

Article

Theoretical Prediction Model of the Explosion Limits for Multi-Component Gases (Multiple Combustible Gases Mixed with Inert Gases) under Different Temperatures

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Abstract: Combustible gases often lead to fire and explosion accidents due to their unsafe characteristics. Furthermore, their explosion limits are influenced by various factors. In the industrial production process, the operating unit is often in a high-temperature environment, and the multi-component gas explosion limits under this condition are difficult to determine. Therefore, it is urgent to have a universal theoretical prediction model to rapidly predict the multi-component gas explosion limits at high temperatures. This paper proposes a theoretical prediction model for the lower explosion limit of multi-combustible gases containing inert gases at different temperatures based on the heat balance equation and radiation heat loss, which can be used to solve the lower explosion limit of the “multiple combustible gases + multiple inert gases” mixture at different temperatures. It solves the explosion limits of methane, ethylene, propane, and propylene mixed with nitrogen with relative errors of 2.66%, 5.98%, 6.82%, and 5.88%, respectively, compared with experimental data. It also obtained theoretically predicted gas explosion limits for methane, ethylene, propane, and propylene mixed with carbon dioxide, with relative errors of 3.24%, 5.13%, 6.19%, and 5.58%, respectively. Although the reference experimental data made the model validation somewhat limited, validation with data for multiple single gases and temperatures still gave the model considerable reliability.

Keywords: explosion limits; multi-component gases; high temperature; inert gas; theoretical model



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1. Introduction

Currently, the proportion of fires and explosions caused by combustible gases in the total number of accidents is as high as 46%, 42%, and 60% in the petrochemical, plastics, and natural gas industries, respectively. The explosion limits of combustible gases are influenced by temperature, pressure, inert gas, experimental equipment, and operating environment [1–7]. In actual production operations, multi-component gas mixtures are often under high-temperature and high-pressure conditions. In contrast, there is little systematic research on the explosion limits of multi-component gas mixtures in this environment. Therefore, the explosion limits of multi-component gas mixtures under such extraordinary conditions of high temperature have become a top priority for research by experts and scholars. With the development of industrial production technology, multi-component gas mixtures are often encountered at high temperatures, but only a small amount of experimental data has been published due to poor experimental equipment conditions, high workloads, and high costs. Markus et al. [8] studied the effect of temperature on the explosion limits of multi-component gas mixtures by selecting CH₃OH/CH₄/air mixtures and measuring their explosion limits at 323 K and 373 K. Chen et al. [9] conducted an experimental study of the explosion limits of dimethyl ether, CH₄, and their mixtures with different mixing ratios at 25–80 °C and 0.1–0.3 MPa. The results showed that the variation

in the multiple mixture's explosion limits with temperature and pressure was the same as that of a single combustible gas. The U.S. Bureau of Mines [10] cited the inadequacy of existing devices and designed a transparent container with a diameter of 5 cm and a length of 125–150 cm, using electric spark ignition. Kondo et al. [11] conducted an experimental study of the effect of temperature gradient changes on the explosive limits of combustible gases. The results showed that the lower explosive limit gradually decreased with the hydrocarbon fuel temperature, while the upper explosion limit gradually increased. Chao Huang et al. [12] determined the explosion limit of C₅–C₁₀ alkanes under high-temperature conditions (25–170 °C) using a cylindrical stainless steel explosion vessel with a volume of 20 L. A linear relationship between the explosion limit and temperature was obtained, and it was concluded that the fuel would thermally crack at higher temperatures to produce other components, so it was impractical to obtain the explosion limit of long-chain polycarbonate hydrocarbons under high-temperature conditions by experimental methods.

In addition, it was also shown that the proportion and type of inert components of combustible gases significantly affected the gas mixture's explosion limit. Besnard [13] measured the explosion limits of mixtures of CH₄, C₂H₆, C₃H₈, and n-C₄H₁₀ with inert gases at normal temperature and pressure and mainly studied the effects of various inert components such as N₂, CO₂, He, and Ar on the explosion limits of the mixtures. The results showed that the inert components significantly differed in their suppression ability depending on their types. Li [14] used experimental methods to study the effect of mixing N₂ and CO₂ in various proportions on the lower explosion limit of the gas mixture at normal temperature and pressure and discovered that when the proportion of inert components exceeded a certain value, the lower explosion limit was significantly increased, reducing the explosion risk significantly. Hu et al. [15–17] measured the explosion limit of CH₄/CO₂/O₂ gases at normal temperature and pressure using a cylindrical experimental setup and studied the effect of CO₂ concentration on the gas mixture's explosion limit. It was shown that the lower explosion limit of the gas mixture increased approximately linearly from 2.5% to 4.3% as the CO₂ concentration increased from 5% to 70%. The lower the explosion limit's heat of combustion was reduced by CO₂ participation, and the higher the CO₂ concentration, the faster the heat of combustion decreased. Rowley [18] analyzed the effect of temperature on the lower explosion limit by improving the Burgess–Wheeler method and obtained an average error of 3.3%, and [19,20] predicted the upper and lower explosion limits for a variety of hydrocarbon and combustible substances based on this method with an average relative error of 2.3%. None of these methods of estimating the explosion limits of multi-component gas mixtures containing inert gases took heat loss into account during combustion. In this paper, we used basic thermodynamic data to derive a prediction model for the explosion limits of multi-component gases containing inert gases that considers heat loss and verified the model's accuracy with corresponding experimental data.

In summary, the current research results are far from meeting the needs of industrial processes. However, it is tough and tedious to determine the explosion limits of multi-component gases at high temperatures through experiments, so a general theoretical prediction model is needed. When the temperature is too high, the combustible gas can be thermally decomposed into other gases, so it is very difficult to measure the explosion limit of multi-component gases at high temperature or high pressure. We have few experimental data at present, and the data that can be referred to are mostly from experiments on a single combustible gas and inert gas. Therefore, this paper proposes a theoretical prediction model of the explosion limits of multi-component gases (multiple combustible gases mixed with inert gases) under different temperatures, aiming to rapidly predict the explosion limits of multi-component gases at high temperature. Due to the lack of reference data, the model's reliability can only be verified on a one-by-one experimental data basis using a single combustible gas mixed with an inert gas, but the obtained results all have minor relative errors. The predictive model's characteristic of predicting multiple component gases and multiple temperatures allows the model to reliably predict lower explosion limits for multiple temperatures and gases.

