

A Thermal Theory for Flammability Diagrams Guiding Purge and Inertion of a Flammable Mixture

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Recently, a thermal method was proposed to recheck the concept of flammability by manipulating the competition between heating and quenching. This method is further explored here to reconstruct flammability diagrams, explaining the contribution of each component toward flammability change for a mixture. Based on the assumption that a diluent will not change the flame temperature at the flammability limits, these isothermal processes lead to a conservative estimation of the flammable zone. Although rough near the inertion point, the theoretical flammability envelop has the potential to guide future purging and diluting operations. It will be a powerful tool for both educational purposes and practical utilities. © 2012 American Institute of Chemical Engineers Process Saf Prog 0000: 000–000, 2012

Keywords: flammability diagram; diluted flammability diagram; diluent/fuel ratio; purge operation; dilution

INTRODUCTION

The role of flammability limits on guiding safe handling of flammable gases has been recognized for more than two centuries. A flammability diagram has the advantage of presenting data figuratively, so it is useful for dealing with multiple species in a flammable mixture. Britton [1] reviewed 200 years of research on flammability limits, stressing the difficulty in making realistic and predictive measurements. Without a consistent theory, all combinations of fuel/diluent have to be experimentally determined [2] to provide the diluted flammability diagram before Le Chatelier's Rule is used to include this pseudo-fuel (fuel/diluent combination). Without a systematic theory to predict the flammability diagram, empirical constants are widely used to reconstruct the flammability diagram from other measurements, such as minimum oxygen concentration [3]. Cheng *et al.* [4] reviewed six methods to determine the mine gas explosibility, all relying on either direct measurement or extrapolation in reconstructing the explosibility diagram.

Recently, a thermal theory was proposed to explain the energy-conservation process in determining the flammability limits of a pure fuel or a flammable mixture [5]. The thermal contribution for each energy term is further clarified in reviewing existing correlations and proposing new correlations [6]. The capability of estimating flame temperature is also explored [7]. Here this thermal method is further utilized

to develop the flammability diagram, with the purpose of guiding future purging and dilution operations.

The inherent assumptions behind this thermal theory are:

- Constant critical adiabatic flame temperature (CAFT) at flammability limits, so the dilution process to flammability is an isothermal process;
- Oxygen calorimetry applies at both lower and upper limits (or the reaction at upper flammability limit [UFL] is complete and similar to the reaction at lower flammability limit [LFL]), so the thermal balance at UFL can be utilized at LFL.

Then a thermal treatment is developed to convert the flammability information into a thermal signature (heating and quenching potentials). After some simple manipulation in energy domain for either mixing or dilution, the energy information is reversed back into the concentration domain, so we get the new flammability limits of any fuel/oxygen/diluent combinations.

The major advantages/contributions of this method are

- A binary view of a tertiary (fuel/oxidizer/diluent) system, so the treatment is consistent for fuel or diluent.
- Nonlinear temperature dependency is preserved in a background species (air) only, so all thermal agents are comparable with each other by an equivalent-air-index. This greatly simplifies the estimation process.

Now the flammability diagram is constructed using this theory, with the purpose of guiding future purging and dilution operations.

STANDARD FLAMMABILITY DIAGRAM

Based on the above assumptions, the theoretical flammability curves are derived in appendix A. The LFL and UFL curves for the flammability diagram are Eq. 1 and 2 with the diluent concentration x_D as the only variable. Subscript 0 is used to represent initial value without dilution.

$$x_L = \frac{1 - (1 - Q_D) \cdot x_D}{1 - Q_F + C_O \cdot H_O} = x_{L,0} \cdot [1 - (1 - Q_D) \cdot x_D] \quad (1)$$

$$x_U = x_{U,0} - \left(x_{U,0} + \frac{Q_D}{Q_F - 1 + 0.2095 \cdot H_O} \right) \cdot x_D \quad (2)$$

The inertion happens at a stoichiometric condition, so a third stoichiometric line is proposed to show where the stoichiometric reaction occurs. Theoretically, the stoichiometric line meets the above two lines at the same point, which is the inertion point (IP) (or isothermal point for inertization).

