

Experimental Study on Flammability Limits Behavior of Methane, Ethane, and Propane with Dilution of Nitrogen

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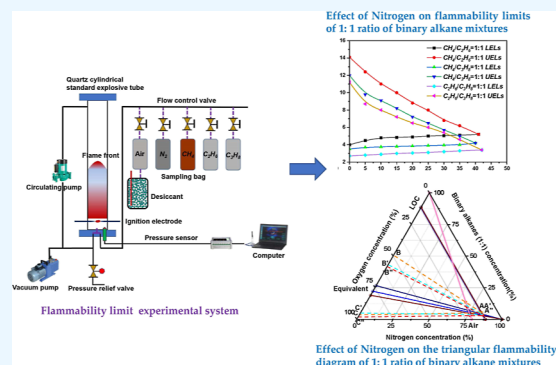
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ABSTRACT: The dilution inerting process of multi-component flammable gaseous mixtures is an important emergency disposal technology that has been widely applied in the explosion-proof field of flammable gases (vapors). In this study, we examined the flammability limits (LFLs and UFLs) of mono and binary alkane mixtures of methane, ethane, and propane when nitrogen is used for dilution inerting. The HY12474B explosion limit test device was used to determine the flammability limits, and the obtained data were compared with the literature data and Chatelier's law. Additionally, the sensitivity coefficient of the chemical reaction chain for LFLs and UFLs of the binary alkane mixtures was analyzed. The minimum inerting concentration (MIC) of methane was found to be sequentially higher than that of ethane and propane when using nitrogen for dilution inerting, and the MIC of the binary alkane mixtures follows the rule of methane/ethane > methane/propane > ethane/propane. Chemical kinetics calculation revealed that the maximum positive sensitivity coefficient of methane/ethane, methane/propane, and ethane/propane are both $R5 H + O_2 \leftrightarrow O + OH$, and the reaction with the maximum negative sensitivity coefficients are both $R34 H + O_2(+M) \leftrightarrow HO_2(+M)$ and $R43 CH_3 + H(+M) \leftrightarrow CH_4(+M)$, respectively. The limiting oxygen concentration (LOC) for both mono alkane and binary alkane mixtures ranged between 10 and 13%. The region of the triangular flammability diagram for methane and ethane was greater than the regions for methane/ethane and methane/propane. In contrast, propane had a smaller region compared to other mono alkane or binary alkane mixtures.



1. INTRODUCTION

Although flammability data for pure fuels are traditionally available, industrial operations dealing with single-phase or multiphase flammable mixtures are even more significant in practical application.¹ The production process of oil exploitation and the chemical industry results in the release of flammable and toxic gases. For example, the processes involved in the volatilization of light-hydrocarbon and hydrothermal pyrolysis reaction between crude oil and steam generate gases such as methane, ethane, C3–C7, and carbon monoxide.^{2,3} The inerting of flammability mixtures with chemically active or inert agents can also result in the formation of such mixtures. Accurate knowledge of flammability limits and the limiting oxygen concentration (LOC) of the mixed fuels allows for evaluating fire and explosion hazards of technological and installation processes and determining safety measures accordingly. Unfortunately, flammability knowledge of mixed fuels is approximately limited to Le Chatelier's law.^{4,5}

Methane, ethane, and propane as important crucial raw materials in the field of energy and chemical engineering, have explosion characteristics analogous to that of other flammability gases. Methane and ethane are the primary components of liquefied and compressed natural gas (LNG and CNG), whereas propane is the primary component of liquefied petroleum gas.

Numerous prior studies have examined the characteristics of alkane flammability and the use of inert gas dilution to prevent explosions. In terms of investigating the flammability limit of mono alkane. Coward and Jones⁶ proposed the method for determining the flammability limits of gases and vapors (USBM, United States Bureau of Mines) and measured the flammability limits of more than 200 pure substances, including methane, ethane, and propane, in air, oxygen, or other atmospheres; these results were arranged, coordinated, and critically reviewed. Subsequently, Zabetakis⁷ from USBM enhanced Coward's testing device and studied the effect of temperature on lower flammability limits (LFLs) of saturated hydrocarbons under atmospheric conditions, the results showed a linear relationship. De Smedt et al.⁸ explored LFLs and upper flammability limits (UFLs) of four hydrocarbon gases (methane, ethane, propane, and butane) and found that in each gas, the explosion range

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based on the DIN 51649 is greater than that estimated in the 20 L sphere. Furthermore, the impact of inert gases on the flammability limit of single alkanes has been conducted. Mitu et al.⁹ investigated the characteristic parameters of laminar deflagrations propagating in methane–Air gaseous mixtures, which were diluted with several inert gases: helium, argon, nitrogen, or carbon dioxide. The results indicated that the inert additive, carbon dioxide is the most efficient, followed by nitrogen, argon, and helium. Adding inert gas addition to any flammable methane–air mixture lowered both experimental and adiabatic explosion pressure, as well as the maximum rate of pressure rise, along with the increase of the explosion time. Abdelkhalik et al.¹⁰ performed a study on the explosion regions of propane when combined with air and inert gases (nitrogen, argon, helium, and carbon dioxide). The results show that propane is highly sensitive to the concentration of the inert gas at the apex of the explosion envelope in a ternary diagram with air acting as an oxidizer. From the following summary of the flammability limit data, there were numerous references to mono alkane flammability limit data for methane, ethane, and propane.

In practice, the flammability limits of mixed fuels need to be measured individually for that particular concentration. For the flammability limit studies of multiple alkane mixtures, Pio and Salzano¹¹ obtained the variation of the flammability range for methane/propane mixtures at ambient temperature and temperatures below 0 °C by using a kinetic model known as KIBO and the limiting burning velocity theory. Significant variations were observed in pure methane for all temperatures measured, the findings indicate that thermal factors dictate the LFLs exclusively at high temperatures; however, kinetic limitations hold greater significance at low temperatures. Kondo et al.¹² measured the flammability limits of binary and ternary mixtures of methane/ethane, methane/propane, and methane/ethane/propane by introducing nitrogen. The LFLs of mixtures were found to be consistent with the values estimated by Le Chatelier's formula; however, the upper limits diverged from the calculated values in some cases. Wan¹³ examined mixed fuels of methane/propane based on the flammability limit theory model, the flammability limits under high temperature and high-pressure coupling conditions were predicted, and the changing law of the flammability limits with temperature and pressure in a variety of environmental atmospheres was explored. Wang et al.¹⁴ investigated the explosion behavior of methane/ethane/propane gas mixtures and the inerting mechanism of carbon dioxide gas in a standard-designed 20 L spherical explosion vessel at ambient temperature and pressure. The results show that a small amount of ethane/propane can significantly intensify the explosion characteristics of methane, and the addition of carbon dioxide has a inerting effect on the explosion behavior of methane/ethane/propane, continuous carbon dioxide addition to the mixture resulted in a linear decline of the UFLs and exponential increase of the LFLs of methane/ethane/propane decreases linearly. Wang et al.¹⁵ investigated the influence of flammable gases and the relative humidity on the methane flammability limit behavior. In a standard cylindrical apparatus, the study measured the flammability limits of methane–air mixtures under varying relative humidity levels, as well as the effects of adding ethane, propane, and nitrogen. The results showed that the combustion risk of methane rises with the increase in volume fractions of added gases but decreases with the increase in relative humidity. These phenomena were attributed to the dual roles of water

