UNIVERSITY OF BUCHAREST
FACULTY OF CHEMISTRY
DOCTORAL SCHOOL IN CHEMISTRY

PhD THESIS
SUMMARY

CHARACTERISTIC PARAMETERS OF FUEL – AIR EXPLOSIONS INITIATIONS

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(according to the PhD thesis)

Introduction

For the last decades, as the oil and natural gas industries have been developing, especially by the appearance and spreading of the offshore structures, besides the detection and alarming systems, due to the restricted space from the platforms and due to some disastrous accidents, there have been imposed as necessary new techniques for limiting explosion effects, the new devices and protective systems being designed based on the maximum explosion pressures and their evolution in time.

Thus, there is justified the interest shown for the explosivity of combustible mixtures issue, illustrated by studies, research projects, reports, worldwide working groups, that try to answer as efficient as possible to the preventing, protection and the limitation of the explosion effects which involve flammable substances in the shape of gases, vapours and dusts. Worldwide research works are following both the theoretical fundamentals aspects of thermodynamics and kinetics of combustion reactions and also the practical applications regarding the design of explosion proof systems.

The doctoral thesis which represents a synthesis of the research activities performed during the doctoral stage is based on a considerable number of tests performed on several flammable systems: gas-air mixtures, air-combustible dust or flammable gas-air-combustible dust. The experimental data can be used in the design of explosion proof systems but also for computer modelling of explosions.

It was followed by an extensive characterization of the laminar deflagration for the gaseous methane – air mixtures throughout the whole combustion process, namely the initiation, propagation and extinction. There were performed comparative experiments in various explosion vessels with different shapes and volumes, using various ignition sources, as well as experiments in the presence of inert additives.

There were also studied the ignition and propagation phenomena for combustible dust – air and hybrid mixtures of combustible dust – air – flammable gas mixtures. Starting from the particularities of the underground mining exploitation from Valea Jiului coal field, where there is the possibility of forming explosive mixtures both of coal-air and hybrid mixtures, within the thesis were studied the influence of the ignition source as well as the variation of the explosion parameters with the dust concentrations and methane gas.

I. DATA FROM LITERATURE

The explosion is a general term which corresponds to a fast energy release. The explosion's violence depends on the velocity of this energy release [1]. The explosion can occur in the form of auto-ignition (homogenous explosion that takes place simultaneously in the entire volume of the explosive mixture), or in the form of heterogeneous process, either as detonation or as deflagration (laminar or turbulent). The explosion of an air-fuel mixture can take place without the intervention of an external energy source and it occurs in the same time within the entire mixture, without the existence of an area of separation between reactants and products. The process is known as auto-ignition and has numerous applications in the Diesel type motors. When the concentration of the flammable mixture is within the explosion range (between the lower and upper explosion limit) its explosion can be locally achieved by a small ignition source (spark, heated body, flame, shock wave, laser beam etc.), the process being called ignition. After the initiation, the explosion propagates in the rest of the mixture in form of combustion wave, which represents a separation area between the reaction products and unreacted mixture. Depending on the characteristics of the ignition source, the explosion propagation can take place in form of laminar deflagration (subsonic speed), turbulent deflagration or detonation (supersonic speed).

The minimum amount of energy which can ignite a flammable mixture is called minimum ignition energy, which represents one of the most important safety parameters regarding the prevention of uncontrolled explosions. It depends mostly on the experimental variables such as gaseous mixture parameters (composition, temperature, volume, pressure), the shape of the ignition source – at the electrical spark ignition, the shape of the electrodes and the discharge time, and for the heated bodies (filaments) the rate of energy dissipation from the source to the explosive mixture [2]. The minimum ignition energy is a very important parameter for safety standards but also for understanding the ignition process of explosive mixtures. The minimum ignition energies for most hydrocarbons are very low (0,3 mJ).

Lewis and von Elbe [3] examined the possibility of correlating the experimental values of the minimum ignition energies with the ones calculated from theoretical considerations, based on the minimum flame concept. Thus, while for the flat combustion wave the difference between the total heat and the one transported by conduction is compensated by the released heat by chemical reaction, in the minimum flame this compensation is incomplete due to the spherical geometry, the energetic difference being compensated by the spark energy.

It was noted that the transition of an explosive mixture from stable conditions, where the reaction is not practically observed, or from stationary conditions, where the reaction is taking place slowly without leading to an explosion, to explosion conditions, is not taking place instantaneously, but after a certain period of time, commonly referred to as the *induction period*.

The knowledge of the explosion pressure variation in closed vessels is an important tool in explosion hazard assessment and for taking measures for explosion protection in a wide range of human activities, connected to fuel production, transportation or use. The explosion parameters characteristic for closed vessels are explosion pressure, explosion time and maximum rate of pressure rise [4].

The normal burning velocity is a basic property of the flame propagation in gaseous air-fuel mixtures, depending on the type of the fuel, its concentration, initial pressure and temperature but also on the inert gases dilution. It is used both for the performance and emission predictions for the combustion engines and for the validations of the kinetic mechanisms used in experimental modelling. The normal burning velocities determined experimentally are used for the calculation of the global reaction order and activation energies that are needed in the CFD modelling of the closed spaces explosions [5]. The normal burning velocity is useful for the design of the venting devices and burning chambers such as combustion engine, or rocket engine, electrical power plants combustion chambers or for turbulent flame propagation [6].

The combustible dust particles which are dispersed in air can form an explosive mixture. In this case, air is the dispersion agent, and the dust particles represent the dispersed phase. These kinds of mixtures are in some way similar to gaseous mixtures. A hybrid mixture is a combination of flammable gas, combustible dust and air. Sometimes, in an explosive mixture, the gas can have a concentration smaller than its lower flammability limit, and the dust can also have a concentration smaller than its minimum explosion concentration [7]. Eckhoff [8], showed that, by adding flammable gas to a dust cloud, the violence and the maximum explosion pressure are increased.

Most of the unwanted explosion events take place inside the process equipment (for example: mills, silos, cyclones, pipes) [9]. In addition, one or more explosions can appear after the first explosion pressure wave. These pressure waves can disperse the deposited dust from the area, forming a new dust cloud that can be initiated by the energy released from the first explosion. The secondary explosions can be more powerful than the first explosion because of the higher quantity of dust or the hybrid mixture that can form. The combustible dusts explosions are frequent and devastating phenomena. Even if it is highly important for the explosion hazard of the first explosion to be eliminated, it is more important to eliminate the possibility for the first explosion to generate other explosions, in other words to prevent the occurrence of the "domino effect", given the fact that secondary explosions are more violent that the primary ones [1,9].

If a flammable gas is present in a dust cloud the latter explosivity is enhanced. The minimum ignition concentration and the minimum ignition energy are smaller and the maximum explosion pressure and normal burning velocity are much higher. Thus, a flammable gas can bring in the explosion range a dust-air mixture which normally is under the minimum explosion concentration, even with a gas concentration under the lower explosion limit [11].

II. ORIGINAL CONTRIBUTIONS

Within the first general objective of the thesis, on the explosivity of homogenous gaseous mixtures, the laminar deflagration phenomenon for methane-air mixtures was studied during all the phases of the combustion process, namely initiation, propagation and extinction (quenching). At the beginning, the minimum ignition energy for the methane-air mixtures was experimentally determined, using an ignition system with capacitive discharge with the generation of high voltage electric sparks. Comparing the obtained data to the similar data from literature, showed that the minimum ignition energy obtained with the experimental set-up is in good agreement with the reported data, these values depending significantly on the experimental technique involved.

