

Estimation of the upper flammability limits for alkanes in air at increased pressures

Xin Wan*, Min Wang, Chunyan Cao, Shuang Zhao, Zhiguo Song

College of Chemistry and Materials, Bohai University, Jinzhou, 121000, China

*Corresponding author: e-mail: wanxinbhu@163.com

A method is proposed to predict the upper flammability limits for alkanes in air at increased pressures. The upper flammability limits for methane, ethane, propane and n-butane/air mixtures at ambient temperature and initial pressure of 0.3 MPa–2.0 MPa are identified through the adiabatic flame temperature calculation model. The association of calculated adiabatic flame temperature with pressure is presented to determine the upper flammability limit. Research shows the good agreement between the forecast upper flammability limits with pressure dependence and the experimental upper flammability limit values. The average relative error of the estimated upper flammability limits for alkanes in air at high pressures reaches 2.52%.

Keywords: Upper flammability limit; Adiabatic flame temperature; High pressure; Alkanes.

INTRODUCTION

Combustible gases have obtained extensive uses in petroleum and natural gas fields as main materials and fuels. Whereas, flammable gas fires and explosion accidents take place occasionally^{1–3}. Flammability limit ranks among the main considerations in the fire and explosion hazards assessment, and its value is subject to multiple factors including pressure, temperature, and inert gas^{4–6}. The unit operation often proceeds at high pressures in industrial production. Thus, flammability limits data provide essential evidence for determining precautionary measures in technical processes.

The flammability limits prescribe the fuel concentration scope, in which the combustible gas-air mixture may burn or be lit. The upper flammability limit (UFL) indicates the boundary in the fuel-rich area, i.e., the maximum fuel concentration at which flame propagation is supported in air⁷.

It is a well-known fact that a higher pressure results in a broader zone of flammability limit. In comparison with a lower flammability limit (LFL), UFL shows greater sensitivity to the effect of pressure⁸. However, it would be very challenging and potentially dangerous to perform experiments on fuel-air mixture under the pressure level of MPa, making it impractical to observe the flammability limit under the pressure of 10 MPa. Thus, the experimental value of UFL at high pressures is barely available.

A few models have been built to assess the UFLs, while they mainly afford the possibility to evaluate the UFLs at atmospheric pressure. Lazzus⁹ put forward a neural network model to predict the UFLs in organic compounds, and Jérôme et al.¹⁰ employed a novel group contribution model for estimating the UFLs in pure compounds at normal pressure and temperature. Wu et al.¹¹ proposed a new model to evaluate the UFLs for propane and isobutene with carbon dioxide in air at 1 atm and 308 K. Tian et al.¹² used the inorganic Rankine cycle to predict the UFLs for mixtures of propane, n-butane, isobutane, pentane and carbon dioxide at high temperature and atmospheric pressure.

There are only a few studies concerning UFL of hydrocarbon at various pressures, and the models involved mainly concentrate on methane-air mixture. Van den

Schoor et al.¹³ studied the pressure and temperature dependence of UFL in methane-air mixture with planar flame, spherical flame, limiting burning velocity, and limiting flame temperature models, respectively, but there were significant differences between their predicted values and experimental values. Benedetto¹⁴ built a thermodynamic model for estimating the explosion limit of methane-air mixture at increased pressure and temperature and discovered the wider flammability limit zone than the experimental values. Liaw and Li¹⁵ developed a mathematical model to predict the upper flammability limits of fuels at subatmospheric pressures, but large deviations were observed between the predicted and experimental values for methane at the pressure range of 0.1–24.9 MPa. At present, a reliable theoretical model that can precisely forecast the UFL in fuel-air mixture at high pressure is still not available.

In this work, we present a model to predict the UFLs for alkanes (methane, ethane, propane and n-butane) in air through thermodynamic equilibrium under the pressure of 0.1–2.0 MPa at ambient temperature. Meanwhile, the relationship between the calculated adiabatic flame temperature and pressure is discussed, and a calculation method of adiabatic flame temperature under high pressure is proposed to determine the upper flammability limit.