vapor and the influence of the added ethane and propane on the initial stage of the methane–air chain reactions. Huang et al.¹⁶ explored the impact of pressure on the flammability limits and explosion pressure of ethane/propane in a 645 mL closed cylinder with an inner diameter of 50 mm. A comparison of the data of lower alkanes indicated that the LFLs decreased as the carbon number increased. Mendiburu et al.¹⁷ analyzed inaccuracies related to the estimation of the UFLs of fuel mixtures (e.g., methane/acetylene, propane/hydrogen, propane/ethylene/carbon monoxide, etc.) in air using the law of Le Chatelier. Moreover, a statistical analysis was performed using available experimental data to determine the LFLs and UFLs of the fuel mixtures. Based on the measurement of laminar flame speeds, the inaccuracies were identified as having arisen due to different heat release rates at the experimental and calculated UFLs.

The above research focused on the effect of inert gases on the flammability limits of alkane mixtures, such as methane, ethane, and propane. The mechanism of the inert medium-aided explosion inerting is based on reducing the oxygen content, thereby minimizing the heat release rate of the chemical reaction, which greatly reduces the reaction heat. The inerting effect of each inert gas is dependent on the consumption of different free radicals.¹⁸ Nitrogen, as the primary component of air, can be easily obtained through air separation units using cryogenic distillation in industries, such as metallurgy, energy, and chemical industries.¹⁹ Therefore, in the disposal of flammability gas leaks and inerting protection applications, nitrogen is commonly used as a dilution inert additive, which can be responded to in many engineering applications, including nitrogen generators in the aircraft fuel tank inert system, nitrogen inerting protection for a clear process of storage tanks.^{20,21} Simultaneously, there was a lack of systematic research on the dilution inerting effect of nitrogen on the flammability limits data of binary alkane mixtures of methane, ethane, and propane with varying ratios. In this study, methane, ethane, propane, and the binary alkane system composed of them were selected as the research objects, nitrogen was used as diluted inerting media, while the flammability limits, LOC, and diluted inerting regulations of methane, ethane, and propane were studied.

2. MATERIALS AND METHOD

2.1. Apparatus. As shown in Figure 1, the HY12474B explosion limit test device of flammability gases was adopted in this experiment, which meets the requirements of Chinese National Standard GB/T 12474–2008: method of Test for Explosion Limits of Combustible Gases in the Air, which is similar to the ISO 10156-2010 standard with exception of the reactor size.²² The experimental device composes a vacuum-pumping, gas distribution system, circulating stirring, spark ignition, explosion glass test tube, pressure relief device, data acquisition, and computer. The explosion glass test tube is a cylindrical quartz explosion tube of 3.4 L (inner diameter 60 mm and length 1200 mm) with a thickness of 5 mm. The tube was closed at the bottom end and vented from the upper end. Before each experiment, the vacuum pump valve needs to be opened to start vacuuming. When the pressure in the explosion tube is lower than 300 Pa, the rotary vane vacuum pump is deactivated. The pressure in the explosion tube is monitored by a pressure sensor installed at the bottom, and the pressure measurement range is 0–200 kPa (absolute pressure) with a resolution of 0.1 kPa, with a sampling frequency of 5 kHz. The experimental

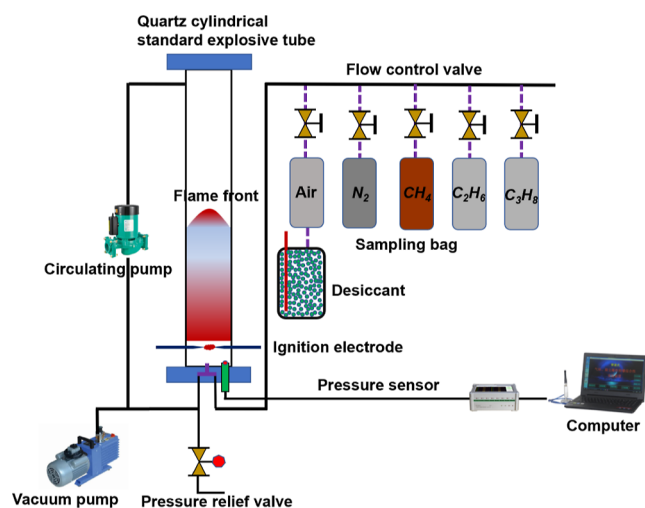


Figure 1. Schematic diagram of the experimental system.

device is equipped with eight precision gas distribution circuits with a gas distribution accuracy of 0.1%, and the partial pressure method is used to obtain the required specified gas distribution concentration. The system automatically adds a gas sample according to the set intake volume. After the sample gas and air volumes are completely added, the circulation pump circulates for 300 s to confirm that the mixture-air was homogeneously mixed. A high-energy pulse electric spark device was installed at a distance of 100 mm from the bottom of the reaction tube, which was required to be in the center of the pipe section with an electrode gap of 3–4 mm. The ignition device adopts high-voltage pulse ignition, generating an arc voltage of 15 kV and an arc current of 20 mA, with a spark discharge time ranging from 0.1 to 1.0 s. When the set ignition delay time is reached, the system automatically ignites the gas mixture. The explosion pressure data acquisition is carried out through a supporting data acquisition system. After a test, the experimental apparatus was flushed three times to avoid the influence of residual exhaust gases. Each group of the experiment was repeated at least three times to confirm the reproducibility.

2.2. Procedures. According to GB/T 12474-2008, the flammability limits of flammable gaseous in the air can be calculated by the following equation

$$\varphi = \frac{1}{2}(\varphi' + \varphi'') \quad (1)$$

When determining LFLs, the change amount of flammability gaseous is not more than 10% of the last injection; when measuring UFLs, the change amount of flammability gaseous shall not be greater than 2% of the last injection amount each time. The following phenomena in the experiment are believed to have occurred: (a) the flame propagated very rapidly to the top of the tube; (b) the flame spreads slowly at a certain speed; and (c) a flame appears around the discharge electrode and goes out, which indicates that the flammability limit occurs around this concentration, in which case the experiment is repeated no least than 5 times with 1 time flame propagation occurs.