In Fig. II. 1 the variation of the minimum ignition energy with the initial pressure, P_0, is given in the interval 80 – 150 kPa, the highest values being obtained for the under atmospheric pressure of 80 kPa, while the smaller values were obtained for the initial pressure of 150 kPa. Regarding the reported data, the minimum ignition energy obtained by capacitive sparks ignition is in good agreement with the data reported in literature, even though the value is double than the one obtained by the classics Lewis and von Elbe [3]. Along the time, a large number of experimental studies were conducted for determining the minimum ignition energy for various hydrocarbons, this depending on the mixture composition, the spark generation method and the electrical circuit properties. It must be mentioned that the values of the minimum ignition energies reported by other researchers, such as Moorhouse and Eckhoff [12], were generally bigger than the ones reported by Lewis and von Elbe [3]. Analyzing the existent literature data about the properties of the coal exploited in the underground of several mines, where the presence of some radioactive elements was signaled, the reproduction in the laboratory of these particular conditions was considered useful. For this purpose, the minimum ignition energy experimental tests were repeated in the presence of a gamma radiation source, with the radioisotope ^{60}Co, embedded in a metal protective shell, and positioned on the transparent window of the explosion vessel. The qualitative results obtained for this experimental tests revealed the influence of the gamma radiation on the minimum ignition energy: its reduction with 15 %, given the experimental conditions used.

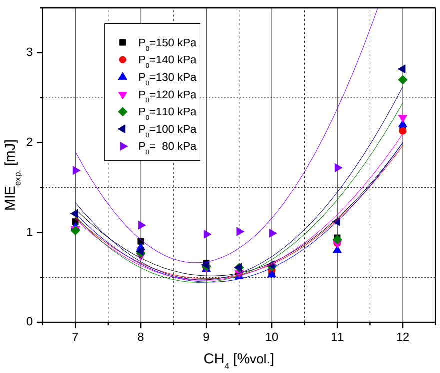


Fig. II.1. The variation of the minimum ignition energy for CH_4-air mixtures at various initial pressures and normal initial temperature

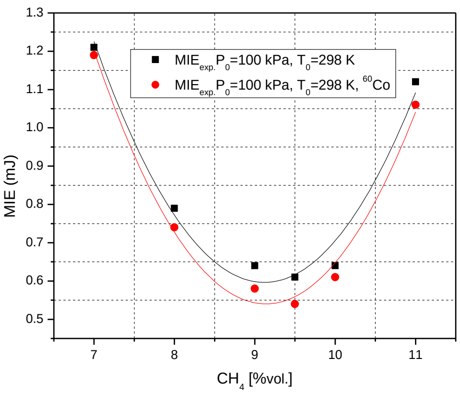


Fig. II.2. The minimum ignition energy, determined in normal conditions and in the presence of the radioactive ^{60}Co source function of the CH_4 concentration, P_0=100 kPa, T_0=298 K

As a result of the minimum ignition energy diminution for the methane-air mixture in the presence of radioactive sources, **it is considered to be necessary a re-evaluation of the explosion hazard** assessment for the workplaces that are endangered by the radiation and flammable gases.

Further, it was studied the propagation of the laminar deflagration of the methane-air mixtures. A typical pressure-time diagram, “1” and its derivative, *dP/dt*, “2”, are given in the Fig. II.3, for a 10 % vol. CH_4-air mixture, at P_0=1 bar and T_0=298 K initial conditions. The maximum explosion pressure growth, ΔP_{max}, and the time to peak pressure, θ_{max}, are measured directly on the recorded diagram. The early stage of pressure evolution was considered for $\Delta P \leq P_0$, when the compression of the unreacted gas was sufficiently small to approximate its temperature equal to the initial temperature. A user defined function of the cubic form was fitted on the resulted curve.

It has been observed long ago that during the initial stage of the flame propagation the pressure rise is proportional with the third power of time:

$$\Delta P = k_3 \cdot t^3 \qquad \text{(II.1.)}$$

where k_3 is related to the normal burning velocity, S_u, measured with reference to the unburned gas [4, 5].

Due to inherent displacements of both abscissa and ordinate during the pressure-time recording, an improved correlation equation with three adjustable parameters proved to fit better the experimental data for $\Delta P \leq P_0$ [13]:

$$\Delta P = a_0 + k_3 \cdot (t - \tau)^3 \qquad \text{(II.2.)}$$

An example is given in Fig. II.4 for 9,5 % vol. methane – air mixture.

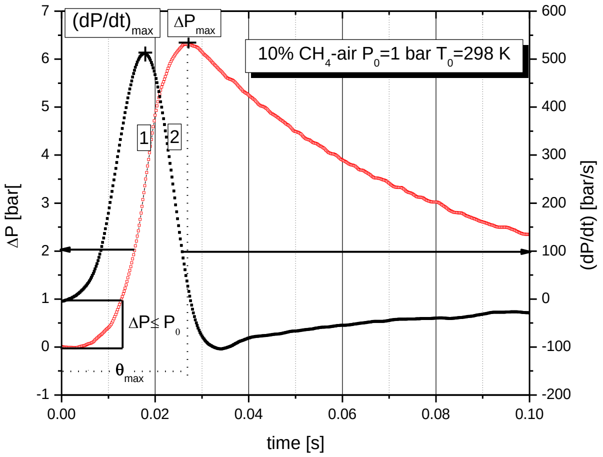


Fig. II.3. Illustration of the experimental pressure-time curve, *ΔP-t*, its calculated derivative (*dP/dt)-t* and resulted characteristic parameters, ΔP_{max}, $(dP/dt)_{max}$, θ_{max}. The initial pressure rise for $\Delta P \leq P_0$ is shown in the lower left side

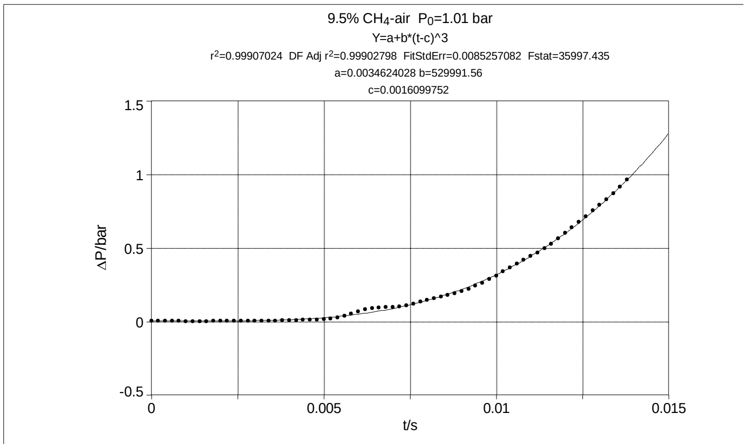


Fig. II.4. Illustration of the third power law for initial pressure rise of 9.5% CH_4/air mixture

The examination of the experimentally determined τ parameter resulted from the pressure-time diagram suggests the possibility for this parameter to be an induction period. Thus, based on the pressure evolution in the initial stage, assuming that this evolution can be governed by the cubic law, **a new method was proposed** for the determination of the induction period *τ*. This method was confirmed by the simultaneous measurement of the pressure variation and the signal generated by an vis-infrared photodiode, placed on the transparent window of the explosion vessel, which follows the variation of the radiation flux generated by the flame kernel in its development. The experimental confirmation of this induction period was based on the analysis of the pressure time-diagrams and the photodiode signal in time, for the initial stage of the explosion. The two curves are given in the Fig. II.5 for the entire combustion process.

In the initial stage the variation of the optical signal is given in Fig II.6 for two initial pressures. The peak signal that appears at the beginning results from the spark used for the ignition. The beginning of the first quasi-linear increase appears to be localized close to the end of the ignition delay period. Significant differences between the signals obtained for two different pressures confirm the existence of a critical period necessary for the formation of the flame kernel. Moreover, the variation of the ignition delay period with initial pressure of a certain mixture follows the same trend as the one found for shock tube or rapid compression experiments. The two verticals lines mark the induction periods determined with the cubic law.

