Impact of Graphite dust on the explosion properties of $H_2/O_2/N_2$ mixtures

Jérémy SABARD*,+, Yao-Chung HSU+,•, Mahmoud IDIR+, Nabiha CHAUMEIX+, Ahmed BENTAIB*
* IRSN, PSN-RES/SAG/BPhAG, BP 17, 92262 Fontenay-Aux-Roses Cedex 2, France
+ ICARE, CNRS Orléans, 1C Avenue de la recherche scientifique, 45071 Orléans Cedex 2
• Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan, 70101, Taiwan, R.O.C.

1 Introduction

The international scientific program, for International Thermonuclear Experimental Reactor, ITER, is one of the first steps for mankind to create tremendous amounts of energy with the help of nuclear fusion. During the normal operation of ITER, a large amount of metallic dust and graphite particles are generated due to the interaction of the plasma with the vacuum vessel walls. In case of loss of coolant and/or vacuum accident scenario, water and/or air may enter the vacuum vessel (VV) of ITER facility. Subsequently, water will (i) vaporize leading to a pressure increase, (ii) react with graphite, beryllium and tungsten dust to generate H_2. In the end, mixtures of $H_2/O_2/N_2$/dust can be obtained in the VV which can lead to flammable atmosphere which can be dangerous for the integrity of the ITER facility. In order to asses this risk, dedicated experiments have been performed to measure pressure loads of $H_2/O_2/N_2$ mixtures and to investigate the impact of the dust concentration on these loads. H_2/O_2/inert gas mixtures have been the target of several studies for different initial temperatures: 300 K [1-5], 523 K [6] and different initial pressures from below the atmospheric one [3,4] up to 6 MPa [2,5,6]. But these studies concerned only the determination of the laminar flame speeds of these mixtures and none of them addressed conditions for which the ratio $O_2/(O_2+N_2)$ was higher than 0.21. Only the study of Tang et al. [7] concerns the explosion parameters (explosion pressure, combustion duration, maximum rate of pressure rise) of hydrogen-air mixtures, diluted with nitrogen, over a wide range of equivalence ratios (Φ=0.6-1.4) at elevated pressures (0.5 MPa) and temperatures (440 K).
The dust may explode if an ignition source delivers enough energy to the mixture. Normally, the energy level to ignite directly the two-phase dust-air mixture is higher than the homogeneous mixture. However, in two-phase mixtures, for example, a weak energy can ignite the gaseous phase which in turn will ignite the dust. In other words, the two-phase mixture is ignited by the flame of the hydrogen-air flame rather than the weak source, like an electrical spark. So the importance of these kinds of studies reveals by degrees. $H_2/O_2/N_2$/graphite mixtures have been studied by Denkevits et al. [8,9]. They showed that the 4 µm diameter graphite particles were the most explosive ones. They measured the explosions parameters of $H_2/O_2/N_2$/graphite mixtures for hydrogen molar percent between 8 and 18 % mol in air at ambient temperature and 1 bar for graphite concentration until 250 g/cm^3. They showed that for a hydrogen content equal or above 10 % mol, the dust can explode with the hydrogen and add extra overpressure that should be taken into account for the security of the ITER installation. The other interests in this issue are the possible negative effects of the dust on the explosion, that is, as

Correspondence to: chaumeix@cnrs-orleans.fr

a heat sink, if less hydrogen or more dust are present. Since the dusts play a role of the inhibitant if the energy of the flame is not high enough to ignite them. The aim of the present work is to discriminate between the two possible regimes according to the initial conditions: temperature, pressure and composition.