The flammable gaseous selected in this experiment were methane, ethane, and propane, which were commonly used in industrial production and daily life, and the dilution inerting gas is nitrogen. The purity of methane, ethane, and propane was 99.99%, and nitrogen was 99.99%. The air used to determine the flammability limits of flammable gaseous was drawn directly

from the ambient environment, and the water vapor in the ambient was removed by the desiccant. The air is considered to contain 21% oxygen and 79% nitrogen. In the case where the flammability limits of methane, ethane, and propane binary alkane mixture were uncertain, the Chatelier's law principle was used to determine the preliminary range of flammability boundaries, which save a lot of time for the experiment.^{23,24} The flammability limits of a flammable gaseous mixture can be expressed as follows

$$\varphi_{\text{mix}} = \frac{1}{\sum_i^n \frac{\varphi_i}{Y_i}} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Satisfaction Analysis Experimental Data of Methane, Ethane, and Propane. The flammability limits of methane, ethane, and propane determined by various methods are listed in Table 1. It was worth mentioning that all these "boundary values" were obtained by using flammability tubes or combustion chambers. The LFLs of methane, ethane, and propane generally ranged between 4.4 and 5.6 (vol %), 2.4 and 3.2 (vol %), 1.7, and 2.3 (vol %), and the corresponding UFLs generally ranged 14.0 and 17.9 (vol %), 12.5 and 15.3 (vol %), and 7.3 and 10.8 (vol %), respectively.

As one of the three elements of combustion, the ignition source has a significant influence on the explosion. Different testing methods have an impact on the experimental data of flammability limits. In the common standard for testing the flammability limits of chemicals (vapors and gases), the spark generator ignition mode is the most selected with an ignition energy of 10–20 J.^{22,25} To assess the satisfaction of the experimental data more accurately, the flammability limit data of mono alkane mixtures obtained from Coward, De Smedt, Burgess, and ISO 10156 were provided as a similar test meant to check the validity of the method in this study. Equations 3 and 4 were used to determine the AE and RE. The result shows that the REs for LFLs of methane, ethane, and propane were 5.4, 6.8, and 15.1%, and the REs for corresponding UFLs were 1.8, 1.4, and 4.5%, respectively. Generally, the RE for LFLs of mono alkane was greater than those for respective UFLs, and the largest RE was observed for LFLs of propane. The main reason that the flammability limits were not an independent parameter is not only related to the flammability limit testing method but also affected by the initial temperature, pressure, limited space, and other factors.²⁶

$$\text{AE} = |\varphi_{\text{exp}} - \varphi_{\text{ave}}| \quad (3)$$

$$\text{RE} = \frac{|\varphi_{\text{exp}} - \varphi_{\text{ave}}|}{\varphi_{\text{ave}}} \times 100\% \quad (4)$$

3.2. Determination of the Flammability Limits of Methane, Ethane, and Propane Binary Gas Alkanes.

The flammability limits of the gaseous alkane mixture were obtained by mixing methane, ethane, and propane in pairs according to the volume ratio of 1:1, 1:2, and 2:1 to form a binary alkane mixture. The flammability limits of the binary alkane mixtures were compared with the theoretical calculation data obtained by eq 2, and the results are shown in Table 2.

Table 2 shows that the RE_{max} between the experimental data and theoretical data of LFLs of the binary alkane mixture of ethane/propane is 12.9%; the RE_{max} of LFLs of ethane/propane

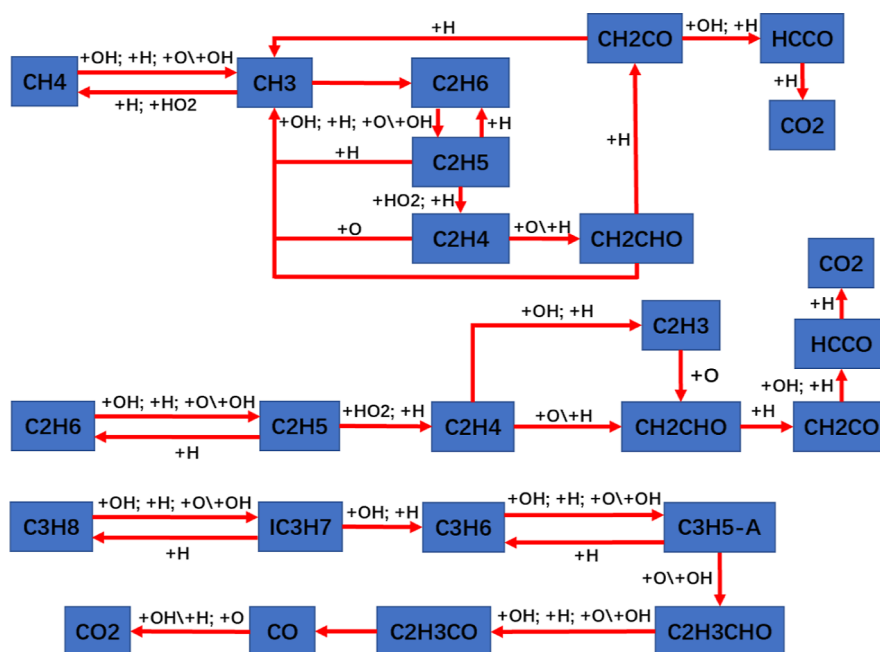
Table 1. Flammability Limits of Methane, Ethane, and Propane (in vol %) Determined with Various Methods

