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Approximation of flammability region for natural gas–air–diluent mixture

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Abstract

The growing implementation of exhaust gas recirculation (EGR) in reducing NO_x emissions of engine is of paramount motivation to perform a fundamental research on the flammability characteristics of fuel–air–diluent mixtures. In this work, the influences of EGR on the flammability region of natural gas–air–diluent flames were experimentally studied in a constant volume bomb. An assumption of critical burning velocity at flammability limit is proposed to approximately determine the flammability region of these mixtures. Based on this assumption, an estimation of the flammability map for natural gas–air–diluent mixtures was obtained by using the empirical formula of burning velocity data. The flammability regions of natural gas–air mixtures with EGR are plotted versus the EGR rate. From the comparison of estimated results and experimental measurements, it is suggested that the accuracy of prediction is largely dependent upon the formula of burning velocity used. Meanwhile, the influence of pressure on the critical burning velocity at flammability limit is also investigated. On the basis of the pressure dependence criterion, the estimation was performed for the circumstance of high temperature and pressure, and the prediction results still agree well with those of experiments.
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1. Introduction

It is well known that nitrogen oxide (NO_x) emissions are primarily functions of combustion temperature, thus the most effective way for reducing NO_x emissions is to perform combustion at low temperature. The addition of the residual gas into the combustible gas is considered to be the simplest practical method to decrease the combustion temperature; therefore the use of the exhaust gas recirculation (EGR) in engines has been promoted recently. However, the combustion temperature strongly influences the burning velocity of combustible gas, which is associated with the phenomenon of flame inhibition. Flame inhibition in a fuel–air mixture can be characterized by the flammability limits of the mixture in general. Flammability limits are known as that region of

fuel–air mixture ratios within which flame propagation can be possible while outside that flame cannot propagate. There are two distinct separate flammability limits for a mixture. The lean fuel limit up to which the flame can propagate is termed as the lower flammability limit (LFL); whereas, the rich limit is called as the upper flammability limit (UFL). The flammability region is namely restricted within the two flammability limits.

It is now acknowledged that flammability limits are physical–chemical parameters of flammable gases and vapors of flammable liquids, which are related to many factors including the heat losses from the flame by conduction, convection and radiation to the apparatus walls, instabilities in the flame front resulting from buoyant convection, selective diffusion and flame stretch, as well as radical loss or their generation on apparatus walls [1,2]. Thus, more attentions have been given to the study the effects of environmental parameters, such as the vessel size, initial temperature and pressure,

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on this fundamental characteristic [3–5]. Flammability limits were discussed extensively in combustion literatures. The standardized measurements of flammability limits are usually conducted in the flammability tubes [6,7] or closed vessels [3,8,9]. Generally, large size of combustion charmer can minimize the wall effects and potentially allow to the use of strong igniters to ensure the absence of ignition limitation, so most of the flammability measurements were conducted in the closed chambers recently. In combustion vessel test, spark igniter is commonly adopted. It is known that the minimum ignition energy is a strong function of the compositions near the flammability limit, and it was reported that the minimum value of ignition energy for hydrocarbon fuels in air would occur in a slightly rich mixture and is usually on the order of 0.2–0.25 mJ [10]. And a relatively stronger igniter used can result in a slightly broader flammability region in general [3,10].

There are several criteria to determine the flammability limits in experimental measurements. A successful attempt can be determined by one or a combination of the following two criteria: (1) visualization inspection of the flame kernel development produced by the spark, namely visual criterion; (2) measurements of the pressure and/or temperature histories in the vessel, where an appropriate pressure or temperature rise criteria can be used to designate flammability rather than the purely visual observation of flame generation. The pressure/temperature rise criteria are helpful in the determination of flammability limits, especially in closed vessels. Nevertheless the observation of flame kernel is generally, still widely used, as the observation of flame kernel is directly visualized.