The importance of the initial stage study of the combustion process in closed vessels is given by the practical applicability of the induction period knowledge, considered to be an important parameter in the design of the equipment with intrinsic safety, limitation of the duration and value for the short-circuit preventing the ignition of an explosive mixture. The induction period calculated using the proposed method can also be used in numerical modelling of the explosion in larger volumes, assuming that the initial stage of the explosion evolution is similar to the combustion process studied in explosion vessels with limited volume.

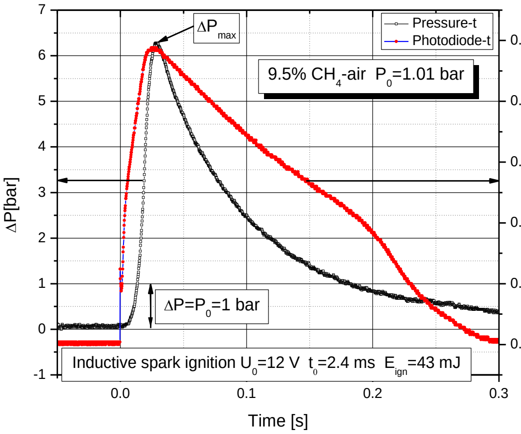


Fig. II.5. Pressure and photodiode signal during laminar propagation of the stoichiometric methane-air mixture

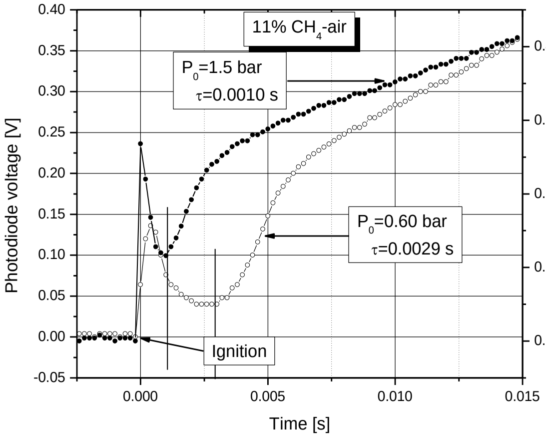


Fig. II.6. Early variations of photodiode signal for the 11% methane-air mixture at two initial pressures (the given ignition delay periods, τ, are obtained from the pressure variation using the cubic law of pressure increase)

For a better understanding of the laminar deflagration phenomenon and its dependence on the shape and volume of the explosion vessel, it was studied in various explosion vessels (one cylindrical with a volume of 0,167 L and two spherical with volumes of 20 L and 0,52 L), following the variation of the propagation parameters of laminar explosion function of the volume and shape at various initial concentrations (from 6 % vol. to 12 % vol.) and various initial pressure (from P_0 = 40 to 200 kPa). The following parameters were measured: the maximum explosion pressure, (P_{max}), maximum rate of pressure rise, $(dP/dt)_{max}$, explosion time (θ_{max}), severity factor (K_{max}) and normal burning velocity (S_u), as well as the evaluated heat losses during the explosions (q_{tr}). Given the fact that in the literature most of the data refers to initial ambient conditions, for this thesis the experiments were also performed at sub and super atmospheric initial pressures in this way a more detailed characterization of the behavior of this type of explosions being possible.

The explosion pressures are significantly influenced by the explosion vessel's shape and volume, as can be seen from the Fig. II.7. For the studied concentrations, the measured values in the spherical vessel of 20 L (considered in most studies reference explosion vessel) are similar with the reported data for the same volume and the values measured in the cylindrical vessel of 0,167 L are closed to the values reported for a cylindrical vessel of 4,2 L [14].

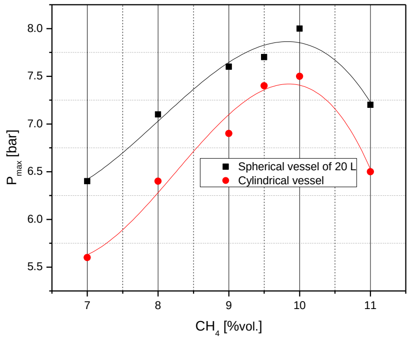


Fig. II.7. The maximum explosion pressure, P_{max}, function of the concentration of CH_4, P_0=1 bar

The differences between the measured values can be explained by the different size and also by the different shape of the two explosion vessels, being known the fact that the sphere has the minimum area corresponding to a maximum volume, leading to heat losses through the cell walls and thus the values obtained for the spherical vessel being lower than those from the cylindrical vessel. There has to be mentioned that the thermodynamic data in adiabatic conditions are higher than all measured data and they are not depending on the volume and shape of the cell.

A comparison between the explosion pressures obtained in three explosion cells, the calculated adiabatic pressure and a few literature data is illustrated in Fig.II.8. The explosion pressures for the stoichiometric CH_4-air in the spherical vessel had values of 7,7 bar in initial ambient conditions. The experimental data are well fitted in the data reported in the literature [15,16, 17, 18, 19, 20].

The explosion adiabatic pressure was calculated with the COSILAB package [21], version 3.0.3, which is based on a general algorithm that calculates the equilibrium composition of the reaction products for every gaseous fuel-air mixture.

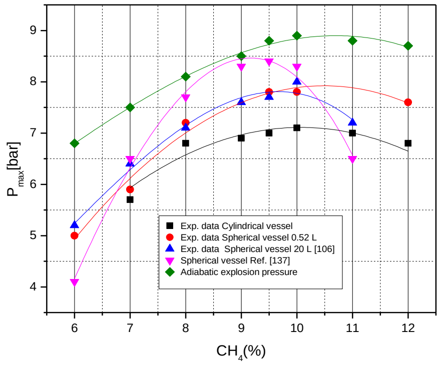


Fig. II.8. Maximum explosion pressure function of CH_4 concentration, initial ambient conditions

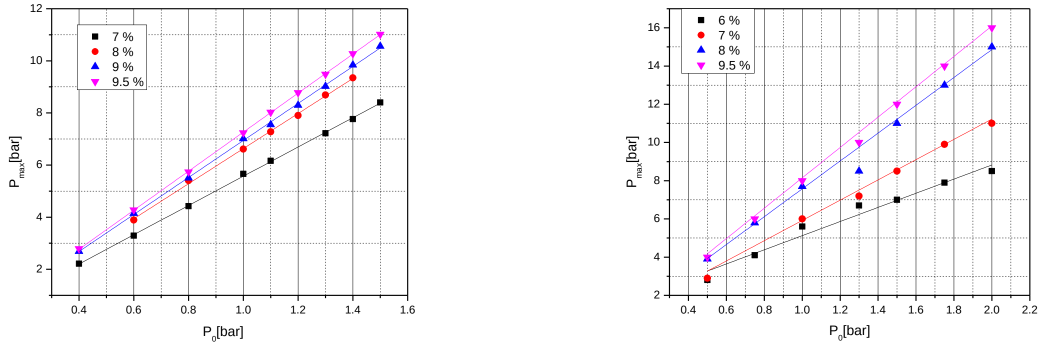
For each explosion vessel and each CH_4 concentration used, linear correlations between the explosion pressure and the initial pressure were identified in the following form:

$$P_{max} = a + b \cdot P_0 \qquad \text{(II.3.)}$$

The values of the explosion pressures, experimentally determined in three explosion vessels, are located in the area of values reported in literature, the other authors using explosion vessels with volumes between 4.2 L and 204 m^3. This fact shows that some relevant explosion properties can be investigated in vessels with small volumes, in this way being significantly reduced the time and materials allocated to the experimental method used.

The linear correlation between the explosion pressure and initial pressure of the gaseous fuel-air mixture was derived from the heat balance of the constant volume explosion [22] and was confirmed by the experimental data obtained from deflagrations of propane-air mixture [23], GPL-air mixture[24] or propylene – air mixture [25] in a spherical vessel with volume of 0,52 L or in a cylindrical vessel with volume of 1,12 L.