method	vessel shape	ignition sources	criterion	methane LFLs	methane UFLs	ethane LFLs	ethane UFLs	propane LFLs	propane UFLs	experimental condition
BAM ²⁶	6.0 dm ³ , cylindrical	exploding wire	5% pressure rise	4.9	17.9					20 °C and 1 bar
TU Delft ²⁶	20 dm ³ , sphere	exploding wire	5% pressure rise	5.0	15.3					20 °C and 1 bar
BASF ²⁶	20 dm ³ , sphere	exploding wire	5% pressure rise	4.9	16.0					20 °C and 1 bar
WUT ²⁶	40 dm ³ , chamber	exploding wire	5% pressure rise	4.5	15.4					20 °C and 1 bar
INERIS ²⁶	8 dm ³ , tube	exploding wire	5% pressure rise	5.0	14.8					20 °C and 1 bar
Mashuga and Crowl ²⁷	20 dm ³ , sphere	exploding wire	7% pressure rise	5.0	14.9	3.0	12.45	2.1	9.5	20 °C and 1 bar
Van den Schoor and Verplaetsen ²⁸	4.2 dm ³ , sphere	exploding wire	1% pressure rise	5.0			15.3		10.4	20 °C and 1 bar
Van den Schoor, et al. ²⁹	4.2 dm ³ , sphere	exploding wire	5% pressure rise	4.6	16.0					room temperature and 1 bar
Van den Schoor, et al. ²⁹	0.848 dm ³ , tube, $\Phi = 30$ mm	spark generator	visual, vertical ^a	4.4	15.8					room temperature and 1 bar
Liu, et al. ³⁰	20 dm ³ , sphere	spark generator	7% pressure rise					2.3	9.4	25 °C and 1 bar
Kondo, et al. ³¹	12 dm ³ , sphere	spark generator	visual, vertical ^a	4.95 ± 0.1	15.7 ± 0.1			2.05 ± 0.02	9.8 ± 0.4	21 °C, 20 °C and 1 bar
Abdelkhalik, et al. ¹⁰	2.5 dm ³ , tube, $\Phi = 80$ mm	spark generator	visual, vertical ^a					1.8	10.7	20 °C and 1 bar
Molnärne, et al. ³²	1.507 dm ³ , tube, $\Phi = 80$ mm	spark generator	visual, vertical ^a					1.7	10.8	20 °C and 1 bar
Cashdollar, et al. ³³	20 dm ³ , chamber	spark generator	7% pressure rise	5.0	15.9					20 °C and 1 bar
Cashdollar, et al. ³³	120 dm ³ , sphere	spark generator	7% pressure rise	5.0	15.7			2.05	9.8	20 °C and 1 bar
De Smedt, et al. ⁸	20 dm ³ , sphere	spark generator	7% pressure rise	4.85 ± 0.11	15.1 ± 0.3	2.53 ± 0.09	13.8 ± 0.2	1.93 ± 0.07	9.4 ± 0.2	room temperature and 1 bar
De Smedt, et al. ⁸	0.848 dm ³ , tube, $\Phi = 30$ mm	spark generator	visual, vertical ^a	4.60 ± 0.06	16.2 ± 0.2	2.39 ± 0.05	14.8 ± 0.2	1.82 ± 0.04	10.5 ± 0.2	room temperature and 1 bar
Coward and Jones ⁶	3.532 dm ³ , tube, $\Phi = 50$ mm	spark generator	visual, vertical ^a	5.24	14.02					room temperature and 1 bar
Coward and Jones ⁶	2.943 dm ³ , tube, $\Phi = 50$ mm	spark generator	visual, vertical ^a			3.15	14.8			room temperature and 1 bar
Coward and Jones ⁶	0.736 dm ³ , tube, $\Phi = 25$ mm	spark generator	visual, horizontal ^b					2.4	7.3	room temperature and 1 bar
Burgess and Wheeler ³⁴	2 dm ³ , sphere	spark generator	visual	5.6		3.1		2.17		room temperature and 1 bar
ISO 10156 ³⁵	2.36 dm ³ , tube, $\Phi = 50$ mm	spark generator	visual, vertical ^a	4.4		2.4		1.7		20 °C and 1 bar
this experiment	3.4 dm ³ , tube, $\Phi = 50$ mm	spark generator	visual, vertical ^a	5.3 ± 0.2	14.7 ± 0.3	3.0 ± 0.1	14.5 ± 0.3	2.3 ± 0.1	9.6 ± 0.2	room temperature and 1 bar

^aUpward propagation of flame. ^bHorizontal propagation of flame.

Table 2. Flammability Limits Data of Methane, Ethane, and Propane Binary Alkane Mixtures Obtained by Experimental Tests and Le Chatelier Law

alkane components		volume ratio						RE _{max} (%)
		experimental data			Le Chatelier law			
		1:1	1:2	2:1	1:1	1:2	2:1	
methane/ethane	LFLs	4.0	3.7	4.2	3.8	3.5	4.1	5.7
	UFLs	14.1	14.2	14.1	14.4	14.2	14.6	3.4
	interval range	10.1	10.5	9.9	10.6	10.7	10.5	5.7
methane/propane	LFLs	3.5	3.0	3.5	3.1	2.7	3.5	12.9
	UFLs	12.0	11.1	12.9	11.6	10.8	12.6	3.4
	interval range	8.5	8.1	9.4	8.5	8.1	9.1	3.3
ethane/propane	LFLs	2.7	2.5	3.0	2.5	2.4	2.7	11.1
	UFLs	11.2	10.2	11.8	11.3	10.6	12.0	3.8
	interval range	8.5	7.7	8.8	8.8	8.2	9.3	6.1

**Figure 2.** Primary reaction path of methane, ethane, and propane near LFLs of methane/ethane, methane/propane, and ethane/propane binary alkane mixtures.

is 11.1%; the RE_{max} of other binary alkane mixtures are within 6%. Meanwhile, the RE_{max} of the flammability limits interval range (i.e., UFLs–LFLs) is within 10%, which indicates that Chatelier's law principle was effective, and the experimental data of binary mixtures are reliable. In addition, the LFLs and UFLs of methane/ethane for the same ratio were greater than those of methane/propane and ethane/propane in turn, and the flammability limits interval range also shows the same pattern, which indicated that the flammability limits of the binary alkane mixtures follow the variation law of mono alkane gas. Gas combustion reaction have a complex mechanism, which can be explained by either a thermal explosion or chain mechanisms. Thus, to reveal the combustion and explosion process of binary mixtures, the sensitivity analysis using a Premixed Laminar Flame in CHEMKIN-PRO with AramcoMech 2.0 was performed.³⁶ AramcoMech 2.0 has been developed to characterize the kinetic and thermochemical properties of a large number of C1–C4 based hydrocarbon and oxygenated fuels over a wide range of experimental conditions, it contains 493 species and 2176 elementary reactions, which has been verified by a large number of researchers and achieved good results.³⁷ Sensitivity

analysis is a method of revealing the effect of the elementary reaction on each reactant during the reaction.³⁸ The sensitivity analysis was assumed a variable

$$\frac{dZ}{dt} = F(Z, t, a) \quad (5)$$

$$\omega_{l,i} = \frac{\partial Z_l}{\partial a_i} \quad (6)$$

Limited by the length of the article, only the primary reaction path of methane, ethane, propane, and oxygen near the LFLs of methane/ethane, methane/propane, and ethane/propane binary alkane mixtures (five max species count were selected) are displayed, see Figure 2. As a result, the chain-branching and chain-propagating reactions initiated by free radicals play an important role in the chemical reaction. The reaction paths of CH₄ → CO₂, C₂H₆ → CO₂, and C₃H₈ → CO₂ in the combustion process are shown in Figure 2. For CH₄ → CO₂, the main reaction pathway is CH₄ → CH₃ → C₂H₆ → C₂H₅ → C₂H₄ → CH₂CHO → CH₂CO → HCCO → CO₂. There is one more step to form CO₂ for methane comparing with ethane and