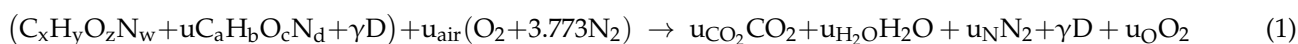
2. Materials and Methods

2.1. Prediction Model of Lower Explosion Limit of Two Combustible Gases Mixed with Inert Gas at Different Temperatures

The addition of inert gases to combustible gases is often used in production processes to reduce the risk of fire and explosion, and commonly used inert gases are nitrogen (N_2), carbon dioxide (CO_2), or water vapor (H_2O). Previous studies of flammability limit estimation methods for inert gas mixtures have ignored the heat loss during combustion [21–23]. This paper uses basic thermodynamic data to derive a prediction model for the lower explosion limits of inert gas mixtures of combustible gases considering heat radiation loss.

When the combustible gas concentration is constantly decreasing due to consumption, the excess air will directly cause the flame not to continue spreading [24]. In addition, once the combustible gas concentration is below its own lower explosive limit, it will not ignite. Therefore, this paper calculates the lower explosion limits of multi-component gases by establishing a fuel-lean (oxygen-rich) reaction, since there is enough oxygen to completely convert the fuel ($C_xH_yO_zN_w$, $C_aH_bO_cN_d$) into carbon dioxide (CO_2) and vapor (H_2O) when in the critical state of the lower explosion limit. This study considers fuel compounds consisting of C, H, O, and N.

Thus, the chemical reaction of two combustible gases ($C_xH_yO_zN_w$, $C_aH_bO_cN_d$) mixed with inert gas in the air and reaching equilibrium leads to the following equations:



$$u_{air} = \frac{v_{air}}{\phi} = \frac{1 + u + \gamma}{4.773(fuel/air)_{stoich}} = \frac{1 + u + \gamma}{4.773(L/1 - L)} = \frac{(1 + u + \gamma)(1 - L)}{4.773L} \quad (2)$$

$$u_{CO_2} = x + ua \quad (3)$$

$$u_{H_2O} = \frac{y + ub}{2} \quad (4)$$

$$M_L = \frac{w + ud}{2} \quad (5)$$

$$u_O = 0.21(1 - L) + u_{air}L \quad (6)$$

$$u_N = 0.79(1 - L) + M_L L \quad (7)$$

Taking as a basis the state of the combustion mixture that continues to increase by 1 mol at the critical state of the lower explosive limit, Table 1 lists the concentrations of the components before and after combustion. Table 1 lists the content of each component of the mixture before and after combustion. The standard heat of reaction at 298 K is shown in the following equation:

$$\Delta H_{298}^0 = L(\Delta h_{c1}^0 + u\Delta h_{c2}^0) \quad (8)$$

where L is the lower explosive limit of the fuel; Δh_c^0 is the standard heat of combustion of 1 mol of fuel at 298 K.

Table 1. Composition of mixtures before and after combustion.

Compound	Mole Fraction before Combustion	Mole Fraction after Combustion
$C_xH_yO_zN_w$	$\frac{L}{1+u+\gamma}$	0
$C_aH_bO_cN_d$	$\frac{uL}{1+u+\gamma}$	0
Inert gas	$\frac{\gamma L}{1+u+\gamma}$	$\frac{\gamma L}{1+u+\gamma}$
Nitrogen	$0.79(1 - L)$	$0.79(1 - L) + M_L L$
Oxygen	$0.21(1 - L)$	$0.21(1 - L) - v_{air}L$
Carbon dioxide	0	$u_{CO_2}L$
Water	0	$u_{H_2O}L$

Taking as a basis the state of the combustion mixture that continues to increase by 1 mol in the critical state of the lower explosive limit, the molar fraction of each component before and after combustion according to Table 1 to find the change in the heat of reactants and products is shown in the following equations:

$$\begin{aligned}\sum_{\text{reactants}} n_i c_{p,i} &= \frac{L}{1+u+\gamma} c_{p,f1} + \frac{uL}{1+u+\gamma} c_{p,f2} + \frac{\gamma L}{1+u+\gamma} c_{p,D} + 0.21(1-L)c_{p,O_2} + 0.79(1-L)c_{p,N_2} \\ &= L \left[\frac{1}{1+u+\gamma} c_{p,f1} + \frac{u}{1+u+\gamma} c_{p,f2} + \frac{\gamma}{1+u+\gamma} c_{p,D} - (0.21c_{p,O_2} + 0.79c_{p,N_2}) \right] + 0.21c_{p,O_2} + 0.79c_{p,N_2} \\ &= L(R_L - P_L) + P_L\end{aligned}\quad (9)$$

$$\begin{aligned}\sum_{\text{products}} n_i c_{p,i} &= \left[0.79(1-L) + \left(\frac{w+ud}{2} \right) L \right] c_{p,N_2} + [0.21(1-L) - u_{\text{air}} L] c_{p,O_2} + u_{\text{CO}_2} L \cdot c_{p,\text{CO}_2} + u_{\text{H}_2\text{O}} L \cdot c_{p,\text{H}_2\text{O}} + \frac{\gamma L}{1+u+\gamma} c_{p,D} \\ &= L \left[\frac{w+ud}{2} c_{p,N_2} - 0.21u_{\text{air}} c_{p,O_2} + u_{\text{CO}_2} c_{p,\text{CO}_2} + u_{\text{H}_2\text{O}} c_{p,\text{H}_2\text{O}} + \frac{\gamma}{1+u+\gamma} c_{p,D} - (0.79c_{p,N_2} + 0.21c_{p,O_2}) \right] + 0.79c_{p,N_2} + 0.21c_{p,O_2} \\ &= L(Q_L - P_L) + P_L\end{aligned}\quad (10)$$

and

$$R_L = \frac{1}{1+u+\gamma} c_{p,f1} + \frac{u}{1+u+\gamma} c_{p,f2} + \frac{\gamma}{1+u+\gamma} c_{p,D} \quad (11)$$

$$P_L = 0.21c_{p,O_2} + 0.79c_{p,N_2} \quad (12)$$

$$M_L = \frac{w+ud}{2} \quad (13)$$

$$Q_L = M_L c_{p,N_2} - 0.21u_{\text{air}} c_{p,O_2} + u_{\text{CO}_2} c_{p,\text{CO}_2} + u_{\text{H}_2\text{O}} c_{p,\text{H}_2\text{O}} + \frac{\gamma}{1+u+\gamma} c_{p,D} \quad (14)$$

When the pressure is maintained at atmospheric pressure, the total heat exchange is linked to the heat loss from the combusted gas to the unburned gas through thermal convection and thermal radiation. According to the Stefan–Boltzmann law, at high temperatures, heat radiation is more dominant than heat convection [25]. The radiant heat loss Q_r is considered in this study. Thus, the energy balance equation is shown as follows:

$$\Delta H \approx Q_r \quad (15)$$

Based on the energy balance equation, a model considering heat radiation losses and constant flame temperature was developed to predict the lower explosion limit for fuel-air-dilution mixtures at constant pressure. The heat is considered positive when transferred from the environment to the system. The initial temperature of the mixture is T_i , and the final temperature after combustion is T . Then, the above equation can be re-expressed as:

$$\Delta H_{298}^0 + \sum_{\text{reactants}} \int_{T_i}^{298} n_i c_{p,i} dT + \sum_{\text{products}} \int_{298}^T n_i c_{p,i} dT = Q_r \quad (16)$$

Radiant heat loss per mole of combustible mixtures is:

$$Q_r = -\alpha e A_s \sigma (T^4 - T_i^4) \Delta t \quad (17)$$

where σ is the Stefan–Boltzmann constant of $5.67 \times 10^{-8} \text{ W}/(\text{m}^2 \cdot \text{K}^4)$, e is the radiance with a value between 0 and 1, determined by the surface properties of the object, A_s is the heat exchange surface area per mole of mixtures, and Δt is the flame propagation duration; α is the surface radiant heat transfer coefficient.