2 Experimental setup and procedure

2.1 The spherical bomb

Two different spherical bombs, which differ only by their size (respectively 8.18 and 56 L), have been used during these experiments. The larger one (56 L) has been utilized for $H_2/O_2/N_2$ mixtures experiments and the smallest one (8.18 L) for the two-phase ones. Each bomb is equipped with two opposite windows used to visualize the flame during its expansion. Each bomb is also equipped with a Kistler pressure sensor mounted flush with the inner surface of the vessel to measure the pressure variation during the combustion. This recording allows the determination of the maximum combustion pressure (P_{MAX}) and the maximum pressure rise rate $(dP/dt)_{MAX}$ from which the deflagration index (K_G for the gas phase mixtures and K_{ST} for the gas-dust mixtures) is derived. P_{MAX} is also compared to the theoretical one which is calculated with the Equil Code of the Chemkin II library [10].

2.2 Ignition systems

The ignition source for this study is produced at the center of the spherical bombs either by (i) a spark initiated between 2 electrodes or (ii) the focusing of a pulsed laser beam (Figure 1).

When the spark ignition is used, for each run, the current and the high voltage of the electric discharge are measured via a current probe (Bergoz® CT-D1.0-B) and a high voltage probe (Tektronix® P6015A) respectively. The recording of these signals on a digitizing scope allows the estimation of the energy deposited in the gaseous phase by the electric discharge: $E = \int |U * I| dt$. Two different sources have been used. The first one delivers a weak energy, between 1 and 2 mJ, while the second one delivers energy around 20 mJ. In case of gaseous mixtures of $H_2/O_2/N_2$, the first ignition device was used since the energy deposited was more than needed to ignite the mixture. The second one was used when dust were added to the mixture.

In the case of laser ignition, the laser used is a prototype made by CILAS®. It consists of a Q-switched DPSS Nd-Yag laser working at 1064 nm with a pulse duration of 20 ns. It can deliver up to 90 mJ. The laser beam is TEM_{00} with a diameter of 3.2 mm and a $M^2=1.6$. The laser energy delivered by pulse is adjustable via a variable attenuator. The laser latter consists of a half wave plate and a Glan-Taylor polarizer. In order to obtain sufficient laser energy densities at the focal point, before focusing, the beam diameter is expanded by a beam expander (Melles Griot®, HEB-4.0-10X) with a 10X magnification ratio. The energy delivered by the laser was measured for each test using a photodiode which receives only a small fraction of the incident beam before entering the spherical bomb. A careful calibration of this photodiode was performed using a laser Joule meter (Gentec®, QE12SP). A second photodiode was set to detect the occurrence of the laser induced breakdown in the center of the spherical bomb. A digital delay generator (BNC®, 575) is used to trigger the laser shot and the acquisition system of the camera. The maximum energy that could be reached is in the range of 60-70 mJ. Moreover, due to the electrical properties of graphite particles, the use of the laser beam to ignite the combustion proved to be easier than the spark between 2 electrodes. Indeed, it appeared that dust layer could cover the electrodes and their insulation parts inducing the formation of a short circuit. Hence, the maximum dust concentration for which the spark ignition is feasible was limited to 100 g/m^3. In the case of laser ignition, concentrations as high as 330 g/m^3 have been reached.

2.3 Particle size meter

The particle size have been measured in real conditions injections (the injector is a cyclone system) with the help of a particle size meter HELOS from Sympatec®. The graphite particles have been bought from Alfa Aesar® with a purity of 99.9995%. The values obtained in these tests (SMD ≈ 17 - 18 µm) are higher than the one given by Alfa Aesar® (Manufacturer size: 2-15 µm). This difference can be explained by the measurement protocol and by the particles agglomeration that could happen during the injection process.

