



Analysis of fire and explosion hazards of some hydrocarbon–air mixtures

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Abstract

Hazards caused by leakage of hydrocarbons have long been a problem. In this paper, the critical initiation energy and explosion limits of some hydrocarbon–air mixtures have been measured in confined (rectangle shock tube) and unconfined (plastic bag) condition tests. Two dimensionless parameters are suggested to compare the fire and explosion hazards of different hydrocarbons. Additionally, a series of experiments was performed to determine the influence of chemical additives on the fire and explosion hazards of some hydrocarbon–air mixtures in confined (rectangle shock tube) tests. These results relate directly to flammability and reactivity of hydrocarbon air mixtures. Such measurements are very important for hydrocarbon safety. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Any operation handling flammable materials in considerable quantities must, or at least should, make every effort to understand as much as possible the nature and magnitude of the fire and explosion hazard posed by these materials. Regulatory authorities require assurance that all reasonable precautions have been taken for safety in the handling of these dangerous chemicals.

However, the hazard can never be reduced to zero. As inventories of hazardous materials in process plants increase, along with the size of plants, the measurable risk to many members of the public has increased simultaneously.

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Historically, the probability of fire and explosion and the magnitude of the resultant consequences have been assessed based on past experience. In modern large petrochemical, oil and similar industries, however, there are too few such plants in existence to yield reliable data.

Generally speaking, hydrocarbons are easily combustible and form explosive mixture. When their vapors or sprays mix with air within the lower flammability limit, they support combustion or yield an explosion. Some vapors may even support detonation, which is a remote but significant hazard. Khan and Abbasi [1] briefly reviewed some of the major accidents in the chemical process industry which occurred during the 1926–1997 period. As can be seen in their paper, many disasters involved hydrocarbons. These accidents resulted in a huge loss of life and property. Perhaps the most macabre accident occurred on 3 June 1989, near Nizhnevartovsk in Western Siberia. The accident left 462 dead and 796 hospitalized with 70–80% burn injuries [1].

The resultant fire and explosion of hydrocarbon–air mixtures can injure and/or kill people, damage property and cause poisonous materials to be released into the atmosphere. The problems associated with, and the need to control detonation of these mixtures, have long been recognized [2,3]. Much valuable information that has been incorporated in practical guidance for industry has been obtained. However, many problems still remain despite of all this work. Petrochemical production is on the increase. Raw materials, intermediate and final products of the petrochemical industry are all linked to the hydrocarbons and accidents involving them may occur unexpectedly.

The paper deals with hazard analysis of some hydrocarbon–air mixtures. Many tests were carried out in confined (rectangle shock tube) and unconfined (plastic bag) tests. These experimental results are the base of comparison for the hazard of fire and explosion of different hazardous materials.

2. Experimental details

The following two principal characteristics are considered in assessing the hazard of different hydrocarbons:

- *Explosion limit*: The explosion limit is the concentration range within which combustible mixture can be ignited.
- *Critical initiation energy*: The critical initiation energy is the minimum energy, which can ignite mixtures and propagate detonation. The parameter reflects the sensitivity of the hydrocarbon–air mixtures.

The paper mainly discusses these two parameters. Experiments for this analysis were carried out in shock tubes as well as in the field.

2.1. Shock tube tests

The shock tube consisted of four parts: (1) detonation tube, (2) temperature control system, (3) test system and (4) gas supply system. The tube is described simply in this paper. A more complete description of the device is given in [4].

The length of the shock tube was 3.68 m, with a cross-section $0.082 \text{ m} \times 0.082 \text{ m}$. The entire length of the shock tube was insulated and could be heated electrically, and temperature controlled. The tube outer surface temperature was monitored by several surface-mounted thermocouples. Four piezoelectric transducers, mounted flush with the tube wall, sensed the arrival of a detonation front. Signals from the transducers were amplified and captured on digital oscilloscopes and transient recorders at a sampling rate of 0.5 MHz per channel. The computer received the signals from the transient recorder.

