

Analysis of Fire and Explosion Hazards of some Hydrocarbon-Air Mixtures

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ABSTRACT

This paper describes fire and explosion hazards of some hydrocarbon-air mixtures. The minimum critical energy and explosion limits measurements are made on mixtures of air and butane, naphtha, JC5,1-pentene and 1-hexene in the rectangle shock tube. The experiments are carried out at 1 atmosphere initial pressure and 60 °C. The experimental results may be used to compare the relative risk sensitivity of these hydrocarbons. These results are also explained using molecular orbital theory of quantum chemistry. Some parameters, including enthalpy of formation, ionization potential, energies of highest occupied molecular orbit (HOMO) and lowest unfilled molecular orbit (LUMO), are calculated using PM3 method. Calculated results show clearly that the hazards of hydrocarbons can be conveniently assessed using this method.

1. INTRODUCTION

People all over the world are menaced by all kinds of disasters. Fire and explosion accidents are the most common and serious, many of which cause heavy casualties and tremendous property loss. Therefore, it is a matter of great importance concerning the safety of people's life and properties to know the importance of fire safety. So is this for chemical industry.

Hydrocarbons are widely used in chemical industry. Generally speaking, hydrocarbons are combustible and explosible substances, that is, when their vapors or sprays mix with air to produce the lower flammability limit, the mixtures can support combustion or explosion. Following the deposition of energy, combustion or explosion can happen. Fire and explosion statistical data indicate that the number of fires caused by hydrocarbons are about 14% of the total fires. Thus, this kind of fire is the principal risk to be avoided and more attention must be paid to hazards of materials to prevent accidents.

The different the fuel's structure are, the different their hazard. A ranking of the risk of some hydrocarbons will provide valuable safety information, in addition to gaining an understanding of how chemical structure affects risk. The risk of hydrocarbon-air mixtures with hydrocarbon molecular containing less than five carbon atoms has been studied extensively^[1].

Explosion limits and autoignition temperature (for gas) or flash-point (for liquids) are the main factors that are commonly used to evaluate the risk of fire and explosion of chemicals^[2]. However, the minimum critical energy of fuel-air mixture is also an important factor to influence their risk.

In this paper, many tests are completed in rectangular shock tube at 1 atmosphere initial pressure and 60 °C to measure explosion limits and the minimum critical energy of hydrocarbon-air mixtures. Then we evaluate fuel-air mixtures' fire and explosion risk by analyzing their the critical energy and explosion limits. We also calculate the risk of different group hydrocarbon using PM3 method, which is one of the molecular orbital theory of quantum chemistry.

2. EXPERIMENTAL DETAILS

Experiments were carried out in rectangular shock tube. The setup is introduced briefly in this article. Further details on the facility, including figure, are detailed by Yang Lizhong^[3].

The shock tube system consists of four parts: shock tube, temperature control system, measuring system and gas supply system. The length of the shock tube is 3.68m and the cross-sectional area is 0.082m × 0.082m. The upper of the tube has two holes, which are used to inject the fuel and to sample the final mixture. The end of the tube was fitted with two valves, one is used for air entering, the other for waste-air exhausting.

The entire length of the shock tube is insulated and can be heated electrically and regulated by temperature control instruments. The tube outer surface temperature is monitored by several surface-mounted thermocouples. Four piezoelectric transducers, mounted flush with the tube wall, sense the arrival of a combustion (or explosion) front. Signals from the transducers are amplified and captured on digital scopes and transient recorders at a sampling rate of 0.5 MHz per channel. The computer samples the signals from the transient recorder.

The distance of four piezoelectric transducers from the initiation end is separately: 2.2m, 2.5m, 3.1m, 3.4m. The experimental method is Bruceton or up-and-down method, i.e.,

$$E_c = c + d(A / N \pm 1/2)$$

$$S = 1.620d((NB - A^2) / N^2 + 0.029)$$

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 primary initiation energy, d is interval of energy level, S is standard variation, E_c is critical energy of 50% explosion ratio, n_i is number explosion (or non-explosion) in given initiation energy, i is the number of basic point.

The test begins by heating the facility to the desired temperature, i.e. 60 °C. The tube is evacuated to a few torr and the fuel is injected into the tube. Next, heated, dry and compressed air is introduced and allowed to mix. After mixing for some time, the mixture is sampled and analyzed using gas chromatography. The analyzed results indicate that the mixtures become homogeneous after mixing for half an hour. Therefore, the mixture is allowed to mix about 30 minutes in the tube prior to initiating the mixture. According to the results of Tieszen et al.^[4], thermal degradation of the fuels is not considered to be a problem at these temperature. Second, it is found that the amount of liquid fuel required to achieve the desired gas-phase fuel concentration is 1.25 times the amount predicted.

3. RESULTS AND RISK ANALYSIS

Based on the calculated results of Gordon-McBride programme, the critical energies and explosion limits of some equivalence ratio mixtures are measured in the shock tube. The data are given in Table 1 and Table 2 for the mixtures initially at room pressure. The tested fuels include butane, naphtha, JC5, 1-pentene, 1-hexene. JC5 and naphtha are blended fuels composed of many hydrocarbon compounds. JC5 is mainly composed of alkenes. Naphtha is mainly composed of alkanes with hydrocarbon molecular containing five and six carbon atoms.