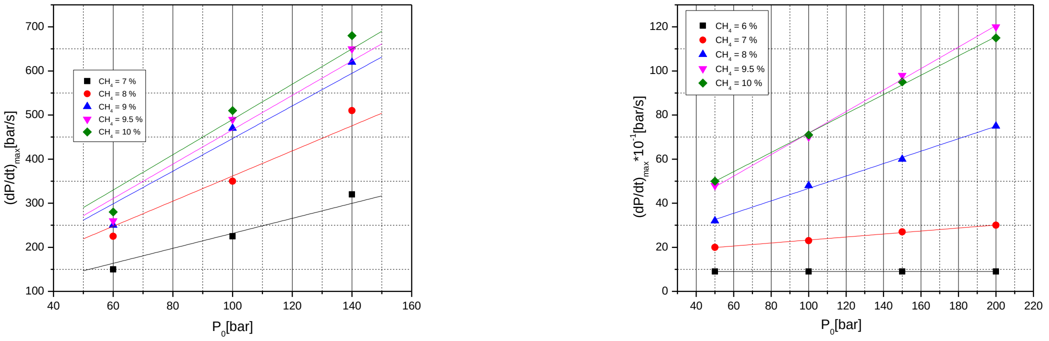
The experimental data discussed before show a common characteristic, respectively that both the slope and intercept of the linear correlation depend on the initial composition of the explosive mixture and can be used to extract additional information on closed vessel combustion.



a) b)

Fig. II.9. The maximum explosion pressure function of initial pressure CH_4-air: a) cylindrical vessel; b) spherical vessel 0,52 L

At constant initial pressure, the maximum rates of pressure rise for the spherical and cylindrical vessels are correlated quasi linearly with the initial pressure, as shown by the plots in Fig. II.10.



a) b)

Fig. II.10. The maximum rate of pressure rise function of initial pressure P_0 and CH_4 concentration: a) cylindrical vessel of 0,167 L; b) spherical vessel of 0,52 L

The linear correlation:

$$\left(\frac{dP}{dt}\right)_{max} = \alpha + \beta \cdot P_0 \tag{II.4.}$$

with the coefficients α and β depending on the vessel's size and aspect ratio and on methane concentration is valid only for a restricted range of pressure variation.

Such correlations have been found for explosions of methane–air and hydrogen–enriched methane–air mixtures at ambient initial temperature, in a cylindrical vessel with central ignition [26, 27]. The importance of these linear correlations is given by the possibility of their extrapolation to higher initial pressures to estimate the explosivity parameters, which can be used either as input parameters for CFD modeling or for developing explosion protection measures for the workplaces endangered by the presence of the flammable substances, or for the design of the explosion pressure relief systems used in the installations from the classified Ex areas.

The influence of inert gases (He, Ar, N_2 and CO_2) on the laminar deflagrations of CH_4-aer was also studied. The experiments were performed in two spherical vessels of different volumes (20 L and

0,52 L) with central ignition, at ambient initial conditions. The inert gases determined the decrease of the maximum explosion pressures, the maximum rates of pressure rise and the increase of the explosion times, regardless of the initial flammable gas concentrations.

For all the studied methane-air mixtures, the carbon dioxide was identified as the most efficient inert additive, followed by nitrogen, helium and argon; the reason could be the dimensions and the heat capacity of the molecule bigger than of the other studied inert gases. Also, the dilution with any of the four studied gases determined the decrease of the calculated adiabatic flame temperature.

Differences between experimental explosion pressures from the two vessels were observed for all studied mixtures, by varying both the flammable gas and inert gas-concentrations. One possible explanation for these differences could rely on the burned gases floatability, favored by the bigger explosion vessel dimensions, which allows the flame front to contact the upper wall of the explosion vessel when the explosion process is still in progress, fact that determines additional heat losses by transfer to the walls, with a longer contact time, finally the explosion pressures being bigger in the vessel with lower volume.

For some data sets, linear correlations have been found between the peak explosion pressure and the amount of inert additive. Linear correlations hold especially for the lean CH_4 – air mixtures, as shown for instance by He-, and CO_2- diluted CH4 –air mixtures in Fig. II.11.

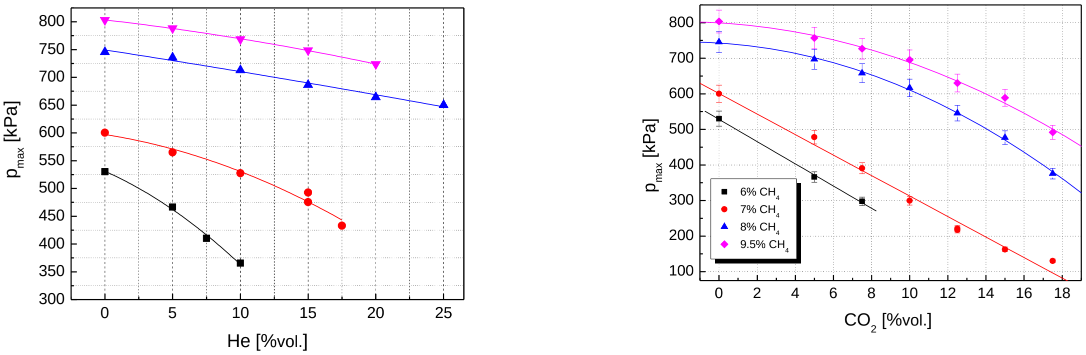


Fig. II.11. Explosion pressures measured in explosion vessel with 0,52 L volume for CH_4 –air mixtures diluted with various concentrations of inert gases

In the case of stoichiometric or near-stoichiometric CH_4–air mixtures, the dependencies of the peak explosion pressures on the inert concentration are better fitted by 2nd order polynomials. For these mixtures, linear variations of the peak explosion pressure can be accepted only over restricted ranges of inert concentration, e.g. between 0 and 10 vol.%.

The linear variation of peak explosion pressures against the inert concentration can be explained by rearranging the correlation between the explosion pressure and initial pressure of the mixture, derived from the heat balance of the isochoric combustion of a fuel-air mixture under non-adiabatic conditions [22, 28]:

$$\mathrm{P_{max}} = \mathrm{P_0}\left(\xi + \frac{\mathrm{r_l}}{\nu_\mathrm{l}} \cdot \frac{\Delta_\mathrm{c}\mathrm{U}'}{\mathrm{C_{e,V}} \cdot \mathrm{T_0}}\right) - \mathrm{q_{tr}}\frac{\gamma_\mathrm{e} - 1}{\mathrm{V_0}}, \tag{II.5.}$$

where P_{max} is the maximum (peak) explosion pressure reached in explosion at pressure P_0; ξ is the ratio of final to initial mole numbers; $\mathrm{r_l}$ is the ratio of the number of moles corresponding to the limiting component of the mixture and the total initial number of moles; ν_l is the stoichiometric coefficient of the limiting component in the mixture (either fuel – in lean to stoichiometric mixtures, or oxygen- rich mixtures); $\Delta_\mathrm{c}\mathrm{U}'$ is the heat of combustion (at constant volume and T_0) corrected by taking into account the accompanying secondary reactions; $\mathrm{C_{e,V}}$ is the molar heat capacity of the end gaseous mixture, averaged for the end components and for the temperature range T_0 to $T_{e,V}$; $\mathrm{q_{tr}}$ is the heat amount transferred by the gas to the vessel before the end of combustion and γ_e is the adiabatic coefficient of the burned gas, at the end of combustion. As long as for the heat balance of the isochoric combustion of a fuel-air mixture the ideal gas law was assumed and P_{max} was considered approximately equal to the pressure at the end of combustion, it is expected that equation II.5 is only a first approximation for an explicit dependence of P_{max} on P_0. For real gases, containing polyatomic molecules with many degrees of freedom, and having higher and temperature dependent heat capacities, significant deviations from those predicted by equation are expected.