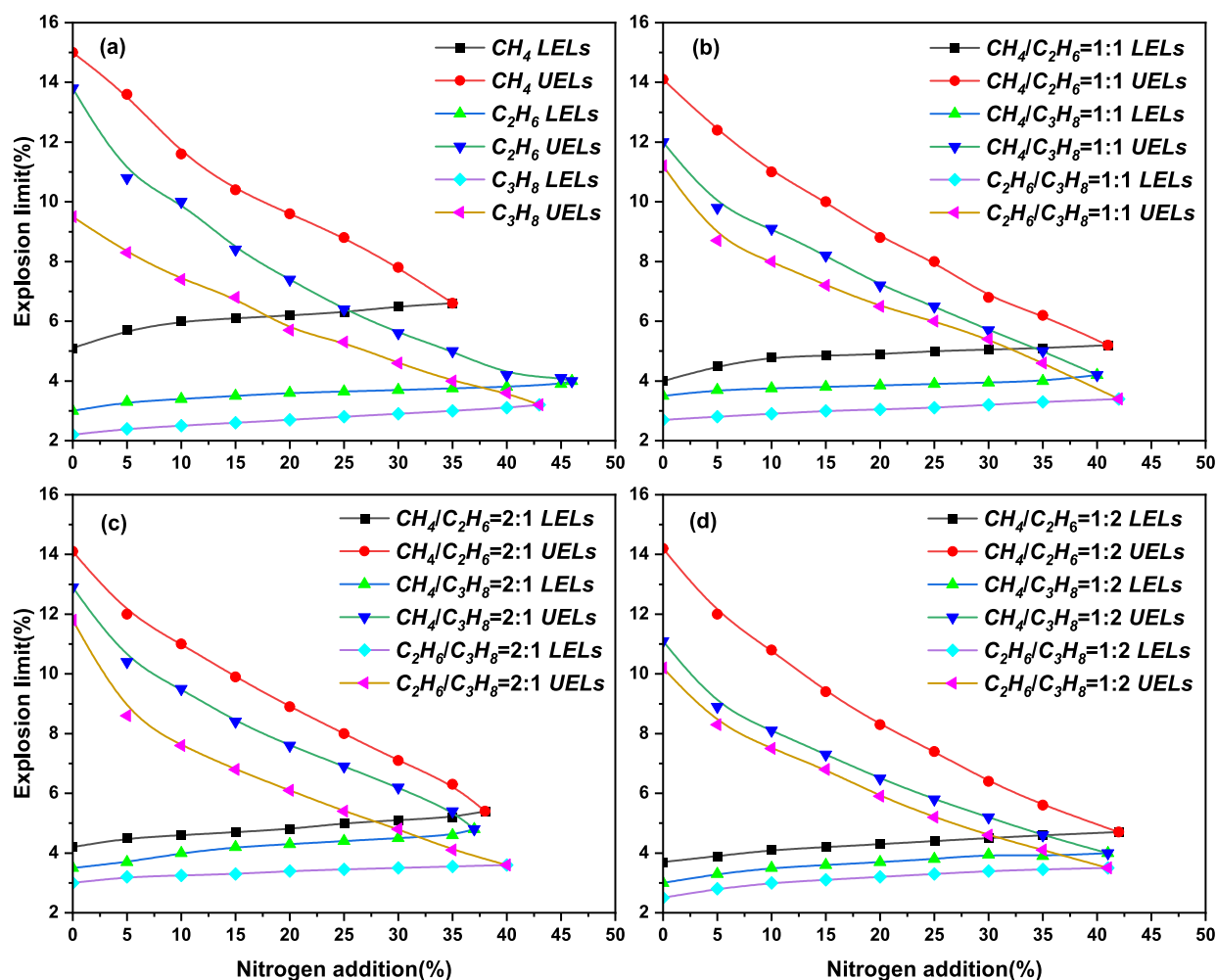


Figure 3. Effect of nitrogen on flammability limits of (a) mono alkane, (b) 1:1 ratio of binary alkane mixtures, (c) 2:1 ratio of binary alkane mixtures, and (d) 1:2 ratio of binary alkane mixtures.

propane. This is caused by the higher CH_4 content in the methane/ethane binary alkane mixture near LFLs.³⁹ These reactions contribute to the product amounts of free radicals O and OH. When the mixed gas absorbs enough energy, the molecular chain breaks, leading to an increase in the number of free radicals H, O, and OH begin to soar to form a chemical reaction active center with a high concentration of free radicals, which eventually form sustained combustion reactions.¹⁵

3.3. Effect of Nitrogen on the Flammability Limits of Methane, Ethane, and Propane Binary Alkanes. Figure 3 illustrates the effect of nitrogen on the flammability limits of methane, ethane, propane mono alkane, and binary alkane mixtures. It shows that as the concentration of nitrogen was continuously increased, the flammability limits area gradually narrows until the LFLs and UFLs completely coincided. This coincidence point is known as the minimum inerting concentration (MIC) point, which indicates that nitrogen has achieved dilution inerting of the flammable alkanes.⁴⁰ In theory, the area surrounded by the LFLs and UFLs curves is the flammability zone, and outside the flammability zone, the mixture is non-flammable. Figure 3a shows that under the condition of nitrogen dilution inerting, the MIC of methane was sequentially higher than those of ethane and propane. Figure 3b–d demonstrates that under the conditions of alkane ratios of 1:1, 2:1, and 1:2, respectively, the MIC of the binary alkane

mixtures follows a rule of methane/ethane > methane/propane > ethane/propane, indicating that mono alkane will provide a greater contribution to the MIC of the binary gaseous alkane mixture.

When the inert gas is added, the probability of flammable alkane molecules and oxygen molecules contacting and reacting was reduced. Nitrogen acted as a barrier role between molecules, increasing the probability of collision between activated molecules and nitrogen molecules, the reaction between molecules cannot proceed normally. Therefore, it is necessary to increase the content of flammable alkanes to maintain combustion and explosion. The substantial decrease in UFLs of mono alkane and binary alkane mixture results from the increasing inert gas of nitrogen, which reduces the oxygen content. Meanwhile, nitrogen also performs an endothermic role, which reduced the activity of activated molecules in the system. As seen in Figure 3, nitrogen dilution inerting has little effect on the LFLs of flammable alkanes, while its effect on UFLs was obvious. There are two main reasons for this phenomenon. On the one hand, with a continuously increased concentration of nitrogen, the oxygen content in the fuel components of UFLs decreases faster than that of LFLs, that is, the same volume of nitrogen is added, and the oxygen content in the fuel components of LFLs is richer, the LFLs of mono alkane and binary alkane mixtures rise slightly, so the dilution inerting effect

