

1 **Abstract**

2 The explosion properties of alkane/nitrous oxide mixtures were investigated and were compared
3 with those of the corresponding alkane/oxygen and alkane/air mixtures. The explosion properties
4 were characterized by three parameters: the explosion limit, explosion pressure, and deflagration
5 index. For the same alkane, the order of the lower explosion limits (LELs) of the mixtures was found
6 to be alkane/oxygen \approx alkane/air $>$ alkane/nitrous oxide. In addition, the mixtures containing nitrous
7 oxide exhibited higher explosion pressures than the corresponding mixtures containing oxygen. The
8 Burgess–Wheeler law was also observed to hold for the mixtures containing nitrous oxide.

9

10 Keywords: Nitrous oxide, Explosion limit, Explosion pressure, Burgess–Wheeler law

11

12 **1. Introduction**

13 Industrial accidents, such as explosions, fires, and gas leaks, are serious hazards (Porto and de
14 Carvalho, 1996) in the petrochemical and semiconductor industries. Hence, knowing the explosion
15 properties is of major importance for assessing the risks and for achieving safety in operations.

16 Nitrous oxide (N₂O) is widely used as an oxidizing or nitriding gas in numerous industries (Zakirov
17 and Sweeting, 2001; Carr et al., 1995). Unfortunately, accidental explosions in facilities storing and
18 handling nitrous oxide have led to deaths and injuries (Hirano, 2004). These incidents occurred

1 because nitrous oxide readily decomposes to oxygen and nitrogen at elevated pressures and
2 temperatures ($> 625\text{ }^{\circ}\text{C}$ (Parres-Esclapez et al., 2010)):

3



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6 A number of studies have been published on the explosion characteristics of various compounds
7 in air (Tang et al., 2014; Coronado et al., 2012; Kondo et al., 2008). For commonly used
8 hydrocarbon/air mixtures, the enthalpy of combustion (ΔH) of the hydrocarbon multiplied by its
9 lower explosion limit volume percent at ambient temperature and pressure ($\text{LEL}(T_0)$) is
10 approximately constant, reflecting a constant flame temperature at its lower limit; this is known as
11 the Burgess–Wheeler law (Eq. 2) (Rowley et al., 2010; Britton, 2002). At temperatures other than
12 ambient temperature, the modified Burgess–Wheeler law (Zabetakis, 1965) is employed (Eq. 3),
13 which assumes that the adiabatic flame temperatures of lower-limit mixtures are also temperature
14 independent (Rowley et al., 2011):

15

$$16 \quad \text{LEL}(T_0) \cdot (-\Delta H) = k; \quad (2)$$

17

$$18 \quad \text{LEL}(T) / \text{LEL}(T_0) = 1 - (100 \cdot c_p \cdot (T - T_0)) / (\text{LEL}(T_0) \cdot (-\Delta H)), \quad (3)$$

1

2 where k , $LEL(T)$, and c_p are a constant, the LEL at a given temperature, and the specific heat of the
3 fuel/air mixture at a constant pressure, respectively. The law in both forms is important for
4 estimating the LEL of a fuel/air mixture. In contrast, the explosion characteristics of fuel/N₂O
5 mixtures have been reported by few studies (Shebeko et al., 2013). For instance, Vandebroek et al.
6 (2005) demonstrated that the LEL values of toluene/N₂O mixtures are less than those of toluene/air
7 mixtures at an initial temperature of 70 °C and 1 bar. Koshiha et al. (2010) reported that fuel/N₂O
8 mixtures have narrower flammability ranges and higher explosion pressures compared with those of
9 corresponding fuel/oxygen mixtures.

10 The present study describes the results of an investigation of the explosion characteristics of
11 alkane/N₂O mixtures at ambient temperature and pressure using three primary parameters: the
12 explosion limit, the explosion pressure, and the rate of the explosion rise. The results were compared
13 with those for corresponding alkane/O₂ mixtures. Finally, the Burgess–Wheeler law was assessed if
14 it holds for flammable mixtures containing nitrous oxide.