In the presence of an inert gas of molar fraction r_i, assuming the same approximations, equation II.5 becomes:

$$\mathrm{P_{max}} = \mathrm{P_0}\left(\xi + \frac{\mathrm{r_l}(1-\mathrm{r_i})}{\nu_\mathrm{l}} \cdot \frac{\Delta_\mathrm{c}\mathrm{U}'}{\overline{\mathrm{C}_{\mathrm{e,V}}} \cdot \mathrm{T_0}}\right) - q^{*}_{\mathrm{transf}}\frac{\gamma_\mathrm{e} - 1}{\mathrm{V_0}} \tag{II.6.}$$

Here, $q^{*}_{\mathrm{transf}} = f(\mathrm{r_l}, \mathrm{r_i})$ is expected to be a function of mixture composition. Eq. II.6 can be rearranged as:

$$\mathrm{P_{max}} = \left[\mathrm{P_0}\left(\xi + \frac{\mathrm{r_l}}{\nu_\mathrm{l}} \cdot \frac{\Delta_\mathrm{c}\mathrm{U}'}{\overline{\mathrm{C}_{\mathrm{e,V}}} \cdot \mathrm{T_0}}\right) - q^{*}_{\mathrm{transf}}\frac{\gamma_\mathrm{e} - 1}{\mathrm{V_0}}\right] - \left(\mathrm{P_0}\frac{\mathrm{r_l}}{\nu_\mathrm{l}} \cdot \frac{\Delta_\mathrm{c}\mathrm{U}'}{\overline{\mathrm{C}_{\mathrm{e,V}}} \cdot \mathrm{T_0}}\right) \cdot \mathrm{r_i} = \mathrm{m} - \mathrm{n} \cdot \mathrm{r_i} \tag{II.7.}$$

In this way P_{max} can be defined as a linear function on r_i where the intercept is m $= P_0\left(\xi + \frac{r_l}{\nu_l} \cdot \frac{\Delta_c U'}{\overline{C_{e,V}} \cdot T_0}\right) - q^{*}_{transf}\frac{\gamma_e - 1}{V_0}$, and the slope is n=$\left(P_0\frac{r_l}{\nu_l} \cdot \frac{\Delta_c U'}{\overline{C_{e,V}} \cdot T_0}\right)$.

Over a restricted range of inert gas concentrations, one can assume that the coefficients *m* and *n* are constant, when both the initial pressure *p*0 and the initial composition of fuel-air mixture (characterized by ξ, $\mathrm{r_l}$ and ν_l) are constant. In such a case the peak explosion pressure P_{max} depends linearly on the molar fraction of inert gas, *ri* .

Outside the mentioned range, it is observed that the term $q^{*}_{transf}\frac{\gamma_e - 1}{V_0}$ is dependent by the nature and composition of the inert gas, determining in this way the variation of P_{max} as nonlinear function of r_i. Moreover, the inherent variation of $\Delta_c U'$, as a consequence of the inert gas concentration change, shows a nonlinear dependence of P_{max} function of r_i, like in the case of CH_4–air mixtures diluted with CO_2.

A comparison between the explosion pressures obtained for the stoichiometric CH_4–air mixture diluted with various N_2 concentrations in both explosion vessels with the volumes of 0,52 L and 20 L, with the corresponding pressure obtained by Sapko [29] for experiments in spherical vessel of 25 m^3, with central ignition, is presented in Fig. II.12, along with the calculated adiabatic explosion pressures.

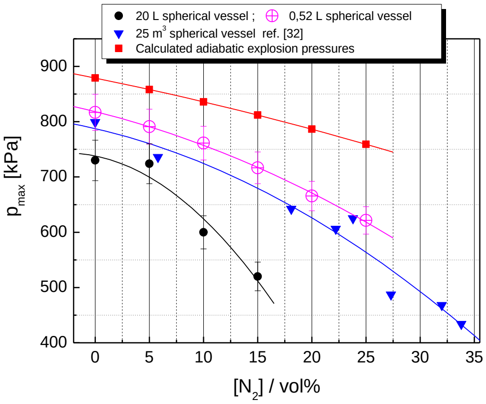


Fig. II.12. Explosion pressures obtained for stoichiometric CH_4–air mixture diluted with various N_2 concentrations (experimental data for both spherical explosion vessels, calculated data and reported data)

The buoyancy of the burned gas sphere, favored by the higher dimensions of vessel with 20 L volume and vessel with $V = 25$ m^3 (as compared to vessel with 0,52 L) results in higher heat losses from the burned gas to the explosion vessel before the end of combustion and can explain the lower explosion pressures reached in these vessels in comparison with vessel with lower volume. Similar results based on experiments in two spherical vessels with volumes of 5 L and 20 L have been given by Zhang [19].

Since the explosivity of a flammable gaseous mixture is primarily determined by the fuel content, it is expected that the inerting efficiency is also dependent on it. For lean to stoichiometric mixtures this efficiency should increase when the fuel content decreases.

The influence of the inert gases was observed also over the normal burning velocity, calculated by the method of analysis of the initial stage of pressure evolution; in the presence of the inert gases the normal burning velocity was diminished with 50 %, the data obtained being in good agreement with the literature data.

A comparison between the inerting effect of three additives (He, N2 and CO2) over the explosion time is shown in Fig. II.13, where data measured in vessel with 20 L volume for a lean CH4–air mixture have been plotted. Compared to He and N2, the addition of CO2 determines the largest inerting effect as seen from the significant increase of the explosion time. The influence of the spherical vessel size is seen from Fig. II.14, where the explosion times of CH4–air–N2 mixtures measured in three spherical vessels are plotted versus the concentration of added nitrogen. For each vessel, the addition of nitrogen results in the increase of explosion times, strongly influenced by vessel's size (i.e. the amount of flammable mixture).

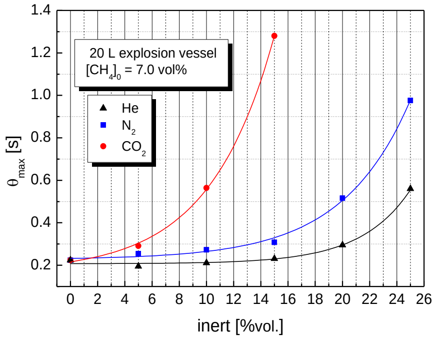


Fig. II.13. Explosion times for 7 % CH_4–air mixtures diluted with inert gases in the 20 L explosion vessel

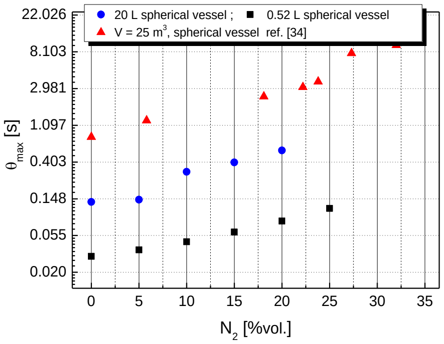


Fig. II.14. Explosion times measured at stoichiometric concentration for CH_4–air - inert mixtures in three explosion vessels

A specific objective of the PhD thesis was the experimental validation of the previously proposed model for the correlation between the minimum ignition energy and the reversible expansion work. In order to observe the pressure variation during the ignition process it was necessary to use explosion vessels with low volume, comparable with the minimum flame volume.