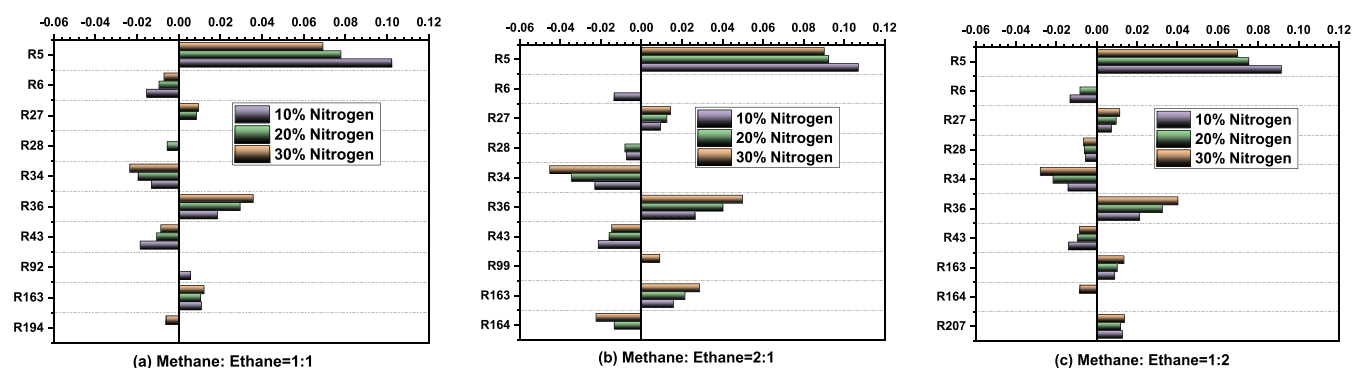


Figure 4. Normalized sensitivity coefficient of (a) methane/ethane = 1:1, (b) methane/ethane = 2:1, and (c) methane/ethane = 1:2 near LFLs when nitrogen dilution inerting.

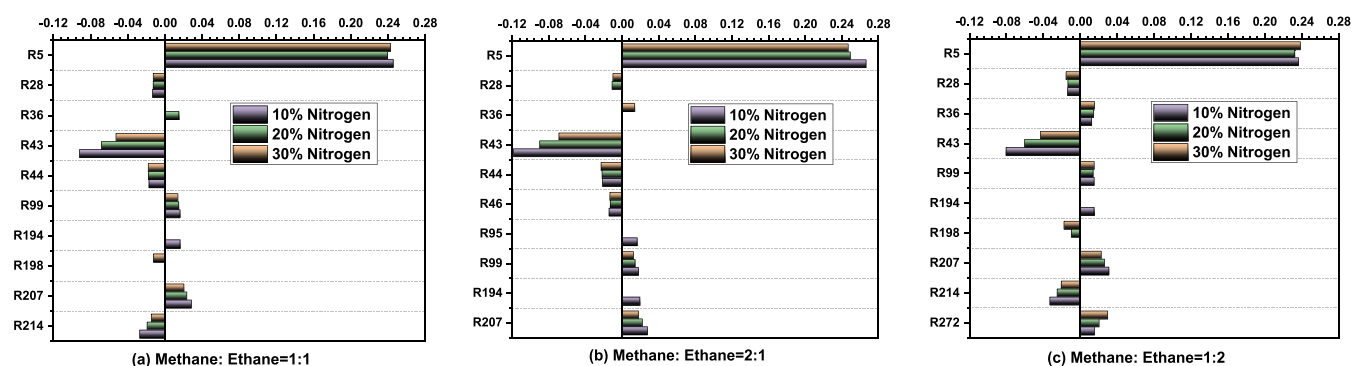


Figure 5. Normalized sensitivity coefficient of (a) methane/ethane = 1:1, (b) methane/ethane = 2:1, and (c) methane/ethane = 1:2 near UFLs when nitrogen dilution inerting.

of nitrogen is not significant. On the other hand, the effect of nitrogen on UFLs of alkane mixtures is more significant because the near UFLs belongs to the fuel-rich and oxygen-lean state. Even if a small amount of nitrogen is added, it will cause a serious decrease in the relative oxygen content in the fuel atmosphere, causing a sharp decrease in UFLs; the slight increase of LFLs is due to the fact that the near LFLs belongs to the oxygen-rich and fuel-lean state; the addition of nitrogen has little effect on the dilution inerting of LFLs, and a small increase in the concentration of fuel components can be combusted.⁴¹

From the perspective of chemical reaction kinetics, the sensitivity analysis of flame temperature was a method to determine the sensitivity factors that have an important impact on the overall response from multiple uncertain factors.⁴² The same chemical kinetic mechanism in Section 3.2 was used. Limited by the length of the article, only the normalized sensitivity coefficients of flame temperature of methane/ethane near LFLs and UFLs are displayed, respectively, see Figures 4 and 5.

As seen from Figures 4 and 5, 10, 20, and 30% nitrogen were added to methane/ethane = 1:1, methane/ethane = 2:1, and methane/ethane = 1:2, respectively. Near LFLs and UFLs, the reaction of methane/ethane with the maximum positive sensitivity coefficients are both R5 $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$, and the reaction with the maximum negative sensitivity coefficients are R34 $\text{H} + \text{O}_2(+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$ and R43 $\text{CH}_3 + \text{H}(+\text{M}) \leftrightarrow \text{CH}_4(+\text{M})$, respectively. In addition, it can be concluded that the reaction of methane/propane and ethane/propane with the maximum positive sensitivity coefficient are also R5 $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$; the reaction with the maximum negative sensitivity coefficients are both R34 $\text{H} + \text{O}_2(+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$ and R43

$\text{CH}_3 + \text{H}(+\text{M}) \leftrightarrow \text{CH}_4(+\text{M})$, respectively. Simultaneously, as shown in Figure 4, near LFLs, the maximum positive sensitivity coefficient of methane/ethane binary alkane mixture with the same ratio when adding 10% nitrogen is sequentially greater than of adding 20 and 30% nitrogen, while its maximum negative sensitivity coefficient is sequentially smaller than that of adding 20 and 30% nitrogen, which indicates that nitrogen has an inerting effect on the maximum positive reaction sensitivity coefficient and a promoting effect on the maximum negative reaction sensitivity coefficient. As shown in Figure 5, nitrogen concentration has little effect on the maximum positive sensitivity coefficient, and has a promoting effect on the maximum negative reaction sensitivity coefficient, indicating that the combustion reaction is suppressed due to rich fuel near UFLs.

Law and Egolfopoulos⁴³ proposed that as the flammability limit approached the maximum termination rate occurs in the same physical region as that of the maximum branching rate, thereby allowing for the most efficient radical scavenging. As seen from Figures 4 and 5, there is a gap between the maximum positive sensitivity coefficient and negative sensitivity coefficient, but it has also reached the physical region as close as possible, mainly because the chemical reaction kinetics are calculated under the adiabatic condition, which cannot be achieved during the experiment test. Chemical reaction kinetics reveals that O and OH radicals produced by R5 $\text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH}$ increase the chemical reaction activity, and consumes H radicals that reduced the chemical reaction activity. On the one hand, nitrogen does not participate in the chemical reaction, but as a stable gas molecule, it participates in third-order collision reactions, increases the concentration of (+M) in the step of gas

phase chain termination, and exchanges the resonance energy. Therefore, the effective third party of nitrogen molecular formula (+M) increases the reaction rate of $R34 \text{ H} + \text{O}_2(+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$ and $R43 \text{ CH}_3 + \text{H}(+\text{M}) \leftrightarrow \text{CH}_4(+\text{M})$, which reduces the concentration of H radicals in the reaction system,⁴⁴ indicating that the increase of nitrogen has a dilution inerting effect on the overall reaction system. On the other hand, the addition of nitrogen can reduce the concentration of fuels and oxygen, absorb the heat released in the reaction process, collide with the key free radicals (O, H, and OH), reduce the activity of these free radicals, accelerate the extinction of these free radicals, and decrease the chemical reaction rate. The important elementary reaction along with the step numbers are showed in Table 3.