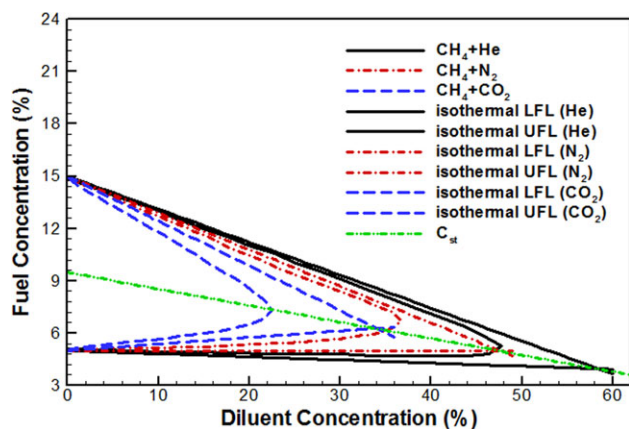


Figure 1. Static dilution diagram for methane flammability. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$x_{st} = \frac{1 - x_D}{1 + 4.773 \cdot C_O} = x_{st,0}(1 - x_D) \quad (3)$$

Applying this theory to a simple fuel (methane), the flammability diagram for different thermal agents is shown in Figure 1. Each thermal agent (Helium, Nitrogen, Carbon Dioxide) is represented by its quenching potential (or equivalent-air-index [7]), which is directly computable from the enthalpy data with reference to that of air. The theoretical flammability diagram is generally encompassing the measured flammability diagrams, since the mixing/diluting process is assumed to be isothermal in nature, while the true flame temperatures at inertion may not be constant. A discussion on the deviation from theory is supplied in Discussion on Uncertainty Section.

For a static flammability problem, the purpose of inertization is to create an inert environment so that no ignition can happen; that means the minimum allowable inertion concentration (MIC) should be reached. In a real flammability diagram, that is called the IP [8]. Without a real flammability measurement, here the cross point of LFL/UFL/Stoichiometric lines can be treated as a conservative estimation of MIC, which is a result of isothermal process and always larger than the limiting concentration. Fortunately, we have three estimations for this upper limit, since all above three lines meet at this point. Using x_D as the only variable, we can solve the limiting x_D (IP) by pairing the above equations. The limiting dilution concentration is determined below. Note the subscript 0 (initial value without dilution) is dropped for simplicity.

$$\begin{aligned} x_D &= \frac{x_{st} - x_L}{Q_D \cdot x_{st} - x_L + Q_D \cdot x_L} \\ &= \frac{x_U - x_{st}}{x_U - Q_D \cdot x_{st} + \frac{Q_D}{Q_F - 1 + 0.2095 H_O}} \\ &= \frac{x_U - x_L}{x_U - x_L + x_L Q_D + \frac{Q_D}{Q_F - 1 + 0.2095 H_O}} \end{aligned} \quad (4)$$

Here is one example to apply this theory.

Problem #01[7]. A methane leak fills a 200 m³ room until the methane concentration is 30 vol%. How much nitrogen is needed to dilute the fuel so there is no danger of explosion? What happens if the agent is replaced by carbon dioxide?

Solution:

- a. The stoichiometric coefficient of methane is directly computable from its oxygen coefficient in chemical reaction.

$$x_{st} = \frac{1}{1 + 4.773 \cdot C_O} = 0.0948$$

- b. Next, the limiting/inertion concentration of nitrogen

$$\begin{aligned} x_D &= \frac{x_{st} - x_L}{x_{st} - x_L + Q_D x_L} = \frac{0.0948 - 0.05}{0.0948 - 0.05 + 0.992 \times 0.05} \\ &= 0.4746 \end{aligned}$$

- c. Then, find the final limiting fuel concentration

$$x_F = (1 - x_D) \cdot x_{F,0} = (1 - 0.4746) \times 0.3 = 0.1576$$

- d. The total volume of needed nitrogen is a function of initial room volume. Assume the room is always well mixed, the volume needed to decrease the fuel concentration is (purging equation, see Beyler's chapter in SFPE Handbook [8])

$$V_{N_2} = -V_0 \cdot \ln\left(\frac{x_C}{x_0}\right) = -200 \times \ln\left(\frac{0.1576}{0.3}\right) = 128.7 \text{ m}^3$$

If the diluent is carbon dioxide ($Q_D = 1.75$), then the above results are recalculated as $x_D = 0.3386$, $x_F = 0.1984$, $V_{CO_2} = 82.7 \text{ m}^3$.

