Benedetto, A., and Sanchirico, R. Theoretical evaluation of the explosion regimes of hybrid mixtures. *Chemical Engineering Transactions*, 26:51–56, 2012.

[223] Li, G., Shang, R. X., Yu, Y. J., Wang, J. Z., and Yuan, C. M. Influence of coal dust on the ignition of methane/air mixtures by friction sparks from rubbing of titanium against steel. *Fuel*, 113:448–453, 2013. DOI: 10.1016/j.fuel.2013.05.082.

[224] Zhang, Q. and Tan, R. Effect of aluminum dust on flammability of gaseous epoxypropane in air. *FUEL*, 109:647–652, 2013. DOI: 10.1016/j.fuel.2013.03.043.

[225] Soo, M., Julien, P., Goroshin, S., Bergthorson, J. M., and Frost, D. L. Stabilized flames in hybrid aluminum-methane-air mixtures. *Proceedings of the Combustion Institute*, 2013. DOI: 10.1016/j.proci.2012.05.044.

[226] Skjold, T. An experimental investigation of flame propagation in clouds of silicon dust dispersed in air, hydrogen-air mixtures, and hybrid Si-H2-air mixtures. *24th ICDERS Proceedings*, 2013.

[227] Addai, E. K., Gabel, D., and Krause, U. Lower explosion limit of hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 36:497–504, 2014. DOI: 10.1016/j.jlp.2015.02.014.

[228] Hossain, M. N., Amyotte, P., Abuswer, M., Dastidar, A., Khan, F., Eckhoff, R., and Chunmiao, Y. Influence of liquid and vapourized solvents on explosibility of pharmaceutical excipient dusts. *Process Safety Progress*, 33:4, 2014. DOI: 10.1002/prs.11673.

[229] Julien, P., Soo, M., Goroshin, S., Frost, D. L., Bergthorson, J. M., Glumac, N., and Zhang, F. Combustion of Aluminum Suspensions in Hydrocarbon Flame Products. *Journal of Propulsion and Power*, 30(4):1–8, 2014. DOI: 10.2514/1.B35061.

[230] Redlinger, R. Numerical simulation of hybrid dust/gas explosion experiments in the standard 20-L sphere. *Fusion Engineering and Design*, 100:419–424, 2015. DOI: 10.1016/j.fusengdes.2015.07.006.

[231] Norman, F., Hosseinzadeh, S., den Bulck, E. V., Berghmans, J., and Verplaetsen, F. Dust explosion severity characteristics of Indonesian Sebuku coal in oxy-fuel atmospheres. In *7th European Combustion Meeting*, 2015.

[232] Liu, X., Zhang, Q., and Wang, Y. Influence of particle size on the explosion parameters in two-phase vapor–liquid n-hexane-air mixtures. *Process Safety and Environmental Protection*, 95:184–194, 2015. DOI: 10.1016/j.psep.2015.03.006.

[233] Palecka, J., Julien, P., Goroshin, S., Bergthorson, J. M., Frost, D. L., and Higgins, A. J. Quenching distance of flames in hybrid methane-aluminum mixtures. *Proceedings of the Combustion Institute*, 35(2):2463–2470, 2015. DOI: 10.1016/j.proci.2014.06.116.

[234] Jiang, J., Liu, Y., Mashuga, C. V., and Mannan, M. S. Validation of a new formula for predicting the lower flammability limit of hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 35:52–58, 2015.

[235] Julien, P., Whiteley, S., Goroshin, S., Soo, M. J., Frost, D. L., and Bergthorson, J. M. Flame structure and particle-combustion regimes in premixed methane–iron–air suspensions. *Proceedings of the Combustion Institute*, 35(2):2431–2438, 2015. DOI: 10.1016/j.proci.2014.05.003.

[236] Sanchirico, R., Russo, P., Di Sarli, V., and Di Benedetto, A. On the explosion and flammability behavior of mixtures of combustible dusts. *Process Safety and Environmental Protection*, 94:410–419, mar 2015.

[237] Sanchirico, R., Russo, P., Saliva, A., Doussot, A., Di Sarli, V., and Di Benedetto, A. Explosion of lycopodium-nicotinic acid–methane complex hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 36:505–508, jul 2015.

[238] Torrado, D., Cuervo, N., Pacault, S., and Dufour, A. Explosions of Gas / Carbon Black Nanoparticles Mixtures : an Approach to Assess the Role of Soot Formation. *Chemical Engineering Transactions*, 48:379–384, 2016.

[239] Ajrash, M. J., Zanganeh, J., and Moghtaderi, B. Methane-coal dust hybrid fuel explosion properties in a large scale cylindrical explosion chamber. *Journal of Loss Prevention in the Process Industries*, 40:317–328, 2016. DOI: 10.1016/j.jlp.2016.01.009.

[240] Ajrash, M. J., Zanganeh, J., and Moghtaderi, B. Effects of ignition energy on fire and explosion characteristics of dilute hybrid fuel in ventilation air methane. *Journal of Loss Prevention in the Process Industries*, 40:207–216, 2016. DOI: 10.1016/j.jlp.2015.12.014.

[241] Moron, W., Ferens, W., and Czajka, K. M. Explosion of different ranks coal dust in oxy-fuel atmosphere. *Fuel Processing Technology*, 148:388–394, 2016. DOI: 10.1016/j.fuproc.2016.03.007.

[242] Yang, L., Yao, J., Yang, Z., Xie, L., Peng, J., and Rao, G. Experimental investigation into the detonation characteristics of hybrid RDX–ethylene–air mixtures. *Shock Waves*, 26:611–619, 2016. DOI: 10.1007/s00193-016-0622-7.

[243] Addai, E., Gabel, D., and Krause, U. Models to estimate the lower explosion limits of dusts, gases and hybrid mixtures. *Chemical Engineering Transactions*, 48:313–318, 2016. DOI: 10.3303/CET1648053.

[244] Addai, E. K., Gabel, D., Kamal, M., and Krause, U. Minimum ignition energy of hybrid mixtures of combustible dusts and gases. *Process Safety and Environmental Protection*, 102:503–512, jul 2016. DOI: 10.1016/j.psep.2016.05.005.

[245] Addai, E. K., Gabel, D., and Krause, U. Experimental investigations of the minimum ignition energy and the minimum ignition temperature of inert and combustible dust cloud mixtures. *Journal of Hazardous Materials*, 307:302–311, apr 2016. DOI: 10.1016/j.jhazmat.2016.01.018.

[246] Addai, E. K., Gabel, D., and Krause, U. Experimental investigation on the minimum ignition temperature of hybrid mixtures of dusts and gases or solvents. *Journal of Hazardous Materials*, 301:314–326, 2016. DOI: 10.1016/j.jhazmat.2015.09.006.

[247] Addai, E. K., Gabel, D., and Krause, U. Models to estimate the minimum ignition temperature of dusts and hybrid mixtures. *Journal of Hazardous Materials*, 304:73–83, 2016. DOI: 10.1016/j.jhazmat.2015.10.015.

[248] Ray, S. K., Kumar, A., Mohalik, N. K., Sahay, N., Khan, A. M., and Singh, R. V. K. CFD Application on coal dust explosiility - An overview. In *Proceedings of NexGen Technologies for Mining and Fuel Industries*, 2017.

[249] Ajrash, M. J., Zanganeh, J., and Moghtaderi, B. The flame deflagration of hybrid methane coal dusts in a large-scale detonation tube (LSDT). *Fuel*, 194:491–502, 2017. DOI: 10.1016/j.fuel.2017.01.038.

[250] Ajrash, M. J., Zanganeh, J., and Moghtaderi, B. Impact of suspended coal dusts on methane deflagration properties in a large-scale straight duct. *Journal of Hazardous Materials*, 338:334–342, 2017. DOI: 10.1016/j.jhazmat.2017.05.030.

[251] Ajrash, M. J., Zanganeh, J., and Moghtaderi, B. The flame deflagration of hybrid methane coal dusts in a large-scale detonation tube (LSDT). *Fuel*, 194:491–502, 2017. DOI: 10.1016/j.fuel.2017.01.038.

[252] Vasil'ev, A. A., Pinaev, A. V., Trubitsyn, A. A., Grachev, A. Y., Trotsyuk, A. V., Fomin, P. A., and Trilisa, A. V. What is Burning in Coal Mines - Methane or Coal Dust? *Combustion, Explosion, and Shock Waves*, 53:8–14, 2017. DOI: 10.1134/S0010508217010026.

[253] Cuervo, N., Dufaud, O., and Perrin, L. Determination of the burning velocity of gas/dust hybrid mixtures. *Process Safety and Environmental Protection*, 109:704–715, 2017. DOI: 10.1016/j.psep.2017.06.009.

[254] Fischer, S., Markus, D., and Maas, U. Numerical investigation of the ignition of diethyl ether-air and propane-air mixtures by hot jets. *Journal of Loss Prevention in the Process Industries*, 49:832–838, 2017. DOI: 10.1016/j.jlp.2017.03.010.

[255] Vickery, J., Julien, P., Goroshin, S., Bergthorson, J. M., and Frost, D. L. Spherically-Expanding Flames in Hybrid Aluminum-Methane-Oxidizer Mixtures at Atmospheric Pressure. In *26th ICDERS*, 2017.

[256] Yu, L., Li, G., Liu, W., Yu, J., and Yuan, C. Experimental investigations on ignition sensitivity of hybrid mixtures of oil shale dust and syngas. *Fuel*, 210:1–7, 2017. DOI: 10.1016/j.fuel.2017.06.082.

[257] Addai, E. K., Addo, A., Abbas, Z., and Krause, U. Investigation of the minimum ignition temperature and lower explosion limit of multi-components hybrid mixtures in the Godbert-Greenwald furnace. *Process Safety and Environmental Protection*, 111:785–794, oct 2017. DOI: 10.1016/j.psep.2017.09.003.

[258] Addai, E. K., Gabel, D., and Krause, U. Lower Explosion Limit/Minimum Explosible Concentration Testing for Hybrid Mixtures in the Godbert-Greenwald Furnace. *Process Safety Progress*, 36:81–94, 2017. DOI: 10.1002/prs.11825.

[259] Moon, S. B., Lim, S. M., and Bang, I. C. Analysis of hydrogen and dust explosion after vacuum vesselrupture - Preliminary safety analysis of Korean fusiondemonstration reactor using MELCOR. *International Journal of Energy Research*, 42:104–116, 2017. DOI: 10.1002/er.3793.

[260] Cloney, C. T., Ripley, R. C., Pegg, M. J., and Amyotte, P. R. Evaluating regime diagrams for closed volume hybrid explosions. *Journal of Loss Prevention in the Process Industries*, 49:912–918, 2017. DOI: 10.1016/j.jlp.2017.03.004.

[261] Vickery, J., Julien, P., Goroshin, S., Bergthorson, J. M., and Frost, D. L. Propagation of isobaric spherical flames in hybrid aluminum-methane fuel mixtures. *Journal of Loss Prevention in the Process Industries*, 49:472–480, 2017. DOI: 10.1016/j.jlp.2017.05.027.

[262] Dobashi, R. Studies on accidental gas and dust explosions. *Fire Safety Journal*, 91:21–27, 2017. DOI: 10.1016/j.firesaf.2017.04.029.

[263] Cloney, C. T., Ripley, R. C., Pegg, M. J., and Amyotte, P. R. Laminar burning velocity and structure of coal dust flames using a unity Lewis number CFD model. *Combustion and Flame*, 190:87–102, 2018. DOI: 10.1016/j.combustflame.2017.11.010.

[264] Kundu, S. K., Zanganeh, J., Eschebach, D., and Moghtaderi, B. Explosion severity of methane–coal dust hybrid mixtures in a ducted spherical vessel. *Powder Technology*, 323:95–102, 2018. DOI: 10.1016/j.powtec.2017.09.041.

[265] Cloney, C. T., Ripley, R. C., Pegg, M. J., Khan, F., and Amyotte, P. R. Lower flammability limits of hybrid mixtures containing 10 micron coal dust particles and methane gas. *Process Safety and Environmental Protection*, 120:215–226, 2018. DOI: 10.1016/j.psep.2018.09.004.

[266] Cloney, C. *Burning Velocity and Lower Flammability Limits of Hybrid Mixtures Containing Combustible Dust and Flammable Gas*. PhD thesis, Dalhousie University, 2018.

[267] Sanchirico, R., Sarli, V. D., and Benedetto, A. D. Volatile point of dust mixtures and hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 56:370–377, 2018. DOI: 10.1016/j.jlp.2018.09.014.

[268] Ji, W., Yu, J., Yu, X., Hou, Y., and Yan, X. Explosion venting of hybrid mixtures: A comparison of standards NFPA 68 and EN 14491. *Journal of Loss Prevention in the Process Industries*, apr 2018.

[269] Gan, B., Li, B., Jiang, H., Zhang, D., Bi, M., and Gao, W. Ethylene/polyethylene hybrid explosions: Part 1. Effects of ethylene concentrations on flame propagations. *Journal of Loss Prevention in the Process Industries*, 54:93–102, jul 2018.

[270] Gan, B., Li, B., Jiang, H., Zhang, D., Bi, M., and Gao, W. Ethylene/polyethylene hybrid explosions: Part 2. Effects of polyethylene particle size distributions on flame propagations. *Journal of Loss Prevention in the Process Industries*, 55:134–143, 2018. DOI: 10.1016/j.jlp.2018.06.006.

[271] Palecka, J., Goroshin, S., and Bergthorson, J. M. Propagation and quenching of dual-front flames inbinary-fuel mixtures. *Combustion Science and Technology*, 2018. DOI: 10.1080/00102202.2018.1459583.

[272] Deng, J., Qu, J., Wang, Q.-H., Xiao, Y., Cheng, Y.-C., and Shu, C.-M. Experimental data revealing explosion characteristics of methane, air, and coal mixtures. *RSC Advances*, 42:24627–24637, 2019. DOI: 10.1039/C9RA04416G.

[273] Song, S.-x., Cheng, Y.-f., Meng, X.-r., Ma, H.-h., Dai, H.-y., Kan, J.-t., and Shen, Z.-w. Hybrid CH4/coal dust explosions in a 20-L spherical vessel. *Process Safety and Environmental Protection*, 122:281–287, 2019. DOI: 10.1016/j.psep.2018.12.023.

[274] Abbas, Z., Zinke, R., Gabel, D., Addai, E., Darbanan, A., and Krause, U. Theoretical evaluation of lower explosion limit of hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 2019. DOI: 10.1016/j.jlp.2019.05.014.

[275] Pak, S., Jung, S., Roh, C., and Kang, C. Case Studies for Dangerous Dust Explosions in South Korea during Recent Years. *sustainability*, 11(4888):1–13, 2019. DOI: 10.3390/su11184888.

[276] Maier, P., Hartlieb, P., and Brune, J. F. Laboratory Scaled Coal Dust Explosions and Physical Test Results for CFD Explosion Models. *Berg- und Huettenmaennische Monatshefte*, 165(6):265–269, 2020. DOI: 10.1007/s00501-020-00985-0.