All objects emit electromagnetic radiation by the Stefan–Boltzmann law, which states that the flux density Φ of the radiation emitted by a black body is proportional to the fourth power of its absolute temperature T .

$$\Phi = \sigma T^4 \quad (18)$$

Substituting Equations (8)–(10) and (18) into Equation (16) obtains the following:

$$L(\Delta h_{c1}^0 + u\Delta h_{c2}^0) + \int_{T_i}^{298} [L(R_L - P_L) + P_L] dT + \int_{298}^T [L(Q_L - P_L) + P_L] dT = \alpha e A_s \sigma (T^4 - T_i^4) \Delta t \quad (19)$$

$$L = \frac{\alpha e A_s \sigma (T_L^4 - T_i^4) \Delta t + \int_{T_i}^{T_L} P_L dT}{(\Delta h_{c1}^0 + u \Delta h_{c2}^0) + \int_{T_i}^{298} R_L dT + \int_{298}^{T_L} Q_L dT - \int_{T_i}^{T_L} P_L dT} \quad (20)$$

where T_i is the initial temperature; T_L is the flame temperature of LFL.

2.2. Prediction Model of the Lower Explosion Limit of Multiple Combustible Gases Mixed with Inert Gases at Different Temperatures

Through the deduction process of the theoretical prediction model of the lower explosion limit of two or more combustible gases, the theoretical prediction model of the lower explosion limit of multiple combustible gases mixed with inert gases at a high temperature can be derived as follows:

$$\Delta H_{298,m}^0 = L (\Delta h_{c1}^0 + u_1 \Delta h_{c2}^0 + u_2 \Delta h_{c3}^0 + \dots + u_i \Delta h_{ci+1}^0) \quad (21)$$

where L is the lower explosion limit of fuel, and Δh_c^0 is the standard heat of combustion for 1 mole of fuel at 298 K.

In the critical state of the lower explosion limit, the heat change of reactants and products can be calculated according to the mole fraction of each component before and after combustion:

$$\begin{aligned} \sum_{\text{reactants}} n_i c_{p,i} &= \frac{L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f1} + \frac{u_1 L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f2} + \dots + \frac{u_i L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f_{i+1}} \\ &+ \frac{\gamma_1 L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D1} + \frac{\gamma_2 L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D2} + \dots + \frac{\gamma_i L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D_i} + 0.21(1-L)c_{p,O_2} \\ &+ 0.79(1-L)c_{p,N_2} \\ &= L \left[\frac{1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f1} + \frac{u_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f2} + \dots + \frac{u_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f_{i+1}} \right. \\ &\quad \left. + \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D1} + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D2} + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D_i} \right] + 0.21c_{p,O_2} + 0.79c_{p,N_2} \\ &= L(R_{L,m} - P_L) + P_L \end{aligned} \quad (22)$$

$$\Delta H_{298,m}^0 = L (\Delta h_{c1}^0 + u_1 \Delta h_{c2}^0 + u_2 \Delta h_{c3}^0 + \dots + u_i \Delta h_{ci+1}^0) \quad (23)$$

$$u_{\text{air}} = \frac{v_{\text{air}}}{\varphi} = \frac{1+u+\gamma}{4.773(\text{fuel/air})_{\text{stoich}}} = \frac{1+u+\gamma}{4.773(L/1-L)} = \frac{(1+u+\gamma)(1-L)}{4.773L} \quad (24)$$

$$u_{\text{CO}_2} = x + ua \quad (25)$$

$$u_{\text{H}_2\text{O}} = \frac{y + ub}{2} \quad (26)$$

$$u_N = 0.79(1-L) + M_L L \quad (27)$$

$$M_L = \frac{w + ud}{2} \quad (28)$$

$$u_O = 0.21(1-L) - u_{\text{air}} L \quad (29)$$

The total number of each atom in the reaction equation is as follows:

$$\begin{aligned} C &= x + u_1 a + u_2 e + \dots; H = y + u_1 b + u_2 f + \dots \\ O &= z + u_1 c + u_2 g + \dots; N = w + u_1 d + u_2 h + \dots \end{aligned}$$

$$\begin{aligned} R_{L,m} &= \frac{1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f1} + \frac{u_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f2} + \dots + \frac{u_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,f_{i+1}} \\ &+ \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D1} + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D2} + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D_i} \end{aligned} \quad (30)$$

and

$$P_L = 0.21c_{p,O_2} + 0.79c_{p,N_2} \quad (31)$$

$$M_L = \frac{w + ud + \dots}{2} = \frac{N}{2} \quad (32)$$

$$u_{CO_2} = x + u_1a + u_2e + \dots = C \quad (33)$$

$$u_{H_2O} = \frac{y + u_1b + u_2f + \dots}{2} = \frac{H}{2} \quad (34)$$

$$Q_L = \frac{N}{2}c_{p,N_2} - 0.21u_{air}c_{p,O_2} + C \cdot c_{p,CO_2} + \frac{H}{2}c_{p,H_2O} + \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_1} \\ + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_2} + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_i} \quad (35)$$

$$\sum_{products} n_i c_{p,i} = \left[0.79(1-L) + \left(\frac{w+ud+\dots}{2} \right) L \right] c_{p,N_2} + [0.21(1-L) - u_{air}L] c_{p,O_2} + u_{CO_2}L \cdot c_{p,CO_2} + u_{H_2O}L \cdot c_{p,H_2O} + \frac{\gamma_1 L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D_1} \\ + \frac{\gamma_2 L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D_2} + \dots + \frac{\gamma_i L}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i} c_{p,D_i} \quad (36)$$

$$= L \left[\frac{N}{2}c_{p,N_2} - 0.21u_{air}c_{p,O_2} + C \cdot c_{p,CO_2} + \frac{H}{2}c_{p,H_2O} + \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_1} + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_2} \right. \\ \left. + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_i} - (0.79c_{p,N_2} + 0.21c_{p,O_2}) \right] + 0.79c_{p,N_2} + 0.21c_{p,O_2}$$