Note the handbook solution is $x_F = 0.13$ ($x_D = 0.5236$, $V_{N_2} = 167.3 \text{ m}^3$) for nitrogen inertion, which is read from the experimental flammability diagram. The error is believed to be the difference in theoretical and experimental flammability diagrams and reading error ($0.1576 - 0.13 = 0.0276$, so the total error = 2.76%, which is acceptable in reading diagrams.). This method is more precise than Beyler's method since the result is directly computable and there is no human error involved.

DILUTED FLAMMABILITY DIAGRAM

The above diagram depicts a purging problem for a static compartment. There is another scenario where some diluent is needed to inertize a fuel stream. Then a dimensionless dilution ratio is introduced so the diluent can be treated along with the fuel. This diluted flammability diagram (also called modified Coward diagram, see Ref. 4) has already been incorporated into the Le Chatelier's rule [2], which is unable to capture the contribution of a diluent. Such a flammability diagram based on dilution ratio is more useful in industrial practices, since it deals with a dynamic inertion problem and diluents directly.

For the diluted flammability diagram, the governing equations for LFL and UFL are derived in appendix B/C and listed below.

$$x_L = \frac{1}{1 + \left(\frac{C_O H_O}{1+R} - \frac{Q_F}{1+R} - \frac{Q_D \cdot R}{1+R}\right)} \quad (5)$$

$$x_U = \frac{(0.2095 \cdot H_O - 1)}{(0.2095 \cdot H_O - 1) + \frac{Q_F}{1+R} + \frac{Q_D \cdot R}{1+R}} \quad (6)$$

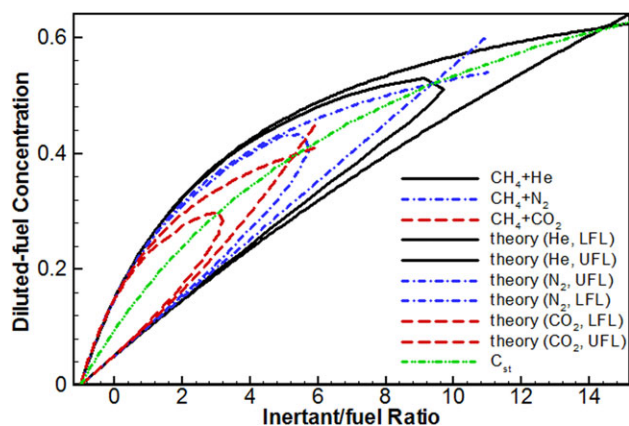


Figure 2. Diluted flammability diagram for inertising a methane stream. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Using R as the only variable, the theoretical flammability diagram is shown in Figure 2. A comparison with the real (measured) flammability diagram [4] is supplied. The stoichiometric line (Eq. E2) is also imposed for completeness.

Forcing $x_L = x_U$, the inerting R or the limiting R can be derived, which can be solved using Eqs. 5 and 6.

$$R = \frac{0.2095C_OH_O^2 - C_OH_O - 0.2095H_OQ_F}{Q_D + 0.2095H_O - 1} \quad (7)$$

This is the minimum inerting concentration or ultimate diluting concentration, beyond which no fuel at whatever concentration is ignitable.

The advantage of this diagram is that a dilution ratio can be easily read from the diagram, so the dynamic dilution process is clearly demonstrated.

Here is another example [8] to demonstrate this function (estimating minimum inerting concentration).

Problem #02. A 1 kg/s flow of methane is being dumped into the atmosphere. How much nitrogen must be mixed with methane to avoid a flammable mixture in the open? What happens if the agent is replaced by carbon dioxide?

Solution:

- The thermal signature of methane is computable from its flammability limits

$$\begin{aligned} H_O &= \frac{x_U - x_L}{C_O \cdot x_U \cdot x_L - \frac{(1-x_U) \cdot x_L}{4.773}} \\ &= \frac{0.15 - 0.05}{2 \times 0.15 \times 0.05 - 0.2095 \times (1 - 0.15) \times 0.05} \\ &= 16.38Q_F = 1 - \frac{1}{x_L} + C_OH_O = 1 - \frac{1}{0.05} + 2 \times 16.38 \\ &= 13.94 \end{aligned}$$

- Apply Eq. 7 for the limiting R , we have

$$R = \frac{0.2095 \cdot C_OH_O^2 - C_OH_O - 0.2095 \cdot H_OQ_F}{Q_D + 0.2095 \cdot H_O - 1} = 9.34$$

- The mass flow rate of Nitrogen should be corrected by its molecular weight.