[277] Li, H., Deng, J., Chen, X., Shu, C.-M., Kuo, C.-H., Zhai, X., Wang, Q., and Hu, X. Qualitative and quantitative characterisation for explosion severity and gaseous–solid residues during methane–coal particle hybrid explosions - An approach to estimating the safety degree for underground coal mines. *Process Safety and Environmental Protection*, 141:150–166, 2020. DOI: 10.1016/j.psep.2020.05.033.

[278] Tan, X., Schmidt, M., Zhao, P., Wei, A., Huang, W., Qian, X., and Wu, D. Minimum ignition temperature of carbonaceous dust clouds in air with CH4-H2-CO below the gas lower explosion limit. *FUEL*, 264, 2020. DOI: 10.1016/j.fuel.2019.116811.

[279] Pico, P., Ratkovich, N., Munoz, F., and Dufaud, O. CFD-DPM and experimental study of the dynamics of wheat starch powder-pyrolysis gases hybrid mixtures in the 20-L Sphere. *Powder Technology*, 372:638–658, 2020. DOI: 10.1016/j.powtec.2020.05.108.

[280] Pico, P., Ratkovich, N., Munoz, F., and Dufaud, O. Analysis of the explosion behaviour of wheat starch-pyrolysis gases hybrid mixtures through experimentation and CFD-DPM simulations. *Powder Technology*, 374:330–347, 2020. DOI: 10.1016/j.powtec.2020.07.016.

[281] Heilmann, V., Taiwo, A., Hirsch, W., Grosshans, H., Zakel, S., and Krause, U. Prenormative Study on the Safety Characteristics of Explosion Protection for Hybrid Mixtures of Dusts and Vapours. In *13th ISHPMIE*, 2020.

[282] Wang, X., Wang, Z., Ni, L., Zhu, M., and Liu, C. Explosion characteristics of aluminum powder in different mixed gas environments. *Powder Technology*, 2020. DOI: 10.1016/j.powtec.2020.04.056.

[283] Kim, W., Anraku, S., Endo, T., and Choi, K. Flammability and flame propagation of propane-L-leucine powder hybrid mixtures. *Powder Technology*, 372:694–702, 2020. DOI: 10.1016/j.powtec.2020.05.107.

[284] Qi, Y., Gan, X., Li, Z., Li, L., Wang, Y., and Ji, W. Variation and Prediction Methods of the Explosion Characteristic Parameters of Coal Dust-Gas Mixtures. *Energies*, 14(2), 2021. DOI: 10.3390/en14020264.

[285] Li, J., Guo, Z., Chen, X., and Zhou, F. Rapid and efficient removal of CO in CH4 and CH4-coal dust hybrid explosions - A novel approach of spraying catalyst powder. *FUEL*, 290, 2021. DOI: 10.1016/j.fuel.2020.119790.

[286] Pang, L., Cao, J., Zhao, Y., Yuan, C., Yang, K., and Zhang, Z. Minimum ignition energy of LDPE dust-ethylene hybrid mixture. *Journal of Loss Prevention in the Process Industries*, 72, 2021. DOI: 10.1016/j.jlp.2021.104546.

[287] Yao, N., Bai, C., Wang, L., and Liu, N. Investigation on the Explosion Characteristics of an Aluminum Dust-Diethyl Ether-Air Mixture. *ACS Omega*, 6:18868–18875, 2021. DOI: 10.1021/acsomega.1c02081.

[288] Yang, K., Cao, J., Zhao, Y., Pang, L., and Ma, R. Inerting effect of N2 on explosion of LDPE dust-ethylene hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 70, 2021. DOI: 10.1016/j.jlp.2021.104431.

[289] Tsai, Y.-T., Fu, T., and Zhou, Q. Explosion characteristics and suppression of hybrid Mg/H2 mixtures. *International Journal of Hydrogen Energy*, 46(78):38934–38943, 2021. DOI: 10.1016/j.ijhydene.2021.09.145.

[290] Gabel, D., Geoerg, P., Franken, F., and Krause, U. Nex-Hys: minimum ignition temperature of hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 2021. DOI: 10.1016/j.jlp.2021.104502.

[291] Yu, X., Yu, J., Wang, C., Lv, X., Wang, Y., Hou, Y., and Yan, X. Experimental study on the overpressure and flame propagation of hybrid hydrogen-aluminum dust explosions in a square closed vessel. *FUEL*, 285, 2021. DOI: 10.1016/j.fuel.2020.119222.

[292] Khudhur, D. A., Ali, M. W., and Abdullah, T. A. T. Mechanisms, Severity and Ignitability Factors, Explosibility Testing Method, Explosion Severity Characteristics, and Damage Control for Dust Explosion - A Concise Review. *Journal of Physics - Conference Series*, 1892:1–21, 2021. DOI: 10.1088/1742-6596/1892/1/012023.

[293] Palecka, J., Park, J., Goroshin, S., and Bergthorson, J. M. Aluminum-propane-air hybrid flames in a Hele-Shaw cell. *Proceedings of the Combustion Institute*, 38(3):4461–4468, 2021. DOI: 10.1016/j.proci.2020.09.017.

[294] Lin, S., Liu, Z., Qian, J., Li, X., and Zhang, Q. Flammability and Explosion Risk of Post-explosion CH4-air and CH4-coal dust-air Mixtures. *Combustion Science and Technology*, 193(8):1279–1292, 2021. DOI: 10.1080/00102202.2019.1688313.

[295] Jing, G., Peng, L., and Mu, L. Research on the propagation of pressure and CO gas of methane and coal dust coupled explosion. *Thermal Science*, 2022. DOI: 10.2298/TSCI211010012J.

[296] Li, H., Zhai, F., Li, S., Lou, R., Wang, F., Chen, X., Shu, C.-M., and Yu, M. Macromorphological features and formation mechanism of particulate residues from methane-air-coal dust gas–solid two-phase hybrid explosions - An approach for material evidence analysis in accident investigation. *FUEL*, 315, 2022. DOI: 10.1016/j.fuel.2022.123209.

[297] Ren, K., Guo, Y., Huang, W., Wei, A., and Wu, D. Explosion characteristics of coal dusts in O2-N2 ambience - A novel method to determine limiting oxygen concentration. *FUEL*, 324, 2022. DOI: 10.1016/j.fuel.2022.124673.

[298] Jiang, H., Bi, M., Gao, Z., Zhang, Z., and WeiGao. Effect of turbulence intensity on flame propagation and extinction limits of methane-coal dust explosions. *Energy*, 2022. DOI: 10.1016/j.energy.2021.122246.

[299] Jiang, H., Bi, M., Huang, L., Zhou, Y., and Gao, W. Suppression mechanism of ultrafine water mist containing phosphorus compounds in methane-coal dust explosions. *Energy*, 239, 2022. DOI: 10.1016/j.energy.2021.121987.

[300] Wang, H., Zhang, Y., Xu, J., Li, J., Fan, C., and Hu, Y. Experimental study on effect of dilute coal dust on gas explosion pressure-flame evolution process. *Powder Technology*, 404, 2022. DOI: 10.1016/j.powtec.2022.117450.

[301] Pietraccini, M., Glaude, P.-A., Dufour, A., and Dufaud, O. Making hybrid mixtures explosion a common case. In *14th ISHPMIE*, 2022.

[302] Yao, J., Bai, C., and Zhang, C. Explosion Performance of Al Powder - Liquid Fuel Mixtures under Different Ambient Conditions. *ACS Omega*, 7:32489–32495, 2022. DOI: 10.1021/acsomega.2c03970.

[303] Abbas, Z., Gabel, D., Krietsch, A., and Krause, U. Quasi-static dispersion of dusts for the determination of lower explosion limits of hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 2022. DOI: 10.1016/j.jlp.2021.104640.

[304] Yu, M., Li, S., Zhai, F., Lou, R., Li, H., and Zheng, K. Effects of volatile contents on the deflagration characteristics and soot formation of methane/coal volatiles hybrid explosion using reaction kinetics simulation. *FUEL*, 2022. DOI: 10.1016/j.fuel.2022.123767.

[305] Wei, L., Su, M., Wang, K., Chen, S., Ju, Y., Zhao, S., Kong, X., Chu, Y., and Wang, L. Suppression effects of ABC powder on explosion characteristics of hybrid C2H4/polyethylene dust. *FUEL*, 2022. DOI: 10.1016/j.fuel.2021.122159.

[306] Ji, W., Wang, Y., Yang, J., He, J., Wen, X., and Wang, Y. Methods to predict variations of lower explosion limit associated with hybrid mixtures of flammable gas and dust. *FUEL*, 310, 2022. DOI: 10.1016/j.fuel.2021.122138.

[307] Wu, W., Huang, W., Wei, A., Schmidt, M., Krause, U., and Wu, D. Inhibition effect of N2/CO2 blends on the minimum explosion concentration of agriculture and coal dusts. *Powder Technology*, 2022. DOI: 10.1016/j.powtec.2022.117195.

[308] Geoerg, P., Spitzer, S., Gabel, D., and Krause, U. Where one plus one equals three - the MIT of hybrid mixtures. In *14th ISPHPMIE*, 2022.

[309] Spitzer, S., Askar, E., Hecht, K. J., Gabel, D., Zakel, S., and Krietsch, A. Requirements for a Hybrid Dust-Gas-Standard - Influence of the Mixing Procedure on Safety Characteristics of Hybrid Mixtures. *fire*, 5(4), 2022. DOI: 10.3390/fire5040113.

[310] Yu, M., Wang, F., He, T., Li, H., Han, S., Lou, R., Zheng, K., and Yu, Y. Experimental exploration and mechanism analysis of the deflagration pressure of methane/pulverized coal blenders inhibited by modified kaoline-containing compound inhibitors. *FUEL*, 333, 2023. DOI: 10.1016/j.fuel.2022.126353.

[311] Yu, M., Li, S., Li, H., Han, S., Wang, F., Lou, R., Zheng, K., and Yu, Y. Numerical evaluation of the influence of initial pressure/temperature on the explosion properties and soot formation of methane-coal volatiles mixtures. *FUEL*, 331(1), 2023. DOI: 10.1016/j.fuel.2022.125698.

[312] Chuang, L., Guoxun, J., and Yue, S. Research on deflagration behavior of gas and gas-coal dust in a vertical pressure relief pipeline system. *Thermal Sciences*, pages 1–14, 2023. DOI: 10.2298/TSCI221104050L.

[313] Cao, X., Wei, H., Wang, Z., Fan, L., Zhou, Y., and Wang, Z. Experimental research on the inhibition of methane-coal dust hybrid explosions by the ultrafine water mist. *FUEL*, 2023.

[314] Ji, W., Wang, Y., Yang, J., He, J., Lu, C., Wen, X., and Wang, Y. Explosion overpressure behavior and flame propagation characteristics in hybrid explosions of hydrogen and magnesium dust. *FUEL*, 332, 2023. DOI: 10.1016/j.fuel.2022.125801.

[315] Wu, D., Zhao, P., Spitzer, S. H., Krietsch, A., Amyotte, P., and Krause, U. A review on hybrid mixture explosions: Safety parameters, explosion regimes and criteria, flame characteristics. *Journal of Loss Prevention in the Process Industries*, 82, 2023. DOI: 10.1016/j.jlp.2022.104969.

[316] Xiong, X., Gao, K., Mu, J., Ji, C., Li, B., Zhang, D., Xu, Y., and Xie, L. Experimental study on the explosion destructive ability of magnesium powder-hydrogen hybrids in large space. *Process Safety and Environmental Protection*, 173:237–248, 2023. DOI: 10.1016/j.psep.2023.02.091.

[317] Yu, X., Zhang, Z., Yan, X., Wang, Z., Yu, J., and Gao, W. Explosion characteristics and combustion mechanism of hydrogen/tungsten dust hybrid mixtures. *FUEL*, 332, 2023. DOI: 10.1016/j.fuel.2022.126017.

[318] Spitzer, S. H., Askar, E., Benke, A., Cloney, C., D'Hyon, S., Dufaud, O., Dyduch, Z., Gabel, D., Geoerg, P., Heilmann, V., Jankuj, V., Jian, W., Krause, U., Krietsch, A., Mynarz, M., Norman, F., Skrinsky, J., Taveau, J., Vignes, A., Zakel, S., and Zhong, S. 1st international round robin test on safety characteristics of hybrid mixtures. *Journal of Loss Prevention in the Process Industries*, 81, 2023. DOI: 10.1016/j.jlp.2022.104947.

[319] Settles, G. S. *Schlieren and Shadowgraph Techniques*. Springer Verlag Berlin, 2001.

[320] Settles, G. S. and Hargather, M. J. A review of recent developments in schlieren and shadowgraph techniques. *Measurement Science and Technology*, 28, 2017. DOI: 10.1088/1361-6501/aa5748.

[321] Ballal, D. R. and Lefebvre, A. H. The Influence of Flow Parameters on Minimum Ignition Energy and Quenching Distance. *15th Symposium (International) on Combustion*, 15(1):1473–1481, 1975. DOI: 10.1016/S0082-0784(75)80405-X.

[322] DIN EN ISO/IEC 80079-20-1:2015. Explosive atmospheres – Part 20-2: Material characteristics for gas and vapour classification. International Standardization Organisation, 2016.

[323] EN 15794. Determination of explosion points of flammable liquids. CEN, 2009.

[324] prEN 14034 - 1. Determination of explosion characteristics of dust clouds - Part 1: Determination of the maximum explosion pressure pmax and the maximum rate of pressure rise of dust clouds. CEN, 2020.

[325] Cao, Y., Guo, J., Hu, K., Xie, L., and Li, B. Effect of ignition location on external explosion in hydrogen–air explosion venting. *International Journal of Hydrogen Energy*, 42(15):10547–10554, 2017. DOI: 10.1016/j.ijhydene.2017.01.095.

[326] Garcia-Agreda, A. *Study of hybrid mixture explosions.* Dissertation, Università Degli Studi Di Napoli Federico II, 2010.

A. Appendix I - Exploding wire

In this chapter the exploding wire is described and construction notes are presented. If everything is built correctly the ignition device shall form two light arcs, that are a similar ignition source, than two chemical igniters (see figure A.1).