Simplification gives the following:

$$u_{air} = \frac{(1 + u_1 + u_2 + \dots + u_i + \gamma_1 + \gamma_2 + \dots + \gamma_i)(1-L)}{4.773L} \quad (37)$$

$$\sum_{production} n_i c_{p,i} = L \left[\frac{N}{2}c_{p,N_2} - 0.21 \frac{(1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i)}{4.773} \left(\frac{1-L}{L} \right) c_{p,O_2} + C \cdot c_{p,CO_2} + \frac{H}{2}c_{p,H_2O} + \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_1} \right. \\ \left. + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_2} + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_i} - (0.79c_{p,N_2} + 0.21c_{p,O_2}) \right] \\ + 0.79c_{p,N_2} + 0.21c_{p,O_2} \quad (38)$$

$$= L \left[\frac{N}{2}c_{p,N_2} + 0.044(1 + u_1 + u_2 + \dots + u_i + \gamma_1 + \gamma_2 + \dots + \gamma_i)c_{p,O_2} + C \cdot c_{p,CO_2} + \frac{H}{2}c_{p,H_2O} + \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_1} \right. \\ \left. + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_2} + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_i} - (0.79c_{p,N_2} + 0.21c_{p,O_2}) \right] \\ + 0.79c_{p,N_2} + 0.21c_{p,O_2} - 0.044(1 + u_1 + u_2 + \dots + u_i + \gamma_1 + \gamma_2 + \dots + \gamma_i)c_{p,O_2}$$

$$\sum_{production} n_i c_{p,i} = L(Q_{L,m} - P_L + S_L) + P_L - S_L \quad (39)$$

$$Q_{L,m} = \frac{N}{2}c_{p,N_2} + C \cdot c_{p,CO_2} + \frac{H}{2}c_{p,H_2O} + \frac{\gamma_1}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_1} \\ + \frac{\gamma_2}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_2} + \dots + \frac{\gamma_i}{1+u_1+u_2+\dots+u_i+\gamma_1+\gamma_2+\dots+\gamma_i}c_{p,D_i} \quad (40)$$

$$S_L = 0.044(1 + u_1 + u_2 + \dots + u_i + \gamma_1 + \gamma_2 + \dots + \gamma_i)c_{p,O_2} \quad (41)$$

Radiant heat loss per mole of combustible mixtures is as follows:

$$Q_r = -\alpha \epsilon A_s \sigma (T^4 - T_i^4) \Delta t \quad (42)$$

$$\Delta H_{298,m}^0 = L_m (\Delta h_{c_1}^0 + u_1 \Delta h_{c_2}^0 + u_2 \Delta h_{c_3}^0 + \dots + u_i \Delta h_{c_{i+1}}^0) \quad (43)$$

$$\Delta H_{298,m}^0 + \sum_{reactants} \int_{T_i}^{298} n_i c_{p,i} dT + \sum_{products} \int_{298}^T n_i c_{p,i} dT = Q_r \quad (44)$$

Substituting Equations (21)–(42) into Equation (43) yields the following:

$$\Delta H_{298,m}^0 + \sum_{reactants} \int_{T_i}^{298} n_i c_{p,i} dT + \sum_{products} \int_{298}^T n_i c_{p,i} dT = Q_r \quad (45)$$

$$L_m (\Delta h_{c_1}^0 + u_1 \Delta h_{c_2}^0 + u_2 \Delta h_{c_3}^0 + \dots + u_i \Delta h_{c_{i+1}}^0) + \int_{T_i}^{298} [L_m (R_{L,m} - P_L) + P_L] dT + \int_{298}^{T_L} [L_m (Q_{L,m} - P_L + S_L) + P_L - S_L] dT \\ = -\alpha \epsilon A_s \sigma (T_L^4 - T_i^4) \Delta t \quad (46)$$

In the case of initial temperature, T_i is a specific temperature (e.g., ambient temperature T_0), and T_L is the flame temperature of the LFL. Then, Equation (46) estimates the variation in the lower explosion limit of the multi-component gases with the initial temperature. Therefore, the prediction model for the lower explosion limit of multi-component gases (multiple combustible gases mixed with inert gases) at high temperatures is as follows:

$$L_m = \frac{\alpha e A_s \sigma (T_L^4 - T_i^4) \Delta t + \int_{T_i}^{T_L} P_L dT - \int_{298}^{T_L} S_L dT}{\left(\Delta h_{c1}^o + u_1 \Delta h_{c2}^o + u_2 \Delta h_{c3}^o + \dots + u_i \Delta h_{ci+1}^o \right) + \int_{T_i}^{298} R_{L,m} dT + \int_{298}^{T_L} (Q_{L,m} + S_L) dT - \int_{T_i}^{T_L} P_L dT} \quad (47)$$

3. Results

3.1. Model Verification

According to Kondo [26–28], methane, ethylene, propane, and propylene explosion limits with nitrogen or carbon dioxide inert gases were tested in a 12 L spherical glass flask sealed in an air bath with a temperature of 35 °C. From the different databases of the Poling and DIPPR [29,30], it is clear that when considering each different heat loss, the proportion of radiative heat loss is highest at a value of $\alpha e A_s \sigma \Delta t$ of $3 \times 10^{-9} \text{ J} \cdot \text{K}^{-4} \cdot \text{mol}^{-1}$, so this value was chosen to obtain the critical flame temperature and the standard heat of generation of the compound. Therefore, this model uses these parameters to calculate the explosion limits of methane, ethylene, propane, and propylene mixed with nitrogen or carbon dioxide. The calculated results are compared with the Kondo experimental results. These results are shown in Table 2.

Table 2. Theoretical predicted values and experimental values of lower explosion limits.