PREDICTION THEORY AND NUMERICAL METHODS

UFL prediction method

The flammability limit is linked to a given critical reaction temperature, which is presumably the equivalent of adiabatic flame temperature. The adiabatic flame temperature represents the highest combustion temperature in condition that fuel composition equals the flammability limit. Thus, the flammability limit is estimated to be a function for calculated adiabatic flame temperature (CAFT)^{16–18}. This method is proposed to estimate the flammability limits for combustible gas-air mixtures at high temperatures^{19–20}. Nevertheless, previous studies rarely focus on the impact of initial pressure on CAFT, which makes it even more difficult to predict the UFL.

The correlation of pressure with the calculated adiabatic flame temperature that corresponds to the UFL

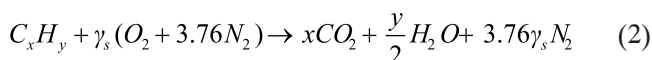
is examined, and a numerical model is constructed to calculate the adiabatic flame temperature at high pressure and determine the UFLs for alkanes in air at increased pressures.

As reported by Hasen and Crowl²¹, the value of CAFT depends upon the mechanism, while the mechanism for UFL and LFL varies. The burning mechanism for combustible gases at the UFL concentration is far more complex than at the LFL concentration, and thus, various problems should be taken into account before giving accurate predictions. As is well-known, combustible gases do not burn adequately in the UFL, and thus, a variety of products can be produced in fuel-air combustion. Hansen and Crowl²¹ further added that CO and H₂O are the major combustion products of methane in air at the UFL. It is assumed that oxygen has a complete reaction in the estimation of UFL concentration. In accordance with the results, the combustion reaction of alkanes in air at the UFL is indicated by:



where γ refers to the number of moles in air per mole of fuel in the mixture at the UFL. Additionally, CH₄, C₂H₄, and C₂H₂ are considered when evaluating the combustion products generated from the thermal decomposition of combustible substance at high temperature. Besides, NO, OH, O, H and N should also be taken into account.

Arnaldos et al.²² predicted the flammability limits for alkanes with the combustion rate at the stoichiometric ratio in the condition that environmental pressure was lower than atmospheric pressure. The main reason is the better accessibility of thermodynamic parameters at a stoichiometric ratio compared with excessive oxygen or excessive fuel. Thus, the concept of adiabatic flame temperature at stoichiometric ratio is used to predict the adiabatic flame temperature at increased pressure. The combustion reaction of alkanes in air at stoichiometric ratio is indicated by:



The CAFT approach is used with the assumption that no heat loss occurs or the reaction does not rely heavily on kinetics. With these assumptions, the energy balance can be expressed as:

$$\sum_i h_{reac,i}(T_i, p) = \sum_j h_{prod,j}(T_{ad}, p) \quad (3)$$

where $h_{reac,i}$ and $h_{prod,j}$ mean the enthalpy of reactant and product, respectively. T_i and T_{ad} suggest the initial temperature and the adiabatic flame temperature, respectively.

The enthalpy and the formation enthalpy can be indicated by:

$$h(T, p) = \Delta h_f(T_{ref}, p) + \Delta h_s(T, p) \quad (4)$$

where Δh_f represents the enthalpy of formation in the reference state, and Δh_s indicates the sensible enthalpy derived from $\bar{C}_p(T - T_{ref})$. Consequently, Eq. (3) is extended as,

$$\sum_{reac} n_i \Delta h_{f,i}(T_i, p) = \sum_{prod} \{n_j \Delta h_{f,j}(T_j, p) + \int_{T_i}^{T_{ad}} n_j \bar{C}_{p,j} dT\} \quad (5)$$

where \bar{C}_p stands for the average heat capacity at constant pressure, which can be estimated using theoretical methods. The research shows that thermodynamic parameters are identified as the function of temperature and pressure, while rare data at high pressures are retrieved from the database. Other thermodynamic parameters can also be estimated under numerical models because of the shortage of database at high pressures, such as entropy, entropy, and Gibbs free energy²³⁻²⁴.