Table 3. Elementary Reaction and Step Number of Methane/Ethane near LFLs and UFLs

elementary reaction	step number	elementary reaction	step number
$\text{O}_2 + \text{H} \leftrightarrow \text{O} + \text{OH}$	R5	$\text{CH}_3 + \text{OH} \leftrightarrow \text{CH}_2\text{OH} + \text{H}$	R95
$\text{H} + \text{OH} + \text{M} \leftrightarrow \text{H}_2\text{O} + \text{M}$	R6	$\text{CH}_3 + \text{HO}_2 \leftrightarrow \text{CH}_3\text{O} + \text{OH}$	R99
$\text{HO}_2 + \text{H} \leftrightarrow 2\text{OH}$	R27	$\text{HCO} + \text{M} \leftrightarrow \text{H} + \text{CO} + \text{M}$	R163
$\text{HO}_2 + \text{H} \leftrightarrow \text{H}_2 + \text{O}_2$	R28	$\text{HCO} + \text{O}_2 \leftrightarrow \text{CO} + \text{HO}_2$	R164
$\text{H} + \text{O}_2(+\text{M}) \leftrightarrow \text{HO}_2(+\text{M})$	R34	$2\text{CH}_3(+\text{M}) \leftrightarrow \text{C}_2\text{H}_6(+\text{M})$	R194
$\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}$	R36	$\text{C}_2\text{H}_6 + \text{H} \leftrightarrow \text{C}_2\text{H}_5 + \text{H}_2$	R198
$\text{CH}_3 + \text{H}(+\text{M}) \leftrightarrow \text{CH}_4(+\text{M})$	R43	$\text{C}_2\text{H}_6 + \text{H}(+\text{M}) \leftrightarrow \text{C}_2\text{H}_5(+\text{M})$	R207
$\text{CH}_4 + \text{H} \leftrightarrow \text{CH}_3 + \text{H}_2$	R44	$2\text{CH}_3 \leftrightarrow \text{H} + \text{C}_2\text{H}_5$	R214
$\text{CH}_4 + \text{OH} \leftrightarrow \text{CH}_3 + \text{H}_2\text{O}$	R46	$\text{C}_2\text{H}_5 + \text{O}_2 \leftrightarrow \text{CH}_2\text{CHO} + \text{O}$	R272
$\text{CH}_3 + \text{O} \leftrightarrow \text{CH}_2\text{O} + \text{H}$	R92		

3.4. Effect of Nitrogen on Flammable Triangular Diagram of Methane, Ethane, and Propane Binary Gaseous Alkanes. The LOC is defined as the minimum concentration of oxygen in a mixture of fuel, air (or oxygen), and inert gas that will not support an explosion. In this study, the obtained LOC is represented as

$$\text{LOC} = (100\% - C_{\text{fuel}} - C_{\text{inert}}) \times 0.21 \quad (7)$$

The LOC for mono alkane and binary alkane mixtures were obtained using eq 7. With the increased concentration of nitrogen, the LOC for both mono alkane and binary alkane mixtures gradually decreased, and the variation pattern was similar to the trend of nitrogen on the flammability limits of mono alkane and binary alkane mixtures. For the mono alkanes of methane, ethane, and propane, the corresponding nitrogen concentrations required to achieve LOC were 35, 46, and 43%, respectively. Methane required the least nitrogen, while ethane required the most. The results corresponding flammability limits were 6.6, 4.0, and 3.2%; and LOCs were $\text{LOC}_{\text{CH}_4} = 12.3\%$, $\text{LOC}_{\text{C}_2\text{H}_6} = 10.5\%$, and $\text{LOC}_{\text{C}_3\text{H}_8} = 11.3\%$, respectively, which were basically consistent with the data of literature.⁵ In summary, the LOC for mono alkane and binary alkane mixtures were distributed 10–13%.

A triangular flammability diagram with axes for fuel, oxygen, and nitrogen is a useful tool for displaying the flammability region and identifying the presence of flammable mixtures during plant operations.⁴⁵ Figure 6 shows the triangular

flammability diagram for mono alkane and binary alkanes under nitrogen dilution inerting. The vertices of the triangles represent 100% mono alkane or binary alkane mixtures, oxygen, and nitrogen, respectively, and the direction of the scale marks represents the change in the concentration of each substance. The LOC is parallel to the fuel concentration axis and represents the line of the LOC (dark solid line). Air represents the airline (pink solid line), which indicates the oxygen concentration corresponding to different concentrations of mono alkane or binary alkane mixtures in the air. Equivalent is the chemical equivalent line (dark solid line), representing the combustion reaction of a mono alkane or binary alkane mixtures in an equivalence ratio.

The regions enclosed by the dashed line represent the flammability range for mono alkanes or binary alkane mixtures in this diagram. Figure 6a regions ΔABC , $\Delta A'B'C'$, and $\Delta A''B''C''$ indicate the flammable region of methane (orange dashed region), ethane (bright green dashed region), and propane (red dashed region), respectively; Figure 6b regions ΔABC (orange dotted region), $\Delta A'B'C'$ (bright green dashed region), and $\Delta A''B''C''$ (red dotted region) indicate the flammable region of methane/ethane, methane/propane, and ethane/propane with ratio of 1:1, respectively; Figure 6c,d were also the same as described above. The intersection points between these regions and air line represent the LFLs and UFLs of the combustible substance, respectively. As shown in Figure 6, nitrogen has a relatively little impact on the LFLs for the mono alkanes or binary alkane mixtures, that is, the trend of changes in line segment AC ($A'C'$ or $A''C''$); however, the effect on its UFLs was obvious, that is, the trend of changes in line segment AB ($A'B'$ or $A''B''$). The region of the triangular flammability diagram can be quickly reduced to achieve dilution inerting by injecting nitrogen. The region of ΔABC and $\Delta A'B'C'$ in Figure 6a were larger than those in (b), (c), and (d), respectively, it indicates that the region of the triangular flammability diagram of mono alkanes methane and ethane were greater than that of the binary alkane mixtures methane/ethane and methane/propane under the same conditions; the region of $\Delta A'B'C'$ in Figure 6a was relatively small, which means that the region of the triangular flammability diagram of propane was smaller than that of other mono alkane or binary alkane mixtures. Therefore, during the process of nitrogen dilution inerting, for instance, the possibility of methane being ignited was greater than that of propane from the perspective of the larger range of combustion and explosion.