Gas Mixture	Inert Gas Ratio X/%	Poling T_L/K	DIPPR T_L/K	Model Prediction L_m	Kondo Experiment L_m	Relative Error/%	Kondo Experiment U_m
Methane + Nitrogen	0	1264	1264	4.90	4.90	0	15.8
	0.15			4.98	4.94	0.8	14.9
	0.25			5.01	4.94	1.4	14.3
	0.30			5.08	5.00	1.6	13.94
	0.50			5.16	4.98	3.6	12.19
	0.625			5.25	5.02	4.6	10.6
	0.75			5.31	4.98	6.6	8.7
Ethylene + Nitrogen	0	1209	1209	2.74	2.74	0	31.5
	0.25			2.80	2.74	2.2	25.0
	0.50			2.89	2.73	5.9	18.4
	0.75			3.01	2.74	9.8	10.5
	0.80			3.08	2.75	12	7.0
Propane + Nitrogen	0	1287	1287	2.03	2.03	0	10.0
	0.25			2.10	2.03	3.3	9.1
	0.50			2.18	2.03	7.4	8.2
	0.725			2.22	2.05	8.3	7.53
	0.75			2.25	2.03	10.8	6.4
	0.85			2.30	2.07	11.1	4.96
Propylene + Nitrogen	0	1294	1294	2.16	2.16	0	11.0
	0.25			2.22	2.16	2.8	9.8
	0.50			2.29	2.16	6	8.8
	0.625			2.32	2.17	6.9	7.9
	0.75			2.38	2.17	9.6	6.7
	0.85			2.43	2.21	9.95	5.2
Methane + Carbon dioxide	0	1264	1264	4.9	4.90	0	15.8
	0.20			5.13	5.05	1.6	14.06
	0.40			5.38	5.15	4.3	12.2
	0.60			5.62	5.35	4.8	10.08
	0.70			5.86	5.65	5.5	8.7

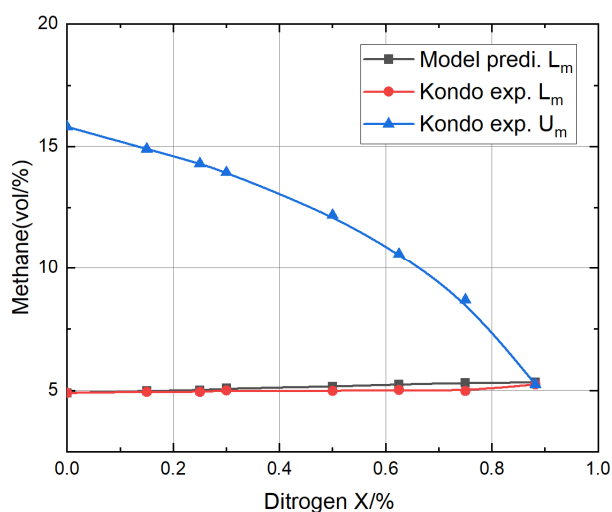
Table 2. Cont.

Gas Mixture	Inert Gas Ratio X/%	Poling T_L/K	DIPPR T_L/K	Model Prediction L_m	Kondo Experiment L_m	Relative Error/%	Kondo Experiment U_m
Ethylene + Carbon dioxide	0	1209	1209	2.74	2.74	0	31.5
	0.20			2.79	2.74	1.8	24.1
	0.40			2.87	2.77	3.6	18.5
	0.60			3.04	2.83	7.4	12.75
	0.75			3.15	2.92	7.9	8.8
	0.85			3.23	3.08	10.1	6.03
Propane + Carbon dioxide	0	1287	1287	2.03	2.03	0	10
	0.20			2.11	2.02	4.5	9.2
	0.25			2.14	2.02	5.9	8.9
	0.40			2.19	2.03	7.9	8.3
	0.60			2.25	2.07	8.7	7.15
	0.75			2.28	2.14	6.5	5.8
Propylene + Carbon dioxide	0	1294	1294	2.16	2.16	0	11
	0.20			2.26	2.18	3.7	9.7
	0.40			2.30	2.17	6.0	8.8
	0.60			2.41	2.22	8.6	7.35
	0.75			2.47	2.30	7.4	6.13
	0.85			2.64	2.45	7.8	4.75

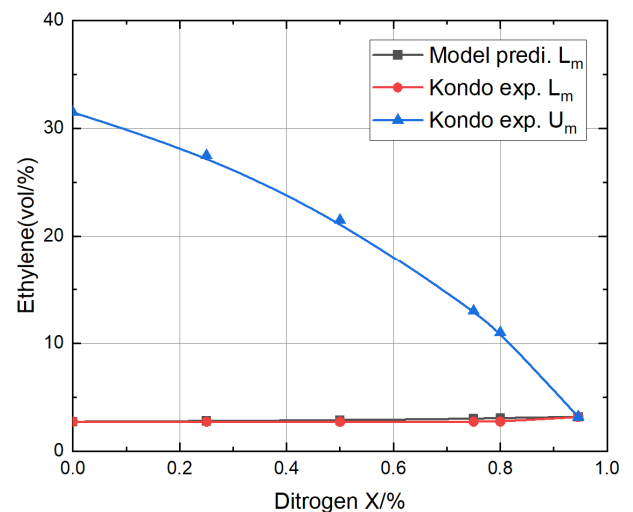
3.2. Analysis

The standard flammability diagram [31] is used to describe the flammability state of the mixture in terms of the diluent/fuel combination and demonstrate the diluent's influence in the gas mixture on the explosion limits. In this paper, standard flammability diagrams were used to analyze the eight gas mixtures “methane + nitrogen”, “ethylene + nitrogen”, “propane + nitrogen”, “propylene + nitrogen”, “methane + carbon dioxide”, “ethylene + carbon dioxide”, “propane + carbon dioxide”, and “propylene + carbon dioxide” in different dilution ratios of the explosion limit range.

The results of the explosion limit calculations for different combustible gases mixed with nitrogen are shown in the explosion limit range in Figure 1. The average relative errors were 2.66% for “methane + nitrogen”, 5.98% for “ethylene + nitrogen”, 6.82% for “propane + nitrogen”, and 5.88% for “propylene + nitrogen”, which were all within the acceptable range.

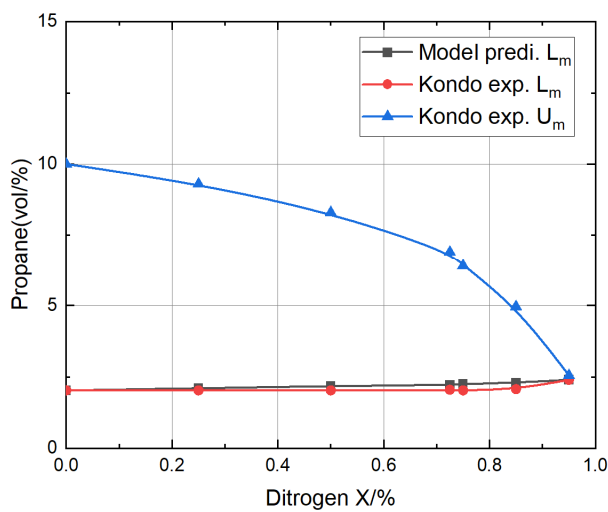


(a)

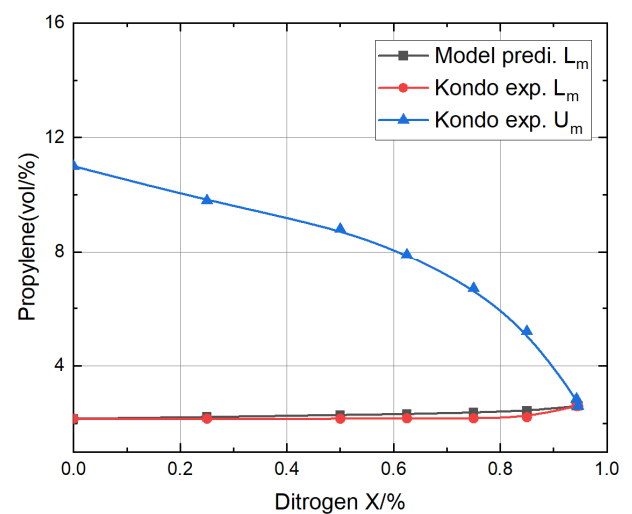


(b)

Figure 1. Cont.



