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An Experimental Study on Vapor Cloud Explosion of Propane-Oxygen Stoichiometric Mixture

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Vapor cloud explosions (VCEs) are serious hazards in refining and petrochemical industries. Statistics indicate that 75% of the total losses were caused by explosion so that considerable research effort has been focused on this subject. Consequences of an explosion are aerial overpressure and impulse, responsible for injury to humans and structures. Many studies were performed with fuel-air explosions but few works focused on fuel-oxygen mixtures explosion.
In this study, experiments were performed on a large experimental field. In order to represent realistic conditions, the shape of the gas envelope was elongated like the dispersion shape from leakage with small wind. The flammable cloud was ignited with SEMTEX explosive charges put at the center of the gas volume envelopes. Overpressure values were collected at different positions on the field. Flame propagation was recorded by high speed camera and gave a constant velocity of 2384 $m.s^{-1}$, indicating a detonation regime.

1. Introduction

Vapor cloud explosions (VCEs) are serious hazards in refining and petrochemical industries (Alonso et al., 2005). Statistics indicated that 75% of the total losses were caused by explosion, fires only about 20%, and the rest belongs to toxic releases (Pelaski et al., 2005). Flammable clouds may be triggered by primary events or domino effects (Heymes et al., 2014). Therefore, a considerable research effort focused on this subject (Strehlow, 1979; Van den Berg, 1985). Regarding the dynamics of an explosion, the two most important and dangerous factors are overpressure and impulse (the latter depending on overpressure and positive phase time duration), which are chiefly responsible for injury to humans, and structural and environmental damage. These factors depend on the rapidity of the combustion: blast waves overpressures associated with detonations are of the order of 15 atmospheres, whereas the corresponding values for deflagrations are typically two orders of magnitude less (100 mbar) (Lee, 1980). Thus, the explosion hazard of the fuels mainly depends on the relative ease with which a given mixture can detonate. From experience, certain fuels (acetylene, ethylene oxide) are known to be more sensitive than others (eg propane, butane, and ethane). A method to evaluate the sensitivity of a mixture of fuel to detonate is to consider the 'direct initiation', a fast mode of generating a detonation wave, in contrast to the deflagration to detonation transition. In this mode the detonation is formed instantaneously via the rapid deposition of a large amount of energy in a small volume of the combustible mixture. This minimum energy is called the critical initiation energy. This critical energy depends on the nature of the fuel, the concentrations of fuel and oxygen. It was shown previously (Matsui et al., 1979) that detonation occurs with a lower amount of initiation energy with an oxygen-fuel mixture, compared to air-fuel mixtures which highlights the destruction potential of fuel-oxygen mixtures.
Vapor cloud explosions involving gaseous fuel and pure oxygen may happen from the growing tendency towards the use of fuel–oxygen mixture as energy source (Hendershot et al., 2010) and since the chemical industry uses vast amounts of oxygen every year in a variety of chemical synthesis reactions. One of the most important use of oxygen in petrochemical plants is the cracking of hydrocarbons by oxygen. Under most circumstances, heating a hydrocarbon with oxygen results in combustion, with carbon dioxide and water as the main products. However, if the rate at which oxygen is fed into a hydrocarbon mixture is carefully

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controlled, the hydrocarbon is "cracked," or broken apart to produce other products, such as acetylene, ethylene, and propylene. Indeed, oxygen is widely used in refineries to increase the capacity of Fluid Catalytic Cracking (FCC) plants.
Due to wind effect gas clouds may not be hemispherical but elongated shaped. This point was rarely studied in literature. The directionality of blast effects depends on the flame velocity and cloud shape. In case of deflagrations, the acoustic analogue explains that a gas explosion will develop blast only if it increases its volume source strength, i.e. the products of its flame surface area and its burning speed. In an elongated flammable vapor cloud of more or less constant cross-sectional area, consumed by a constant velocity flame, there will be hardly any blast (Terao et al., 2014). Substantial blast could be produced only by acceleration of the flame propagation process. Pickles et al. (1983) used a simple model to describe the blast pressure in the explosion of an elongated vapor cloud. They main feature of their results was a marked asymmetry in the blast wave, overpressure along the direction of the flame propagation were four times greater than those in the reverse direction, even at long range.
In case of detonation, the dynamics is different but directional differences could also happen. This work aimed therefore to perform stoichiometric propane-oxygen mixtures explosion experiments, ignited by a SEMTEX explosive charge in order to provoke a direct initiation of detonation regime. Aerial overpressures are discussed and the TNT equivalent energy was calculated.