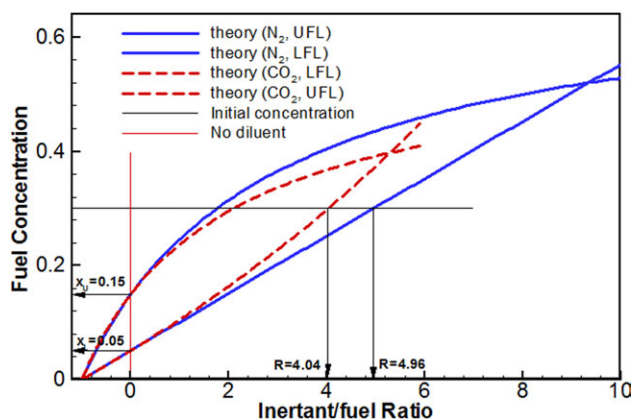


Figure 3. Graphical representation of a dilution process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$m_{N_2} = m_F \cdot R \cdot \frac{MW_{N_2}}{MW_{CH_4}} = 1 \times 9.3 \times \frac{28}{16} = 16.3 \text{ kg/s}$$

Note Beyler [8] estimated $R = \frac{0.82}{0.18} = 4.56$ and $m_{N_2} = 7.97 \text{ kg/s}$. This result is not conflicting here, since an isothermal process is assumed for the dilution operation, while his limits are estimates based on readings from the real flammability diagram.

However, there are some cases where a diluted fuel needs to be diluted a little further to go below its LFL. If the initial concentration is just flammable, then there is no need to get the MIC at the IP. In this case, we can find a smaller threshold for diluting to LFL instead of diluting to the IP. Real dilution problems may need both values and use whichever is smaller. Fortunately, LFL value is also estimated easily with simple algebraic expressions. The critical dilution ratio for a diluted fuel of initial concentration x_0 is expressed as Eq. 8 (see Appendix D).

$$R = \frac{x_0 C_OH_O - x_0 Q_F + x_0 - 1}{x_0 Q_D + 1 - x_0} \quad (8)$$

Here is another modified example for inertion with a smaller concentration.

Problem #03. A 1 kg/s flow of 30% methane/air mixture is being dumped into the atmosphere. How much nitrogen must be mixed with methane to avoid a flammable mixture in the open? What happens if the agent is replaced by carbon dioxide?

Solution:

- Same as previous problem
- Apply Eq. 8, we have a smaller diluting ratio

$$\begin{aligned} R &= \frac{x_0 C_OH_O - x_0 Q_F + x_0 - 1}{x_0 Q_D + 1 - x_0} \\ &= \frac{0.3 \times 2 \times 16.38 - 0.3 \times 13.94 + 0.3 - 1}{0.3 \times 0.992 + 1 - 0.3} = 4.96 \end{aligned}$$

- Again, the required mass flow rate of nitrogen should be corrected by its molecular weight.

$$m_{N_2} = m_F \cdot R \cdot \frac{MW_{N_2}}{MW_{\text{mix}}} = 1 \times 4.96 \times \frac{28}{16 \times 0.3 + 28.84 \times 0.7} = 5.56 \text{ kg/s}$$

Table 1. Thermal balance method for flammability range of a fuel/diluent mixture.

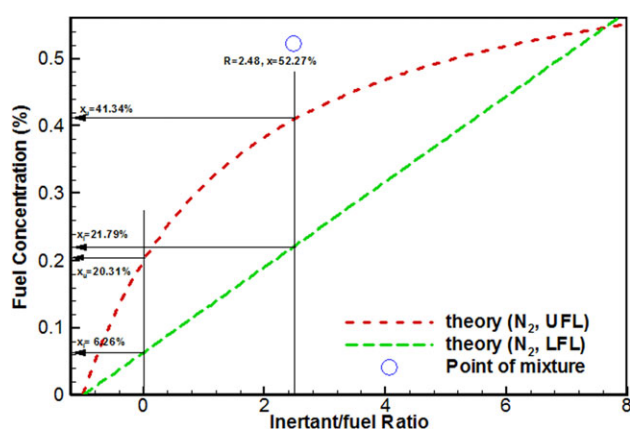
	C_O	x_L	x_U	Q_D	H_O	H_F	Composition
Methane	2.00	5.00%	15.00%	13.81	16.38	32.77	19.13%
Carbon monoxide	0.50	12.50%	74.00%	0.80	15.59	7.80	9.57%
Nitrogen				0.99	0.00	0.00	71.30%
Mixture	0.43	21.79%	41.34%	3.43	4.63	7.01	100.00%

These bold values are computed results, while other values are inputs or intermediate results.