15

16 **2. Material and methods**

17 The purity of the methane, ethane, n-propane, n-butane, nitrous oxide, oxygen, and nitrogen used in
18 this study was >99.7%. The dried alkanes used in this study (i.e., n-pentane, n-hexane, n-heptane,

1 and n-octane) were of reagent grade (>98.0%).

2 The explosion experiments were conducted using the experimental apparatus illustrated in Fig. 1
3 and following previously described procedures (Koshiha et al., 2010). The closed cylindrical
4 explosion vessel had a diameter of 100 mm and a height of 120 mm; it included tungsten electrodes
5 for ignition, a fan, and two pressure transducers. The vessel was connected to a vacuum pump and
6 gas-supply units. Explosion experiments have frequently been conducted in vessels recommended by
7 testing standards, such as ASTM E 681-04 (2009) and EN 1839 (2003a; 2003b). Explosion
8 properties likely exhibit sensitivity to the experimental conditions (e.g., vessel size) because the
9 flame-quenching effect of the vessel wall is not negligible when the vessel volume is small. The
10 explosion vessel used in the present study was a non-standard device, and the ratio of the surface
11 area of the vessel to its volume was relatively higher than that of standard vessels. This condition
12 results in enhanced heat loss to the vessel wall, thereby potentially influencing the explosion
13 characteristics. However, using this explosion vessel, the LEL and UEL (Upper Explosion Limit) of
14 a methane/air mixture were determined to be 5.2% and 15.3%, respectively, which are nearly the
15 same as the values reported in the literature for the same mixture (LEL: ca. 5%; UEL: ca. 15%)
16 (Pfahl et al., 2000; Kuchta, 1985). Thus, the energy loss in the small-volume vessel was considered
17 to be small.

18 Each measurement was performed at ambient pressure and temperature and repeated thrice to

1 confirm its reproducibility. Prior to each experiment, the explosion vessel was evacuated. The
2 flammable mixture was then created in the vessel using the partial-pressure method, and the mixture
3 was mechanically stirred. After a brief interval, each mixture was ignited at the center of the vessel
4 with an electrical spark (18 J), and the explosion pressure was measured using a pressure transducer
5 (PGM-H, Kyowa Electronic Instruments, Japan) placed on the side wall of the vessel via a strain
6 measuring unit (NR-ST04, Keyence, Japan). A 7% pressure rise criterion for explosion was applied.

7 Thermochemical equilibrium calculations to determine the adiabatic flame temperatures were
8 performed using the CHEMKIN ver. 4.1.1 program (Kee et al., 2007). For the fuel/N₂O mixtures, the
9 following 34 chemical species were considered: H, H₂, OH, HO₂, H₂O, H₂O₂, O, O₂, HCO, C, CO,
10 CO₂, CH, CH₂, CH₃, CH₄, C₂, C₂H₂, C₂H₄, C₂H₅, C₂H₆, C₃, C₄, C₅, C₆H₆, the fuel, CN, N, N₂, NO,
11 NO₂, N₂O, NH, and HNO; for the fuel/O₂ mixtures, 26 equilibrium species (those without nitrogen
12 atoms) were used for the calculations. The thermodynamic data for these species were extracted
13 from the NASA database (2001).

14

15 **3. Results and discussion**

16 *3.1 Explosion limits*

17 Fig. 2a and b illustrate the UELs and LELs as a function of the carbon number of the alkanes,
18 respectively. For the fuel/O₂ mixtures, these values for the LELs and UELs agree well with those

1 reported in the literature (Coward and Jones, 1952). As the carbon number increases, the UELs and
2 LELs of the alkane/O₂ mixtures decreases. For reference, the UELs and LELs of alkane/air mixtures
3 reported in the literature (Crowl and Louvar, 2011) are shown in Fig. 2a and b, respectively. The
4 UEL and LEL of the CH₄/N₂O mixture were found to be 42.4% and 2.5%, respectively, and are in
5 good agreement with those reported by Pfahl and co-workers (2000). As seen in these figures, the
6 UELs and LELs decreases as the carbon number increases, similar to those observed for the
7 alkane/O₂ mixtures described above.