The distances of the four piezoelectric transducers from the initiation end were: 2.2, 2.5, 3.1, and 3.4 m. Detonation was initiated directly by an explosive charge. The experimental method is termed the Bruceton or up-and-down method. The test began with the primary initiation energy. If a detonation is established, the initiation energy was decreased a finite amount. If there was no detonation, it was increased by the same amount. Many tests (at least 20) were carried out for the same equivalence ratio mixture. The results are expressed by:

$$E = c + d \left(\frac{A}{N} \pm \frac{1}{2} \right) \quad (1)$$

$$S = 1.620d \left(\frac{NB - A^2}{N^2 + 0.029} \right) \quad (2)$$

where $N = \sum_{i=1}^k n_i$, $A = \sum_{i=1}^k i n_i$, $B = \sum_{i=1}^k i^2 n_i$, c is the primary initiation energy (MJ/m^2), d the interval of energy level (MJ/m^2), S the standard variation (MJ/m^2), E the critical initiation energy of 50% detonation ratio (MJ/m^2), n_i is the detonation (or non-detonation) number for a given initiation energy, and k is the number of uniform increment above the basic point.

In a group of tests, there are two possible outcomes: detonation, indicated by $n(+)$ and non-detonation, indicated by $n(-)$. When conducting calculations using the above equation, the smaller of $n(+)$ and $n(-)$ should be chosen. When $n(+)$ > $n(-)$, $-$ is chosen, vice versa.

The test is started by heating the tube to 60°C . The tube is then evacuated to a few Torr and the fuel injected, followed by heated, dry, compressed air; these materials are allowed to mix. After mixing for approximately 30 min, the mixture is sampled and analyzed using gas chromatography.

Whether or not a detonation is produced is deduced from the pattern of the pressure wave history and the absolute values of pressure and velocity. If a sudden change appears in the initial form of the pressure wave, and if the values of pressure and velocity are high enough, detonation is assumed to have been established.

2.2. Plastic bag tests

Field tests were carried out in plastic bags, which approximated unconfined conditions.

The lengths of the plastic bag were 2, 4 and 8 m, respectively, with a diameter 0.68 m. At the beginning of the experiment, the plastic bag was evacuated to a few Torr using vacuum pump, then fuel and compressed air was added until the pressure of plastic bag equaled the atmospheric pressure. Finally, the detonator was installed at the end. The test protocol

includes high-speed photography, high-speed video recorder, and a transient pressure and velocity measurement system.

3. Results and analysis

3.1. Experimental results from the shock tube tests

3.1.1. Results of determination of critical initiation energy

Based on the calculated results using the Gordon–McBride program [5], the critical initiation energy for that equivalence ratio that produces the largest detonation pressure was measured in the shock tube. The critical initiation energies of different fuels are given in Table 1 for the mixtures initially at room pressure. The tested fuels included butane, naphtha, JC5, 1-pentene, 1-hexene. Naphtha and JC5 are blended fuels composed of many different kinds of hydrocarbons. Typical components of JC5 include 3-methyl-1,2-butadiene; 1-*cis*-3-pentadiene; isopentene; *n*-pentane; 1,2-butadiene; 1-pentene; vinyl acetylene and isopentane, etc. Its molecular mass is 67.7. Tables 2 and 3 give critical initiation energies of different equivalence ratios of butane–air and pentene–air mixtures, respectively.

In comparing the relative ease with which a given hazardous fuel and air mixture can be ignited, it was proposed that a dimensionless number “ R_1 ” be defined as follow [6]:

$$R_1 = \frac{E_c}{E_a} \quad (3)$$

where E_c is the minimum critical energy of fuel–air, and E_a is the minimum critical energy of acetylene–air (0.019 MJ/m²).

Table 1
Critical initiation energy of different fuel–air mixtures

Mixture	Equivalence ratio	Volume concentration (%)	Critical energy (MJ/m ²)	Standard variation (MJ/m ²)
C ₄ H ₁₀ + air	1.19	4.0	0.971	0.006
Naphtha + air	1.27	3.0	0.986	0.009
JC5 + air	1.51	4.2	0.686	0.01
1-C ₅ H ₁₀ + air	1.12	3.0	0.689	0.016
1-C ₆ H ₁₂ + air	1.14	2.6	0.689	0.016

Table 2
Critical initiation energy of different equivalence ratio butane–air mixtures

Equivalence ratio	Volume concentration (%)	Critical initiation energy		Standard variation (MJ/m ²) (only for shock tube tests)
		Confined (MJ/m ²)	Unconfined (MJ)	
0.89	3.0	1.081	3.58	0.009
1.19	4.0	0.971	2.81	0.006
1.80	6.0	1.330	>10.22	0.010