There exist large array of experimental data on flammability limits for ternary gaseous mixtures of fuel–air–diluent, and the diluent gases considered herein were nitrogen gas, carbon dioxide or their mixture, which are different from the real residual gaseous in combustion chamber, and most of previous studies were conducted at atmospherical conditions. For engineering application, the fundamental research on flammability characteristics of fuel–air mixtures with EGR, especially at high temperature and pressure like those of engine combustion is worthwhile. Practically, due to the time consumed in measurements, it is desirable to choose some reliable criteria for quick estimation of flammability limits. Shebeko et al. proposed an analytical method to evaluate flammability characteristics for various fuel–oxidizer–diluent mixtures [11], by considering energy balance in the chemical reaction of combustion, however this method has only been validated under the atmospheric pressure and temperature conditions. A commonly accepted view is that flames fail to propagate as the burning velocity becomes too low to overcome the dissipation processes during combustion [1]. Burgess and Hertzberg [12] emphasized that at least, burning velocity at the lean limit would tend to be the approximate value for many fuels. Lovachev et al. [2] predicted that 5–7 cm/s is the minimum possible flame speed for lean limit hydrocarbon flames, and Huang et al. [13] found that the laminar flame speed at the maximum diluent level is on the order of 1–2 cm/s at elevated pressures. Blint [14] calculated laminar burning flame speeds for adiabatic one-dimensional propane/air flames over a range of pressures, initial temperatures, and diluent levels, and an arbitrary flame speed (10 cm/s) was defined to determine flammability limit.

In this work, the flammability characteristics of natural gas–air–exhaust gas are evaluated using the critical burning velocity criteria. In order to validate the estimations, the experimental measurements were also performed, where the visual criterion of flame kernel is adopted to determine the mixture flammable or not.

2. Experimental method

In this work, the experimental study is conducted in a constant volume combustion bomb, as shown in Fig. 1. The cubic combustion bomb has an inside size of 108 mm × 108 mm × 135 mm, with 1.571 in volume. Two sides of this bomb are fixed quartz glasses to make the inside observable, which are to provide the viewing access for the observation of flame growth. The combustible mixture was prepared within the closed vessel by adding gases at the required partial pressures scaled by a mercury manometer whose sensitivity is about 0.13 kPa/mmHg. A thermocouple with accuracy of 1 K was used to measure the initial temperature of combustion vessel. The deviation associated with determining flammability limit using this method is controlled within a limited value by accurately scaled the pressure and initial temperature.

Two extended stainless steel electrodes are used to form the spark gap at the center of this bomb, to make center ignition. It should be noted that, in order to relate the flammability limit to that of practical engine conditions, an igniter,
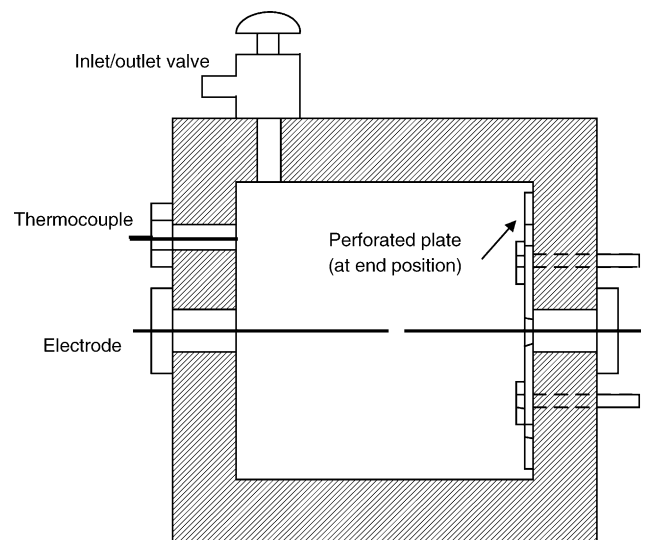

Fig. 1. Flammability region of NG–air–diluent mixture at 300 K and atmospheric pressure.

45 mJ energy in a conventional battery–coil ignition system, is adopted.

The origin of the natural gas selected for the present study is north of the Shannxi province of China. This NG consists of 96.160% volume fraction of methane, 1.096% of ethane, approximate 0.189% of hydrocarbon components higher than C3, and the remains includes carbon dioxide, nitrogen, sulfurated hydrogen and water that totally occupies about 2.555% in volume. The diluent gases considered here are the combustion products of NG–air mixture. The detailed procedure for producing air–fuel–exhaust gas mixture includes two steps as given in [15]. Initially, the combustion vessel makes vacuum using a vacuum pump, and then to introduce the fresh air–fuel mixture in the bomb; the exhaust gases are produced after combustion. Secondly by regulating the partial pressures of the exhaust gases and the fresh air–fuel mixture, the mixture with a desired diluent ratio can be realized. The diluent ratio ϕ_r denotes the volumetric fraction of dilution addition in the total mixture.