The equilibrium compositions in combustion products depend upon the minimum of the overall Gibbs free energy²⁵. When the adiabatic flame temperature at the high pressure is identified, the UFL will be derived through solving energy balance.

Thermodynamic model

In line with the numerical model, the thermodynamic parameters for substances at high pressures are found to be able to determine the equilibrium composition, as well as calculate energy balance. Hence, it is of great significance to apply accurate thermodynamic parameters to the prediction model. Theoretical methods are usually applied in the prediction of thermodynamic properties at abnormal pressures due to the huge and tedious workload in the experiment.

Enthalpy and Entropy

A few mathematical methods are used to evaluate the variations of the thermodynamic properties of gases at abnormal pressure and temperature^{23, 24}. The deviation functions h^R and S^R are introduced to estimate enthalpy and entropy at high pressure, which can be expressed as:

$$h^R = pV - RT - \int_{V \rightarrow \infty}^V p dV + T \int_{V \rightarrow \infty}^V \left(\frac{\partial p}{\partial T} \right)_V dV \quad (6)$$

$$S^R = R \ln Z + \int_{V \rightarrow \infty}^V \left[\left(\frac{\partial p}{\partial T} \right)_V - \frac{R}{V} \right] dV \quad (7)$$

Here, Poling et al.²³ point out that the Peng-Robinson cubic equation of state can be applied to express the pressure-volume-temperature relationships of real gas.

$$p = \frac{RT}{V-b} - \frac{a\alpha(T_r)}{V^2 + 2bV - b^2} \quad (8)$$

In this expression,

$$a = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (9)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (10)$$

$$\alpha(T_r) = [1 + m(1 - T_r^{0.5})]^2 \quad (11)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (12)$$

where p_c means the critical pressure and T_c represents the critical temperature.; $T_r = T/T_c$ denotes the reduced temperature and ω is the acentric factor. The values of p_c , T_c and ω for various substances are obtained from chemical and physical databases. Then, the deviation enthalpy and entropy can be acquired by Eq. (6) and Eq. (7) with a computer program. Finally, the enthalpy

and entropy of gases involved at increased pressures are calculated,

$$h(T, P) = h_0^{ig} + \int_{T_0}^T C_p^{ig} dT + h^R \quad (13)$$

$$S(T, P) = S_0^{ig} + \int_{T_0}^T \frac{C_p^{ig}}{T} dT - R \ln \frac{P}{p_0} + S^R \quad (14)$$

where h_0^{ig} , S_0^{ig} and C_p^{ig} are the enthalpy, entropy and constant pressure heat capacity for ideal gas at atmospheric pressure, respectively. And the Gibbs free energy used in this model can be obtained by calculating enthalpy and entropy under different pressures.

By taking methane as an example, we calculated the enthalpy and entropy of pure substances by deviation function. The comparison between the estimated values and the experimental data reported by Younglove and Ely²⁶ at various conditions are presented in Table 1.

We can see clearly that the calculated values of enthalpy and entropy for methane are approximate to experimental values, where the range of relative error is 0–1.40%. The results show that it is reasonable to estimate the thermodynamic properties using the deviation function and PR equation under high pressures.