Table 2. Thermal balance method for the thermal signature of a fuel-only mixture.

	C_O	x_L	x_U	Q_D	H_O	H_F	Composition
Methane	2.00	5.00%	15.00%	13.81	16.38	32.77	66.67%
Carbon monoxide	0.50	12.50%	74.00%	0.80	15.59	7.80	33.33%
Mixture	1.50	6.26%	20.31%	9.47	16.12	24.44	

These bold values are computed results, while other values are inputs or intermediate results.

**Figure 4.** A dilution flammability diagram presenting the dilution process. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

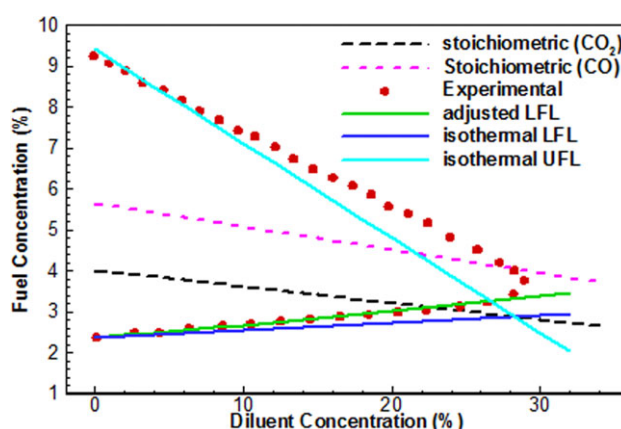
For carbon dioxide, the above calculation is updated with $Q_D = 1.75$, then we get $R = 4.04$, $m_{CO_2} = 7.11$ kg/s. This shows that less volume, or more mass is needed if a heavier thermal agent is adopted to inertize the fuel. The above process can be demonstrated graphically in Figure 3.

= 9.3, but to its LFL value $R = 4.96$. If using CO_2 , these two values are $R = 5.3$ and $R = 4.04$, respectively. The flammability zone/envelop and the dilution requirements are clearly demonstrated in this diluted flammability diagram.

Problem #04 [4]. A sample taken from a sealed area yields the mixture composition as follows: $CH_4 = 10\%$, $CO = 5\%$, $N_2 = 75\%$, $O_2 = 10\%$. Is this gas-mixture flammable?

Solution: The thermal balance method will deal the mixing problem (a flammable mixture with diluent) in the following approach.

- This is a dilution problem where a fuel/diluent mixture (10% CH_4 , 5% CO and 37.27% N_2) is immersed in 47.73% of air (10% O_2 + 37.73% N_2).

**Figure 5.** Experimental flammability diagram for propane deviates from the isothermal processes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

- For this fuel/diluent mixture, the thermal balance method is adopted to find the flammability range using a spreadsheet (Table 1, see also Ref. 5).

- Get the thermal signature from flammability limits of each component.
- Sum up each individual thermal signature into a lump-sum signature for the mixture.
- Get the flammability limits from the mixture signature.
- Current fuel mixture has a concentration of 100%–47.73% = 52.27%, well above the flammability range of 21.79%–41.34%. So this sample is too rich to ignite.

Another solution: A pseudo-fuel is composed of two fuels and diluted by a third agent.

- Get the thermal signature of two fuels (Table 2) without dilution first.
- Then a dilution diagram (Figure 4) is reconstructed from this mixture signature using Eqs. 5 and 6.

c. The same flammability range will be reached by either reading the diagram or solving Eqs. 5 and 6 using a given $R = 37.27\%/15\% = 2.48$.

The above two treatments are consistently represented in Figure 4. As the sample point lies above the flammable zone, this sealed area is too rich to ignite.

Tables 1 or 2 are also explained in Figure 4. So Figure 4 is a good presentation of the mixing/diluting process, no matter it is a static (purge) or a dynamic (dilution) problem.