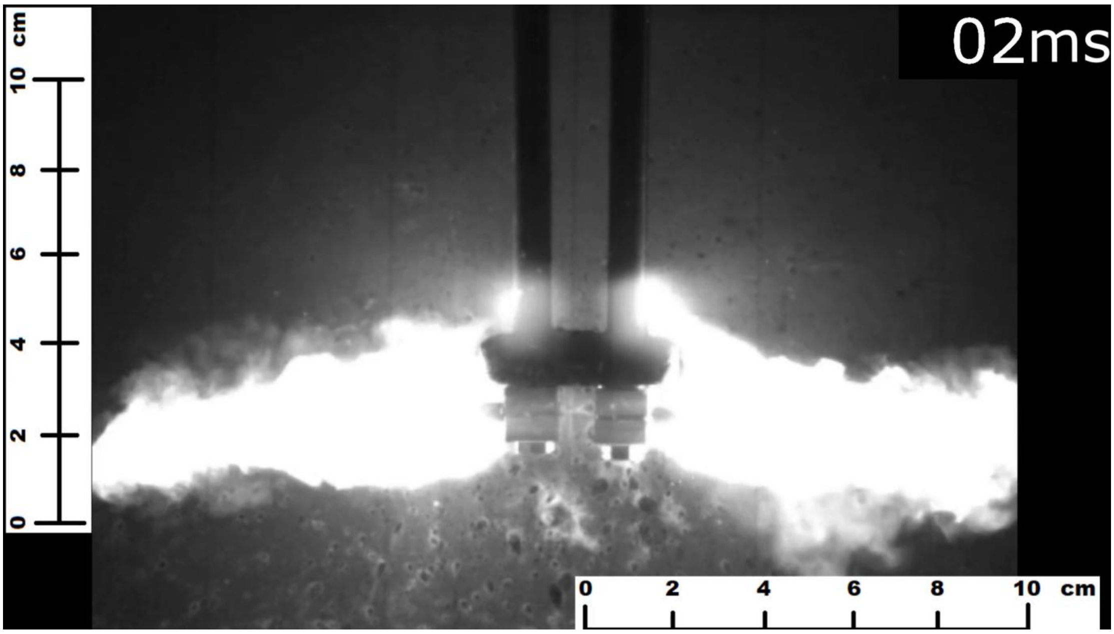

Figure A.1.: Exploding wire fired in two opposing directions with 1 kJ each two milliseconds after triggering

A list of all suitable stock devices is also presented. Since it is dangerous and complex for someone not familiar with electricity it should only be built by electricians. However, the full schematic of the high voltage circuit is rather simple (see figure A.2).
The **C**apacitor **I**gnition **S**ystem (CIS1) consists of a voltage source, capacitors, one inductance per channel, electrodes, probes and cables, one thyristor per channel, 2 isolation amplifiers per channel (one for voltage, one for current), and the control unit.

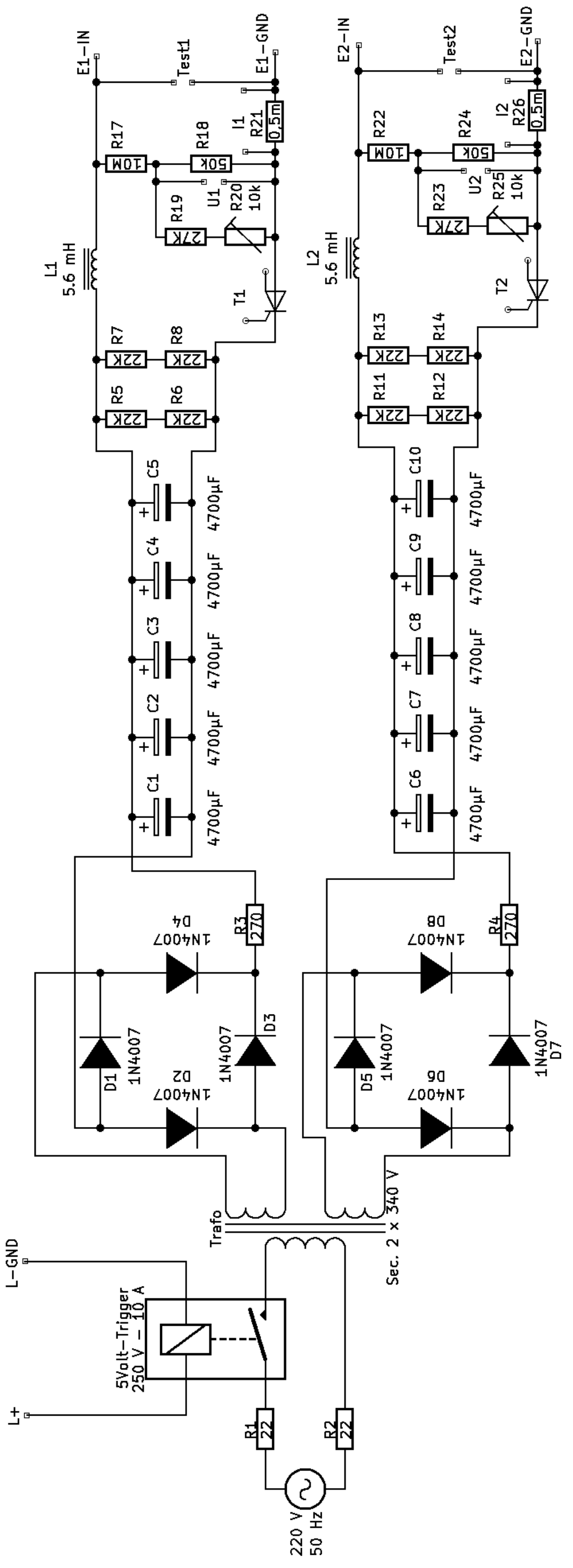

Figure A.2.: Schematic of the CIS1 without control unit and isolation amplifiers

A.1. Voltage source

The Voltage source consists of a transformer with 230 Volts on the primary side and two times 340 Volts on the secondary side. This is the nominal voltage, so the peak value is

$$Voltage_{Peak} = Voltage_{Nominal} * \sqrt{2} = 480 Volts^{1} \tag{A.1}$$

The transformer is switched on by a relay with a maximum rated voltage of 250 Volts, a maximum Current of 10 A and triggerable by a 5 Volts-signal. After the transformer the voltage is rectified by four 1N4007-Diodes. After the rectification a high power resistor with 270 Ohms protects the voltage source against break-down (and short-circuit current) in the first moment of loading (see figure A.3).

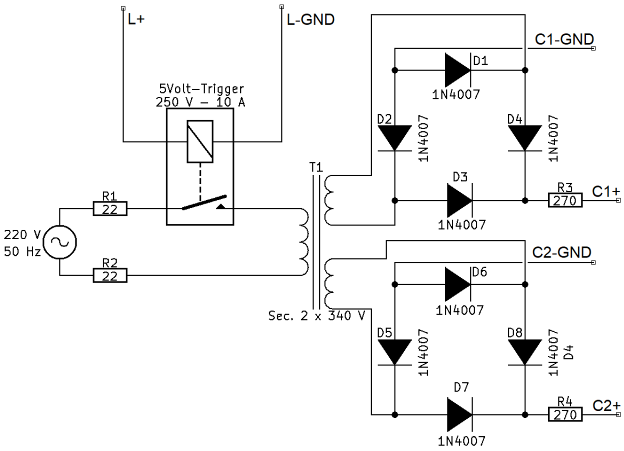

Figure A.3.: Schematic of the high voltage source

A.2. Capacitors

Five capacitors with a capacity of 4700 μF and a loading voltage of 450 Volts are used per channel. The capacitors are wired in parallel so the overall capacitance is 23 500 μF per channel. To ensure a full discharge at the end of the tests and if accidently loaded the capacitors are connected with six 22 kOhm resistors with a power rating of 11 watts (see figure A.4).

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[1] Because of the safety resistors and other losses the maximum loading voltage should not exceed the 450 Volts stated on the capacitors.

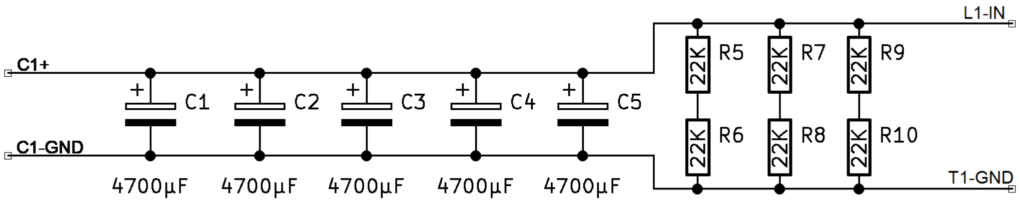


Figure A.4.: Schematic of one line of capacitors; this device has to be built twice

A.3. Inductance

To stretch the circuit breakdown and with that the duration of the light arc to 8 - 15 ms it is necessary to place either a resistor or an inductance into the circuit. For this circuit a so called "zero-Ohm-inductance" with an inductance of 5.6 mH and a resistance of 0,05 Ohm was chosen. It is placed between the capacitor bank (L1-IN) and the electrodes (L1-OUT).

A.4. Electrodes, probes and cables

The electrodes are connected to the ignition device with cables of 4 mm^2 cross section, when they are shorter than 4 m and 10 mm^2 when they are under 10 m. The voltage can be measured by a voltage divider (R17-R20) with a ratio of 500:1. The potentiometer (R20) is for the fine adjustment of the voltage divider. The current can be measured by a shunt resistor (R21) with a ratio of 2000:1 (see figure A.5).

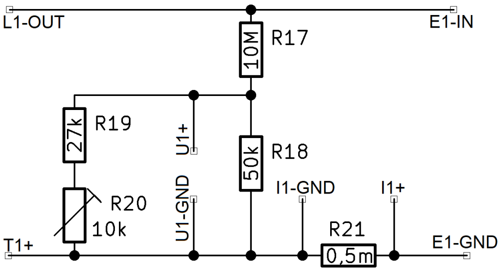


Figure A.5.: Schematic of one line of electrodes with the resistors and probes necessary to measure the voltage and the current; this device has to be built twice

A.5. Thyristor

The ignition is switched by a thyristor with a voltage rating of more than 1kV and a maximum peak one-cycle surge current of more than 1800 kA under full voltage. The thyristor is placed between the ground of the capacitor bank (T1-GND) and the ground of the electrodes(T1+) after the probes.

A.6. Isolation amplifier

PCB for the measurement unit available under `https://aisler.net/p/AAESKNFR`

A.7. Control unit

The control unit has to switch the two thyristors galvanically isolated with the required current and voltage. In this case it is at least 150 mA and 9 Volts. The different 20L-spheres have different triggersignals (or better fusing voltages) for the chemical igniters: Kühner has 24 Volts for 2 seconds, ANKO Lab has 12 Volts for 1 second and the chinese manufacturer gives a range of 5-10 volts. Using a z-diode an optocoupler and a mosfet this is realized.
A PCB for the control unit is available under `https://aisler.net/p/VMVPSICC`

A.8. List of suitable stock parts

The following list provides suitable parts for the building of the CIS1. If the parts are commonly used and not rare they are not specified further. If the parts are very special a potential supplier and the URL is stated.

- 8 Diodes 1N4007
- 1 Transformer with two 340 Volts secondary voltages. `https://www.buerklin.com/de/Netztransformator-Netz--110%C2%A0V-240%C2%A0V/p/12C160`
- 10 capacitors with 4700 μF and 450 V
  `https://de.rs-online.com/web/p/aluminium-elektrolytkondensatoren/1251084`
- 2 Inductances with 5.6 mH and 0.05 Ohm `https://www.mundorf.com/audio/de/shop/coils/ei_coils/MCoil-FERON-Null-Ohm/?card=6130`
- 2 Thyristors
  `https://www.tme.eu/de/details/t100n12-gg/thyristoren-mit-schraubverb/greegoo/t100n12/`
  or `https://www.semic-shop.de/skt-100-18e-15/`
- 12 Resistors with 22 kOhm and 11 Watt
- 8 Resistors with 270 Ohm and 17 Watt
- 1 Relay with 250 Volts, 10 A and 5 V control voltage
- 2 Resistors with 10 MOhm
- 2 Resistors with 50 kOhm

- 2 Resistors with 27 kOhm
- 2 Potentiometers with 10 kOhm
- 2 Shunt resistors with 0,5 mOhm or 3,3 mm^2 copper wires with soldered connections 98 mm apart from each other
- 1 Arduino nano
- 2 Moving iron voltmeters to show the loading voltage

B. Appendix II - Bomb Calorimeter

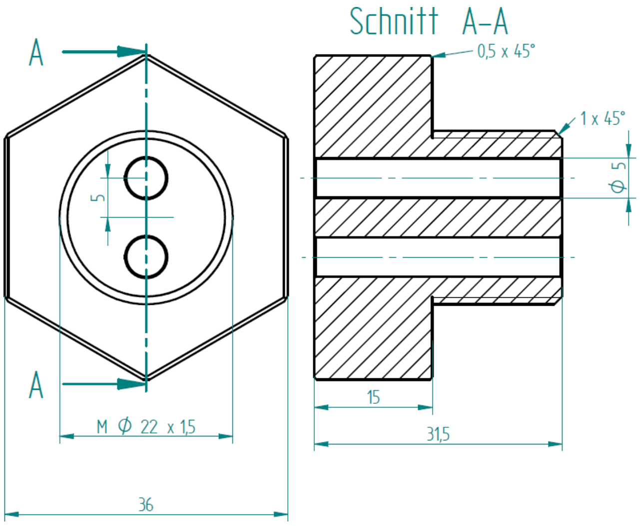


Figure B.1.: Closure of the calorimeter with holes for insulated electrodes

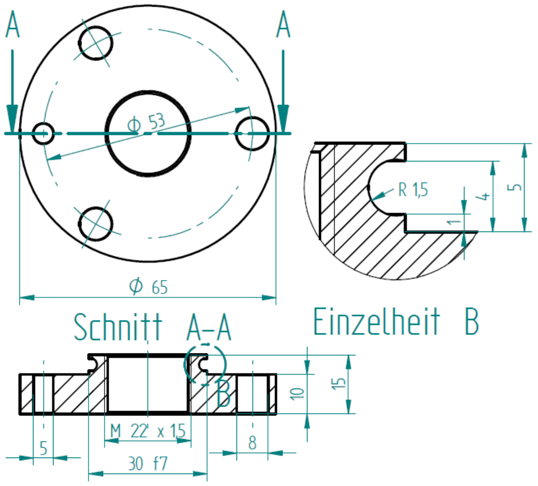


Figure B.2.: Top of the calorimeter with thread for the cap

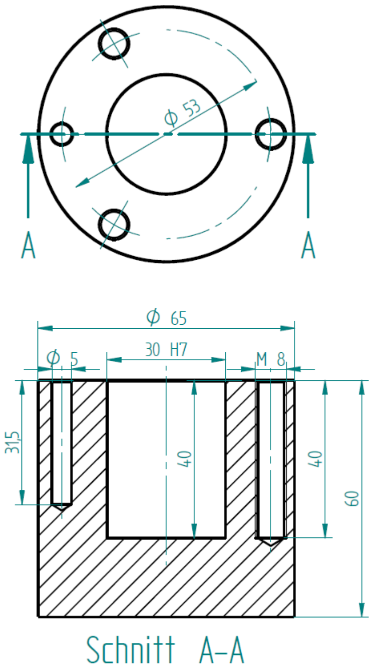


Figure B.3.: Hollow cylinder with threads for fastening the top and hole for the measuring sensor

Figure B.4.: PCB for the calorimeter, available under `https://aisler.net/p/EWHXKDFG`

The calorimetric energy was a calculation of the determined value - 0.0698 mV/J or its reciprocal value 14.33 J/mV - and the difference between the measured voltage before triggering the ignition source and the new stabilized value after about 5 minutes, when the energy was fully distributed inside the brass cylinder.