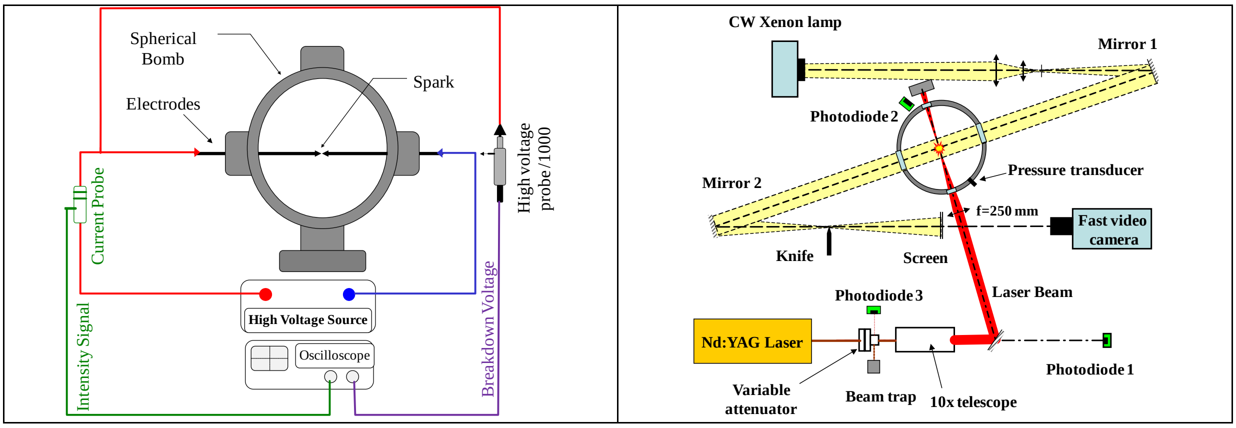


Figure 1: Scheme of the different ignition systems. On the left: spark ignition; On the right: laser beam focalization

2.4 Injection system and validation of the dust concentration by laser extinction

For the two-phase mixtures experiments, the filling of the spherical bomb was done with the help of mass flow meter for the gas phase. A cyclone (25mm i.d. and 100mm in length) is used for the injection of the dusts. The dust concentration is calculated directly from the gravimetric measurements of the cyclone before and after each test. However due to sticky properties of graphite and to the velocity of the flow during the filling procedure, the graphite mass that is really in suspension can be different from the mass released by the cyclone. Part of this mass can be lost to the walls. In order to limit these dust losses, the filling procedure has been carefully optimized. Before the starting of the injection, all the system (spherical bomb, pipeline and cyclone) is vacuumed. Two stages of injection are used in order to obtain the best dispersion of the dusts. The first injection only includes the gas mixture, whereas the second one injects the mixture of gas and dusts. A rough evaluation of the dust concentration in the bomb is made through extinction measurement using a 3.3 µm HeNe laser and a fast HgCdTe detector. We could measure a linear dependence of the extinction coefficient for dust concentrations, determined through initial graphite mass derived from the gravimetric measurements of the cyclone, lower than 22.5 g/m^3. However, the maximum concentration graphite used in this study is 330 g/m^3.

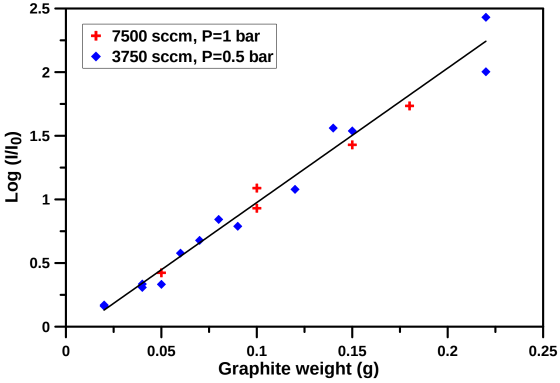


Figure 2: The ratio of transmitted intensity to the incident intesity in a logarithm versus the the dust weight

2.5 Gas chromatography

In order to characterize the burnt gases composition for the two-phase mixtures experiments, after each experiment, a sample was taken using a 1 L glass bulb and analyzed off-line with a gas chromatographer (HP 6890). The chromatographer is equipped with two columns. The first one is a molecular sieve with a porosity of 5 Å which allows the separation of H_2, CO, CH_4, O_2 and N_2 and the second one is a HP-Plot Q with a mixture of divinylbenzene and styrene with porosity equals to 40Å. This column permits the separation of the CO_2. A TCD detector is added to the gas chromatographer for the analysis. A system of injection is installed near the GC which allows us to inject the samples and the standard ones at the desired pressure.