Heat capacity

The deviation function is also be applied to determine the heat capacity of substance under elevated pressure, which can be represented as²³,

$$\frac{C_p}{R} = \frac{C_p^{ig}}{R} + \frac{T}{R} \int_{V \rightarrow \infty}^V \left(\frac{\partial^2 p}{\partial T^2} \right)_V dV - \frac{T}{R} \left(\frac{\partial p}{\partial T} \right)_V \left/ \left(\frac{\partial p}{\partial V} \right)_T \right. - 1 \quad (15)$$

where C_p refers to the heat capacity at constant pressure of real gas. The Peng-Robinson cubic equation of state is also used to represent the relationships among their pressure, volume and temperature. This method is well established for determining the heat capacities for substances at increased pressures and temperatures²⁰.

According to the previous methods, the constant pressure heat capacity will have an impact on establishing the heat balance in the CAFT model, so the changes of the constant pressure heat capacity of substances with pressure and temperature are also discussed. As can be indicated from Fig. 1 that the pressure has a more significant influence on the constant pressure heat capacity of methane at room temperature, where the value of C_p decreases by 3.082 kJ/mol · K when pressure increases from 0.1 MPa to 3.0 MPa.

It also shows that the higher the pressure, the larger the constant pressure heat capacity, which is mainly because the force between molecules becomes stronger and their distance becomes shorter as pressure increases, more gas deviates from the ideal state. However, increased temperature has a completely opposite effect

on the gas molecules, thus making the value of heat capacity remain substantially constant with the change in pressure. Therefore, the influence of pressure on the

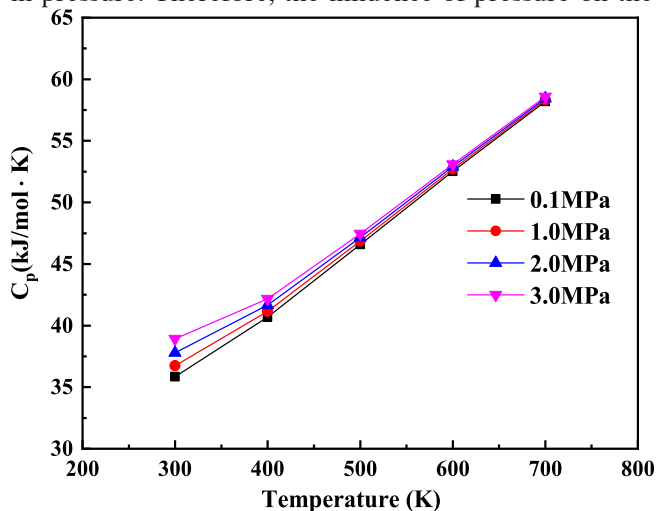


Figure 1. The graphs of constant pressure heat capacity at various pressures and temperatures for methane

constant pressure heat capacity at ambient temperature cannot be ignored.

RESULTS AND DISCUSSION

The prediction for CAFT

The calculated adiabatic flame temperature has a direct impact in determining the upper flammability limit in this method, but the adiabatic flame temperature at the UFL concentration under high pressure has not been reported yet. We propose that the adiabatic flame temperature at the stoichiometric ratio (T_S) can be applied to the estimation as a critical factor. Consequently, the calculated adiabatic flame temperature at the UFL concentration under ambient temperature should be expressed as a function of T_S . But the influence of pressure needs to be taken into account in the determination of the calculated adiabatic flame temperature. This is mainly because as pressure increases, the more likely the molecules are to effectively collide, thus resulting in easier combustion, especially near the UFL. It indicates that the influence of high pressure on the combustible gas at the UFL concentration cannot be reflected by only applying T_S . Therefore, the calculation formula of the CAFT should be described as a function of T_S at the stoichiometric ratio and pressure, i.e. $CAFT = f(T_S, p)$.