Table 1 Critical energies of different fuel-air mixtures

Mixtures	Equivalence ratio	Fuel % by volume	Critical energy (MJ/m ²)	Standard variation(MJ/m ²)
Butane+air	1.29	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-Pentene+air	1.12	3.0	0.689	0.016
1-Hexene+air	1.14	2.6	0.689	0.016

Table 2 Explosion limits of different fuels

Fuels	Lower limit(L _L)(vol.%)	Upper limit(L _U)(vol.%)
Butane	2.5, 1.98 ^[3]	7.2, 6.18 ^[3]
Naphtha	1.1	4.8
JC5	1.4	7.7
1-Pentene	1.2	8.7 ^[4]

3.1 Discussion of the minimum critical energy

In comparing the relative ease with which a given fuel-air mixture can be ignited, it was proposed that a dimensionless number “R₁” be defined as follow^[5]:

$$R_1 = \frac{E_c}{E_a} \quad (2)$$

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

The minimum critical energy of acetylene-air mixture is chosen since it is found that acetylene has the lowest ignition energy obtained to-date among most of the common explosion gas mixtures. The value of R₁ thus provides a quantitative number for measuring the fire and explosion hazards of the fuel-air mixtures. The smaller the value of R₁, the higher the hazard of the mixtures. The values of R₁ for the various fuels tested are given in Table 3.

Table 3

Mixtures	Butane/Air	Naphtha/Air	JC5/Air	1-Pentene/Air	1-Hexene/Air
R ₁	51.1	51.9	36.1	36.3	36.3

Butane and naphtha are found to have about the same value of R₁. The value of R₁ for JC5, 1-pentene and hexene is also similar. However, R₁ 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 olefin group.

Since other fuels in the alkane group are found to have the same values of R₁ as butane and naphtha^[5], it may be concluded that the alkane group should have the same fire and explosion risk with a value of R₁=50. Moreover, we may predicted that olefins group maybe also shows the same hazard.

3.2 Discussion of explosion limit

Also a dimensionless parameter R₂, which is called risk sensitivity, is defined as follow^[11]:

$$R_2 = (L_U - L_L) / L_L \quad (3)$$

The bigger 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 4.

Table 4

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

As can be seen from table 4, of the four fuels, risk of butane is the lowest and that of 1-pentene is the highest. Naphtha and JC5 show a different regular compared with the above analysis based on the minimum critical energy. This is related to the composition of these two fuels. Naphtha includes little quantities of olefins, which may increase its risk. JC5 includes little quantities of alkane, which may decrease its risk.

Owing to expense to measure the risk of hydrocarbons, it is convenient to calculate the hazard of different hydrocarbons. For comparison of risk of hydrocarbon, some parameters, including enthalpy of formation, ionization potential, energies of highest occupied molecular orbit (HOMO) and lowest unfilled molecular orbit (LUMO), are calculated using molecular orbit method of quantum chemistry theory, i.e., PM3 method. The calculated results are shown as Table 5.

HF and IP of table 5 refer to enthalpy of formation and ionization potential, respectively. E_{HOMO} and E_{LUMO} of table 5 refer to the energy of highest occupied molecular orbit and lowest unfilled molecular orbit, respectively.

The greater the enthalpy of formation and energy of LUMO are, the lower the risk. The enthalpy of formation and ionization potential of alkane are higher than alkene for the calculated fuels, especially the enthalpy of formation is much obvious (the enthalpy of formation of alkane is higher 130kJ/mol than that of alkene). The energy of LUMO of alkane is twice as high as that of alkene. These results indicate that alkane can't easily lose its electrons because of its higher ionization potential and can't easily obtain electrons because of its higher energy of LUMO. Therefore risk of alkane is lower than that of alkene. The conclusion is correspond to that deduced by the experiments. Thus we can conclude that risk of different group of hydrocarbons can be conveniently predicted using molecular orbital theory, i.e., PM3 method.

CONCLUSIONS

The fire and explosion risks of some hydrocarbon-air mixtures are studied both experimentally and analytically. Enthalpy of formation, ionization potential, energies of HOMO and LUMO of the tested fuels are calculated using PM3 method. Hazard of alkane and alkene are compared by PM3 method. We can deduced from experiment and calculation that the risk of alkane is much lower than that of alkene. The implication of these conclusions is that the relative risk of hydrocarbon-air mixtures can be deduced using calculated results of PM3 method. Thus, we can easily assess the hazards associated with the hydrocarbons that are used in the transportation, storage and chemical process industries under accident conditions. Appropriate precautions are taken against fire and explosion.

Table 5 Calculated results of PM3 method

Moleculars	Molecular patter	HF (kJ/mol)	IP (ev)	E _{HOMO} (ev)	E _{LUMO} (ev)
1-Butane		-121.483	11.35	-11.35	3.56
1-Butene		7.462	10.032	-10.032	1.177
1-Pentane		-144.262	11.298	-11.298	3.448
1-Pentene		-15.261	10.03	-10.03	1.17
n-Hexane		-166.944	11.280	-11.280	3.366
1-Hexene		-37.912	10.030	-10.030	1.168

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