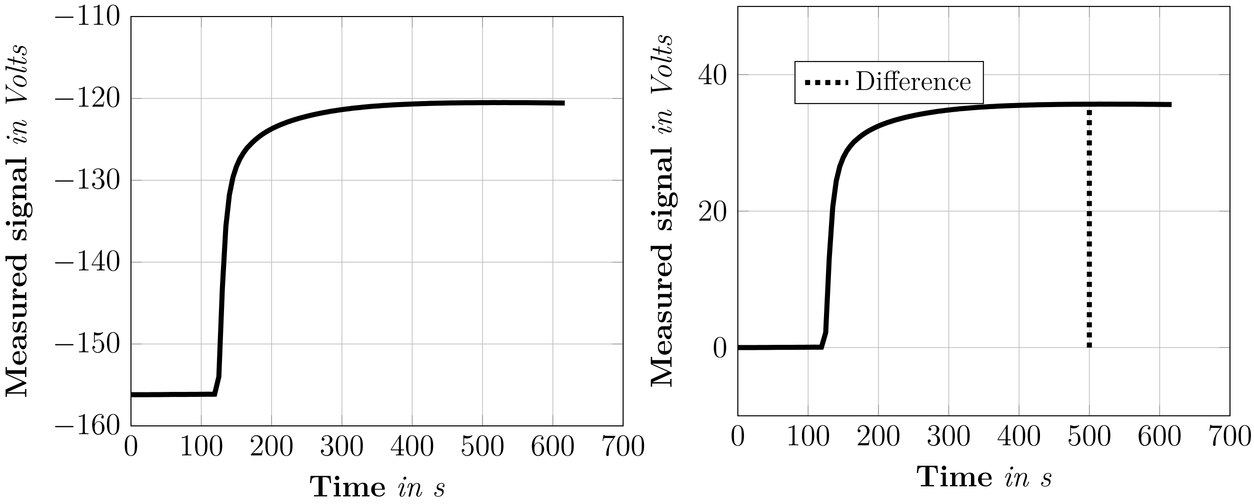


Figure B.5.: Measured voltage of the brass calorimeter for one single test, on the right the offset value is subtracted

In figure B.5 the calculated energy is 35.7 mV * 14.33 J/mV = 497 J.

C. Appendix III - History of Hybrids

1844	[2]
...	
1876	[3]
1879	[154]
1881	[155], [156]
1882	[6]
1884	[157]
1885	[5]
1886	[158]
1887	[159], [8]
1891	[160]
1892	[161]
1907	[4]
1910	[162], [163]
1911	[164], [165], [166]
1913	[7]
1927	[167], [168]
1929	[169]
1930	[170]
1933	[171]
1940	[172]
1941	[173]
1956	[174]
1957	[175]
1960	[176]
1961	[177]
1963	[178]
1964	**[10]**
1977	[9], [179]
1978	[180], [63]
1979	**[12]**,**[11]**

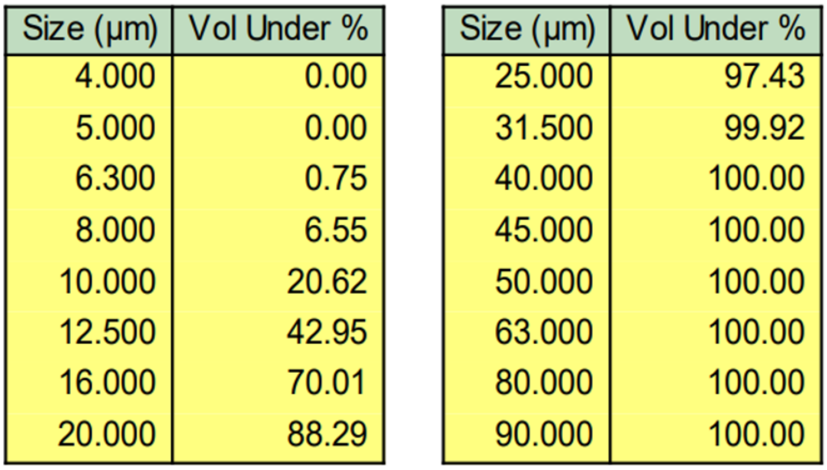
Table C.1.: History of publications for hybrid mixture explosions until 1980, only coal and methane, **gas amount was verified**

1980	**[72]**
1981	[181]
1982	[81]
1983	[149]
1985	[26], [1], [182]
1987	[183], [184], **[13]**
1990	[185]
1991	[82],[186]
1992	[89]
1993	[187], [188]
1994	[32]
1995	[189]
1996	[105],[190], [191],[192], [193]
1997	[194]
1998	[195], [196]
1999	[197], [198]
2000	[199], [200]
2001	[201]
2002	[202], [203]
2003	[204], [205], [206]
2004	[207]
2005	[208], [209]
2006	[210], [98], [21]
2007	[211], [17], [212]
2008	[28]
2009	[86], [84], [144]
2010	[213], [114], [214]
2011	[215], [216], [88], [145], [217], [218]
2012	[219], [220], [221], [222]
2013	[223], [224], [14], [225], [226], [146]
2014	[227], [15], [228], [229]
2015	[230], [231], [232], [18], [233], [85], [234], [235], [236], [237]
2016	[238], [239], [240], [241], [242], [243], [244], [245], [246], [247]
2017	[153], [248], [249], [250], [251], [252] [253], [254], [255], [256], [257], [258], [30], [259], [260], [261], [262], [151]
2018	[263], [264], [265], [266], [94], [267], [268], [269], [270], [271]
2019	[272], [273], [87], [92], [274], [275], [20]
2020	[276], [27], [91], [277], [278], [279], [280], [281], [96], [282], [283], [279]
2021	[284], [285], [286], [287], [288], [289], [290], [291], [292], [293], **[294]**
2022	[295], [296], [297], [298], [299], [300] [301], [302], [303], [31], [304], [305], [306], [307], [308], **[309]**
2023	[310], [311], [312], [313], [314], [315], [316], [317], **[318]**

Table C.2.: History of publications for hybrid mixture explosions since 1980, only coal and methane, **gas amount was verified**

D. Appendix IV - Sample data

Corn Starch



Size (µm)	Vol Under %
4.000	0.00
5.000	0.00
6.300	0.75
8.000	6.55
10.000	20.62
12.500	42.95
16.000	70.01
20.000	88.29
25.000	97.43
31.500	99.92
40.000	100.00
45.000	100.00
50.000	100.00
63.000	100.00
80.000	100.00
90.000	100.00

Figure D.1.: Values of the particle size distribution tested in December 2021

Date	Moisture content *in weight-%*	Median diameter *in μm*
03.09.2020	6.57	13
10.09.2020	6.28	-
17.09.2020	6.52	-
24.09.2020	5.78	-
01.10.2020	7.08	-
06.10.2020	6.41	-
07.04.2021	7.70	13.789
12.04.2021	7.43	-
19.04.2021	7.56	13.869
26.04.2021	7.46	13.866
01.05.2021	7.50	13.788
18.05.2021	7.23	13.324
26.05.2021	7.94	13.261
04.06.2021	7.55	13.253
06.07.2021	7.35	-
10.07.2021	7.31	13.595
14.07.2021	7.19	-
22.07.2021	7.37	-
17.09.2021	7.28	13.079
24.09.2021	7.28	13.078
09.10.2021	7.23	13.556
20.12.2021	7.4	13
20.01.2022	7.5	-
21.01.2022	7.9	-
09.02.2022	7.7	-
10.03.2022	7.6	-
16.03.2022	7.1	-
31.03.2022	7.7	-
06.04.2022	7.7	-

Table D.1.: Moisture content and particle size distribution over time

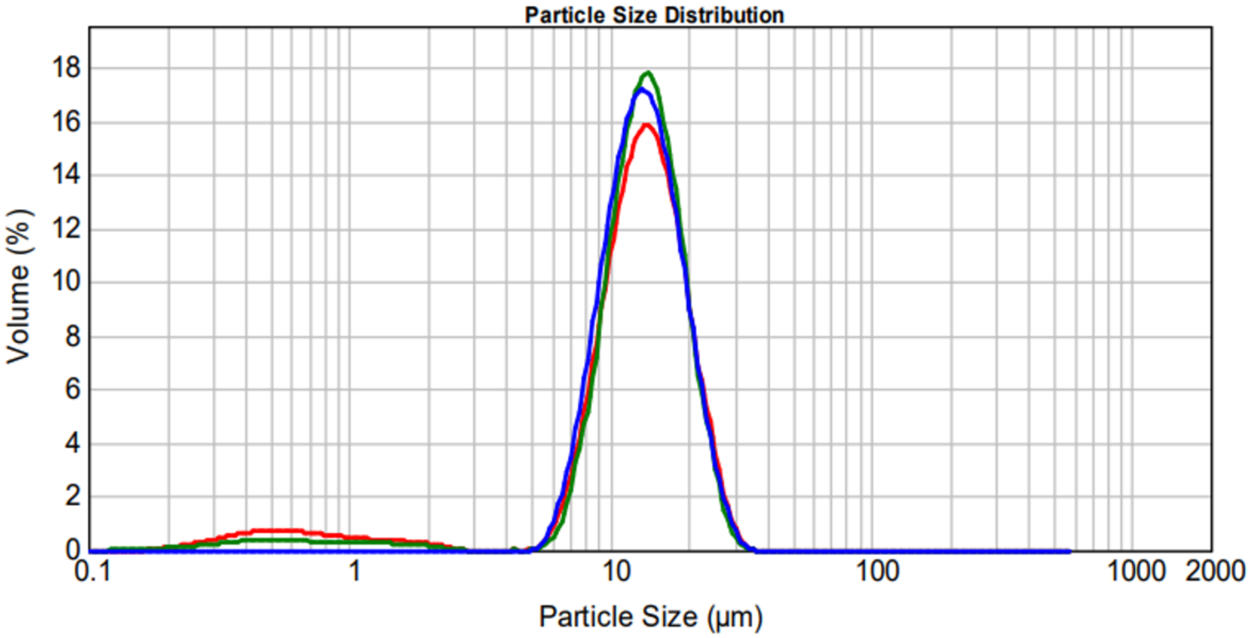


Figure D.2.: Particle size distribution tested in December 2021

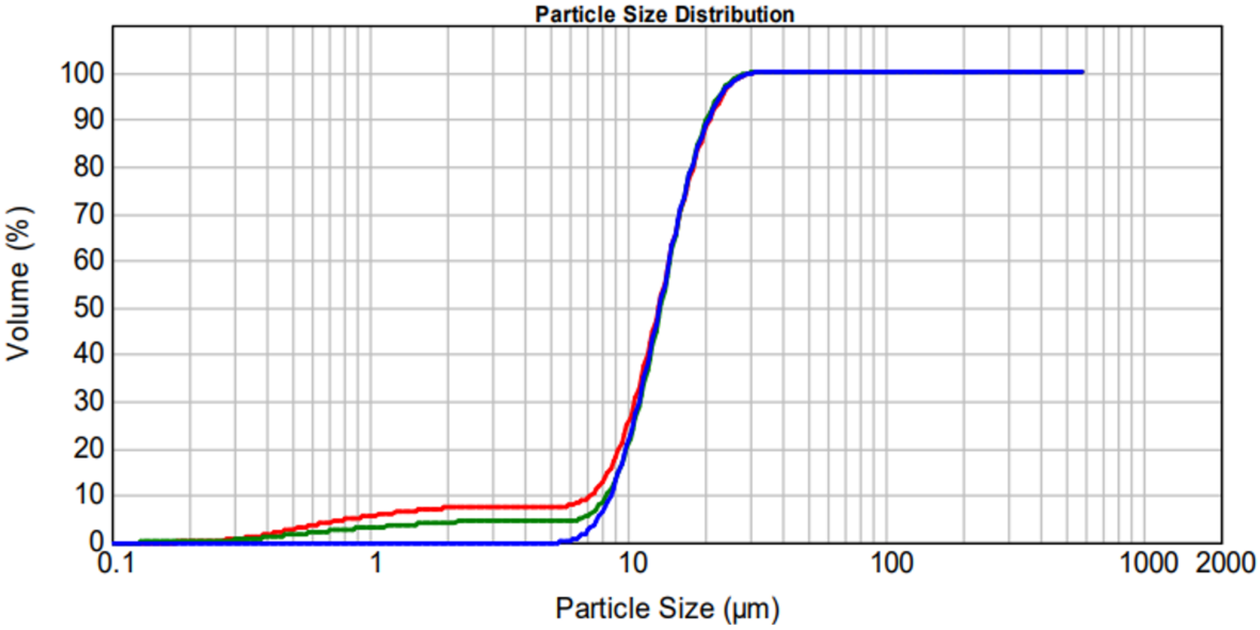


Figure D.3.: Summed particle size distribution tested in December 2021

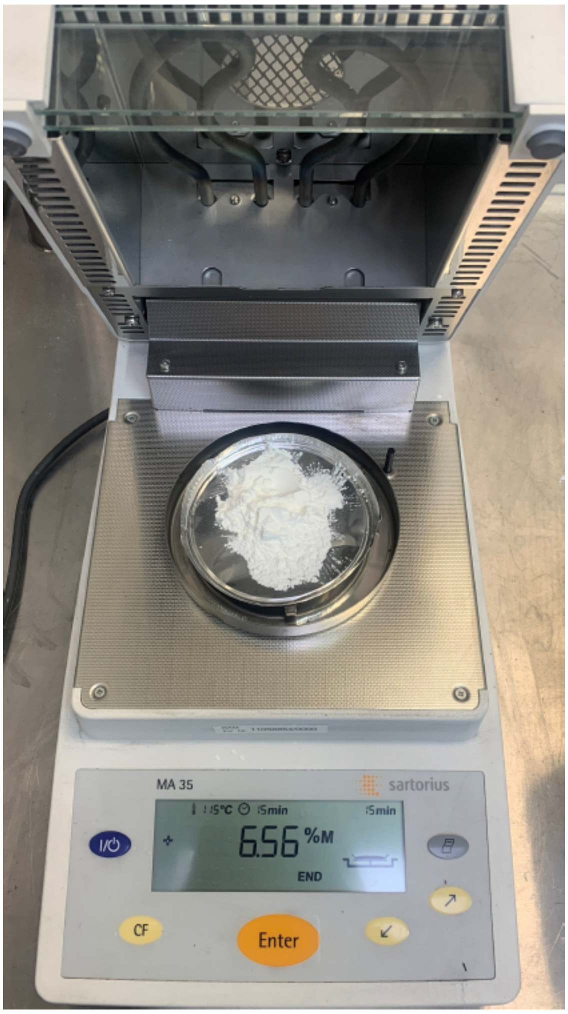
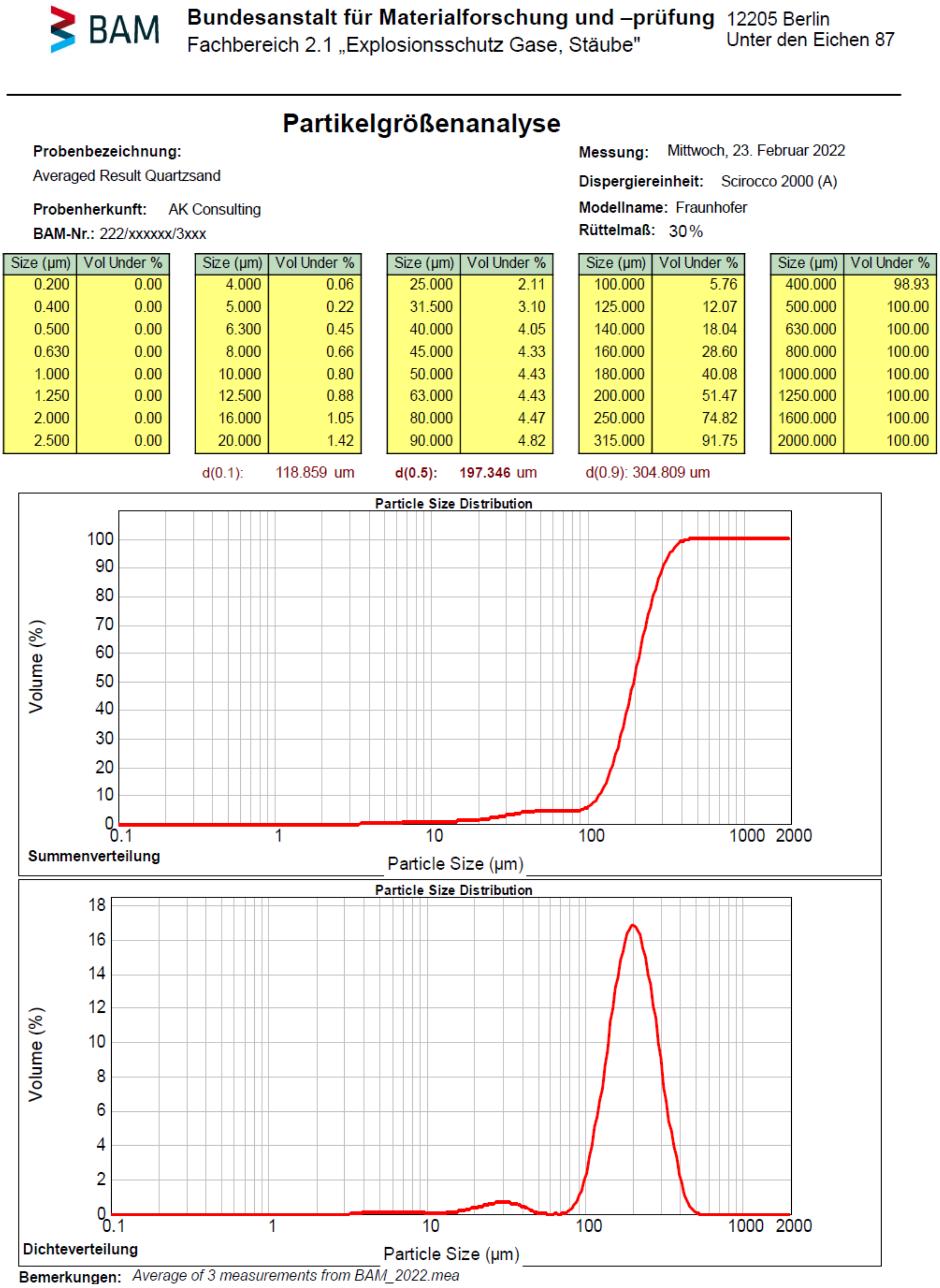