Table 1. Calculated enthalpy and entropy of methane under various pressures at ambient temperature

P/MPa	Enthalpy/ kJ · mol ⁻¹			Entropy/kJ · kmol ⁻¹ · K ⁻¹		
	Calc. values	Exp. values	Error/%	Calc. values	Exp. values	Error/%
0.5	9.98	10.01	0.30	173.01	173.0	0
1.0	9.89	9.93	0.40	167.03	167.1	0.04
2.0	9.70	9.77	0.72	160.84	160.9	0.04
5.0	9.16	9.29	1.40	151.91	152.1	0.12

$$Error(\%) = |Exp. - Calc. / Exp. \times 100$$

Under the adiabatic condition, the heat balance of combustion reaction can also be represented as:

$$\Delta H_{298}^{\ominus} + \sum_{\text{reac}} \int_{T_i}^{298} n_i \bar{c}_{p_i} dT + \sum_{\text{prod}} \int_{298}^{T_{ad}} n_i \bar{c}_{p_i} dT = 0 \quad (16)$$

At ambient temperature and increased pressures, the adiabatic flame temperature at stoichiometric ratio can be expressed as:

$$T_s^p = \frac{\sum_{\text{reac}(s)} \int_{T_i}^{T_i} n_i \bar{c}_{p_i} dT - \Delta H_{298,p}^{\ominus}(s)}{\sum_{\text{prod}(s)} n_i \bar{c}_{p_i}} + 298 \quad (17)$$

The adiabatic flame temperatures at upper flammability limit are calculated,

$$T_{ad}^p = \frac{\sum_{\text{reac}(U)} \int_{298}^{T_i} n_i \bar{c}_{p_i} dT - \Delta H_{298,p}^{\ominus}(U)}{\sum_{\text{prod}(U)} n_i \bar{c}_{p_i}} + 298 \quad (18)$$

In real gas treatment, the corresponding states principle is applied in investigating how temperature and pressure affect thermodynamic parameters, including reduced temperature and reduced pressure in the cubic equation of state. The corresponding states principle stipulates that appropriate dimensionless properties for all matters abide by general variation in proper dimensionless variables

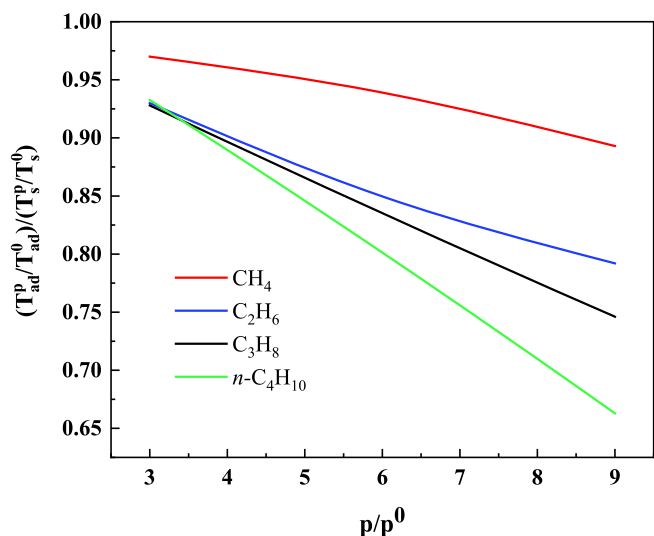


Figure 2. The relationship curves between T_{ad}^p/T_{ad}^0 and T_s^p/T_s^0 for alkanes in air with increasing pressures

for state and other dimensionless parameters²³. Thus, a dimensionless quantity of pressure is chosen by the paper, together with the adiabatic flame temperature at stoichiometric ratio as the reduced temperature. The relationship curves between T_{ad}^p/T_{ad}^0 , T_s^p/T_s^0 and p/p^0 are plotted in Fig. 2.