8 Under fuel-lean conditions, a flammable gas or vapor undergoes complete combustion due to the
9 presence of excess oxidant, and similar combustion processes are observed in oxygen and air
10 atmospheres. Thus, nearly the same LELs were obtained for both the alkane/O₂ and corresponding
11 alkane/air mixtures (Chen, 2011). However, differences in the LEL values were observed for the
12 alkane/N₂O and corresponding alkane/O₂ mixtures. The UEL value for a flammable gas in oxygen is
13 also remarkably larger than that for the same gas in air because of the fuel-rich conditions (Shu and
14 Wen, 2002). A similar result was obtained for the alkane/N₂O mixtures; the UELs were significantly
15 lower than those for the corresponding oxygen mixtures.

16 The tested mixtures were ranked in the following order in terms of their explosion ranges:
17 alkane/O₂ > alkane/N₂O >> alkane/air; their LEL values were in the following order: alkane/O₂ ≈
18 alkane/air > alkane/N₂O, indicating that flammable mixtures were formed under N₂O atmospheres

1 more readily than under oxygen and air atmospheres, even for small amounts of the alkane gases or
2 vapors.

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4 *3.2 Burgess–Wheeler law*

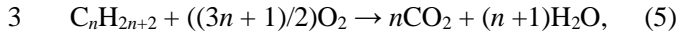
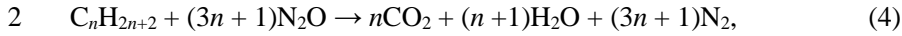
5 Eq. (2) suggests that the Burgess–Wheeler law trivially holds for alkane/N₂O mixtures if ΔH varies
6 approximately linearly with respect to the reciprocal of its lower explosion limit: 1/LEL. Fig. 3
7 shows the variations of the enthalpies as a function of 1/LEL for the three types of mixtures. These
8 plots were approximately linear with high coefficients of determination: 0.97 for the alkane/N₂O
9 mixtures, 0.99 for the alkane/O₂ mixtures, and 0.98 for the alkane/air mixtures. These results
10 indicate that the decomposition enthalpy of nitrous oxide had little impact, and hence, the
11 Burgess–Wheeler law holds for *n*-alkane/N₂O mixtures. The different slopes of the lines shown in
12 Fig. 3 indicate that the parameters of the Burgess–Wheeler law should be changed. However, this
13 paper does not address the issue because there may be no significant differences in the slopes due to
14 the somewhat greater variations in the adiabatic flame temperatures shown in Table 1.

15

16 *3.3 Explosion pressure and rate of pressure rise*

17 Fig. 4a depicts the observed explosion pressures for alkane/N₂O/N₂ mixtures as a function of the
18 equivalence ratio (ϕ). The equivalence ratio was calculated based on the following overall reactions:

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5 When the equivalence ratio is just 1, the reaction is stoichiometric; if $\phi > 1$ and $\phi < 1$, the mixtures
6 are at the fuel-rich and fuel-lean conditions, respectively. The nitrogen concentration was fixed at 30
7 vol%. The explosion pressure can be seen to initially increase with an increase in the equivalence
8 ratio to reach a maximum, and then declines gradually under fuel-rich conditions. In Fig. 4b, the
9 explosion pressures of the alkane/O₂/N₂ mixtures are plotted as a function of the equivalence ratio.
10 The nitrogen concentration was also set to 30 vol%. Similar pressure behavior was observed for the
11 mixtures containing O₂ as was seen for the corresponding mixtures containing N₂O; however, a
12 slight difference was found when $\phi < 1$. That is, while the number of carbon atoms did not affect the
13 explosion pressure for mixtures containing readily-decomposable N₂O under fuel-lean conditions
14 ($\phi < 1$), the explosion pressures for the corresponding mixtures containing O₂ varied significantly
15 with the carbon number under these conditions. These results also imply that the presence of excess
16 nitrous oxide at $\phi < 1$ caused the pressure rise because of decomposition of nitrous oxide to dominate
17 the reaction. In fact, chemical equilibrium calculations confirmed that the N₂O fraction at $\phi < 1$ was
18 on the order of 10⁻⁶, indicating that most of the N₂O decomposed to N₂ and O₂ according to Eq. 1.