Table 3
Critical initiation energy of different equivalence ratio pentene–air mixtures

Equivalence ratio	Volume concentration (%)	Critical energy (MJ/m ²)	Standard variation (MJ/m ²)
0.95	2.5	0.693	0.014
1.12	3.0	0.689	0.016
2.01	5.4	1.10	0.010

The minimum critical energy of an acetylene–air mixture was chosen since it has been found that acetylene has the lowest ignition energy measured to-date of most of the common explosion gas mixtures. The value of R_1 thus provides a quantitative number for measuring the fire and explosion hazards of fuel–air mixtures. The smaller the value of R_1 is, the higher the hazard of the mixtures. The values of R_1 for the various fuels tested are given in Table 4.

Butane and naphtha were found to have approximately the same value of R_1 . The value of R_1 for JC5, 1-pentene and hexene is also similar. However, R_1 of the former is about two times greater than the corresponding value of the latter. Thus, fire and explosion risk of JC5, 1-pentene and 1-hexene is much higher than that of butane and naphtha. This characteristic is related to chemical structure of hydrocarbons. Butane and naphtha belong to alkane group, JC5; 1-pentene and 1-hexene belong to alkene group.

Since other fuels in the alkane group are found to have the same values of R_1 as butane and naphtha [6], it may be concluded that the alkane group should have the same fire and explosion risk with a value of $R_1 = 50$ (except methane). Moreover, we may predict that olefins group may also pose the same hazard.

As can be seen from Tables 2 and 3, the critical initiation energy for the same chemical depends on the equivalence ratio of mixtures. It can be deduced that the critical energy decreases with the equivalence ratio initially and increases with the ratio. There must exist a minimum ratio at which the critical initiation energy is the smallest. The minimum ratio is slightly higher than unity. Mixtures of the minimum ratio may easily ignite and cause a major accident. For butane and pentene, the tested minimum ratio is 1.19 and 1.12, respectively.

3.1.2. Results of determination of detonation limit

Table 5 gives the detonation limits of the different mixtures. Values obtained by other researchers are also given in the table.

A dimensionless parameter R_2 , which is called risk sensitivity, has been defined as follow [7]:

$$R_2 = \frac{(L_U - L_L)}{L_L} \quad (4)$$

where L_U is upper detonation limit and L_L is lower detonation limit.

Table 4
List of R_1

Mixture	Butane–air	Naphtha–air	JC5–air	1-Pentene–air	1-Hexene–air
R_1	51.1	51.9	36.1	36.3	36.3

Table 5
Detonation limits of different fuels

Fuel	Lower detonation limit (L_L) (vol.%)	Upper detonation limit (L_U) (vol.%)
Butane	2.5 (this paper), 1.98 [6]	7.2 (this paper), 6.18 [6]
Naphtha	1.1	4.8
JC5	1.4	7.7
1-Pentene	1.2	8.7 [7]

Table 6
Value for risk sensitivity

Fuels	Butane	Naphtha	JC5	1-Pentene
R_2	1.9	3.4	4.5	6.2

The larger the value of R_2 is, the higher the hazard of the mixtures. Values of R_2 of the tested fuels are listed in Table 6.

As can be seen from the data in Table 6, of the four fuels, the hazard posed by butane is the lowest and that by 1-pentene is the highest. Naphtha and JC5 show a different ranking compared with the above analysis based on the minimum critical energy. This result is related to the composition of these two fuels. Naphtha includes small concentration of alkenes, which may increase its hazard. JC5 includes small concentration of alkanes, which may decrease its hazard.

3.2. Effect of additives on the explosion hazard of hydrocarbons

The effect of additives on the fire, explosion and detonation hazard of hydrocarbon–air mixtures has been a research topic for several years. Research has proved that additives play an important role in the explosion hazard of hydrocarbon–air mixtures [8–10]. Of course, different additives have different affects. Some additives act as an inhibitor and some as a sensitizer. Effects of three additives, NT (RONO₂), PO (1,3-epoxypropane) and BPO (benzoyl peroxide), on the explosion hazard of hydrocarbon–air mixtures have been tested in the work. The results of NT and PO experiments are given in Table 7. This table also shows the results of BPO experiments.