If we consider that an explosive mixture occupies a sphere with a volume V_0, at P_0 and T_0, and if V_f^* represents the volume of the minimal spherical flame, which normally is much lower than V_0, it is assumed that the ignition stage takes place at constant pressure P_0. The burned gases from the volume V_f^* has the pressure P_0 and the temperature T_f, equal with the flame temperature at pressure P_0, resulted from the burning of a volume V_i of unburned gases at pressure P_0 and temperature T_0. During the ignition process of the explosive mixture, the expansion of the unburned gases from the volume V_i to the minimal flame volume, V_f^*, is accompanied by the expansion work consumed by the burned gases. As a first approximation [30], this quantity can be calculated as reversible expansion work from V_i to V_f^*:

$W_{e,rev} = P_0 \Delta V = P_0 V_f^* (E_0\text{-}1)/E_0$ where $E_0 = V_f^*/V_i$ is the expansion coefficient at pressure P_0.

If it is assumed that the ignition takes place only in the moment when the loss of energy as expansion work of burned gases from the minimal flame is compensated by the spark energy, then the reversible expansion work is equal to the minimum ignition energy.

Since the minimum flame volume is $V_f^* = \pi d_s^3/6$ where d_s is the quenching distance and the ratio $(E_0\text{-}1)/E_0$ can be approximated with 0,85, then:

$$W_{e,rev} = MIE_{calculated} = P_0 \cdot \pi \cdot \frac{d_s^3}{6} \cdot 0{,}85 \cong 0{,}445 \cdot P_0 \cdot d_s^3 \qquad \text{(II.8.)}$$

If it is considered that the ignition stage takes place at variable pressure, $P \neq P_0$, then for an intermediate volume V, there is a reacted gas fraction $x = (P-P_0)/(P_{max}-P_0)$, and the expansion work from Vi to V_f^*, is given by the following approximation:

$$W_{e,rev} = MIE_{calculated} = (P_0 V_0/K) \cdot ln \frac{1 - K \cdot V^*/(V_0 \cdot E_0)}{1 - K \cdot V^*/V_0} \qquad \text{(II.9.)}$$

Where the constant K is given by $K = (k_V-1)/E_0$ with $k_V = P_{max}/P_0$.

For this purpose, the validation of the proposed model of correlating the minimum ignition energy with the reversible expansion work, there were determined experimentally the minimum ignition energies and the quenching distances both in the normal volume of the explosion cell (V_0 = 0,167 L), and for a reduced volume (V_0' = 0,018 L). The quenching distances and the minimum ignition energies, determined for the established methane concentrations had minimum values near the stoichiometric concentration, and an ascending trend towards the explosion limits, tendency that was observed in both explosion vessels. By comparing the obtained results, it was observed that the minimum ignition energy and the quenching distances are higher in the case of the explosions performed in the reduced volume explosion vessel. It was shown that the variation of the minimum ignition energy it is due to the variation of the expansion work to the minimal flame against the external pressure. Since the quenching distance is directly correlated with the minimum ignition energy, it is expected that its variation to be in the same direction.

The results given in fig. II. 5 indicate the variation of the quenching distance with both composition and pressure. The minimum value of the quenching distance was observed for the most reactive system, situated near 10 % vol. methane – air mixture. It can be also observed that the increase of the initial pressure leads to the explosion propagation through increasingly narrow spaces.

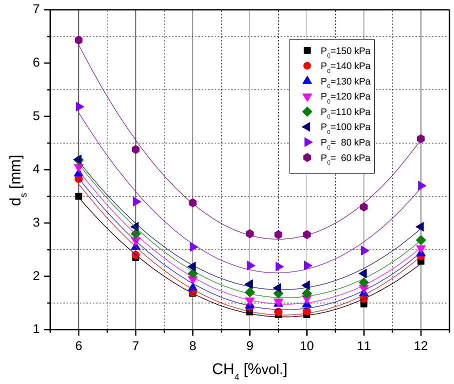


Fig. II.15. The variation of the quenching distances, d_s, with CH_4 concentration, experimentally determined in the normal volume explosion vessel, V_0=167 cm^3

In order to compare the obtained results by indirect measure of the minimum ignition energy as reversible expansion work, the minimum ignition energy was experimentally determined in two different situations: large volume and small volume of the explosion vessel. The minimum ignition energies were determined from 7 % to 12 % vol. methane in air. Larger values were obtained in the lower volume explosion cell. The experimental data obtained were used for the validation of equation II.9, which is used for evaluation of the minimum ignition energy, taking into account its dependence on the pressure increase during the ignition stage.

As expected, by applying the equations based on the experimental quenching distance, higher values were obtained from the reversible expansion work for the experiments performed in the explosion cell with the reduced (lower) volume. In Fig. II.16 are presented the experimental data obtained for the minimum ignition energy determinations and the values calculated based on the quenching distances for the reversible expansion work.

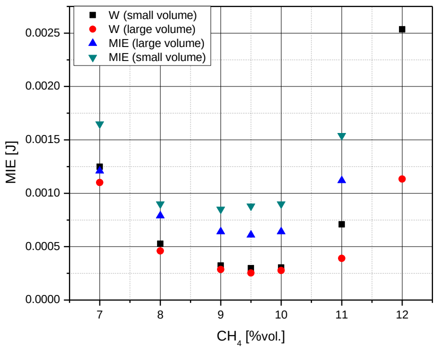


Fig. II.16. The reversible expansion work, W_{exp}, and the minimum ignition energy, *MIE*, for experiments performed in the normal and lower volume explosion vessel, for methane air mixtures, T_0= 298 K , P_0=100 kPa

One can observe that the values obtained for the reversible expansion work, W_{rev}, for the lower volume explosion cell keep the same trend in terms of concentration and size, namely with the increase of the initial volume, the value for the expansion work decreases, as well as for the minimum ignition energy.

The measured quenching distances allow the calculation of the reversible expansion work and, indirectly, of the corresponding minimum ignition energies, having almost the same values with those reported in the literature, as can be seen in the Fig. II.17.

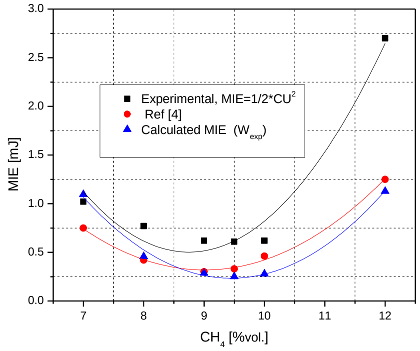


Fig. II.17. Minimum ignition energies of CH_4-air mixtures for initial ambient conditions

The PhD thesis undertakes **for the first time** the validation of the indirect method for determination of the minimum ignition energy based on the presumption of its equivalence with the reversible expansion work, using the experimental data for quenching distances. This validation was performed firstly by comparing the obtained data with the minimum ignition energies from literature and then from the linear correlation of the ratio between the calculated expansion work and minimum ignition energy with the fuel concentration.

For the **second general objective of the thesis**, regarding the explosivity of the coal dust -air -methane mixtures, it was investigated the phenomenon of explosive combustion for mixtures of combustible dust-air and hybrid mixtures of combustible dust-air flammable gas.

Starting from the particularities of the underground mining exploitation from Valea Jiului coal field, where there is the possibility of explosive mixtures occurrence, both of coal dust -air and of hybrid mixtures, the influence of the ignition source on the explosion behavior of such mixtures and the variation of the explosion parameters depending on the coal dust and methane gas concentrations were studied.

The coal dust was characterized by its properties (moisture content, ash and volatile matters) and by their influence on the explosion parameters. At the same time, using the Scanning Electron Microscopy and Electron Dispersive X-ray Spectroscopy techniques, a compositional and structural characterization of the coal dust sampled from 3^{rd} layer of Uricani Mine Exploitation from the west area of the coal basin was made.

SEM analysis can provide information on particle size and morphology at the nanoscale level. The size and the morphological characteristics of coal analyzed in this paper are illustrated in Fig. II.18. The coal sample was analyzed by electron microscopy at various magnitudes and it was observed that it is constituted mainly of particles of irregular shapes. Metal particles such as iron, aluminum and silicon are not evenly distributed in the heterogeneous structure of the coal [31, 32].