1 The fact that the explosion pressures for the N₂O mixtures were higher than those for the
2 corresponding O₂ mixtures at $\phi < 1$ further supports this conclusion.

3 Table 2 lists the deflagration index (K_G) values for the mixtures containing N₂O or O₂ at the
4 equivalence ratio for which the explosion pressure reached a maximum value. K_G was determined
5 using the following equation (NFPA, 2013):

6

$$7 \quad K_G = (dP/dt)_{\max} \cdot V^{1/3}, \quad (6)$$

8

9 where P , t , and V are the explosion pressure, time, and vessel volume, respectively. In these
10 experiments, the nitrogen concentration was once again fixed at 30 vol%. The K_G values for the
11 CH₄/N₂O and CH₄/O₂ mixtures were found to be 379 bar m s⁻¹ and 682 bar m s⁻¹, respectively. K_G is
12 reported to be positively correlated with the oxidant concentration in flammable mixtures (Shu and
13 Wen, 2002) and explosion severity (Crowl and Louvar, 2011). In addition, K_G has been shown to
14 increase as the adiabatic flame temperature increases (Benedetto et al., 2009). The results presented
15 in Table 2 clearly indicate that the K_G increased with the carbon number of the alkane, and the K_G s
16 of the mixtures containing O₂ were significantly larger than those for the corresponding mixtures
17 containing N₂O. These results imply that the mixtures with N₂O exhibited lower mixture activities
18 and explosion severity compared with the corresponding mixtures with O₂. In addition, the mixtures

1 containing N₂O had higher calculated adiabatic flame temperatures than the corresponding mixtures
2 containing O₂, which is in good agreement with the findings of earlier studies (Koshiba et al, 2010).

3

4 **4. Conclusions**

5 The explosion properties of C1–C8 n-alkane/N₂O mixtures were investigated to ensure safe
6 operations when using these types of mixtures. On the basis of their explosion ranges, the tested
7 mixtures with the same alkanes were ranked in the following order: alkane/O₂ > alkane/N₂O >>
8 alkane/air; the order of the LELs of the tested mixtures with the same alkanes was alkane/O₂ ≈
9 alkane/air > alkane/N₂O. In addition, the Burgess–Wheeler law was determined to hold for
10 flammable mixtures containing N₂O. Finally, the N₂O mixtures exhibited larger K_G values than the
11 corresponding O₂ mixtures.

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10 **Figure captions**

11 Fig. 1 Schematic of the experimental apparatus used for the explosion experiments.

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13 Fig. 2 Explosion limits as a function of the carbon number of the alkane: (a) UELs of the mixtures

14 and (b) LELs of the mixtures; squares = alkane/N₂O mixtures, circles = alkane/O₂ mixtures, and

15 triangles = alkane/air mixtures. The data on the alkane/air mixtures were taken from Crowl and

16 Louvar (2011).

17

18 Fig. 3 Enthalpy versus 1/LEL plots; squares = alkane/N₂O mixtures, circles = alkane/O₂ mixtures,

1 and triangles = alkane/air mixtures.

2

3 Fig. 4 Explosion pressures for mixtures containing (a) N₂O and (b) O₂ as a function of the

4 equivalence ratio; circles = CH₄, lozenge = C₂H₆, triangles = n-C₃H₈, squares = n-C₄H₁₀, pentagons

5 = n-C₅H₁₂, hexagons = n-C₆H₁₄, and stars = n-C₇H₁₆.