Figure 2 shows the ratio of T_{ad}^p/T_{ad}^0 to T_s^p/T_s^0 decreases with increased pressures for methane, ethane, propane and n-butane in air, indicating that the pressure has a great influence on the CAFT values. However, the curve slope is different from that of diverse fuel-air mixtures. The curve seems to decrease rapidly with carbon amount from the homologous series of alkanes. Obviously, the number of carbon atoms is also an important factor

affecting the CAFT values. Multiple fitted calculations are subsequently performed with the numerical model. The formula for predicting the CAFT at UFL under high pressures can be generally indicated by:

$$\frac{T_{ad}^p}{T_{ad}^0} = \left[\frac{T_s^p}{T_s^0} \right]^k, k = -\left[1 + \frac{n}{2} \cdot \frac{p}{p^0} \right] \quad (19)$$

where p^0 and p refer to the atmospheric pressure and initial pressure, respectively; T_{ad}^0 and T_{ad}^p denote the CAFT values at the UFL at atmospheric pressure and initial pressure, and T_s^0 and T_s^p denote the CAFT values at the stoichiometric ratio at p^0 and p . The value of n is decided by the amount of carbon atoms in the combustible gas.

Table 2. The calculated adiabatic flame temperature of alkanes in air at various pressures

Fuel	Pressure/MPa	CAFT/K
methane	0.3	1841
	0.6	1786
	1.0	1718
ethane	0.3	1606
	0.6	1495
	1.0	1347
propane	0.3	1641
	0.6	1470
	1.0	1283
n-butane	0.3	1502
	0.6	1323
	1.0	1090

The CAFT values of alkane fuels such as methane, ethane, propane, and n-butane in air are directly measured, with Eq. (19) as a function of pressure at ambient temperature. The results are presented in Table 2, and the experimental upper flammability limits at ambient temperature and atmospheric pressure are taken from Van den Schoor and Verplaetsen²⁷.

Estimation of the UFL

The UFLs of alkane fuels, such as methane, ethane, propane, and n-butane, in air can be estimated by adiabatic flame temperature modeling as initial pressure increases from 0.3 MPa to 2.0 MPa at ambient temperature.

Vanderstraeten et al.²⁸ suggested that experimental values vary with discrepant explosion standards. Cashdollar et al.²⁹ ascribed the difference in measured data to various test instruments. Thus, the UFL values vary with pressure dependence under different test conditions. For verifying model accuracy in an all-round way, a comparison is made between the forecasted UFL values and the experimental values from the literature. However, because of the difference in reported data, particularly the experimental values of UFL at normal pressure and temperature, the predicted CAFT and UFL values at initial pressures are affected. Thus, the UFLs at ambient pressure and temperature in the literature are introduced for calculation.

Figure 3 compares the calculated theoretical UFLs in methane-air mixture, marked in lines, with the experimental data^{27, 28, 30}, marked in individual points.

The UFL values in methane-air mixture agree with the reported values²⁷ and corresponding relative error is 0.32–1.44% as the pressure increases from 0.3 MPa to 1.0 MPa. According to the experimental performed

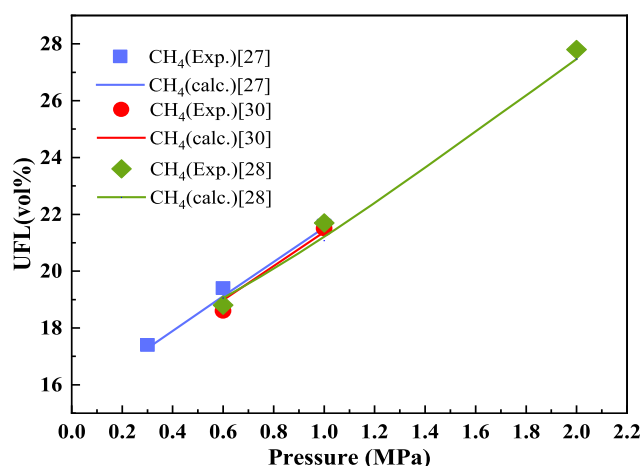


Figure 3. Comparison of the experimental and estimated upper flammability limits for methane/air mixture at various pressures

by Chen and Liu³⁰, the UFL values are 18.6 vol% and 21.5 vol% under the pressure of 0.6 MPa and 1.0 MPa. Meantime, the UFL values estimated using the model are 18.98 vol% and 21.38 vol%, suggesting insignificant differences between the calculated and experimental values. Vanderstraten et al.²⁸ measured the UFL values in methane-air mixture with a broader pressure scope through experiments. The research indicates the UFL