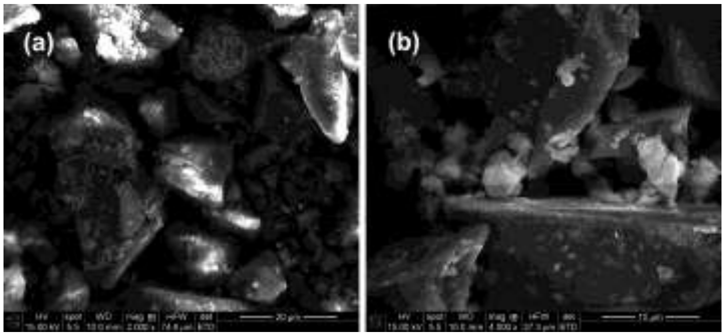


Fig. II.18. SEM analysis of coal sample; particle dimension 0,063 mm, a) magnified of 2000 X, and b) magnified of 4000x

From the compositional analysis SEM/EDX, it has been shown that the coal is constituted mainly from carbon, metallic and nonmetallic formations (Fe, Al, S or Si). Additionally, Na, Mg, S, K and Ti ions were also detected. From the interpretations of the SEM images and the correlation with the EDX analysis, the presence of iron sulphide (pyrite) was highlighted, with a significant spreading in the coal sample, reported to the investigated surface. The ICP-OES analysis revealed a high quantity of Iron, compared with the rest of the analyzed metals, fact that confirms in addition to the EDX analysis the presence of pyrite in the coal sample.

The presence of metals in the coal mass contributes to the increase of the severity of coal dust explosion, being well known the fact that the oxidation temperature of the metals, especially Al and Fe are higher than the oxidation temperatures of the coal.

The minimum explosive concentration (*LEL*) for the coal sample was experimentally determined at 35 g/m^3. The Jiu Valley hard-coal has an average lower explosion limit 40 g/m^3, being considered a reactive coal from the standpoint of explosivity. When a flammable gas is present in a combustible dust cloud, the explosive character of the latter is enhanced [33], fact reflected in higher explosion pressures and rates of pressure rise. Some experiments were performed in order to determine the explosive parameters for coal dust – air – methane mixtures, for CH_4 concentrations below the lower explosive limit between 2 % and 5 % vol. and for the coal dust between 35 to 125 g/m^3. It was observed that, in agreement with the literature data, [33], although both substances were below the explosive limits, their mixture with air, besides the fact that they get-into the explosive range, the generated explosion pressures were greater than the ones obtained for the single substances explosion at explosion limit, as can be seen from Fig. II.19.

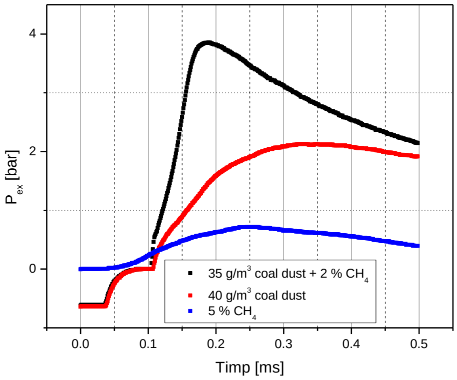


Fig. II.19. Explosion pressure evolution in time for coal dust – air - methane mixtures

Another topic of interest approached for **the first time** on national level was the study of the influence of the ignition source on the explosion parameters of combustible dust – air and hybrid mixtures.

In order to study the influence of the ignition source, a series of experiments for hybrid mixtures with concentrations of CH_4 between 2 and 5 % vol. and of coal dust between 75 and 250 g/m^3 were performed using as ignition chemical igniters of 5 kJ energy and electrical sparks of 10 J energy.

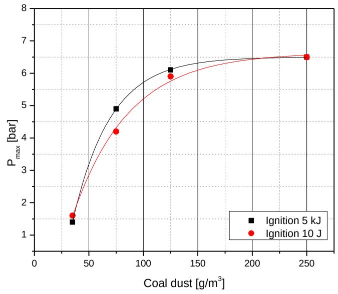


Fig. II.20. The maximum explosion pressure for coal dust – air mixtures depending on the energy of the ignition source

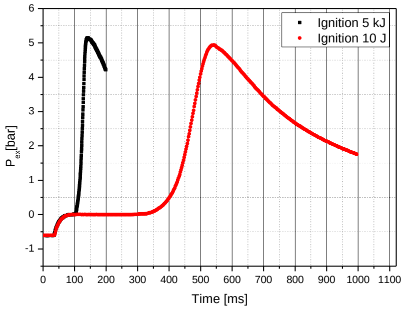


Fig. II.21. Explosion pressure evolution in time for 125 g/m^3 coal dust-air mixture

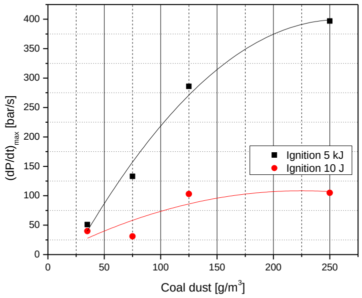


Fig. II.22. *(dP/dt)$_{max}$* for mixtures of coal dust -air depending on the energy of the ignition source

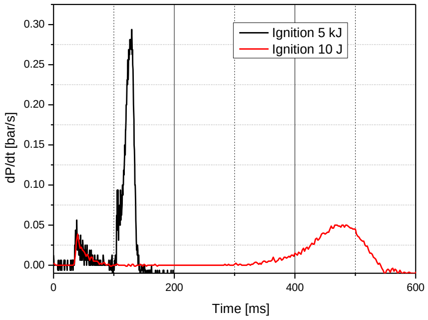
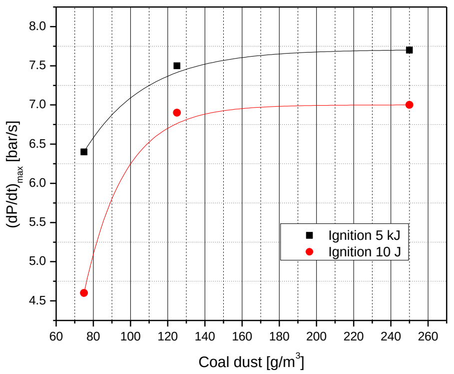


Fig. II.23. The evolution of *(dP/dt)* in time for 125 g/m^3 coal dust-air mixture



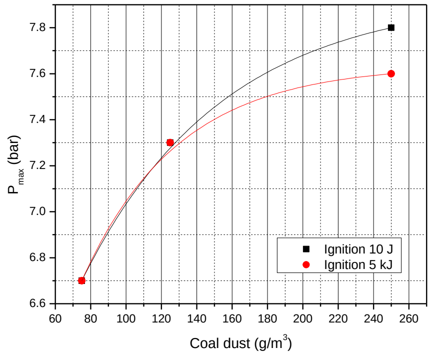


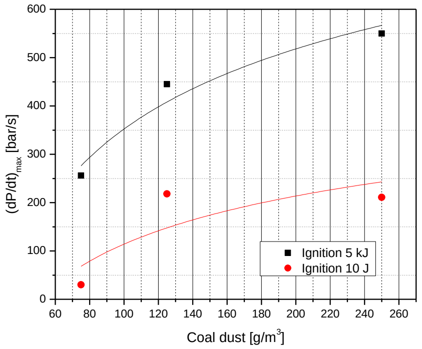
Fig. II.24. P_{max} function of the dust concentration for coal dust and 2 % CH_4

Fig. II.25. P_{max} function of the dust concentration for coal dust and 5 % CH_4

It was observed that, for the coal dust mixed with air, the ignition with different energy sources does not have a significant influence on the explosion pressure, the results being comparable; however, the explosion time is approximately 4 times lower in the case of 5 kJ chemical igniter. This can be explained by the fact that the electrical energy source of 10 J performs an increase in temperature for a smaller volume of the explosive mixture, at the ignition moment, compared to the chemical igniter, the reaction rate being significantly influenced.