4. CONCLUSIONS

In this study, the flammability limits of mono alkanes of methane, ethane, and propane, the binary alkane mixtures of methane/ethane, methane/propane, and ethane/propane with ratios of 1:1, 2:1, and 1:2 were tested, respectively. The detection data were compared with the literature data and theoretical calculations. In addition, the dilution inerting effect of nitrogen on mono alkane or binary alkane mixtures was studied, and the kinetic mechanism of nitrogen inerting on the combustion reaction was analyzed. The main conclusions were summarized as follows:

- (1) According to the experimental test results of the flammability limits for the mono alkane and binary alkane mixtures of methane, ethane, and propane, it can effectively meet the results calculated using the Chatelier's law principle, and the flammability limits of binary

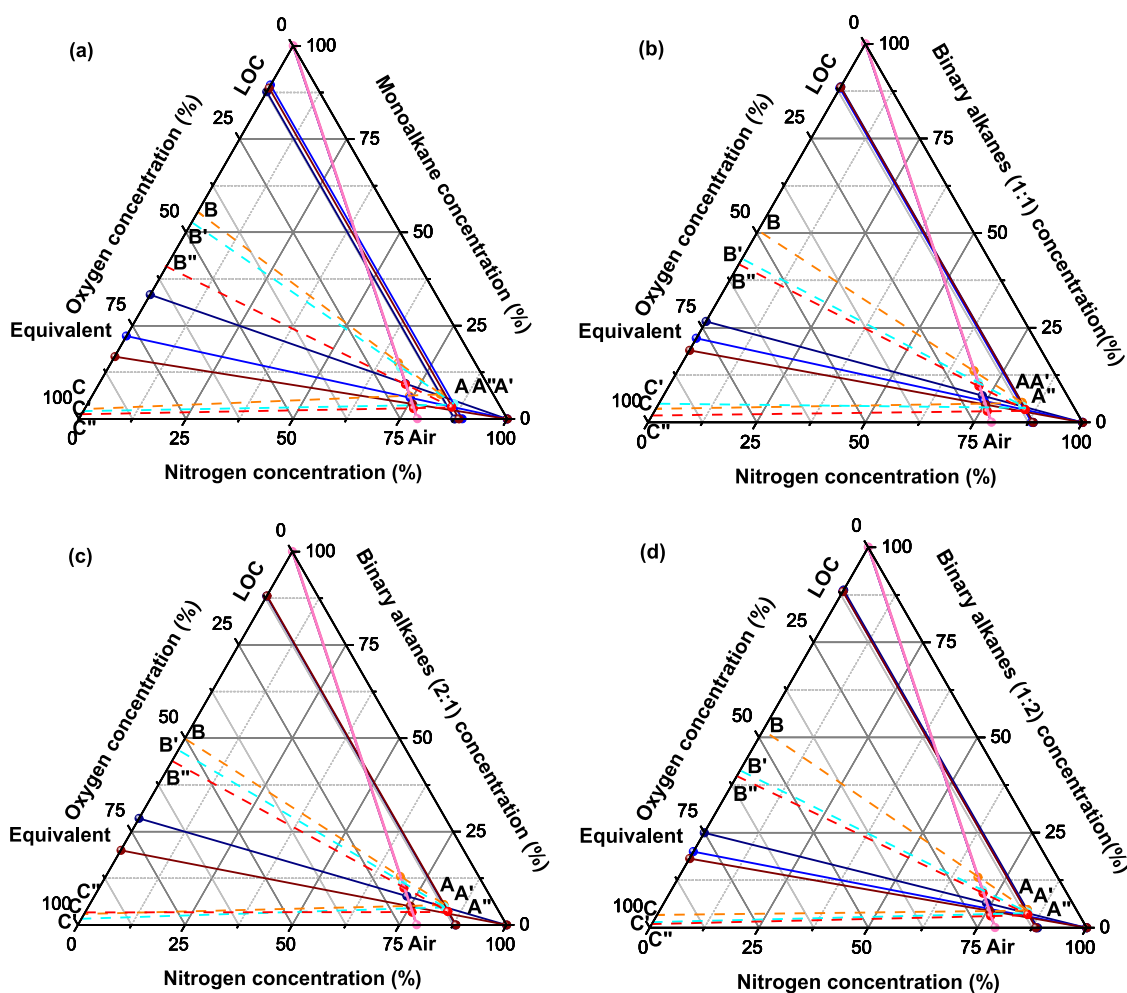


Figure 6. Effect of nitrogen on the triangular flammability diagram of (a) mono alkane, (b) 1:1 ratio of binary alkane mixtures, (c) 2:1 ratio of binary alkane mixtures, and (d) 1:2 ratio of binary alkane mixtures.

mixtures follow the variation law of mono alkane gaseous. The maximum positive sensitivity coefficient of methane/ethane, methane/propane, and ethane/propane are both $R5 H + O_2 \leftrightarrow O + OH$, and the reaction with the maximum negative sensitivity coefficients are both $R34 H + O_2(+M) \leftrightarrow HO_2(+M)$ and $R43 CH_3 + H(+M) \leftrightarrow CH_4(+M)$, respectively.

- (2) The effect of nitrogen on the UFLs was obvious. Under the condition of nitrogen dilution inerting, the flammability limits of methane reaching the MIC was sequentially higher than those of ethane and propane. The MIC of the binary alkane mixtures follows the rule of methane/ethane > methane/propane > ethane/propane. O and OH radicals produced by $R5 H + O_2 \leftrightarrow O + OH$ increase the chemical reaction activity, and consumes H radicals that reduced the chemical reaction activity.
- (3) The LOC of mono alkane and binary alkane mixtures gradually decreases with the increase of nitrogen. The region of the triangular flammability diagram of mono alkanes methane and ethane was greater than that of the binary alkane mixture methane/ethane and methane/propane under the same operating conditions.

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Notes

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NOMENCLATURE

RE, relative error, %
RE_{max}, maximum relative error, %
Z, mass fraction of each component, %
Z_{*l*}, mass fraction of *l*-th component, %
a, pre-factor of each elementary reaction
a_i, pre-exponential factor of the reactions
 $\omega_{i,j}$, sensitivity coefficient
LOC, limiting oxygen concentration, %
MIC, minimum inerting concentration, %
C_{fuel}, fuel concentration, %
C_{inert}, inert gases concentration, %
air, airline
equivalent, chemical equivalent line
LFLs, lower flammability limits, %
UFLs, upper flammability limits, %
 φ , flammability limits of fuel in air, divided into LFLs and UFLs, %
 φ' and φ'' , two concentration values of fuel–air mixture closest to flame propagation and non-propagation, respectively, %
 φ_{mix} , flammability limits of the fuel mixtures in the air, %
 φ_i , flammability limits of the *i*-th substance component, %
 φ_{ave} , average value of flammability limits, %
 φ_{exp} , experimental value of flammability limits, %
Y_{*i*}, concentration ratio of the *i*-th substance component, %
N, number of flammability gaseous
AE, absolute error, %

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