3. Approximation of flammability limit

Up to now, many studies on fuel–air–diluent flames have been well-explored [16–21], and most works focussed on the burning velocity of fuel–air–diluent mixtures. The empirical formulas were proposed to correlate the burning velocities of those flames, and these formulas are well available in the literatures. In these studies, the burning velocity, u_l, usually were explicitly formulated as a simple power law relations related to the datum temperature T_{u0}, and the datum pressure P_{u0}:

$$u_l = \left(\frac{T_u}{T_{u0}}\right)^{\alpha_T} \left(\frac{P_u}{P_{u0}}\right)^{\beta_P} g(\phi_r) u_{l0} \tag{1}$$

where P_u indicates the initial pressure, T_u for initial temperature, ϕ for equivalence ratio and ϕ_r for diluent ratio, α_T, β_P are fitting coefficients. Note that, u_{l0} denotes the reference burning velocities at datum condition, which is a function of ϕ, and $g(\phi_r)$ reflects the diluent influence on burning velocity.

For a convenient interpretation, Eq. (1) can be described as

$$u_l = f_1(P_u, T_u, \phi, \phi_r) \tag{2}$$

Hence, for given values of ϕ_r, P_u, and T_u, the equivalence ratios at the flammability limits, ϕ_{LFL} and ϕ_{UFL} (corresponding to the upper flammability limit UFL and the lower one, LFL, respectively) can be deduced through resolving Eq. (3):

$$\phi = f_2(P_u, T_u, u_{l,cr}, \phi_r) \tag{3}$$

where $u_{l,cr}$ is the critical burning velocity, determined by the assumption that below the value the flame cannot propagate. Thereby, bisection method can be used to resolve this nonlinear function [22].

The burning velocity data of natural gas–air–diluent mixture is cited from Refs. [19,21,23], and the empirical relation is given in following formula:

$$u_l = u_{l0} \left(\frac{T_u}{300}\right)^{\alpha_T} \left(\frac{P_u}{0.1}\right)^{\beta_P} g(\phi_r) \tag{4}$$

where

$$u_{l0} = -177.43\phi^3 + 340.77\phi - 123.66\phi - 0.2297 \tag{5}$$

$$\alpha_T = 5.75\phi^2 - 12.15\phi + 7.98 \tag{6}$$

$$\beta_P = -0.925\phi^2 + 2\phi - 1.473 \tag{7}$$

and

$$g(\phi_r) = 3.4259\phi_r^2 - 3.6993\phi_r + 1.002 \tag{8}$$

Note that, the validated equivalence ratio range is 0.49–1.43, pressure from 0.05 MPa up to 1.0 MPa, diluent ratio ranging from 0 to 0.43, and tested temperature ranges from 300 to 400 K [23].

4. Results and discussion

The data listed in Table 1 are the results of test for quiescent NG–air mixture at ambient pressure and temperature without diluent, and the available flammability limit data for pure methane–air are presented as well. It can be seen that, the flammability region of this NG–air mixture is from 5.0% to 15.6% of NG by volume. As the concentration of methane in the NG is over 96%, the measured result can well agree with those of previous works even though the test conditions are different. This in other hand verified the experimental certainly. It is known that a dependence of flammability limits of various fuels on diluent concentration, which restricts flammability region of ternary gaseous mixtures (fuel, oxidizer and diluent) in the form of a peninsula

Table 1

Flammability limit data (in vol.%) for methane–air and NG–air mixtures (quiescent condition)

Mixtures	Test conditions	LFL (vol.%)	UFL (vol.%)
NG–air[a]	1.57 L chamber	5.0	15.6
	LeChatelier's rule	4.98	–
Methane–air	8 L chamber[b]	5.0	–
	20 L chamber[c]	4.9	15.9
	120 L chamber[d]	5.0	15.7
	25.5 m³ sphere	4.9[e], 5.1 ± 0.1[f]	–
	Flammability tube[g]	5.2	15.1
	Flammability tube[h]	4.9	15.0

[a] This study.
[b] Hertzberg and Cashdollar (1983) [8].
[c] Cashdollar et al. [8].
[d] Cashdollar (2000) [8].
[e] Burgess et al. (1982) [8].
[f] Furno et al. (1970) and Burgess et al. (1982) [8].
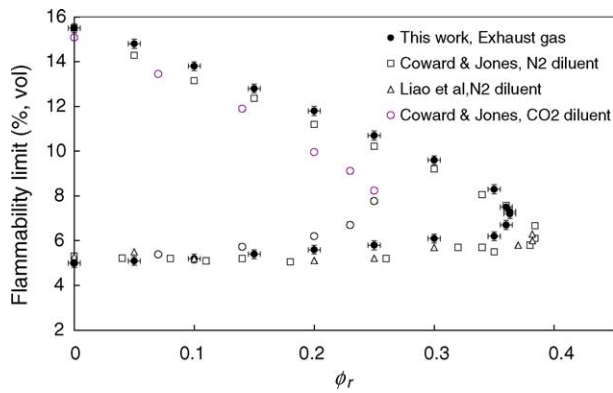[g] Liao et al. [6].
[h] Kuchta [10].