2.6 Experimental conditions

For the $H_2/O_2/N_2$ study, the H_2 content has been ranged from 10 to 60 %mol, for 2 initial temperatures (303 and 343 K) and 2 initial pressures (50 and 100 kPa). The molar ratio N_2/O_2 was varied from 0.66 up to 9. In the following, H_2 content reported was calculated by considering its molar fractions: $\%H_2 = x_{H2}/[x_{H2}+x_{O2}+x_{N2}]$). For the two-phase $H_2/O_2/N_2$/graphite mixtures, the H_2 content has been varied between 10 and 30 %mol, for two initial pressures (50 and 100 kPa) at 300 K. Two molar ratios N_2/O_2 have been studied: 2.33 and 3.76 for dust concentrations from 0 to above 300 g/m^3.

3 Results

3.1 Gaseous $H_2/O_2/N_2$ mixtures

As a first step, the combustion properties of gaseous $H_2/O_2/N_2$ mixtures were measured for different conditions of initial temperature (303 and 343 K), initial pressure (0.5 and 1 bar), hydrogen molar fraction (0.1-0.6) and of dilution (N_2/O_2=2.33; 3.76; 9). Maximum pressure was measured and compared to the theoretical value for an adiabatic isochoric complete combustion (P_{AICC}).

The evolution of the experimental maximum pressure versus the molar fraction of H_2 follows a bell shape curve (Figure 3). A good agreement between the measurements and the calculation is obtained over all the studied range. The difference between P_{MAX} and P_{AICC} is between 1.7 and 9 %. The maximum derivation is observed for the more diluted mixtures. In this case, the combustion time is very large compared to the last diluted one and hence the heat losses are more preeminent. For both initial temperatures, P_{MAX} reaches its highest value at a hydrogen molar fraction that depends on the N_2/O_2 ratio. For N_2/O_2 of 9, the maximum is at XH_2=0.2 and it is shifted to 0.3 and 0.4 when the N_2/O_2 decreased to 3.76 and 2.33 respectively.