6

7

8 **Table captions**

9 Table 1 Calculated adiabatic flame temperatures for alkane/N₂O and alkane/O₂ mixtures.

10

11 Table 2 K_G values for mixtures containing N₂O or O₂.

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Figure 1

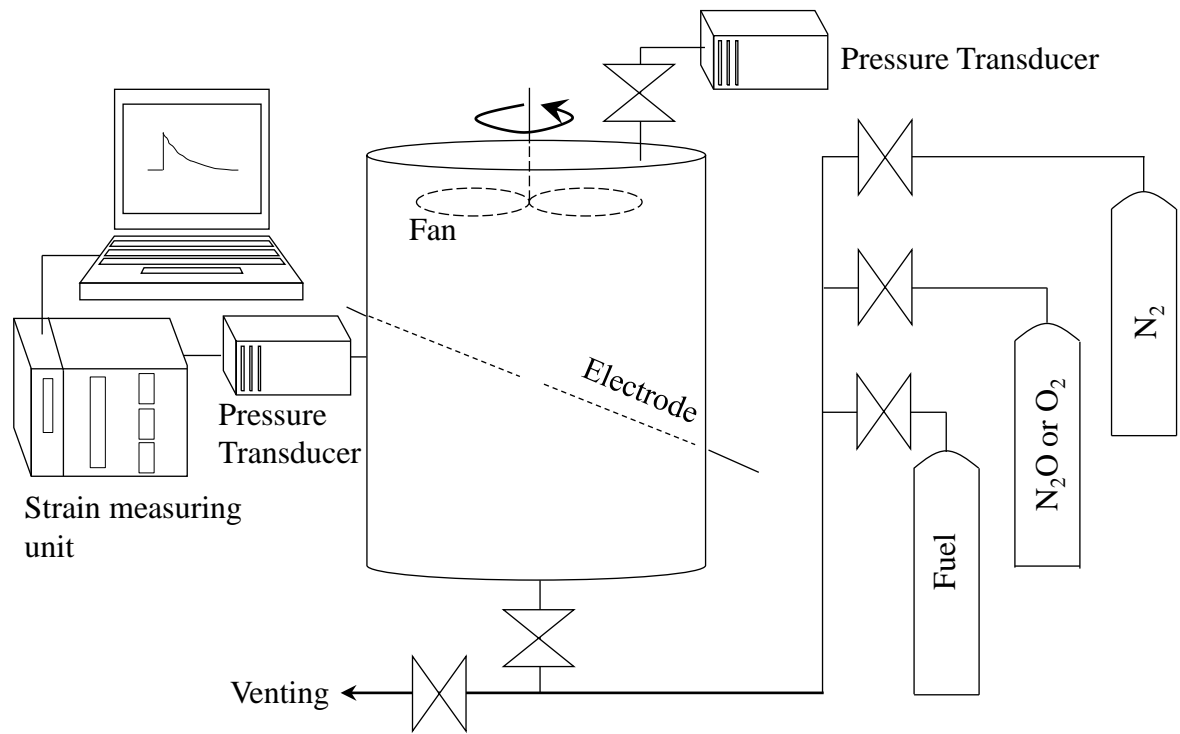


Figure 2a

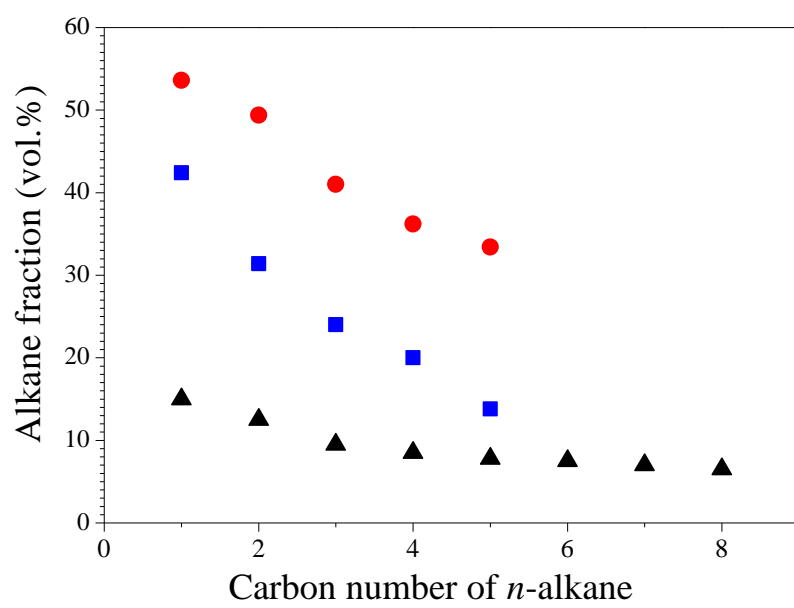


Figure 2b

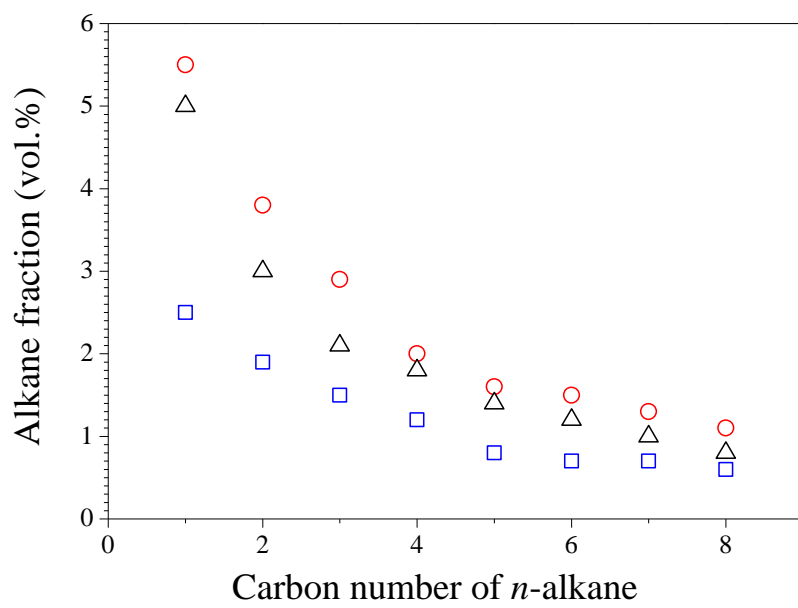


Figure 3

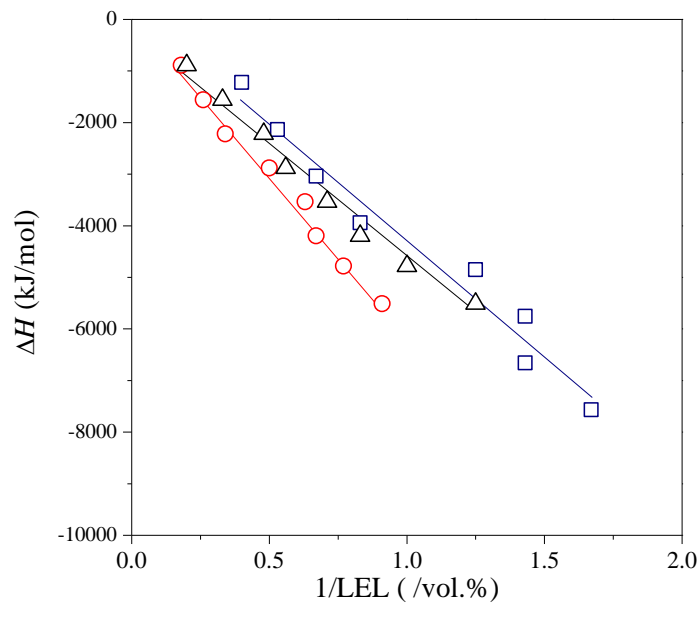


Figure 4a