DISCUSSION ON UNCERTAINTY

The above analysis is based on the assumption of isothermal processes. The critical flames near extinction are not only deviating from the isothermal process but also turning away from the stoichiometric line, as shown in Figure 5. There are two mechanisms contributing to this deviation between a theoretical flammability envelop and the measured envelop. One is the raised flame temperature due to a premixed flame structure near extinction. The other is the incompleteness or chemical equilibrium for a fuel-rich flame. The first deviation can be modeled, while the second part cannot be modeled, as the CO yield is needed to model the incompleteness of reaction in fuel-rich flames, which requires chemical equilibrium to determine.

Here, a temperature-dependent scaling factor is needed to model the effect of the CAFT other than at 1,600 K. Fortunately, this theory is based on a background species (air), which has a clearly defined temperature-dependency in Eq. 12. Note the input temperature should be divided by 1,000, so the correlation coefficients can have more valid digits.

$$E_{\text{air}} = (H_{\text{AFT}}^0 - H_{298.15}^0)_{\text{air}} = f(T) = 1.4893T^2 + 29.862T - 9.381 \quad (9)$$

Next, define a temperature-dependent scaling factor η for the change in CAFT.

$$\eta = \frac{E_i}{E_{\text{air}}} = \frac{(E_{\text{air}}^{\text{AFT}} - E_{\text{air}}^{0.298})}{(E_{\text{air}}^{1.600} - E_{\text{air}}^{0.298})} = \frac{(1.4893T^2 + 29.862T - 9.381) - (-0.35)}{42.21 - (-0.35)} = 0.035 \cdot T^2 - 0.702 \cdot T - 0.212 \quad (10)$$

Then, the heating and quenching potentials are all changed by this scaling factor to account for the impact of a raised critical flame temperature.

$$x_L \cdot Q_F \cdot \eta + (1 - x_L) \cdot \eta = x_L \cdot H_F / \eta \quad (11)$$

Finally, we have the temperature-modified lower flammable limits as

$$x_L = \frac{\eta^2}{\eta^2 + C_O H_O - Q_F \cdot \eta^2} \quad (12)$$

Assume the critical flame temperature near extinction is 1,700 K and this rise happened uniformly with an added diluent, we have a temperature-modified LFL curve in Figure 5, which is closely following the experimental LFL curve.

The second deviation happens to the UFL curve, where incomplete reaction dominates the energy-releasing process. With a few exceptions (such as the above methane flammability diagram), the stoichiometric line for complete reaction to CO_2 is not followed, but the incomplete reaction to CO instead is approached. That means, the flame at extinction is biased toward the CO stoichiometric line instead of CO_2 stoichiometric line (Eq. 13). This shift is attributed to incom-

plete combustion and to preferential diffusion of reactants [8].

$$\begin{aligned} C_{\text{st}} &= 1 + 4.773 \cdot (a + b/4 - c/2) \text{ for reaction to } \text{CO}_2 \\ C_{\text{st}} &= 1 + 4.773 \cdot (a/2 + b/4 - c/2) \text{ for reaction to CO} \end{aligned} \quad (13)$$

Figure 5 shows the impact of two effects (raised flame temperature and incomplete reaction). For dilution problems to find the limiting IP, raised flame temperature leads to a smaller limiting inertion concentration (see Figure 1), while the incomplete reaction does not change the IP much (see Figure 5). So the isothermal processes in this work are usually conservative in guiding dilution operations (see Figures 1 and 2). Propane in Figure 5 is an exception, where the theoretical and the experimental IP is close to each other.

CONCLUSION

Based on previous work on the flammability limits of a flammable mixture, flammability diagrams are established theoretically from the thermal signature of a fuel mixture. The contributions of fuel/diluent are clearly defined and manipulated in the diagrams. By setting-up the standard flammability diagram and the diluted flammability diagram, the purge and dilution problems will be easily solved and demonstrated. No experimental flammability diagrams are needed if their thermal signature is known. As most thermal signatures are derived from LFL and UFL data, this method are self-sufficient to treat any fuel/diluent combination with limited demand on external inputs. These diagrams can serve not only as an educational tool but also as a practical utility tool in daily safety operations involving a flammable gaseous fuel.