Figure D.4.: Moisture analyzer from Sartorius

Quartz Sand



Bundesanstalt für Materialforschung und –prüfung
Fachbereich 2.1 „Explosionsschutz Gase, Stäube"

12205 Berlin
Unter den Eichen 87

Partikelgrößenanalyse

Probenbezeichnung:
Averaged Result Quartzsand

Probenherkunft: AK Consulting

BAM-Nr.: 222/xxxxxx/3xxx

Messung: Mittwoch, 23. Februar 2022

Dispergiereinheit: Scirocco 2000 (A)

Modellname: Fraunhofer

Rüttelmaß: 30%

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.200	0.00	4.000	0.06	25.000	2.11	100.000	5.76	400.000	98.93
0.400	0.00	5.000	0.22	31.500	3.10	125.000	12.07	500.000	100.00
0.500	0.00	6.300	0.45	40.000	4.05	140.000	18.04	630.000	100.00
0.630	0.00	8.000	0.66	45.000	4.33	160.000	28.60	800.000	100.00
1.000	0.00	10.000	0.80	50.000	4.43	180.000	40.08	1000.000	100.00
1.250	0.00	12.500	0.88	63.000	4.43	200.000	51.47	1250.000	100.00
2.000	0.00	16.000	1.05	80.000	4.47	250.000	74.82	1600.000	100.00
2.500	0.00	20.000	1.42	90.000	4.82	315.000	91.75	2000.000	100.00

d(0.1): 118.859 um **d(0.5): 197.346** um d(0.9): 304.809 um

Bemerkungen: *Average of 3 measurements from BAM_2022.mea*

Niacin

BAM **Bundesanstalt für Materialforschung und –prüfung**
Fachbereich 2.1 „Explosionsschutz Gase, Stäube"
12205 Berlin
Unter den Eichen 87

Partikelgrößenanalyse

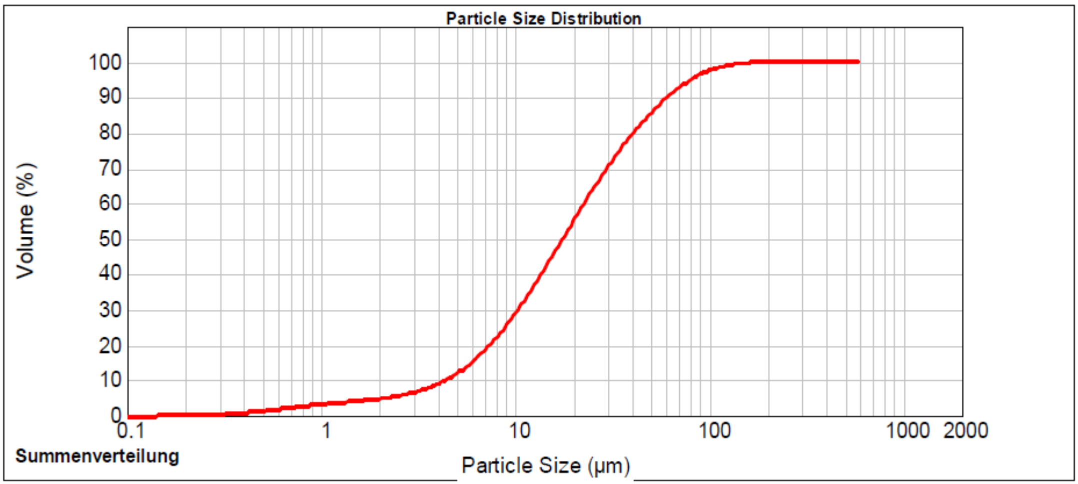
Probenbezeichnung:
Averaged Result Niacin

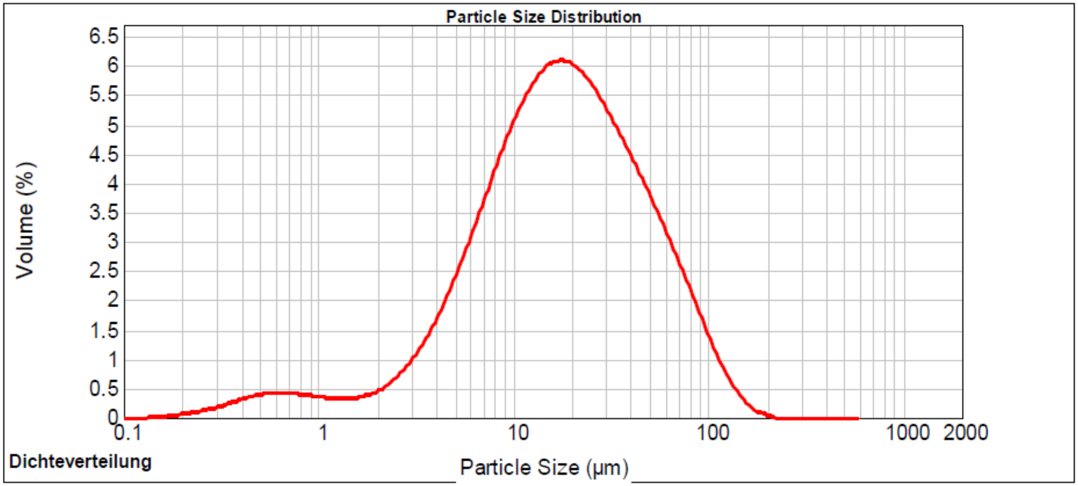
Probenherkunft: AK Consulting
BAM-Nr.: 222/xxxxxx/3xxx

Messung: Mittwoch, 23. Februar 2022
Dispergiereinheit: Scirocco 2000 (A)
Modellname: Fraunhofer
Rüttelmaß: 30 %

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.200	0.08	4.000	9.11	25.000	63.84	100.000	97.57	400.000	100.00
0.400	0.86	5.000	12.05	31.500	72.06	125.000	99.10	500.000	100.00
0.500	1.39	6.300	16.31	40.000	79.58	140.000	99.53	630.000	100.00
0.630	2.03	8.000	22.16	45.000	82.88	160.000	99.82	800.000	100.00
1.000	3.25	10.000	28.94	50.000	85.61	180.000	99.93	1000.000	100.00
1.250	3.75	12.500	36.82	63.000	90.80	200.000	99.99	1250.000	100.00
2.000	4.85	16.000	46.37	80.000	94.93	250.000	100.00	1600.000	100.00
2.500	5.66	20.000	55.25	90.000	96.47	315.000	100.00	2000.000	100.00

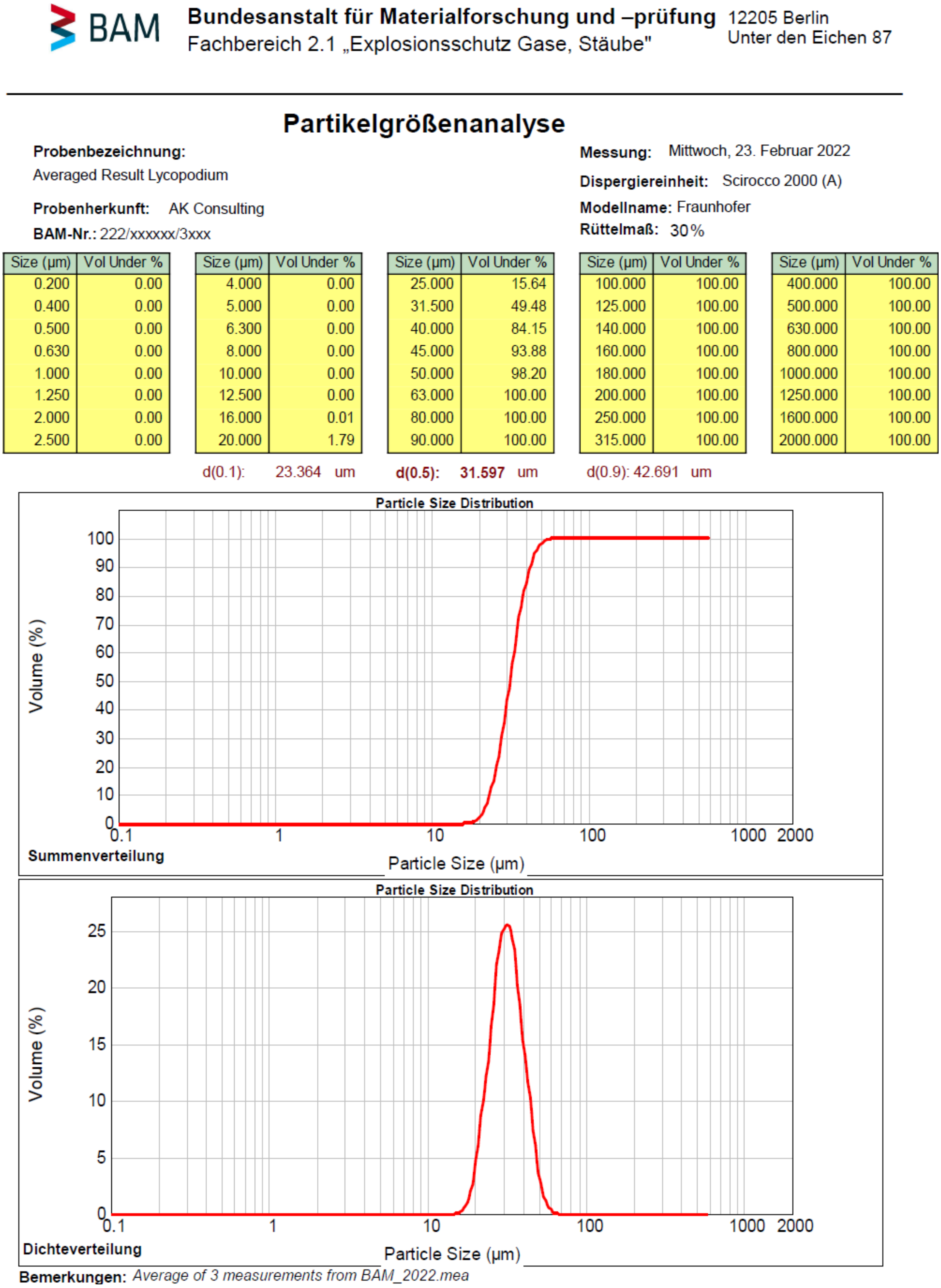
d(0.1): 4.317 um **d(0.5): 17.526** um d(0.9): 60.577 um





Bemerkungen: *Average of 3 measurements from BAM_2022.mea*

Lycopodium



Bundesanstalt für Materialforschung und –prüfung
Fachbereich 2.1 „Explosionsschutz Gase, Stäube"

12205 Berlin
Unter den Eichen 87

Partikelgrößenanalyse

Probenbezeichnung:
Averaged Result Lycopodium

Probenherkunft: AK Consulting

BAM-Nr.: 222/xxxxxx/3xxx

Messung: Mittwoch, 23. Februar 2022

Dispergiereinheit: Scirocco 2000 (A)

Modellname: Fraunhofer

Rüttelmaß: 30%

Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %	Size (µm)	Vol Under %
0.200	0.00	4.000	0.00	25.000	15.64	100.000	100.00	400.000	100.00
0.400	0.00	5.000	0.00	31.500	49.48	125.000	100.00	500.000	100.00
0.500	0.00	6.300	0.00	40.000	84.15	140.000	100.00	630.000	100.00
0.630	0.00	8.000	0.00	45.000	93.88	160.000	100.00	800.000	100.00
1.000	0.00	10.000	0.00	50.000	98.20	180.000	100.00	1000.000	100.00
1.250	0.00	12.500	0.00	63.000	100.00	200.000	100.00	1250.000	100.00
2.000	0.00	16.000	0.01	80.000	100.00	250.000	100.00	1600.000	100.00
2.500	0.00	20.000	1.79	90.000	100.00	315.000	100.00	2000.000	100.00

d(0.1): 23.364 um **d(0.5): 31.597 um** d(0.9): 42.691 um

Bemerkungen: *Average of 3 measurements from BAM_2022.mea*

E. Appendix V - Miscellaneous

E.1. Voltage, Current, Power and Summed Power (=Ignition Energy) of the exploding wire