(c)

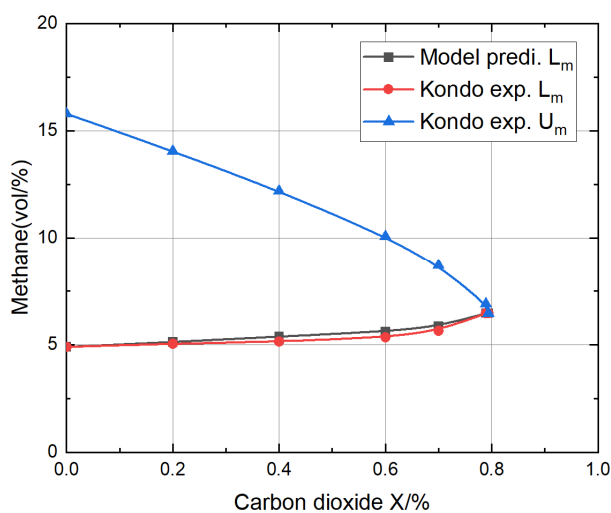


(d)

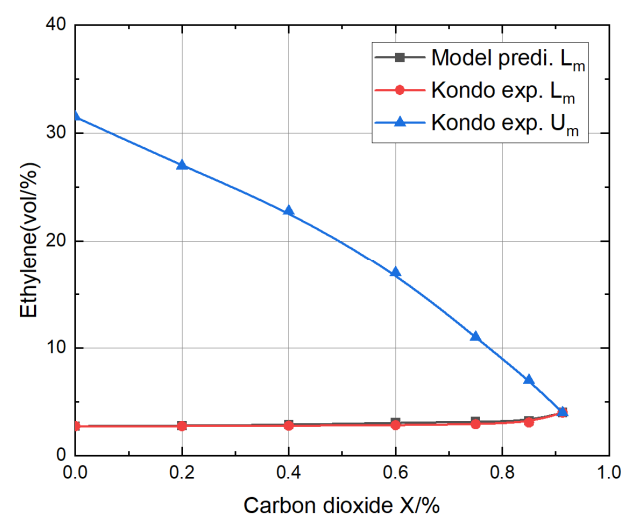
Figure 1. Standard flammability diagrams of methane, ethylene, propane and propylene mixed with nitrogen. Calculation of the explosion limit of (a) “methane + nitrogen”; (b) “ethylene + nitrogen”; (c) “propane + nitrogen”; (d) “propylene + nitrogen”.

The results of the explosion limit calculations for different combustible gases mixed with carbon dioxide are shown in the explosion limit range in Figure 2. The average relative errors were 3.24% for “methane + carbon dioxide”, 5.13% for “ethylene + carbon dioxide”, 6.19% for “propylene + carbon dioxide”, and 5.58% for “propylene + carbon dioxide”, which were all within the acceptable range.

The results in Figures 1 and 2 show that this theoretical model predicted values of the lower explosion limit that coincided with the Kondo experimental values. This theoretical model accurately predicts the explosion limits of multiple gas mixtures containing inert gases with small errors.



(a)



(b)

Figure 2. Cont.

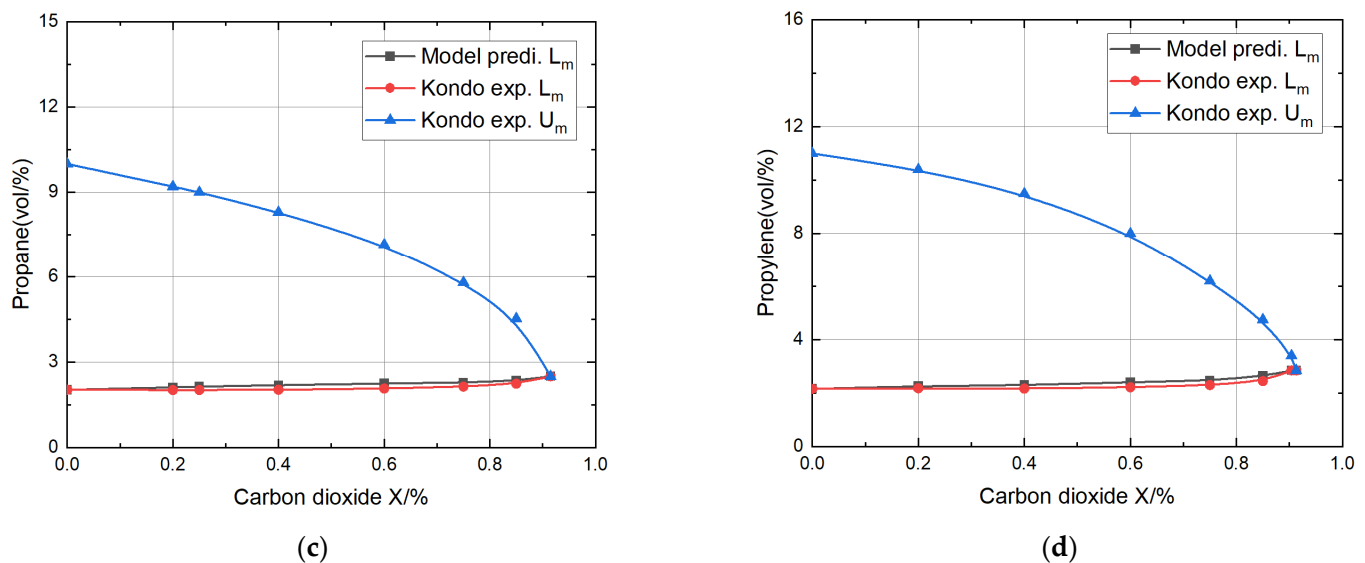


Figure 2. Standard flammability diagrams of methane, ethylene, propane and propylene mixed with carbon dioxide. Calculation of the explosion limit of (a) “methane + carbon dioxide”; (b) “ethylene + carbon dioxide”; (c) “propane + carbon dioxide”; (d) “propylene + carbon dioxide”.