Regarding the maximum rate of pressure rise, when ignited with the chemical igniter, the obtained values were a few times higher than those obtained at the ignition with the electrical spark. This can be explained by the fact that the chemical igniter transfers to the system a higher quantity of energy, 5000 J, determining the heating of the coal particles and the sudden release of the volatiles; in this way the burning rate of the system is accelerated determining the increase of the $(dP/dt)_{max}$ parameter.

At the ignition with chemical igniter, with 5 kJ energy, one can observe that for the hybrid mixtures the maximum rate of pressure rise has higher values than the ones obtained at electrical spark ignition.



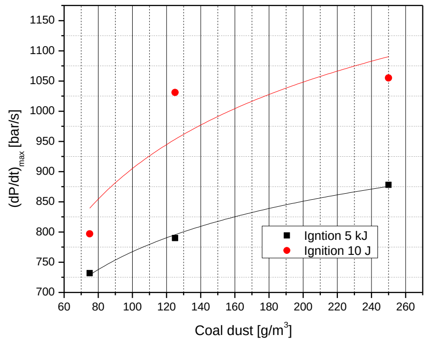


Fig. II.26. Maximum rate of pressure rise function of the coal dust for 2 % CH_4 hybrid mixtures

Fig. II.27. Maximum rate of pressure rise function of the coal dust for 5 % CH_4 hybrid mixtures

The research captured an interesting aspect, specific to the hybrid mixture for all the coal dust concentrations and the CH_4 at 5 % vol., the lower flammability limit, where the gas is explosive. The unexpected result was that the explosion pressure obtained for the 10 J electric spark ignition equals and even exceeds the explosion pressures obtained for the ignition with the 5 kJ chemical igniter. A possible explanation for this phenomenon could be the negative influence of the simultaneously reacted combustible substances through the reaction products with inhibiting role.

The experiments performed for the hybrid mixtures combustible dust – air – flammable gas, using different energy ignition sources, revealed a less predictable behavior for the range of concentration from lower explosive limit, thereby the severity of the explosion was more pronounced in the case of the lower energy ignition source, for the flammable gas, **hence the need for revising and completing the existing standardized method** for determining the explosive parameters for dangerous mixtures.

Another relevant issue is given by the amplification of the explosion severity in the case of the hybrid mixtures compared to single component mixtures, which shows the importance to be given to technical and organizational measures in industrial environments where there is both combustible dusts and flammable gases and where, to avoid explosion of hybrid mixtures, the explosion protection systems are currently designed only on the basis of the most severe explosions of a single component mixture.

Another original contribution of the thesis is the application for the **first time** for this type of systems (combustible dust – air and hybrid mixtures) of a new method for the determination of the normal burning velocity (isothermal conditions for unreacted mixture in the early stage of the explosion evolution), recently described in the literature by the physical chemistry group from University of Bucharest and Ilie Murgulescu Physical Chemistry Institute.

Two methods for the determination of the normal burning velocity were used, namely the one suggested by van den Bulk and the one mentioned before. The new method was successfully applied to a series of experimental data, both in this thesis and in the work group.

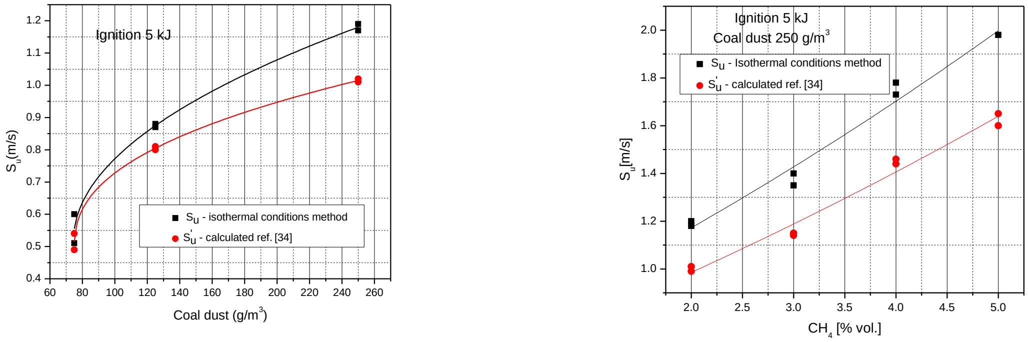
The experimental pressure – time curves were processed for the determination of k_3 constant in order to apply equation II. 10, for ignition of the coal dust -air and hybrid mixtures with both 5 kJ and 10 J sources.

$$S_u = R \cdot \left(\frac{k_3}{\Delta P_{max}}\right)^{1/3} \cdot \left(\frac{P_0}{P_{max}}\right)^{2/3} \tag{II.10.}$$

Where R is the radius of the spherical explosion vessel.

For comparison purpose, the normal burning velocity, S'_{u},, was also calculated, using equation II.11, based on the experimental parameters, K_{st} and P_{max}, suggested by van den Bulk, [34]:

$$S_u' = (K_{max} \cdot 0{,}9)/4{,}836 \cdot \left[\left(\frac{P_{max}}{P_0}\right)^{1/1{,}33} - 1\right] \cdot P_{max} \tag{II.11.}$$



a)

b)

Fig. II.28. Normal burning velocity, S_u, for coal dust – air and hybrid mixtures at ignition with 5 kJ energy ignition source for: a) Coal dust – air function of coal dust concentration; b) Coal dust -air-methane function of added CH_4 concentration

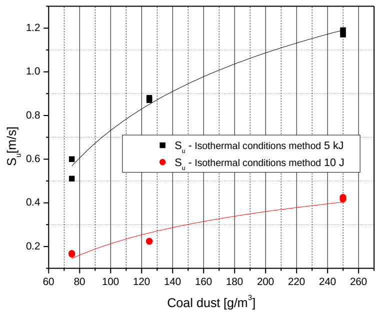


Fig. II.29. Normal burning velocity, S_u, function of coal dust concentration at different energy ignition sources

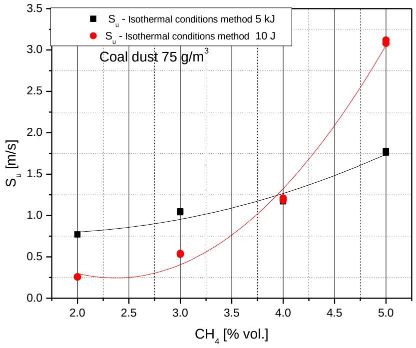


Fig. II.30. Normal burning velocity, S_u, function of methane concentration at different energy ignition sources

The normal burning velocity for the studied systems is in good agreement with the variation of the maximum rate of pressure rise parameter, and also, it can be observed the behavior at the lower explosive limit of methane, where the ignition with lower energy source determines a higher normal burning velocity compared to the 5 kJ chemical igniter. The results obtained with the help of the two equations, namely the one suggested by van den Bulk [34] and the one that is based on the assumption that in the early stage of the explosion evolution the unburned gas temperature is constant, equation that was used and successfully applied on a series of experimental data [4, 23, 28, 35, 36] shows the latter can be used for the estimation of the normal burning velocity for this type of mixtures, respectively combustible dust – air and hybrid mixtures.

After analyzing the results, it was found that by applying the new method, the normal burning velocity values are around those reported in the literature.

The results obtained revealed that the new method can be used to estimate normal burning velocity for combustible dust – air and hybrid mixtures and suggests using these values for the computer modeling of explosions, whether realized in CFD technique for computer modeling of air-fuel explosions or in CFD DESC technique (Dust Explosion Simulation Code).

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