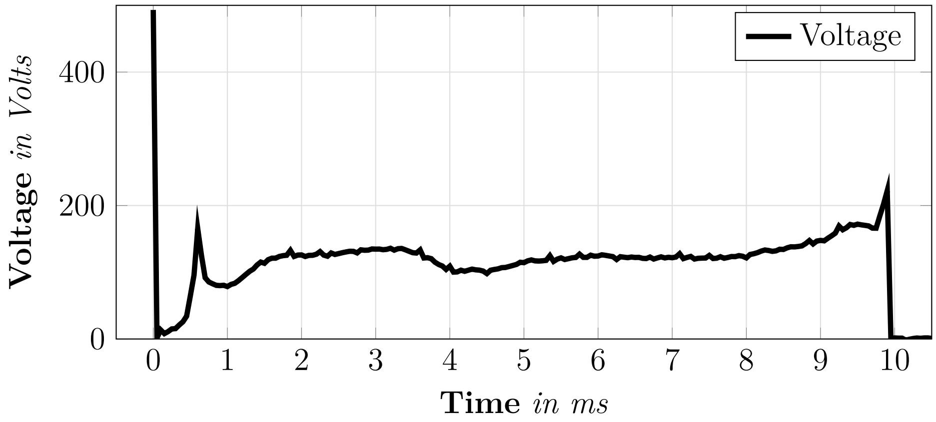


Figure E.1.: Voltage curve at 450 V ignition voltage and 1070 J ignition energy

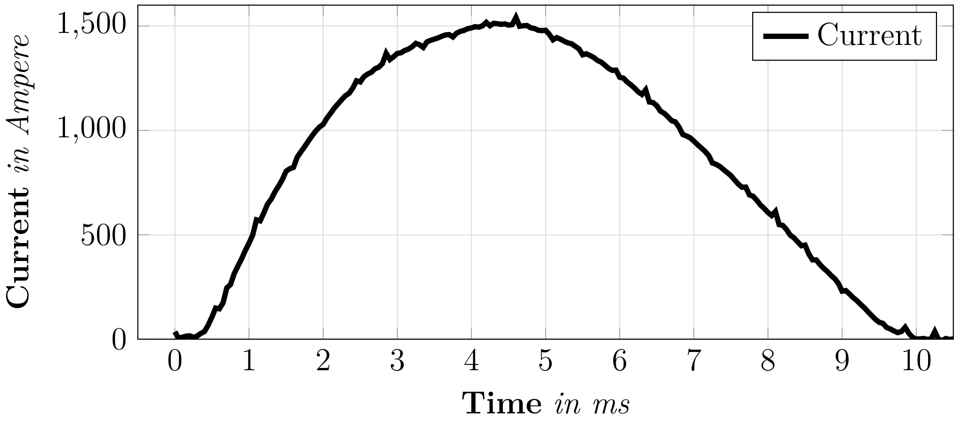


Figure E.2.: Ignition current curve at 450V ignition voltage and 1070 J ignition energy

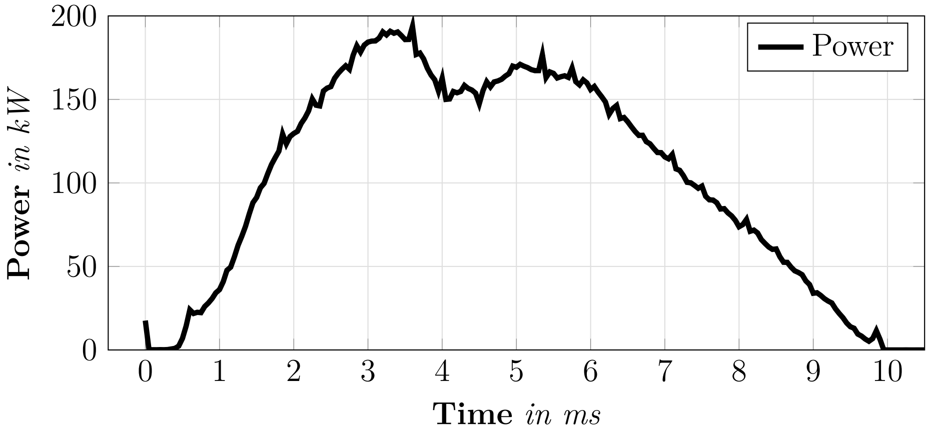


Figure E.3.: Power curve at 450 V ignition voltage and 1070 J ignition energy; product of ignition voltage and ignition current

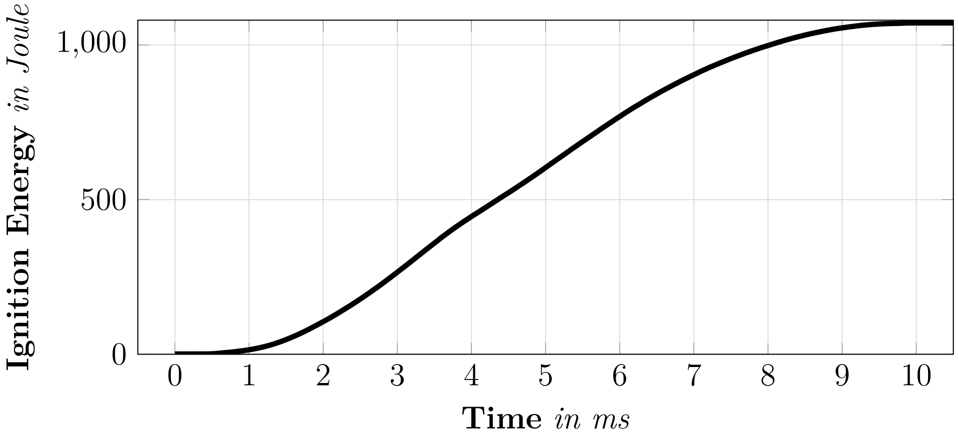


Figure E.4.: Summed power at 450 V ignition voltage and 1070 J ignition energy

E.2. Melting energy for the exploding wire

The distance between the two electrodes was additionally varied between 5 mm and 200 mm. The melting energy of the wire $E_{melting}$ was calculated with the following equation:

$$E_{melting} = l_{wire} * \frac{\pi}{4} * d_{wire}^2 * \rho_{Nickelin} * \Delta T * cp_{Nickelin} \tag{E.1}$$

*with l_{wire}: length of the wire in mm, d_{wire}: diameter of the wire in mm, $\rho_{Nickelin}$: densitiy of nickeln in kg/m^3, Δ T: difference between ambient temperature (21 ° C) and the melting temperature of Nickelin (1180 °) being 1159 K, $cp_{Nickelin}$: specific heat capacity of Nickelin being 0,4 J/(g*K)*

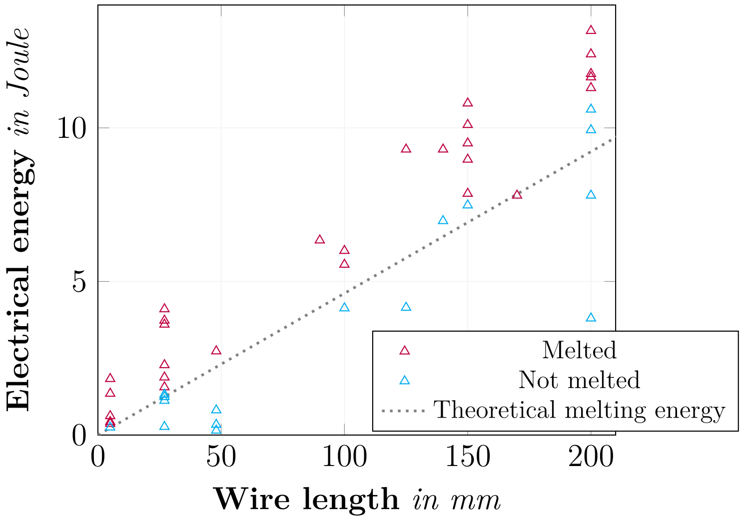


Figure E.5.: Wire length against electrical energy pushed through them

E.3. Influence of the gas on the schlieren images

There is a simple relationship for the air and other gases between the refractive index n and the gas density ρ of a fluid, see Equation E.2:

$$n - 1 = k\rho \tag{E.2}$$

This coefficient k is a constant for a given fluid. For air this coefficient is approximately 0.23 $\frac{cm^3}{g}$ at standard atmospheric conditions, given visible illumination. Other gases may have a variety from 0.10 $\frac{cm^3}{g}$ until 1.5 $\frac{cm^3}{g}$, but the refractive index varies only in the third or fourth decimal place for common gases ([319], [320]). Also, Equation E.2 is not too deeply dependent upon ρ. The refractivity of a gas (n-1) depends upon gas composition, temperature, density and the wavelength of illumination. Simple perfect-gas state Equation E.3 could be used in many cases when the temperature, density and pressure of gases is not too far from atmospheric conditions. In this equation, R is the specific gas constant.

$$p/\rho = R * T \tag{E.3}$$

Due to temperature differences or high gas speeds velocities, flowing gases with variable density can arise. These possibilities lead to the fact, that gases are capable of refracting light. This refraction may be then visualized. In the schlieren image the gradients $\delta n/\delta x$ and $\delta n/\delta y$ are visible which are perpendicular to optical axis and the knife-edge orientation ([319], [320]).

E.4. Influence of the turbulence on the minimum ignition energy

Ballal and Lefebvre investigated the influence of turbulence on the minimum ignition energy and give an explanation for their experimental findings: "Initial passage of the spark creates a cylindrical volume of hot gas between the electrodes. As the spark discharge proceeds the effect of the flow is to extend this volume in a downstream direction, as illustrated in" Fig. 10. "Under favorable conditions, the rate of heat generation by chemical reaction at the kernel surface may exceed the rate of heat loss by turbulent diffusion. If this happens the spark kernel will continue to expand and a successful ignition is assured." [321]

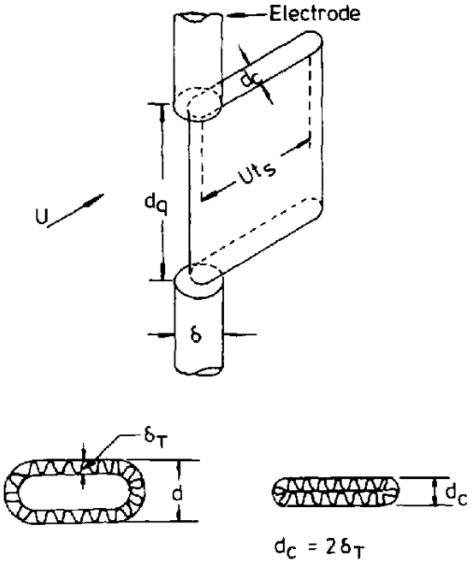


Figure E.6.: Proposed idealized model for formation of spark kernel, taken from [321]

E.5. Burning duration of chemical igniters

Table E.1.: Main burning duration of chemical igniters and time of the last visible glowing particle

Stated energy	(Main) burning duration	last glowing particle
-	*in ms*	*in ms*
100 J, Nr. 1	15	110
100 J, Nr. 2	5	100
100 J, Nr. 3	6	100
250 J, Nr. 1	18	160
250 J, Nr. 2	6	75
500 J, Nr. 1	17	167
500 J, Nr. 2	9	105
1 kJ, Nr. 1	8	205
1 kJ, Nr. 2	9	80
5 kJ, Nr. 1	15	332
5 kJ, Nr. 2	13	260

E.6. The need for an alternative ignition source - political and financial reasons

The need for an alternative ignition source is also visible if the countries having dust testing laboratories are marked. The countries, which are allowed to import chemical igniters that are necessary for the determination of the maximum explosion pressure and the maximum rate of pressure rise, are marked in red (see figure E.7).

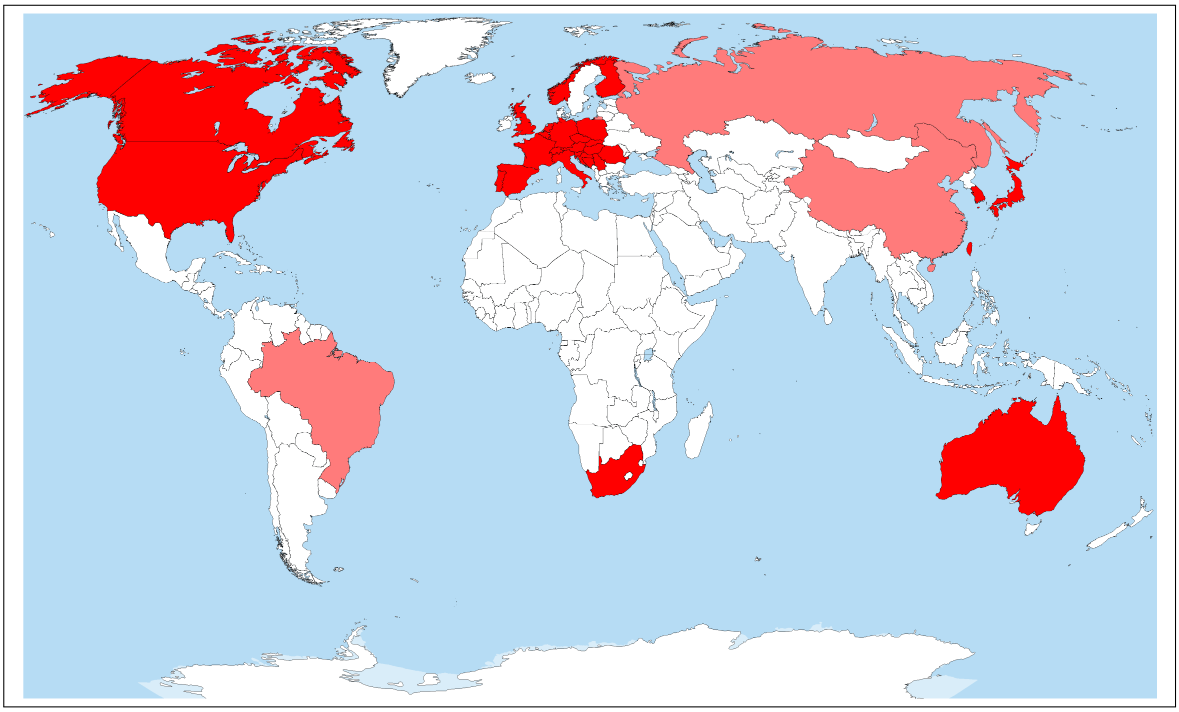


Figure E.7.: Worldmap with the countries, that perform dust explosion tests (CC BY-SA 3.0 `https://en.wikipedia.org/wiki/User:Cbrittain10`, image cut and marked by the author)

Brazil is marked reddish, since there is only one facility that is allowed to import the igniters and they have to be delivered by the military. Chinese dust testing laboratories manufacture their own igniters since the restrictions are very high. In Russia there are dust testing laboratories but the standard igniters are not allowed to be delivered anymore. In India there is no single facility for the determination of p_{max} and $(dp/dt)_{max}$ of dusts since the igniters are prohibited. So the companies have to either ship the dust samples to the United Kingdom or forego the tests. The same applies for Southern America except for the one facility in Sao Paulo. In Africa there is also just one dust testing facility in South Africa, making it almost impossible to implement safety measures all over the continent.