The relative error results are shown in Figure 3. When the proportion of inert gas was lower than 70%, the relative error between the theoretical model predicted value of the lower explosion limit and the experimental value of Kondo was less than 8%, and the accuracy of the model was verified. When the proportion of inert gas was 70–85%, the relative error was 12%. On the one hand, this was due to the high content of inert components in the gas mixture, which will produce a certain inerting effect on the gas mixture to reduce its flammability, thus resulting in a slight increase in the lower explosion limit. On the other hand, only ethylene and propane had relatively high errors, because the chemical properties of these two combustible gases are very different from those of ordinary combustible compounds. Among them, ethylene tends to explode and decompose, and the flammability of propane is a little weaker compared with that of ordinary combustible compounds. The dilution effects of nitrogen and carbon dioxide on methane, ethylene, propane, and propylene are different, and their different effects on the lower explosion limit are due to the different heat capacity values between air and the two inert gases. However, their general trends were consistent with the experimental data. Among them, the theoretical model predicted the dilution effect of CO₂ better than that of nitrogen with less error, mainly because the specific heat of CO₂ is higher than N₂, and CO₂ is directly involved in chemical reactions and thermal radiation. Among the four different combustible gases, the relative errors between the theoretically predicted and experimental values of the explosion limits after methane mixing were the smallest, at only 2.66% and 3.24%, respectively; propane had the most significant errors, reaching 6.82% and 6.19%, respectively.

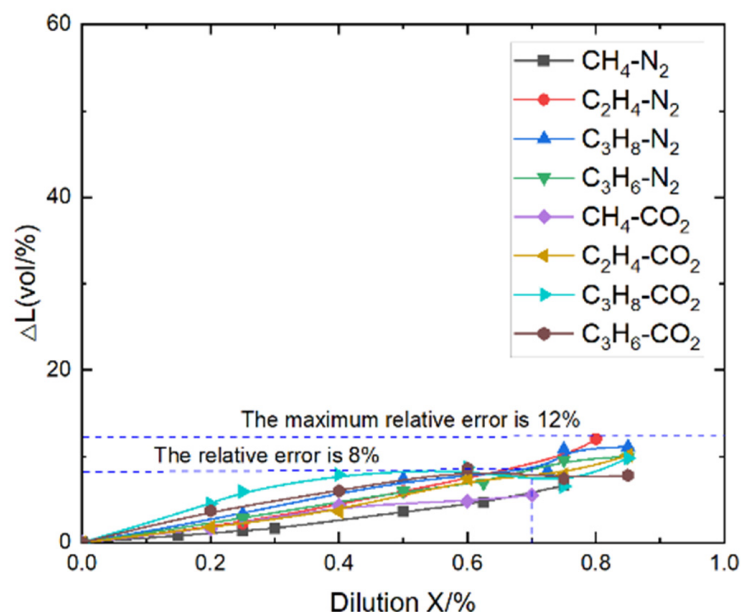


Figure 3. Relative error for lower explosion limit between theoretical predicted value and experimental value.

4. Discussion

Using basic thermodynamic data under constant pressure and different temperature conditions, a model was derived for predicting the explosion limit of a multi-component gas mixture with inert gas considering thermal radiation loss. The explosion lower limit formula for two kinds of combustible gas and inert gas in air was deduced first. Then, the lower explosion limit prediction model for multiple combustible gases mixed with inert gases was derived based on the same principle, and finally, the model's accuracy was verified through comparison with Kondo's experimental data.

5. Conclusions

The research conclusions can be summarized as follows.

1. The relative errors are all less than 8% when the proportion of inert gas is less than 70%, and the model's accuracy was fully verified. Due to the higher specific heat of CO_2 compared to N_2 , and the fact that CO_2 directly participates in chemical reactions and thermal radiation, the theoretical model predicted that the CO_2 dilution effect was better than that of N_2 , and the error was somewhat smaller.
2. Comparing the predicted explosion limits of four different combustible gases mixed with nitrogen with the experimental values, it was found that the relative error for the methane mixture was the smallest, at only 2.66% and 3.24%, respectively; the relative error for the propane mixture was the largest, reaching 6.82% and 6.19%, respectively.
3. The theoretical model's predictions for the lower explosion limits for methane, ethylene, propane, and propylene mixtures with nitrogen or carbon dioxide fell within the acceptable range of relative error compared to the experimental values of Kondo, thoroughly verifying the validity of the theoretical model.

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Nomenclature

L	Lower explosive limit of the fuel	
D	Inert gas	
ΔH_c	Heat of combustion	kJ/mol
ΔH	Enthalpy change	J
$\Delta H_{c,j}$	Heat of combustion of the reactants	J
Δh_c°	Standard heat of combustion for 1 mole of fuel at 298 K	J
$c_{p,i}$	The specific heat capacity of the reactants	J·g ⁻¹ K ⁻¹
Q _r	Heat loss	J
a	Surface radiant heat transfer coefficient	W/(m ² K)
e	Radiance	
A _s	Heat exchange surface area per mole of mixture	m ² /mol
σ	Stefan–Boltzmann constant	W/(m ² ·K ⁴)
Δt	Flame propagation duration	S
Φ	Radiation flux density	
T _i	Initial temperature	K
T _L	Flame temperature of LFL	K
n	Chemical reaction order	