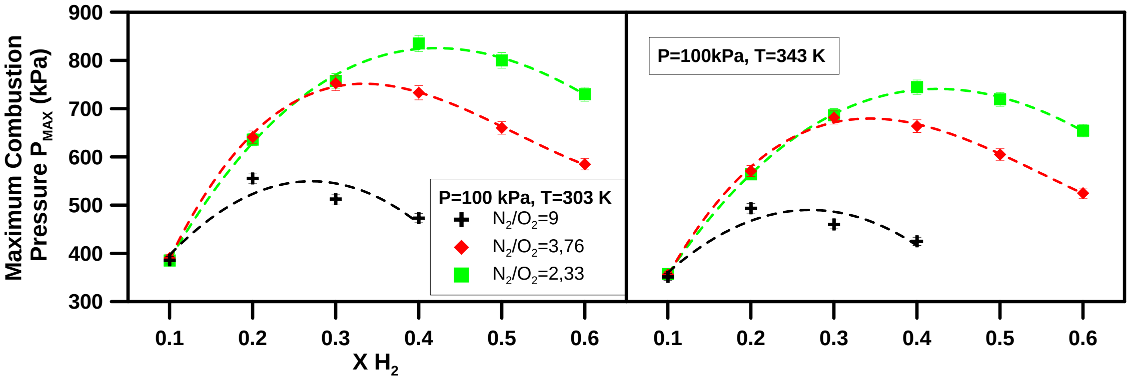


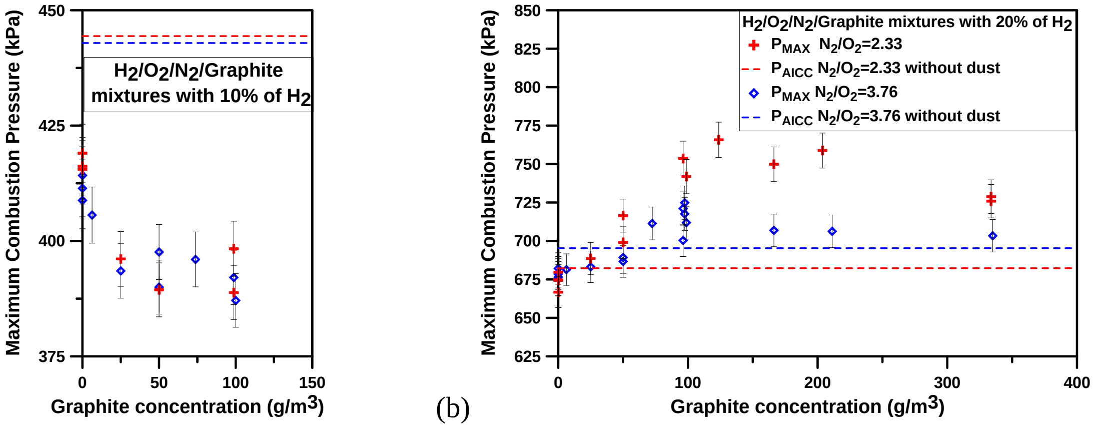
Figure 3: Maximum combustion pressure (P_{MAX}) for $H_2/O_2/N_2$ mixtures in function of the molar fraction in H_2 at 100 kPa and for two initial temperatures: 303 and 343 K

3.2Dust behavior in two-phase mixtures

As graphite particles are added to the mixture, the combustion of this two-phase media will depend strongly on the hydrogen molar fraction since the ignition energy deposited by either the spark generated between 2 electrodes or by the laser is below the critical ignition energy of graphite/air mixtures. For these experiments gaseous samples of the burnt gases were taken after each test and analyzed using a gas chromatographer (Table 1). Since the gaseous fuel is hydrogen and carbon is present only as graphite, the presence of CO and/or CO_2 in the burnt gases is a good indicator that the particles have burnt due to the flame of hydrogen.

H_2 fraction	0.1		0.2		0.3				
N_2/O_2	2.33	3.76	2.33	3.76	2.33	3.76			
[Graphite] (g/m^3)	98.75	98.75	98.75	83.75	77.5	25	48.75	88.75	162.5
Φ	0.934	1.345	1.265	1.634	1.452	1.356	1.679	2.225	3.231
GC results for burnt gases									
H_2	0	0	0	0	4.85	7.04	7.39	8.31	8.37
CO	0	0	0	0	4.3	1.2	1.43	1.88	1.89
CO_2	0	0	7.85	5.17	8.56	1.45	1.72	1.92	1.92
O_2	24.87	16.72	10.51	5.97	0	1.28	1.36	1.46	1.53

Table 1: Analysis of the burnt gases by GC for two-phase mixtures.



(a) (b)

Figure 4: P_{MAX} and P_{AICC} for $H_2/O_2/N_2$/Graphite mixtures with (a) 10 and (b) 20%mol in hydrogen in function of the graphite concentration at 300 K and 1 bar

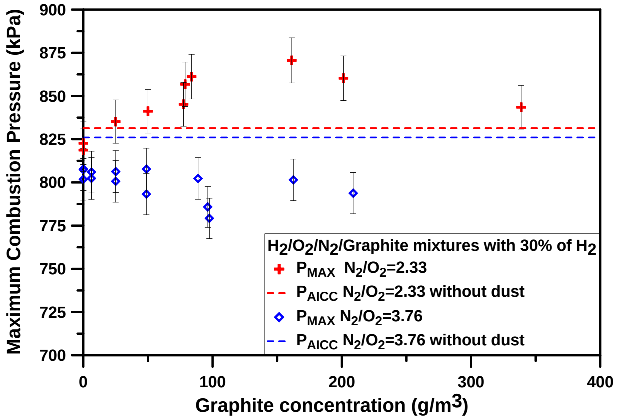


Figure 5: P_{MAX} and P_{AICC} for $H_2/O_2/N_2$/Graphite mixtures with 30%mol in hydrogen in function of the graphite concentration at 300 K and 1 bar