E.7. Standards in which the transformer is specified

Table E.2.: Specifications on the induction spark in different standards; values, that are presumably wrong are in red; calculated values in brackets

Standard	Primary Voltage *in Volt*	Secondary Voltage *in kV*	Stated Current *in mA*	Electrode Distance *in mm*	Spark Duration *in ms*	Power *in Watt*
ISO 80079-1 [322]	-	15	30 (short-circuit)	4	200	-
ISO 80079-2 [58]	-	15	-	4	continuosly	**200**
ISO 10156 [69]	-	15	30 (no further information)	5	200-500	**(1000)** @50Hz **(1200)** @60Hz
EN 1839 [42]	-	15	30 (short-circuit)	5 ± 1	200	10
EN 15967 [43]	-	13 - 16	20 - 30 (short-circuit)	5 ± 0,1	200 or 500	10
EN 15794 [323]	-	13 - 16	20 - 30	5 ± 0,1	200 or 500	10
EN 17624 [71]	-	13 - 16	20 - 30	5 ± 0,1	200 or 500	10
ASTM E 681 [70]	120	15	**30**	6,4	200 - 400	**(450)**
ASTM E 789 [75]	115	12	-	6,35	continuosly	-

There are also new electronic transformers on the market, that change the frequency from 50 Hz to 20 kHz before transforming the voltage to 15 kV. These are smaller and today easier to obtain, produce sparks only at the positive wave (so just 50 instead of 100 sparks per second) but with higher energy. The power and the ignition behavior is similar to the standard type. Since they are the standard today it may even be overseen, that this one is in use instead of the standardized type [1].

E.8. Ignition Criteria

There are several ignition criteria for the determination of safety characteristics of dusts and gases. Since the chemical igniters cause a significant pressure rise that depends also on the test vessel size a clear statement shall be done what was counted as an ignition.

The values vary from 0.05 bar g (EN 1839) to 2.3 bar g (ASTM1226) because the ignition energy is with 2 J and 10 000 J also different by a factor of 5 000. However, to overcome this weakness or as a first approach here are several ignition criteria that are stated in the standards. This may be a first help, if confusion arises about the ignitability of various

---

[1] This occured to two facilities that were not aware of the fact, that they used this type.

Table E.3.: Ignition criteria stated in different standards

Standard	Equation	Pressure *in bar g*	Comment
EN 14034-1:2011 [45]	$p_{Ex} > p_I + 0.5$ bar	0.5	Theoretically every test an ignition since the igniters cause an overpressure of around 1 bar g
	KSEP changes p_{Ex} to p_m	1.96	
EN 14034-2:2011 [46]	$p_{Ex} > p_I + 0.5$ bar	0.5	Theoretically every test an ignition since the igniters cause an overpressure of around 1 bar g
	KSEP changes p_{Ex} to p_m without stating the equation	1.96	
EN 14034-3:2011 [46]	$p_{Ex} > p_I + 0.5$ bar	0.5	
	KSEP changes p_{Ex} to p_m without stating the equation	0.62	
EN 14034-4:2011 [47]	$p_{Ex} > p_I + 0.5$ bar	0.5	
	KSEP changes p_{Ex} to p_m without stating the equation	0.62	
prEN14034:2022 [324]	$p_{Ex} > p_I + p_{CI} + 0.2$ bar	1.2	KSEP would take 1.96 bar g
ASTM1226:2011 [57]	$p_m > 1$ bar	2.3	KSEP would take 1.96 bar g
ISO 80079-2 [58]	$p_{Ex} > p_I + p_{CI} + 0.3$ bar	0.6	KSEP would change value slightly to 0.62 bar g
EN 1839:2017 [42]	$p_{Ex} > p_I * 1.05 + P_{IS}$	0.05	depending on beginning pressure, ignition source and volume of the test vessel

p_{Ex}=Explosion overpressure; p_{CI}=Overpressure caused by chemical igniter
p_{IS}=Overpressure caused by the ignition source; p_m=corrected explosion overpressure
p_I=Initial pressure

concentrations of combustible substances. The author also wants to mention, that there is no right or wrong as long as everybody agrees on the same value and as long as everybody knows, what criterion was chosen for what reason.

Again, it should also always be clearly stated what ignition energy was chosen, what the beginning pressure was, what value for the ignition criterion was chosen and whether the corrected value was taken or the measured one.

E.9. Additional Ignition Delay Time

The effect of the decay of turbulence on the safety characteristics of gases and dusts was investigated several times. The following list might give an overview of what has been investigated:

- The flow characteristics of the dust were simulated [113]
- The effect of the decay of turbulence on the safety characteristics of several dusts was investigated with ignition delay times of 60 ms, 100 ms and above [107],on coal dust with ignition delay times of 15 ms, 30 ms, 60 ms, 90 ms and 150 ms [325] and on methane and nicotinic with ignition delay times of 60 ms, 90 ms and 120 ms [217] and with ignition delay times of 60 ms, 120 ms and 240 ms [326]
- The effect of the decay of turbulence on the safety characteristics of a hybrid dust gas mixture was investigated with ignition delay times of 30 ms, 45 ms, 60 ms, 75 ms, 90 ms, 105 ms and above [91]
- The effect of the decay of turbulence on the safety characteristics of corn dust was investigated in a 5L-sphere with ignition delay times of 60 ms, 80 ms, 100 ms, 150 ms and 200 ms (for the 1m^3 600 ms is the standard) [116]
- The effect of the decay of turbulence on the safety characteristics of several dusts was investigated in the 1m^3 with ignition delay times of 115 ms, 200 ms, 300 ms, 400 ms, 500 ms and 600 ms (for the 1m^3 600 ms is the standard) [118]

Thus, most of the investigations chose a rather coarse step-size. The very narrow variation of the ignition delay time of ± 10 ms (50 ms to 70 ms in total) that might occur due to inertia of the ignition source was not found in the literature.

That this additional delay causes different values for the (dp/dt) of dusts was investigated with a constant concentration of 500 g/m^3 for corn starch, niacin and lycopodium while all other parameters were kept constant. The (dp/dt)-value decreased from 505 bar/s for 60 ms over 452 bar/s with 70 ms to 424 bar/s with 80 ms for corn starch (see figure E.8, all values averaged). The values of the other two samples are also displayed in figure E.9 and E.10 and in table E.4. In general the difference between 60 ms and 80 ms causes a reduction of (dp/dt) of 15 % to 35 %.

The additional delay time of the exploding wire using a simple transformer would be especially annoying since it would be unpredictable and different in every test.

A coupling of the 20L-sphere controller to the power grid is possible but difficult and, since there is the other presented method with capacitors, not necessary.

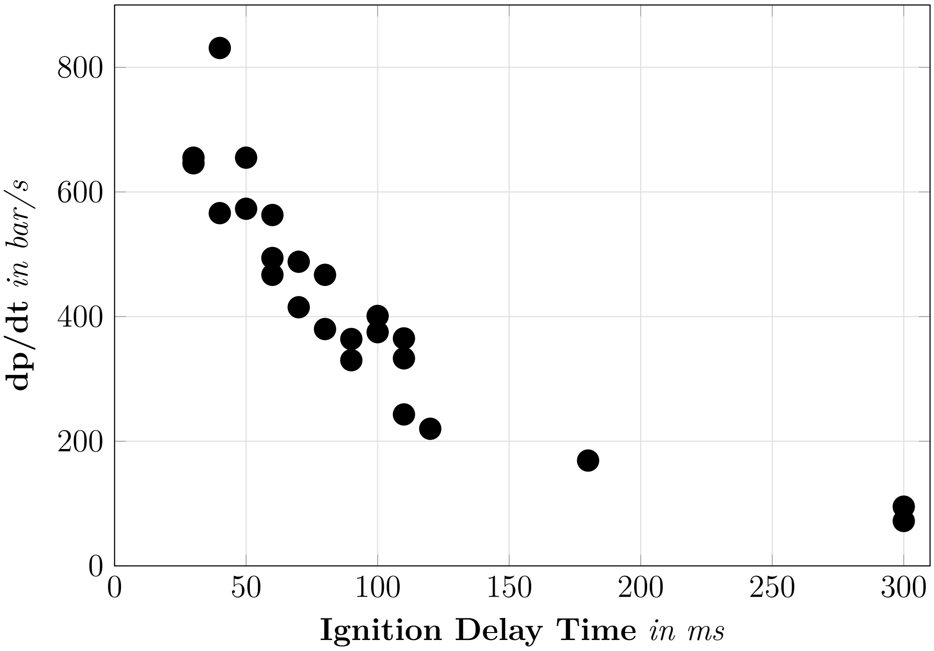


Figure E.8.: Influence of the ignition delay time on the (dp/dt)-value of 500 g/m^3 corn starch

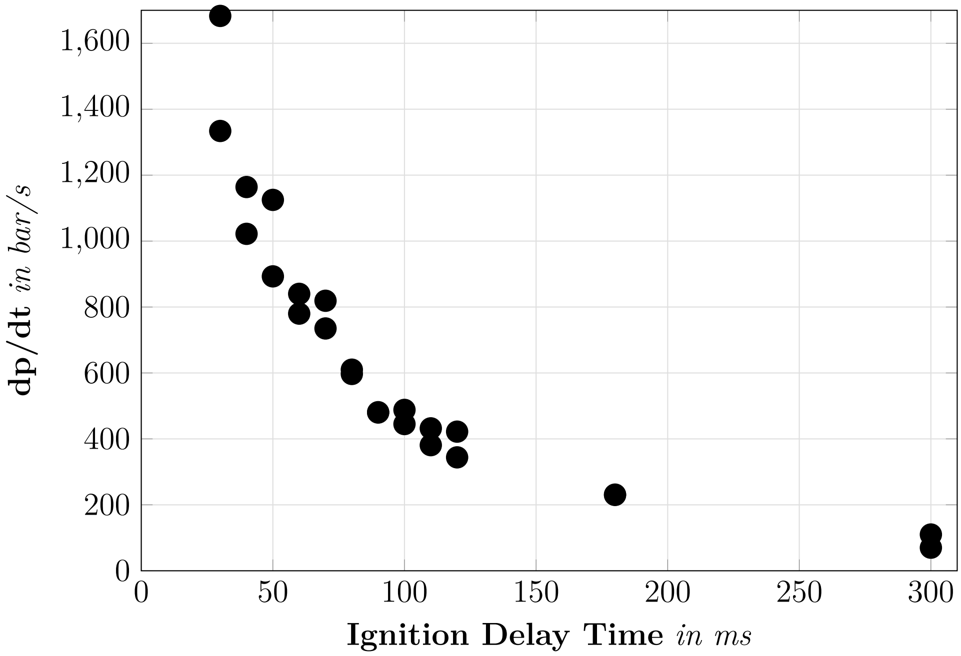


Figure E.9.: Influence of the ignition delay time on the (dp/dt)-value of 500 g/m^3 niacin

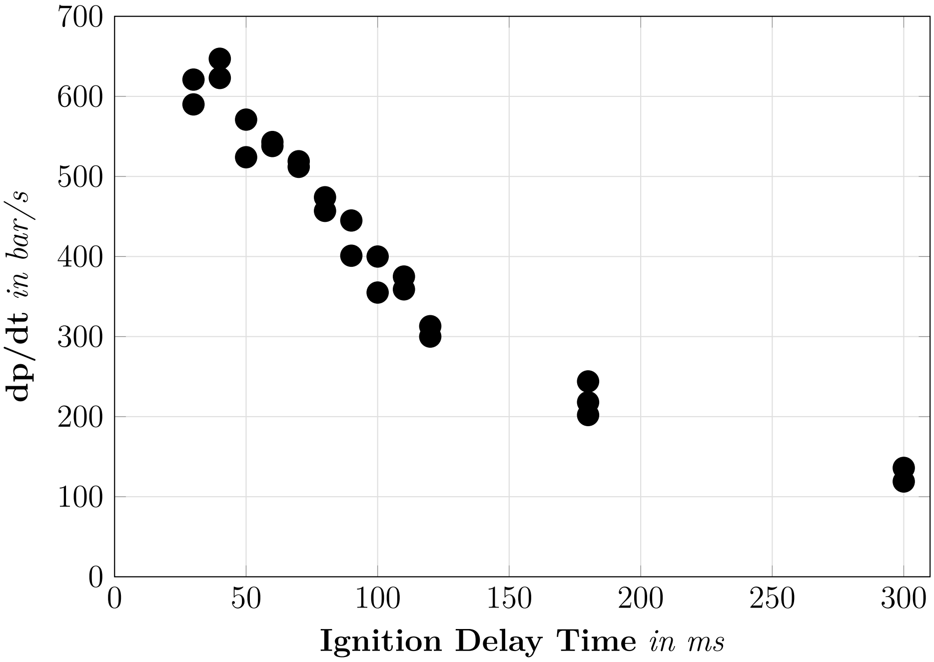


Figure E.10.: Influence of the ignition delay time on the (dp/dt)-value of 500 g/m^3 Lycopodium

Table E.4.: Maximum rate of pressure rise of three different dust samples against ignition delay time

	ignition delay time				
Dust	50 ms	60 ms	70 ms	80 ms	90 ms
Corn Starch	614	505	452	424	347
Lycopodium	548	541	516	466	423
Niacin	1009	810	777	604	481

E.10. Inherent scattering of p_{Ex} and $(dp/dt)_{Ex}$ of dusts

The deviations and scattering of dust explosions are known in the dust explosion community but no statements were found in the literature.
The above mentioned corn starch was tested twenty times at concentrations of 500 g/m^3 and 750 g/m^3.
All other parameters were kept within a very narrow range so that they can be seen as constant:

- Chemical igniters with two times 1 kJ
- Pressure before injection: 400 mbar ± 0.2 mbar
- Pre-ignition pressure rise: 640 mbar ± 15 mbar
- Mass of corn starch: 10 g ± 0.03 g (for the concentration of 500 g/m^3)
- Mass of corn starch: 15 g ± 0.01 g (for the concentration of 750 g/m^3)

The moisture content of the corn starch was tested before each testing day and was between 7.4 weight-% and 7.6 weight-%.
All presented values of the explosion pressures were corrected with the equation 2.2 stated in chapter 2.1.2.
The explosion overpressure and the rate of pressure rise are shown in figure E.11 and E.12 as histograms. This rather unusual way of presenting the values was chosen because most of the points were overlapping in the "standard" way of presenting while the outliers were harder to spot.

The scattering for the explosion pressures is with 8.4 bar g ± 0.4 bar (500 g/m^3) and 9 bar g ± 0.4 bar (750 g/m^3) below 5 %. However, the (dp/dt)-values have with values of 492 bar/s ± 117 bar/s (500 g/m^3) and 493 bar/s ± 113 bar/s (750 g/m^3) a scattering of 24 % respectively 18 %. Since it is mandatory in both standards to perform at least three test series the deviation of the stated values between different test facilities might be smaller because they are averaged but since the influence of other parameters can be excluded here the arising deviations might still be larger than the allowed 20 %.