2. Materials and methods

A series of four experiments were performed on a facility provided by the French Army at the military area Camp des Garrigues (Figure 1). All gas envelopes were constituted by a thin polyvinylchloride (PVC) fabric (Figure 2), inflated using propane and oxygen gas bottles. The two first tests were performed with an explosive charge alone, the third with a small gas volume and the last one with a large gas volume. All experiments were performed in January; the air temperature was 19°C. The experimental details of each of the four tests are provided in Table 1.

Figure 1: Experimental test site

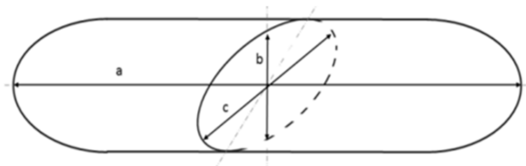

Figure 2: Sketch of the experimental flexible tank

The flowrate of each compound during filling was monitored with a mass flow meter (Brooks type) and mixed with a volume fraction close to stoichiometric ratio before entering the envelope. The inflation was stopped when the static pressure exceeded the atmospheric pressure. The volume was deduced from the mass recordings.

Table 1: Experiments description

Test	Size (m)			Volume (m^3)	Propane mass (kg)	Oxygen mass (kg)	Fuel–air equivalence ratio (φ)	SEMTEX (g)
	a	b	c					
1	-	-	-	-	-	-	-	100
2	-	-	-	-	-	-	-	100
3	0.95	0.47	0.95	0.51	0.17	0.59	1.048	100
4	5.32	0.89	1.01	3.8	1.29	4.35	1.078	100

The combustion was ignited by SEMTEX explosive charges, operated by the French NEDEX (demining team). Aerial blast overpressures were measured at 8 different locations by PCB 137A23 blast gauges (Table 2). The explosive was put at the center but upper surface of the volume (grid at the location (x=0; y=0; z=0.89). The distances between each gauge and the center of the gas cloud are given in Table 2. Data was recorded by a HBM Genesis Gen7t data acquisition system set at 100 kHz.

Table 2: Blast sensors location (z = 1.22m)

Tests 1, 2, 3				Test 4			
Sensor	Sensor position		Distance from explosive charge (m)	Sensor	Sensor position		Distance from explosive charge (m)
	x	y			x	y	
P1	0	15	15	1	-1.3	15.0	15.06
P2	14.14	14.14	20	2	12.8	14.1	19.8
P3	15	0	15	3	13.7	0.0	13.66
P4	14.14	-14.14	20	4	12.8	-14.1	19.08
P5	0	-15	15	5	-1.3	-15.0	15.06
P6	-14.14	-14.14	20	6	-15.5	-14.1	20.97
P7	-15	0	15	7	-16.3	0.0	16.34
P8	-14.14	14.14	20	8	-15.5	14.1	20.97

Two fast cams were used to record the explosion. A Photron SA3 cam recorded the experiments at 6,000 fps (resolution 800x600) and the Phantom V711 was set at 13,000 fps (resolution 800x600). Both cameras and data acquisition system were triggered by the earliest pressure peak at blast gauge. The charge was located at the center of the envelope.