Fig. 2. Experimental flammability region for methane–air and NG–air mixtures.

[11], as shown in Fig. 2, and the results obtained by Liao et al. [6] using tubular burner and Coward and Jones [7] using the Bureau of Mines apparatus, are also plotted in this figure. It is known that flame inhibition by diluent of concentration is $H_2O > CO_2 > N_2 > Ar$, so the peak concentrations for N_2 diluent is greatest, following by the exhaust gas and CO_2 diluent. It is demonstrated that the rich flammability limits of our study is slightly greater than the results of N_2 diluent by flammability tube measurement, Fig. 3 is the comparison of experiments and predictions for methane–air–N_2 mixture. There are three cut-off burning velocity criteria, i.e. 1, 5 and 8 cm/s, selected to determine the flammability region of mixtures considered. It can be seen that, experimental results [6,7] are within the predictions of cut-off values of 1 and 8 cm/s. Generally, the agreement is reached by using cut-off value of 5 cm/s, and the derivation between measured data and prediction is within ±10%. The diluent limit of 5 cm/s critical velocity is 0.364, 5.2% derivation against 0.384 by the measurement. However, for rich flames, the predicting method shows a narrow flammability region, even using 1 cm/s, as shown in Fig. 3, due to the invalidation of fitting burning velocity formula for rich flame. The measurement of Liao et al. [6] reports that the UFL of methane-air flame without diluent is
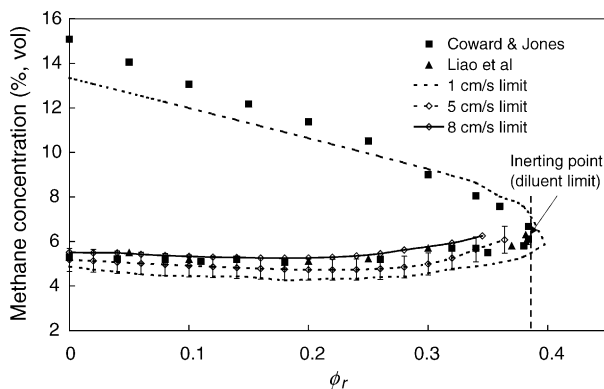

Fig. 3. Flammable region of methane–air–nitrogen mixture at 300 K and atmospheric pressure, where the burning velocity formula for diluting methane–air flames is $u_1 = (-150.84\phi^3 + 287.6\phi^2 - 96.327\phi - 1.2924)(1 - 1.208\phi_r^{0.803})$, derived from those of Law and Stone.
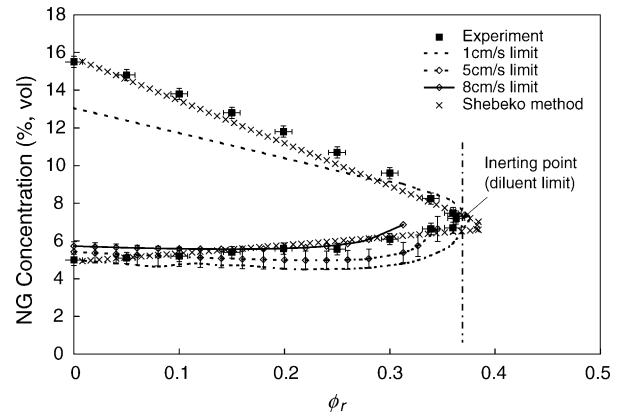

Fig. 4. Flammability region of NG–air–diluent mixture at 300 K and atmospheric pressure.

about 15% volume fraction, corresponding to the equivalence ratio of 2.04. While the empirical relation on methane–air burning velocity, $u_1 = (-150.84\phi^3 + 287.6\phi^2 - 96.327\phi - 1.2924)(1 - 1.208\phi_r^{0.803})$ [16,17], was validated within the equivalence ratio ranges from about 0.46 to 1.46.

The results of NG–air flames with EGR are presented in Fig. 4. Similarly, cut-off burning velocities of 1, 5 and 8 cm/s are used as well. Generally speaking, the measured data are consistent to the prediction by Shebeko method over the diluent ranges, and this reveals that critical velocity criteria are not suitable to determine the rich flammability limit (UFL) due to the invalidation of the empirical relation on burning velocity data for rich flames as well. By comparison between experiment and prediction, an appropriate critical velocity is defined to be 5 cm/s herein.