NOMENCLATURE

CAFT,	critical adiabatic flame temperature (K)
C_O ,	the oxygen coefficient in a reaction, dimensionless
C_{st} ,	the stoichiometric number for a reaction, dimensionless
E_{air} ,	enthalpy difference of air
H_O ,	the heating potential of oxygen based on air, dimensionless
H_F ,	the heating potential of fuel based on air, dimensionless
R ,	Diluent/fuel ratio
x_D ,	diluent concentration, %
x_L ,	LFL, Lower Flammability Limit (volume ratio), %
x_U ,	UFL, Upper Flammability Limit (volume ratio), %
x_{st} ,	stoichiometric concentration, $x_{\text{st}} = \frac{1}{C_{\text{st}}} = \frac{1}{1+4.773 \cdot C_O}$
Q_D ,	the quenching potential of diluent based on air, dimensionless
Q_F ,	the quenching potential of fuel based on air, dimensionless

SUBSCRIPTS

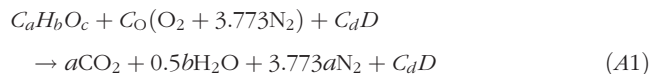
0,	original state without diluent
D,	diluent
F,	fuel
O,	oxygen
i,	component of a mixture
m,	sum of a mixture
st,	stoichiometric
L,	lower flammable limit
U,	upper flammable limit

Table A1. Quenching potentials of some common thermal agents.

	Q_D @ 1600K
Carbon dioxide (CO ₂)	1.75
Water (vapor) (H ₂ O)	1.08
Nitrogen (N ₂)	0.99
Oxygen (O ₂)	1.01
Helium (He)	0.65

APPENDIX A: DERIVATION OF FLAMMABILITY DIAGRAM

For the completeness of the method, the simple and universal reaction is restated here.



$$C_O = a + b/4 - c/2 \quad (A2)$$

$$C_{st} = 1 + 4.773 \cdot C_O$$

Where D stands for diluent, C_O is the oxygen coefficient representing chemistry or stoichiometric oxygen number, C_{st} is the stoichiometric number, while $x_{st} = \frac{1}{C_{st}}$ is the slope of the stoichiometric line [9].

Based on assumptions that most combustion products are similar to air, a non-dimensional variable is introduced by scaling with the enthalpy difference of air from ambient temperature to the critical flame temperature, which is typically 1, 600 K at LFL or UFL. Here the quenching potential of species i is defined as

$$Q_i = \frac{E_i}{E_{air}} = \frac{(H_{AFT}^0 - H_{298.15}^0)_i}{(H_{AFT}^0 - H_{298.15}^0)_{air}} \quad (A3)$$

Where H_{AFT}^0 is the enthalpy value of this species at AFT. For some agents, such as CO₂ and N₂, Q_D can be computed directly using their enthalpy values from the national institute of standards and technology (NIST) chemistry database [5]. Here is a table of Q_D for common thermal agents (Table A1).

Similarly, the heating potential is defined as

$$H_i = \frac{E_i}{E_{air}} = \frac{\text{Energy release}_i}{(H_{AFT}^0 - H_{298.15}^0)_{air}} \quad (A4)$$

Note some diluents (such as CO₂, N₂, O₂) can have its quenching potential derived using (A3) and (A4) using the enthalpy information from NIST website (see Ref. 4), while most fuels have their signature derived from their flammability limits (using Eqs. A7 and A8).

At the critical flame temperature for flammable limits, the energy balances between quenching (left) and heating (right) are established as

$$x_{L,0} \cdot Q_F + (1 - x_L) = x_L \cdot H_F \quad (A5)$$

$$x_{U,0} \cdot Q_F + (1 - x_{U,0}) = \frac{1 - x_U}{4.773} \cdot H_O \quad (A6)$$

Here x stands for the molar concentration, so x_L and x_U are LFL and UFL, respectively. Where Q_F and $H_F = C_O \cdot H_O$ are the quenching/heating potential of fuel scaled by that of air. The subscript 0 represents initial condition without a

diluent involved. Note the energy release in Eq. A6 is based on oxygen availability and heating potential of oxygen. A constitutive relationship $H_F = C_O \cdot H_O$ is needed to solve Eqs. A5 and A6 for the thermal signature: Q_F , H_O and H_F (see Ref. 5).

$$H_O = \frac{x_{U,0} - x_{L,0}}{C_O \cdot x_{U,0} \cdot x_{L,0} - \frac{(1 - x_{U,0}) \cdot x_{L,0}}{4.773}} \quad (A7)$$

$$Q_F = 1 - \frac{1}{x_{L,0}} + C_O \cdot H_O \quad (A8)$$

When a diluent D is added, subscript 0 will drop since x_L and x_U are floating with x_D , as shown in Eqs. A9 and A10.