3. Results

3.1 Experiments with explosive material only

The two first tests were performed in order to check the explosive behavior reproducibility. The reproducibility of the test is very good with a slight difference of 5.5% of measured pressure between both tests (Table 3). The time of arrival of the shock wave between the 15 m and 20 m sensors give an average propagation velocity of 347 $m.s^{-1}$ which is close to the speed of sound in dry air at 20°C (343.21 $m.s^{-1}$). Peak pressure data at all sensor locations are given in Table 3, showing that the blast wave was symmetrical. Considering that the TNT equivalence of SEMTEX is 1.14 (Jeremić et al., 2006), the available energy was equivalent to 114 g of TNT.

Table 3: Peak pressure data for tests 1 and 2

Sensor	Distance (m)	Peak pressure (kPa)		Sensor	Distance (m)	Peak pressure (kPa)	
		Test 1	Test 2			Test 1	Test 2
P1	15	0.360	0.334	P2	20	0.228	0.225
P3	15	0.367	0.321	P4	20	0.226	0.195
P5	15	0.350	0.354	P6	20	0.287	0.283
P7	15	0.349	0.335	P8	20	0.297	0.282

3.2 Explosive + propane-oxygen mixture in small cloud

The same explosive was put at the center of a small stoichiometric oxygen-propane volume (0.51 m^3). Overpressure data are illustrated on Figure 3. The pressure profiles are very similar for all data, which shows that the blast wave was hemispheric. As expected the pressure peaks are more powerful, increased from an average peak pressure of 3.5 kPa (tests 1 and 2) to 5.2 kPa (test 3) at 15 meters. This corresponds to the energy added by the gaseous mixture. All data about pressure peaks are given on Table 4.

The TNT equivalent of an explosive gas mixture is the mass of TNT that causes an explosion with the same pressure field as one kilogram of the explosive. This value is calculated by the ratio of the heat of combustion of the hydrocarbon and the combustion energy of one kilogram of TNT, modified by an explosion yield. This yield was proposed and discussed by Lannoy et al. (1984). A yield value of 10% should be used in a safety analysis to estimate the pressure effects because this value corresponds to a confidence level of 97%. An explosion yield of 10% corresponds to a 1 kg TNT equivalent of 1 kg of hydrocarbon in the atmosphere.

Considering the TNT curve specified in TM5-1300 (Department of the Army, 1990), the best fit between experimental data and the TM5-1300 is observed with the yield of 10% (Figure 7, left). This value corresponds to the equivalent mass of TNT related to propane alone in the cloud (0.17 kg) and by subtracting the energy of SEMTEX.

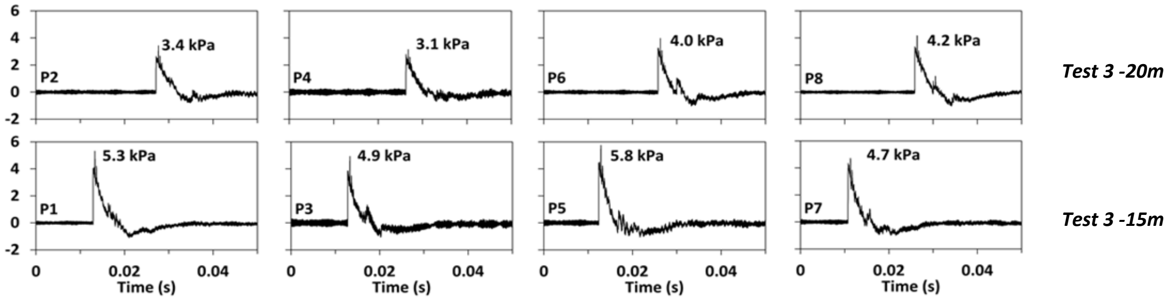

Figure 3: Pressure data for test 3

Table 4: Peak pressure data for test 3

Sensor	Distance (m)	Peak pressure (kPa)	Sensor	Distance (m)	Peak pressure (kPa)
P1	15	5.32	P2	20	3.45
P3	15	4.93	P4	20	3.15
P5	15	5.75	P6	20	3.99
P7	15	4.72	P8	20	4.18

3.3 Explosive + propane-oxygen mixture in an elongated cloud

The explosive was put at the center of a 5.32 meters long, 1 meter wide and 0.8 meters thick elongated envelope. A pictures sequence is given on Figure 4. The flame propagation was symmetric. A video processing enabled to plot the evolution of the flame front characteristics (width, height) of the cloud. After ignition, the flame speed increased quickly up to a plateau at 2384 m.s^{-1}. After two milliseconds the flame reaches the end of the flammable mixture and stops propagating. The size of the cloud continues to grow due to gas expansion. It has to be noted the very intense flame at both ends of the cloud.