As can be seen for pure naphtha, when initiation energy is 0.884 or 1.130 MJ/m², the detonation cannot be produced. However, when NT is added, if the initiation energy is 0.884 MJ/m², detonation may propagate; if the initiation energy is 1.046 MJ/m², all mixtures can support detonation. In our experiments, we found that NT sensitized naphtha–air mixture.

One can see that, adding BPO and PO, can allow initiation when the initiation energy is reduced from 0.892 to 0.486 MJ/m²; If only PO is added, detonation cannot occur when the initiation energy is 0.486 MJ/m². Thus, it can be deduced that BPO has a positive effect on the fire and explosion hazard of JC5–air mixture.

Table 7
Number of tests^a

Additive	Mixtures	Initiation energy (MJ/m ²)	Result				
NT and PO	Naphtha + air	0.884	–	–	–	–	–
	Naphtha + air	1.130	–	–	–	–	–
	A + air	0.884	+	–	+	+	–
	A + air	1.046	+	+	+	+	+
	B + air	0.884	+	+	+	+	+
BPO	JC5 + air	0.486	–	–	–	–	–
	JC5 + air	0.730	–	–	–	–	–
	JC5 + air	0.892	+	+	+	+	+
	D + air	0.486	–	–	–	–	–
	C + air	0.486	+	+	–	+	+

^a ‘+’ denotes detonation, ‘–’ denotes non-detonation, A= naphtha/NT = 80/20 (vol.%), B = naphtha/PO = 50/50 (vol.%), C = JC5/PO/BPO = 68/28/4 (mass ratio), D = JC5/PO = 70/30 (vol.%).

3.3. Field experimental results

Accidents caused by leakage of hydrocarbons occurred mainly in unconfined condition. Results of the critical initiation energy in the field are also given in Table 2.

These data can be used directly to assess the risk of the ignition source. Also, using these data and based on the concept of explosion length [11], the relationship between critical initiation energy of shock tube test and that of field test can be obtained. Lee et al. [11] had concluded that explosion length for the same mixture should be equal for different geometric condition. Thus, the following equation can be derived [12]:

$$E_s = 0.974 \times 10^{-10} E_p^3 \quad (5)$$

where E_s is critical initiation energy for the field test and E_p critical initiation energy for the shock tube test.

For example, for a butane–air mixture whose equivalence ratio is 0.89, the critical initiation energy for the field test is 3.58 MJ; the calculated value using Eq. (5) is 4.03 MJ. Obviously, the value calculated using formula (5) shows a good agreement with experiment results. The same conclusion can also be drawn for other two butane–air mixtures. These results have shown the rationality of Eq. (5).

Because the field test costs are high, utilizing formula (5) is very convenient way to assess the critical initiation energy of hydrocarbon–air mixture in unconfined condition using results of shock tube tests. The same can be said for safety analysis of these mixtures.

4. Summary and conclusions

Hazardous hydrocarbons appear to be generated in ever increasing amounts. Their potential to create acute problems has prompted the public, media, legislators and judiciary to become active in directing industry to manufacture and use these materials more responsibly. Thus, it is very important to determine the potential hazard of hydrocarbons.

Based on the experimental results and analysis presented in this paper, the following general conclusions can be drawn about the hazard analysis of fire and explosion for hydrocarbon–air mixtures.

- Explosion limits and critical initiation energy are the main parameters that are commonly used to evaluate the hazard of fire and explosion of hazardous hydrocarbon. In this paper, the critical initiation energy and explosion limit measurements were determined for mixtures of air and butane, naphtha, JC5, 1-pentene and 1-hexene in a rectangle shock tube. Two dimensionless parameters based on the experimental results are suggested for comparison of the hazard of different hazardous substances. The analysis shows that fire and explosion risk of JC5, 1-pentene and 1-hexene are much higher than that of butane and naphtha. The equivalence ratio corresponding to the most hazardous mixture of butane and pentene is 1.19 and 1.12, respectively.
- Of the factors affecting the fire and explosion hazard of hydrocarbon–air mixtures, additives play an important role. The results of the paper have shown that critical initiation energy of mixtures decreases greatly when NT, BPO and/or PO are added. This means that these additives are positive effect on fire and explosion hazard of hazardous hydrocarbon.
- Numerous tests are carried out in the field. These data are very important for evaluating the hazard of the ignition source. A simple formula for estimating the critical initiation energy under unconfined condition has proven to be simple and practical.

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