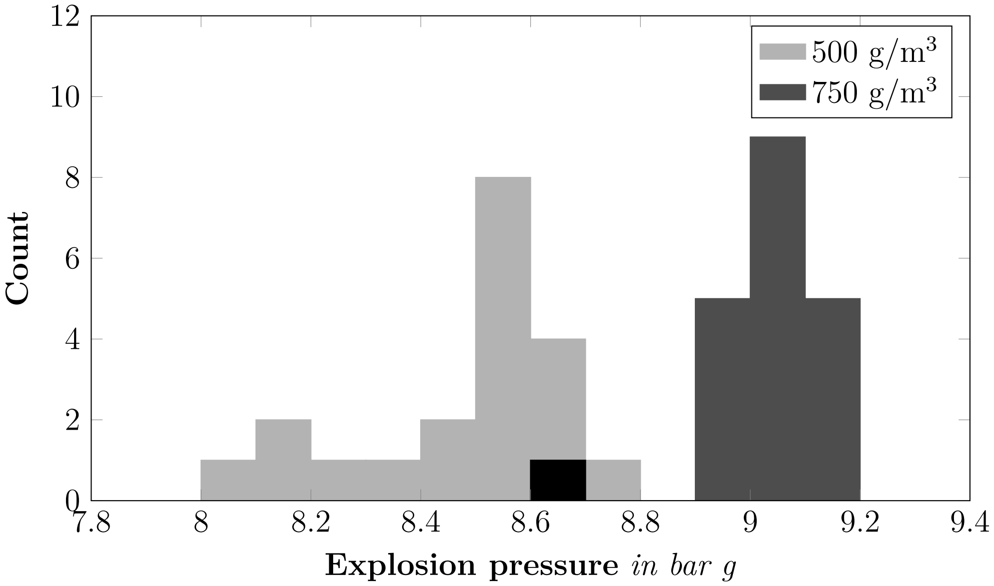


Figure E.11.: Distribution of the explosion pressures of corn starch for two different concentrations

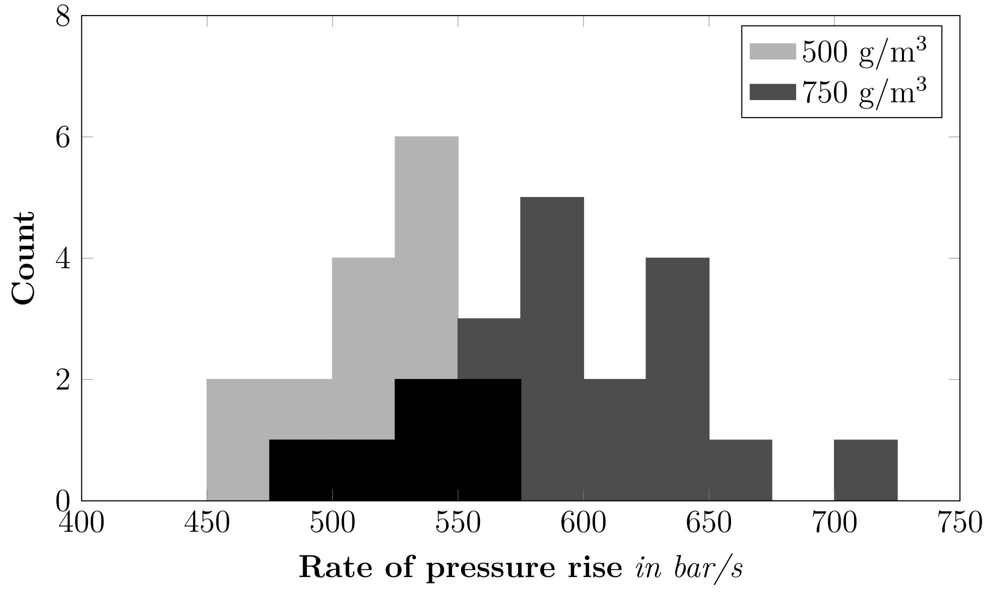


Figure E.12.: Distribution of the rates of pressure rise of corn starch for two different concentrations

F. Appendix VI - Scientific publications

The corresponding author is always marked in bold letters.

F.1. Peer-reviewed 1st author papers published during the dissertation

Comparative study on standardized ignition sources used for explosion testing

Stefan Spitzer, Enis Askar, Arne Krietsch, Volkmar Schröder

This paper compares the chemical igniters, the induction spark, the surface-gap spark and the exploding wire regarding the burning duration and the net energy, that is usually introduced into the test vessel.

Published in July 2021 in *Journal of Loss Prevention in the Process Industries*
`https://doi.org/10.1016/j.jlp.2021.104516`
Previously published in the proceedings of the 13^{th} ISHPMIE

Comparative Study on standardized ignition sources Part 2: Exploration of the initial igniting volume of standardized ignition sources for the determination of explosion characteristics

Stefan Spitzer, Vojtech Jankuj, Arne Krietsch

This paper compares the chemical igniters, the induction spark, the surface-gap spark and the exploding wire regarding their burning volume with a Schlieren-Setup.

Published in May 2022 in *Chemical Engineering Transactions*
`https://doi.org/10.3303/CET2290087`

This paper was chosen for a special Issue of *Process Safety and Environmental Protection.* An extended wersion with the title "Igniting Volume of four Ignition Sources" was published in March 2023 under the following addres:
`https://doi.org/10.1016/j.psep.2022.12.076`

Influence of pre-ignition pressure rise on safety characteristics of dusts and hybrid mixtures

Stefan H. Spitzer, Enis Askar, Alexander Benke, Bretislav Janovsky, Ulrich Krause, Arne Krietsch

The influence of the allowed range of the initial pressures in the different standards is investigated as well as the pressure drop due to the compression when injecting the dust in the 20L-sphere.

Published in March 2022 in *FUEL*
`https://doi.org/10.1016/j.fuel.2021.122495`

The maximum rate of pressure rise of hybrid mixtures

Stefan H. Spitzer, Enis Askar, Kristin J. Hecht, Paul Geoerg, Dieter Gabel, Ulrich Krause, Olivier Dufaud, Arne Krietsch

The first part of this paper focuses on the confusion around the different statements about $(dp/dt)_{max}$ of hybrid mixtures and where they come from. In the second part of this paper experimental results are presented that elaborate how to clarify the different findings of past research and show what to expect as a real worst-case-value for hybrid mixtures.

Published in December 2023 in *Journal of Loss Prevention in the Process Industries*
`https://doi.org/10.1016/j.jlp.2023.105178`
Previously published and presented in July 2022 at the *14th ISHPMIE*

Requirements for a hybrid dust-gas-standard: Influence of the mixing procedure on safety characteristics of hybrid mixtures

Stefan H. Spitzer, Enis Askar, Kristin J. Hecht, Dieter Gabel, Sabine Zakel, Arne Krietsch

Beside the ignition source, the mixing procedure is the main difference between the single-phase standards for dusts and gases. The preparation of hybrid mixtures containing a flammable gas and a combustible dust in the 20L-sphere can be realized in different ways. Either the flammable gas is filled only in the sphere or only in the dust container or in both. In previous works, almost always the first method is applied, without giving any information on the accuracy of the gas mixtures. In this work the accuracy of the gas mixtures and the results of the tests applying two methods of mixing were studied.

Published in August 2022 in *fire*
`https://doi.org/10.3390/fire5040113`

1st International Round Robin Test on Safety Characteristics of Hybrid Mixtures

Stefan H. Spitzer, Enis Askar, Alexander Benke, Chris Cloney, Sebastian D'Hyon, Olivier Dufaud, Zdzislaw Dyduch, Dieter Gabel, Paul Geoerg, Vanessa Heilmann, Vojtech Jankuj, Wang Jian, Ulrich Krause, Arne Krietsch, Miroslav Mynarz, Frederik Norman, Jan Skrinsky, Jerome Taveau, Alexis Vignes, Sabine Zakel, Shengjun Zhong

In this first round robin test on hybrid mixtures ever, with methane as gas component and a specific corn starch as dust sample, the practicality of the whole procedure, the scattering of the results and the deviation between the testing apparatuses is investigated. This paper summarizes the experimental procedure adopted and objectives of the first round-robin phase involving three of the four original German companies, plus volunteering laboratories from Australia, Belgium, Czech Republic, France, Poland and P.R. China.

Published in December 2022 in *Journal of Loss Prevention in the Process Industries*
`https://doi.org/10.1016/j.jlp.2022.104947`
Previously published and presented in July 2022 at the *14th ISHPMIE*

Experimental Parameter Study and Inherent Scattering of Safety Characteristics of Dusts

Stefan H. Spitzer, Arne Krietsch, Vojtech Jankuj

Several laboratory parameters influence the determined values when performing the test series such as the initial pressure, the ignition source, the ignition energy, the burning du-ration and volume or the concentration of the combustible substance. In the different standards for the determination of safety characteristics of dusts there is no statement about the scattering or the deviation when parameters are chosen or occur on the borders of their allowed range. Thus, two laboratories might determine values that are hardly comparable for the same given substance.

This article summarizes some of the influential factors that cause a deviation and shows the inherent scattering of dust tests when all other parameters are kept constant.It also provides some advice how to minimize the deviation and the scattering with very little effort.

Submitted to the *1st International Conference on Fires and Explosions in the Process Industries (FEx23)* and the related *Chemical Engineering Transactions*

F.2. 1st author papers and presentations published during the dissertation

Influence of the pressure difference on the safety characteristics of dusts and potential ignition sources for hybrid mixtures

Stefan H. Spitzer
A presentation about the early key findings of pressure dependencies and the influence of the different mixing procedures.
Presented in March 2021 at the *2021 Global Dust Safety Conference*

Entwicklungen zu Bestimmungsverfahren für sicherheitstechnische Kenngrößen des Explosionsschutzes für hybride Gemische

Stefan Spitzer, Enis Askar, Arne Krietsch, Volkmar Schröder
For the determination of safety characteristics of hybrid mixtures (mixture of at least two combustible phases, eg. dust/gas- or gas/vapor-mixture) there is no existing standard so far. In the standards for the evaluation of the safety characteristics of dusts, gases and vapors there are big differences. For example, in the standards for dusts, gases and vapors different types of ignition sources are listed and there is a difference in the mixture preparation. For the development of a new standard for hybrid mixtures the influence of these two parameters must be investigated to obtain a relationship to the safety characteristics of the single substances and to be able to interpret and evaluate the results of the actual research.
Published and presented in November 2020 at the *VDI-Fachtagung "Sichere Handhabung brennbarer Stäube"*

F.3. Co-authored papers published during the dissertation

Safety of alternative energy sources: A review

Vojtech Jankuj, Stefan H. Spitzer, Arne Krietsch, Petr Štroch, Aleš Bernatík
The article summarizes a short review of the literature focused on safety in the field of alternative energy sources. With an increasing orientation towards sustainable and renewable energy sources, new technologies will come to the fore. These facts must be demonstrated in occupational health and safety. Several studies focused on alternative energy sources are mentioned and show the trends for the future. Especially in the area of hydrogen and battery technologies, systems should pay attention to acquisitions as a normal part of our lives. Safety research is essential for the acceptance of cleaner, efficient, and sustainable future.

Published in May 2022 in *Chemical Engineering Transactions*
`https://doi.org/10.3303/CET2290020`

Where one plus one equals three: the MIT of hybrid mixtures

Paul Geoerg, Stefan Spitzer, **Dieter Gabel**, Ulrich Krause
To determine minimum ignition temperatures for frequently used hybrid mixtures, first, the minimum ignition temperatures and ignition ratios were determined in the modified Godbert-Greenwald furnace for solids (Lycopodium, Corn starch), liquids (n-Heptane), and gases (Methane, Hydrogen). Second, the minimum ignition temperature and ignition ratios were determined for several combinations as hybrid mixtures of dust and liquid or gas.

A noticeable decrease of minimum ignition temperatures below the MIT of the pure gases was observed for the hybrid mixtures. For vapors, the effect is not that strong. The MIT of the hybrid mixture is in the region of the MIT of the dust component. Additionally, more widely dispersed areas of ignition can be achieved. Following previous findings, the results demonstrate a strong relationship between the likelihood of explosion and the amount of added solvent or gas. Consequently, the hybrid mixture is characterized by a different minimum ignition temperature than that of the single components.

These findings and the conclusions during the development of the GG oven are summarized in recommendations for further progressing the underlying standards.

Published and presented in July 2022 at the *14th ISHPMIE*
`https://doi.org/10.7795/810.20221124`

Experimental Investigation of the Consequences of Acetylene Pressure Cylinder Failure under Fire Conditions

Jankuj Vojtech, Miroslav Mynarz, Arne Krietsch, Stefan H. Spitzer, Petr Lepik
Acetylene pressure cylinders are widely used in the industrial sector for welding, flame cutting, or heating. Sometimes during work, not only with acetylene cylinders, fires occur and in this case the risk of destruction increases and the behavior of such an exposed cylinder is unpredictable. The purpose of this study is to identify those critical conditions when acetylene cylinders burst and explode in fires. In the present study, acetylene cylinders were exposed to fire conditions. For this purpose, a woodpile as a source of fire was chosen, tested, and evaluated.

In addition to the fire condition, this option guaranteed reproducibility and similar conditions for all tests. The individual cylinders were equipped with thermocouples measuring the shell temperature, and half of them were prepared in order to measure the temperatures inside the cylinder. An important factor was the measurement of the amount of pressure that was achieved during the destruction of the cylinder. For this purpose, a pressure transducer was attached to the outlet of the cylinder valve. Exposed to direct fire, they can explode in 10 min, which was confirmed. The critical pressure of 40 bar has been reached in 6 min, followed by destruction after 7 min in fire. Cylinders with internal thermocouples were destroyed when lower pressure was achieved.

This confirms the fact that any change of the pressure cylinder affects the original properties. After the tests, the fragments of the selected cylinders were subjected to material tests. The results obtained in these tests are the main source of information for understanding the behavior of acetylene cylinders in fire and the possibility of increasing the safety of intervening rescue services in an emergency.

Published in December 2022 in *Journal of Loss Prevention in the Process Industries*
`https://doi.org/10.1016/j.jlp.2022.104874`

A review on hybrid mixture explosions: Safety parameters, explosion regimes and criteria, flame characteristics

Dejian Wu, Peng Zhao, Stefan H. Spitzer, Arne Krietsch, Paul Amyotte, Ulrich Krause
The hybrid mixture of combustible dusts and flammable gases/vapors widely exist in various industries, including mining, petrochemical, metallurgical, textile and pharmaceutical. It may pose a higher explosion risk than gas/vapor or dust/mist explosions since the hybrid explosions can still be initiated even though both the gas and the dust concentration are lower than their lower explosion limit (LEL) values. Understanding the explosion threat of hybrid mixtures not only contributes to the inherent safety and sustainability of industrial process design, but promotes the efficiency of loss prevention and mitigation. To date, however, there is no test standard with reliable explosion criteria available to determine the safety parameters of all types of hybrid mixture explosions, nor the flame propagation and quenching mechanism or theoretical explanation behind these parameters. This review presents a state-of-the-art overview of the comprehensive understanding of hybrid mixture explosions mainly in an experimental study level; thereby, the main limitations and challenges to be faced are explored. The discussed main contents include the experimental measurement for the safety parameters of hybrid mixtures (i.e., explosion sensitivity and severity parameters) via typical test apparatuses, explosion regime and criterion of hybrid mixtures, the detailed flame propagation/quenching characteristics behind the explosion severities/sensitivities of hybrid mixtures. This work aims to summarize the essential basics of experimental studies, and to provide the perspectives based on the current research gaps to understand the explosion hazards of hybrid mixtures in-depth.
Published in April 2023 in *Journal of Loss Prevention in the Process Industries*
`https://doi.org/10.1016/j.jlp.2022.104969`