When the hydrogen molar fraction was fixed at 0.1, P_{MAX} was lower than both $P_{MAX,no\ dust}$ and $P_{AICC,no\ dust}$, and decreased as the initial graphite content increased in the spherical bomb (Figure 4a). Moreover the analysis of the burnt gases did not show any H_2, CO or CO_2 in the sample (Table 1). Hence, when the hydrogen molar fraction is equal to 0.1, the combustion of the gaseous phase does not ignite the graphite particles, but these acts as a heat sink and therefore the maximum pressure is lower. This behavior is observed for both N_2/O_2 ratios of 3.76 and 2.33.

As the molar fraction of hydrogen is increased to 0.2, the presence of graphite particles induces an increase of P_{MAX} and the obtained values are higher than the corresponding $P_{AICC,no\ dust}$ (Figure 4b). For example, at XH_2=0.2 and N_2/O_2=2.33, the mixture with a graphite concentration equals to 124 g/m^3 gives a P_{MAX} equals to 766 kPa which is 90 kPa higher than $P_{AICC,no\ dust}$. Moreover, the gas chromatography analyses show that the burnt gases are constituted of CO and CO_2. No H_2 could be detected (Table 1). Then for 20 %mol H_2 in the mixture, the initial hydrogen combusted totally and the graphite particles have also burnt. This behavior is observed for both N_2/O_2 ratios of 3.76 and 2.33.

As the hydrogen molar fraction is up to 0.3, the behavior of the graphite particles is not the same for the different N_2/O_2 ratios (Figure 5). For the ratio N_2/O_2=2.33, it is the same than the one observed at 20 %mol H_2, which leads us to conclude that the dust burns. It is corroborated by the results of the analysis of the burnt gases. The results show that CO_2, CO and H_2 are present in the burnt gases (Table 1). The presence of H_2 can be explained by the fact that when more dust is added, the mixtures begin to become rich in combustible and there is a competition between H_2 and graphite for burning.

For the mixtures at N_2/O_2=3.76, the P_{MAX} behavior is different. Indeed, for the entire studied domain, it remains almost constant. The first supposition is that the mixture is too rich and only hydrogen burns because it is supposedly easier to be ignited and the mixture is so fast that the particles do not have enough time to play as heat sinks. However, CO, CO_2, H_2 and O_2 are detected in the burnt gases, which indicate the incompleteness of the combustion (Table 1). In the early stage of the combustion, only hydrogen burns but the combustion is so powerful that the graphite begins to burn rapidly and consumes the remaining oxygen in the mixture. A first visualization, not detailed here, of these experiments supports the ignition in two steps. For example, in the mixture with [Graphite]=162.5 g/m^3, almost 2 %mol of CO and CO_2 were found in the burnt gases and also 8.3 %mol of H_2 (Table 1). In this particular case, almost one-third of the hydrogen is remaining. These two phenomena, the burnt dust and unburnt hydrogen, lead to a pressure profile of P_{MAX} which remains almost flat.

4 Conclusion

In this work, new experimental data concerning the combustion properties were acquired in a spherical vessel of $H_2/O_2/N_2$ and $H_2/O_2/N_2$/Graphite mixtures which are related to the explosion risk assessment in the ITER project. The impact of the N_2/O_2 ratio in the mixture was observed as well as the impact of the presence of dust. For mixtures with 10%mol of hydrogen, the P_{MAX} are always below the P_{AICC} of the mixture without dust and composition of the burnt gases shows that the dusts did not burn in the mixture. However, in the 20 and 30 %mol H_2 cases, the dusts burn with the evidence of the P_{MAX} and composition of the burnt gases, at the exception of 30 %mol H_2 in air. In this particular case, both the H_2 and the graphite have been ignited and their combustion was incomplete since the overall equivalence ratio is higher than one. However, around 1 % of O_2 is found in the burnt gases.

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