It is shown that Shebeko method can give better prediction to the experimental results at both lean and rich flammability limit than does the method based on a critical burning velocity, as shown in Fig. 4. However, the effect of temperature and pressure on flammability limit cannot be derived from Shebeko method. The advantage of the critical burning velocity method is that one can approximately calculate the diluent limit without an excessive amount of experiments when the burning velocities are available. Thus, the pressure and temperature dependencies of the flammability characteristics on temperature and pressure could be well established in principle. As reviewed by Lovachev et al. [2], pressure has important influence on the burning velocity at flammability limit, and its dependence on pressure P_u can be simplified as, $u_{1,\text{lim}} \sim u_{10}(P_u/P_{u0})^{-1/3}$, where subscript 0 denotes the reference conditions. The experimental points are listed in Table 2, it can be seen that the measured results are generally consistent to these experiments, where u_{10} selected as 5 cm/s. Over the test conditions, the maximum derivation is less than 6.0%. Fig. 5 presents the predicted maximum EGR rate for various initial pressures and temperatures. The limits obtained by fixed 5 cm/s critical velocity and pressure dependence criteria are presented as well, the results show that the difference of diluent limits between these two crite-

Table 2
Diluent limits of NG–air–EGR mixture

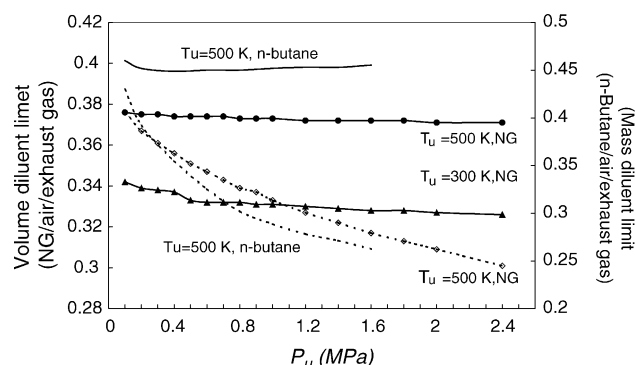| T_u (K)	P_u (MPa)	Measured diluent limit (vol.%)	Predicted diluent limit (vol.%)	Derivations (%)
300	0.1	36.3	34.2	5.78
350	0.1	37.1	35.6	4.04
400	0.1	38.0	36.5	3.94
300	0.5	34.0	33.3	2.05
350	0.5	36.0	35.0	2.78
400	0.5	37.2	36.1	2.96

Fig. 5. Computed diluent limit of EGR NG–air mixture at various initial temperatures and pressures, dashed curves are derived from fixed flame speed criteria and solid cures pressure dependence criteria.

ria becomes more obvious with the increase of pressure. It also can be seen that, although the temperature of the empirical relation used (Eqs. (4)–(8)) is only validated in range from 300 to 400 K, the computation at 500 K still shows the similar trend in diluent limits as that of 300 K. The analogous analysis [13] for *n*-butane/air/residual gas flames is reproduced in this figure, a comparable phenomenon can be observed as well.

However, it should be noted that, the flame speed of 5 cm/s may be too low and this just reflects the lowest loads or idling conditions of engines with EGR. The accuracy of predictions is also primarily dependent on the empirical formula of flame speeds. Since the causes of extinction at limits are very complex, it is believed that the further researches are necessary for better understandings of thermodynamic process and chemical kinetics at flammability limits for better applications of EGR in engines.

5. Conclusions

This study focuses on the flammability characteristics of natural gas–air–exhaust gas mixtures. Experiments and predictions based on critical burning velocity at flammability limits have been performed to explore flammability region for these mixtures. Three different critical burning velocity criteria are used to determine flammability limits at the ambient temperature and pressure, and it is proved that 5 cm/s would be a suitable critical burning velocity for determining the

flammability limit. Extrapolating empirical formula of burning velocity for ternary gaseous mixtures of fuel–air–diluent, the dependencies of diluent limits on initial temperature and pressure can be derived. By using $u_{1,\lim} \sim u_{10}(P_u/P_{u0})^{-1/3}$ to express the dependence of flame speed at flammability limit on pressure P, good agreement of diluent limit between measurements and predictions was obtained, and this has been verified by the calculations reported previously.

Acknowledgments

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