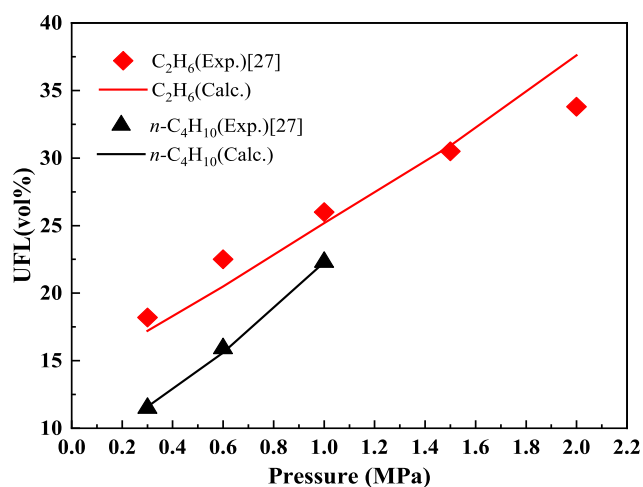


Figure 4. Comparison of the experimental and estimated upper flammability limits for ethane and n-butane in air at various pressures

value reaches 27.8 vol% at 2.0 MPa, and the value predicted by the CAFT model reaches 27.47 vol%, merely 0.33 vol% lower than experimental data. The predicted UFL values approach the experimental values at 0.6 MPa and 1.0 MPa, and the relative error of methane in air is 1.33–2.90%. Therefore, the proposed algebraic method can reasonably estimate the UFL values for methane in air at the initial pressure of 2.0 MPa.

The UFL values in ethane and n-butane in air are measured, and the CAFT model is applied as a function of pressure at ambient temperature. Figure 4 compares the predicted values of ethane and n-butane with previously reported data²⁷. The figure shows that the predicted UFL values of ethane in air are close to the experimental values at 0.3–1.5 MPa, and the average relative error was 4.71%. Whereas, the relative error of

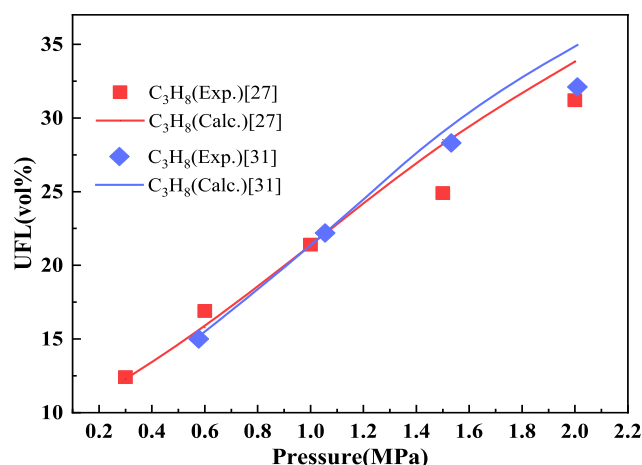


Figure 5. Comparison of the experimental and estimated upper flammability limits for propane/air mixture at various pressures

experimental data reaches 11.24% as the pressure grows to 2.0 MPa, possibly because of underestimated CAFT value measured using Eq.(19).

In n-butane/air mixture, the UFL values seem to agree with the reported values²⁷. The absolute error of this method is 0.02–0.30 vol%, and the average relative error is 0.95% as pressure fluctuates in 0.3–1.0 MPa.

The changes of the UFL in the propane-air mixture can be also determined at increasing pressures and ambient temperature. The comparison between the estimated UFL values and experimental values^{27, 31} can be seen from Fig. 5. The predicted UFLs agree with the data in former research at an initial pressure range of 0.3–2.0 MPa.