$$x_L \cdot Q_F + x_D \cdot Q_D + (1 - x_L - x_D) = x_L \cdot H_F \quad (A9)$$

$$x_U \cdot Q_F + x_D \cdot Q_D + (1 - x_U - x_D) = \frac{1 - x_D - x_U}{4.773} \cdot H_O \quad (A10)$$

Solving the Eqs. A9 and A10 with unknowns x_L and x_U based on input x_D , we have

$$x_L = \frac{1 - (1 - Q_D) \cdot x_D}{1 - Q_F + C_O \cdot H_O} = x_{L,0} \cdot [1 - (1 - Q_D) \cdot x_D] \quad (A11)$$

$$x_U = x_{U,0} - (x_{U,0} + \frac{Q_D}{Q_F - 1 + 0.2095 \cdot H_O}) \cdot x_D \quad (A12)$$

Equations A11 and A12 form the LFL and UFL curves in a flammability diagram, which are the boundaries of the flammable zone. Their cross point is the IP, which is also the cross point with stoichiometric line developed below.

The stoichiometric reaction without and with x_D are developed by

$$x_{st,0} \cdot C_{st,0} = 1 \quad (A13)$$

$$x_{st} \cdot C_{st} + x_D = 1 \quad (A14)$$

Using x_D as the only variable, the stoichiometric line is developed by

$$x_{st} = \frac{1 - x_D}{1 + 4.773 \cdot C_O} = x_{st,0} (1 - x_D) \quad (A15)$$

APPENDIX B: DERIVATION OF LFL DILUTION EQUATION

First, the dilution ratio R is defined as

$$\frac{x_D}{x_F} = R \quad (B1)$$

This definition combined with a conservation equation $x_F + x_D = x_L$

Solve two equations for two variables, we have

$$x_D = \frac{R \cdot x_L}{1 + R} \quad (B2)$$

$$x_F = \frac{x_L}{1 + R} \quad (B3)$$

Submit them into the energy conservation equation at LFL

$$x_F \cdot Q_F + x_D \cdot Q_D + 1 - x_L = x_F H_F \quad (B4)$$

We have

$$\frac{x_L}{1 + R} \cdot Q_F + \frac{R \cdot x_L}{1 + R} \cdot Q_D + 1 - x_L = \frac{x_L}{1 + R} \cdot C_O H_O \quad (B5)$$

Rearranging the terms, we have a new equation for LFL with R as the only input.

$$x_L = \frac{1}{1 + \left(\frac{C_O H_O}{1 + R} - \frac{Q_F}{1 + R} - \frac{Q_D \cdot R}{1 + R} \right)} \quad (B6)$$

APPENDIX C: DERIVATION OF UFL DILUTION EQUATION

Solving

$$\frac{x_U}{1 + R} Q_F + \frac{R x_U}{1 + R} Q_D + 1 - x_U = 0.2095(1 - x_U) H_O \quad (C1)$$

We have a new equation for UFL

$$x_U = \frac{(0.2095 \cdot H_O - 1)}{(0.2095 \cdot H_O - 1) + \frac{Q_F}{1 + R} + \frac{Q_D \cdot R}{1 + R}} \quad (C2)$$

APPENDIX D: DERIVATION OF R

For the energy conservation at LFL,

$$\frac{x_0}{1 + R} \cdot Q_F + \frac{R \cdot x_0}{1 + R} \cdot Q_D + 1 - x_0 = \frac{x_0}{1 + R} \cdot C_O H_O \quad (D1)$$

Solving this equation, we have a dilution ratio with known x_0 as the only input.

$$R = \frac{x_0 C_O H_O - x_0 Q_F + x_0 - 1}{x_0 Q_D + 1 - x_0} \quad (D2)$$

APPENDIX E: DERIVATION OF THE STOICHIOMETRIC LINE FOR THE DILUTED FLAMMABILITY DIAGRAM

For the stoichiometric line in a diluted fuel mixture, Eq. A14 will be modified as following

$$x_{st} \cdot C_{st} + x_D = 1 + R \quad (E1)$$

Note $R = \frac{x_D}{x_{st}}$, or $x_D = x_{st} \cdot R$, so we have

$$x_{st} = \frac{1 + R}{C_{st} + R} \quad (E2)$$

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