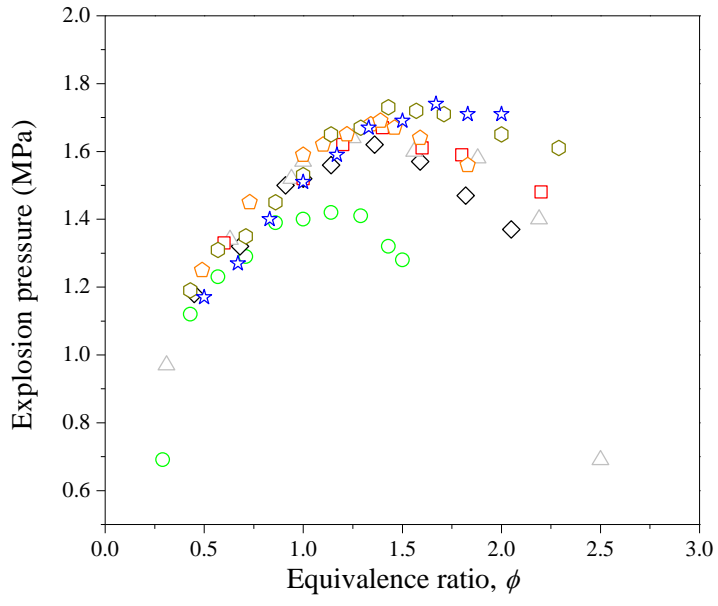


Figure 4b

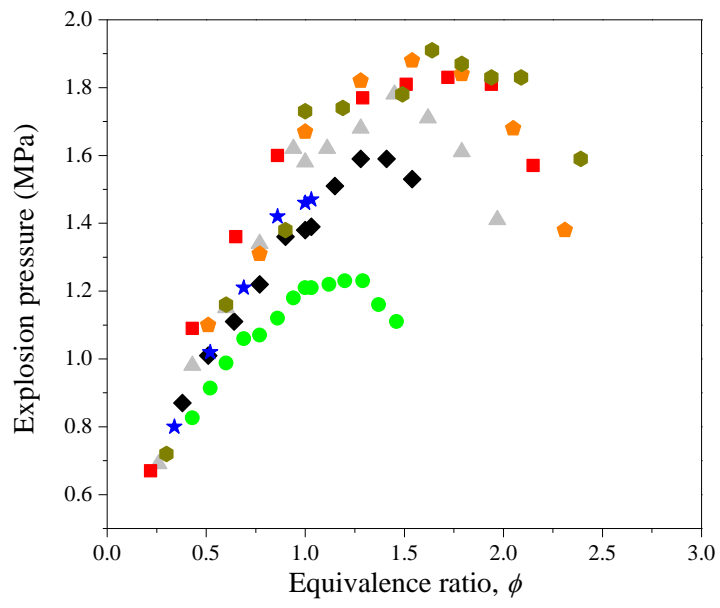


Table 1

Fuel	Adiabatic flame temperature (K)	
	N ₂ O mixtures	O ₂ mixtures
CH ₄	2253	1931
C ₂ H ₆	2332	2015
C ₃ H ₈	2366	2045
n-C ₄ H ₁₀	2377	1858
n-C ₅ H ₁₂	2379	1815
n-C ₆ H ₁₄	2309	1930
n-C ₇ H ₁₆	2366	1924
n-C ₈ H ₁₈	2354	1859

Table 2

Fuel	KG (bar m/s)	
	N ₂ O mixtures	O ₂ mixtures
CH ₄	379	682
C ₂ H ₆	515	1334
C ₃ H ₈	877	2764
n-C ₄ H ₁₀	1294	3420
n-C ₅ H ₁₂	1441	3905
n-C ₆ H ₁₄	1441	4496
n-C ₇ H ₁₆	1560	ND
n-C ₈ H ₁₈	ND	ND

ND: not determined due to the vapor pressure of the alkane.

Highlights

- The explosion properties of n-alkane/nitrous oxide (N₂O) mixtures are investigated.
- N₂O mixtures exhibit higher explosion pressures than the corresponding O₂ mixtures.
- The LEL values are in the following order: alkane/O₂ \approx alkane/air > alkane/N₂O.
- The Burgess–Wheeler law is observed to hold for the alkane/N₂O mixtures.