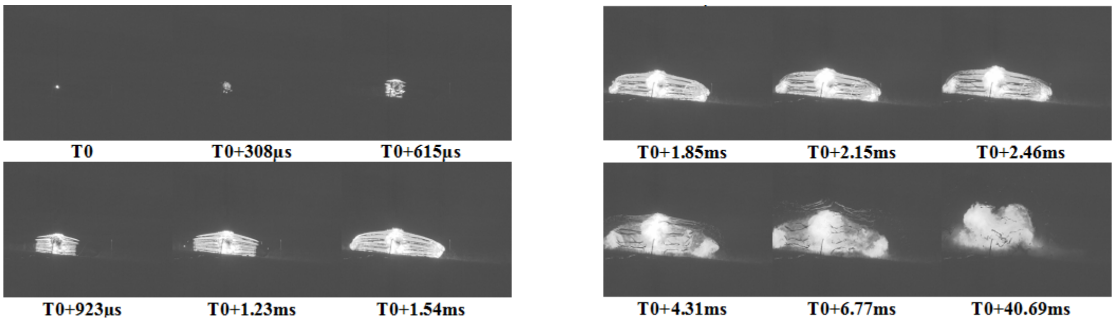

Figure 4: Pictures sequence for test 4

The analysis of the pressure data highlights some key facts:

- The blast wave is not symmetric along both symmetry axis of the cloud: there is a strong difference between overpressure data recorded at the sides of the cloud (29.76 and 25.45 kPa at 15 meters from the center) and in the axis of the cloud (15.39 and 10.85 kPa at 15 meters from the center). This large difference cannot be explained by the distance between the sensor and the center of explosion (Table 1), but is due to the elongated shape of the explosive cloud;
- At the corners of the square defined by the sensors the overpressure recordings are similar (14.28; 10.98; 12.84 and 12.33 kPa) which is logical since these points are located on a similar way in geometry;
- Recordings revealed two pressure peaks, separated by a time step depending on the location of the blast pressure gauge; this observation indicates that the blast cannot be linked with a single explosion center.

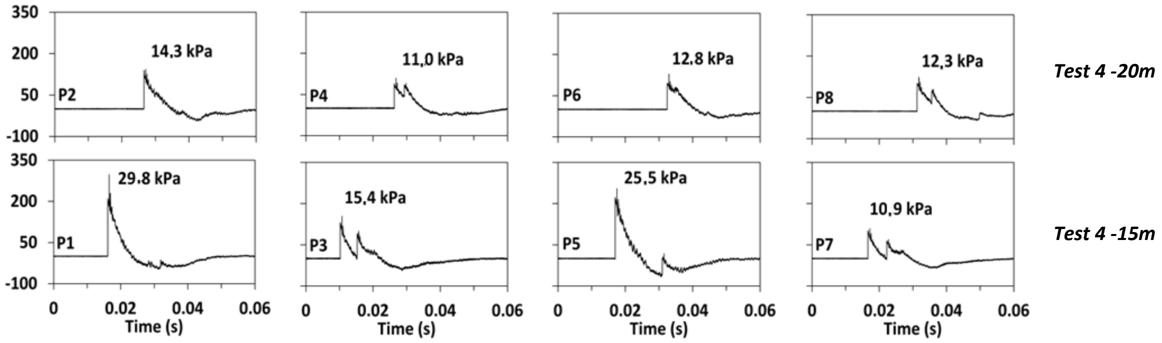

Figure 5: Peak aerial overpressure (test 4)

These observations provide useful information in the purpose of determining the blast pressure from an elongated cloud explosion with the TNT equivalency method. The key assumptions are locating the so called center of the explosion and determining the yield for the released energy.