The estimated UFL values are accurate compared with the experimental values provided by Norman et al.³¹ under the pressure ranging from 0.3 MPa to 2.0 MPa, and the average absolute error and average relative error are 1.26 vol% and 4.24%. However, the experimental UFL reduces more obviously at 1.5 MPa, resulting in a great discrepancy between the predicted value and experimental value given by Van den Schoor and Verplaetsen²⁷. Whereas, the predicted UFL value at 1.5 MPa agrees well with the experimental value reported by Norman et al.³¹, and the relative error reaches 6.00%.

The comparison results of the experimental and estimated UFLs on the strength of the numerical model for methane, ethane, propane and n-butane in air are summarized in Table 3.

Fuel	Max relative error	Min relative error	Average relative error	Literature
methane	1.44%	0.32%	0.80%	27
	2.04%	0.56%	1.30%	30
	2.90%	1.19%	1.81%	28
ethane	11.24%	1.38%	6.01%	27
propane	8.88%	1.20%	4.24%	31
n-butane	0.09%	1.89%	0.95%	27

Table 3. The errors between the experimental and estimated UFLs for alkanes in air at various pressures

In addition, it is obvious that all the curves (Fig. 3–5) for alkane-air mixtures are nearly linearly correlated with pressure, in which the estimated UFL values increase rapidly with elevated initial pressure at ambient

temperature, indicating that the high inflammability and explosion risk during operation. As a result of increasing pressure, there are more molecules per unit volume at the UFL and molecules are more likely to collide, thus increasing chemical reaction rate. Therefore, the influence of pressure on the UFL of combustible substance is more significant than that on the LFL.

Based on the results described above, the predicted UFL values for alkane-air mixture are in agreement with the reported results from 0.3 MPa to 1.5 MPa at ambient temperature. The highly accurate calculated UFL values indicate that the proposed numerical method appears to be reasonable for predicting the UFL for alkanes in air at elevated pressures.

But the variation of UFL values is complicated when initial pressure is increased from 1.5 MPa to 2.0 MPa. The UFL value of methane/air mixture is consistent with the reported value, with a relative error of only 1.18% at 2.0 MPa. The UFL values of other alkane-air mixture seem to be slightly overestimated compared to the reported values at 2.0 MPa.

The reason is possibly that the CAFT value determines the estimated UFL based on the approach presented in this paper. It seems that the variation of the CAFT for ethane and propane with pressure is gradually decreasing, causing the predicted CAFT value to be lower than the experimental value at higher pressure. The UFLs at higher pressure can be slightly overestimated by using underestimated CAFTs. On the other hand, experimental determination standards such as the basis for judging explosion are different, resulting in different experimental values in various literature. Meanwhile, the experimental determination is also affected by container size, ignition source, ignition energy, etc. However, the premise of theoretical calculations only depends on the changes in thermodynamic properties, which results in large discrepancies between predicted and experimental values under certain pressure.

Therefore, the numerical formula of the CAFT will not be applied to predict the UFL of alkanes in air under pressure greater than 2.0 MPa so as to ensure its accuracy.

CONCLUSIONS

A method is proposed for predicting the upper flammability limits of alkane-air mixtures at increased pressures in this study. The numerical model of the CAFT value at UFL for alkane-air mixture is established, and then the UFLs are determined for methane, ethane, propane and n-butane in air at ambient temperature and initial pressure of 0.3–2.0 MPa through calculated adiabatic flame temperature model. The predicted UFL values as a function of pressure shows the good agreement with the experimental data. The average relative error reaches 2.52%, suggesting that the method proposed in this paper is reasonable to determine the UFLs of alkane-air mixture under pressure less than 2.0 MPa.

ACKNOWLEDGMENTS

The research presented in this paper was supported by the Education Department Project of Liaoning Province (No. LQ2017010)

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