References

- Hao, Y.; Peizhi, W.; Xiangyun, W. Current situation and Influencing Factors of Gas and dust explosion accidents in China. *Saf. Environ. Eng.* **2008**, *15*, 97–99. [\[CrossRef\]](#)
- Bond, J. *Sources of Ignition: Flammability Characteristics of Chemicals and Products*; Butterworth-Heinemann: Oxford, UK, 1991; pp. 147–151.
- Lian, P.; Gao, X.; Mannan, M.S. Prediction of minimum ignition energy of aerosols using flame kernel modeling combined with flame front propagation theory. *J. Loss Prevent. Proc.* **2012**, *25*, 103–113. [\[CrossRef\]](#)
- Chen, T.; HU, S. Research progress of combustible gas explosion process. *Sci. Technol. Inf. Dev. Econ.* **2006**, *16*, 171–172. [\[CrossRef\]](#)
- Tian, G.; Ma, Y.; Yang, Z.; Feng, Y.; Wang, Z. Theoretical and Experimental Study on explosion Limit and Suppression of Combustible Refrigerant. *J. Shandong Inst. Civ. Eng. Archit.* **2001**, *16*, 58–63. [\[CrossRef\]](#)
- Barbosa, J.A.; Coronado, C.; Tuna, C.E.; Silva, M.H.; Mendiburu, A.Z.; Junior, J.; de Andrade, J.C. Experimental determination of lower flammability limits of Synthesized Iso-Paraffins (SIP), jet fuel and mixtures at atmospheric and reduced pressures with air. *Fire Saf. J.* **2021**, *121*, 103276. [\[CrossRef\]](#)
- Zhang, K.; Luo, T.; Li, Y.; Zhang, T.; Li, X.; Zhang, Z.; Shang, S.; Zhou, Y.; Zhang, C.; Chen, X.; et al. Effect of ignition, initial pressure and temperature on the lower flammability limit of hydrogen/air mixture. *Int. J. Hydrogen Energy* **2022**, *47*, 15107–15119. [\[CrossRef\]](#)
- Markus, D.; Schildberg, H.P.; Wildner, W.; Krdzalic, G.; Maas, U. Flammability limits of premixed methane/methanol/air flames. *Combust. Sci. Technol.* **2003**, *175*, 2095–2112. [\[CrossRef\]](#)
- Chen, X.; Bi, S.; Wu, J. Experimental study on explosion limit of dimethyl ether, methane and dimethyl ether/methane mixtures. *J. Eng. Thermophys.-Rus.* **2009**, *30*, 1267–1270. [\[CrossRef\]](#)
- Zabetakis, M.G. *Flammability Characteristics of Combustion Gases and Vapors*. US Bureau of Mines: Washington, DC, USA, 1965; pp. 97–107.
- Kondo, S.; Takizawa, K.; Takahashi, A.; Tokuhashi, K. On the temperature dependence of flammability limits of gases. *J. Hazard. Mater.* **2011**, *187*, 585–590. [\[CrossRef\]](#) [\[PubMed\]](#)
- Huang, C.; Yang, X.; Lu, L.; Wang, X. Determination of explosion limit of alkanes at high temperature. *Chem. Ind. Prog.* **2002**, *21*, 496–498. [\[CrossRef\]](#)
- Besnard, S. *Full Flammability Test of Gases and Gas Mixtures in Air*; CERN: Meyrin, Switzerland, 1996; pp. 253–258.
- Li, S.; Zhang, Y.; Qiu, X.; Li, B.; Zhang, H. Effects of Inert Dilution and Preheating Temperature on Lean Flammability Limit of Syngas. *Energ. Fuels* **2014**, *28*, 3442–3452. [\[CrossRef\]](#)
- Hu, X.; Yu, Q.; Sun, N.; Qin, Q. Experimental study of flammability limits of oxy-methane mixture and calculation based on thermal theory. *Int. J. Hydrogen Energy* **2014**, *39*, 9527–9533. [\[CrossRef\]](#)
- Hu, X.; Xie, Q.; Yu, Q.; Liu, H.; Yan, F. Effect of Carbon Dioxide on the Lower Flammability Limit of Propane in O₂/CO₂ Atmosphere. *Energ. Fuels* **2020**, *34*, 4993–4998. [\[CrossRef\]](#)
- Hu, X.; Xie, Q.; Zhang, J.; Yu, Q.; Liu, H.; Sun, Y. Experimental study of the lower flammability limits of H₂/O₂/CO₂ mixture. *Int. J. Hydrogen Energy* **2020**, *45*, 27837–27845. [\[CrossRef\]](#)
- Rowley, J.R.; Rowley, R.L.; Wilding, W.V. Estimation of the lower flammability limit of organic compounds as a function of temperature. *J. Hazard. Mater.* **2011**, *186*, 551–557. [\[CrossRef\]](#) [\[PubMed\]](#)
- Albahri, T.A. Flammability characteristics of pure hydrocarbons. *Chem. Eng. Sci.* **2003**, *58*, 3629–3641. [\[CrossRef\]](#)

20. Albahri, T.A. Prediction of the lower flammability limit percent in air of pure compounds from their molecular structures. *Fire Saf. J.* **2013**, *59*, 188–201. [[CrossRef](#)]
21. Vidal, M.; Wong, W.; Rogers, W.J.; Mannan, M.S. Evaluation of lower flammability limits of fuel–air–diluent mixtures using calculated adiabatic flame temperatures. *J. Hazard. Mater.* **2006**, *130*, 21–27. [[CrossRef](#)]
22. Kondo, S.; Urano, Y.; Tokuhashi, K.; Takahashi, A.; Tanaka, K. Prediction of flammability of gases by using F-number analysis. *J. Hazard. Mater.* **2001**, *82*, 113–128. [[CrossRef](#)]
23. Shebeko, Y.N.; Fan, W.; Bolodian, I.A.; Navzenya, V.Y. An analytical evaluation of flammability limits of gaseous mixtures of combustible–oxidizer–diluent. *Fire Saf. J.* **2002**, *37*, 549–568. [[CrossRef](#)]
24. Zhang, X.; Wang, Z.; Xu, J.; Liu, H.; Hou, P.; He, L. Analysis of combustion characteristics and thermal characteristics of different gas fuels. *Econ. Energy* **2022**, *41*, 15–19. [[CrossRef](#)]
25. Cui, S.; Sun, B.; Sun, X. General formula for the radiative brightness response of black bodies in the infrared band. *Spectrosc. Spect. Anal.* **2020**, *40*, 1329–1333. [[CrossRef](#)]
26. Kondo, S.; Takizawa, K.; Takahashi, A.; Tokuhashi, K. Extended Le Chatelier’s formula and nitrogen dilution effect on the flammability limits. *Fire Saf. J.* **2006**, *41*, 406–417. [[CrossRef](#)]
27. Kondo, S.; Takizawa, K.; Takahashi, A.; Tokuhashi, K. Extended Le Chatelier’s formula for carbon dioxide dilution effect on flammability limits. *J. Hazard. Mater.* **2006**, *138*, 1–8. [[CrossRef](#)] [[PubMed](#)]
28. Kondo, S.; Takizawa, K.; Takahashi, A.; Tokuhashi, K.; Sekiya, A. Flammability limits of isobutane and its mixtures with various gases. *J. Hazard. Mater.* **2007**, *148*, 640–647. [[CrossRef](#)] [[PubMed](#)]
29. Poling, B.E.; Prausnitz, J.M.; Connell, J.P. *The Properties of Gases and Liquids*, 5th ed.; McGraw-Hill: New York, NY, USA, 2001; pp. 133–149.
30. DIPPR, A. *DIPPR Project 801 Pure Component Data*; Public Version; American Institute of Chemical Engineers: New York, NY, USA, 1996; pp. 209–233.
31. Ma, T. Using critical flame temperature for estimating lower flammable limits of a mixture. *Process Saf. Prog.* **2013**, *32*, 387–392. [[CrossRef](#)]