Table 5: Peak pressure data for test 4

Sensor	Peak pressure (kPa)	Sensor	Peak pressure (kPa)
P1	29.76	P2	14.28
P3	15.39	P4	10.98
P5	25.45	P6	12.84
P7	10.85	P8	12.33

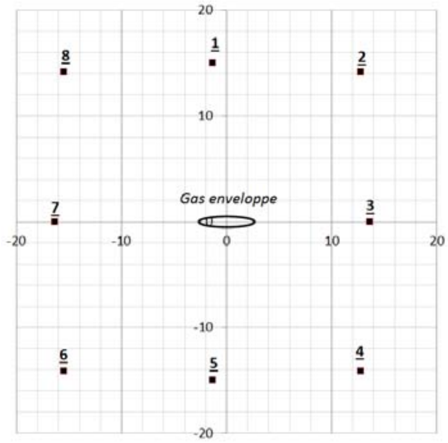

Figure 6: Map of blast sensors (test 4)

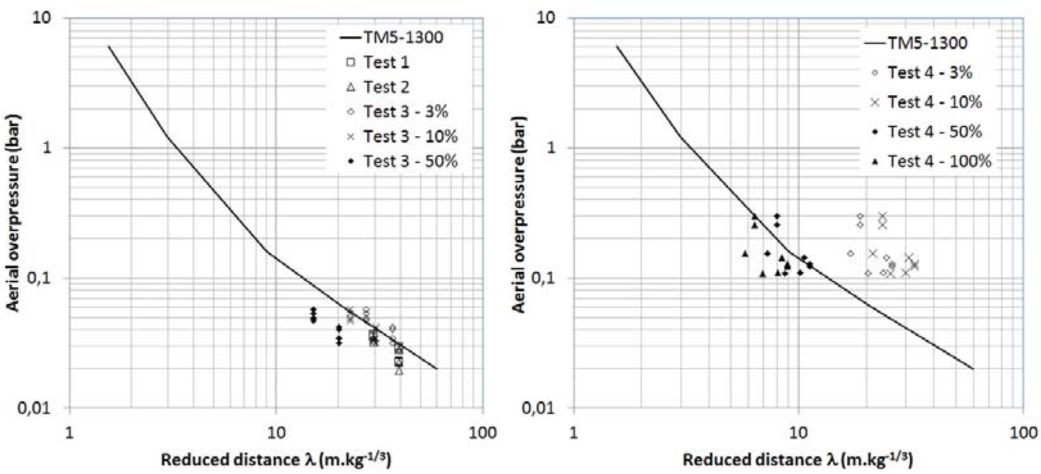

Figure 7: Experimental data on TM5-1300 curve

The symmetry center of the cloud may was considered as the origin of the blast. Considering this point, four different yields were tested (3%, 10%, 50% and 100%) and put on the TM5-1300 TNT curve. The elongated shape of the cloud and the mixture with oxygen instead of air increase the power of the blast. Results reported on Figure 7 indicate that a yield of 3% and 10% underestimate the blast overpressure; indeed the stoichiometric mixture with oxygen releases more energy per kilogram of propane, therefore a yield of 50% is closer to the prediction of the TM5-1300 curve. However, the two side peaks are underestimated. A yield of 100% is required to predict all peaks.

4. Conclusion

In this paper, the blast created by the explosion of propane-oxygen stoichiometric clouds was investigated. The reaction was triggered by SEMTEX explosives, in order to start a detonation regime. This was observed and verified by fastcam images and a combustion velocity of 2384 $m.s^{-1}$ was calculated. It was shown that the reaction with oxygen and the elongated shape of the flammable cloud entailed powerful blast overpressures. The TNT method is able to predict the blast but a yield of 100% has to be employed.

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