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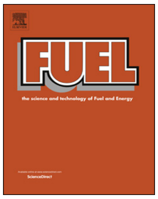

Full Length Article

Method for determination of flammability limits of gaseous compounds diluted with N_2 and CO_2 in air

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ABSTRACT

The present work studies the flammability limits of combustible–diluent–air mixtures at 25 °C and 1 atm pressure. The diluent species, considered in this study, were nitrogen and carbon dioxide. A factor called k_{FL} was obtained from mass and energy conservation, this factor relates the flammability limit of a combustible–air mixture to that of a combustible–diluent–air mixture. The factor k_{FL} varies with diluent concentration. Nevertheless, it was shown that an average value of this factor (k_{FL}^{av}) can represent, with good accuracy, the variation of the flammability limits with diluent concentration.

An empirical method to determine the flammability limits of combustible–diluent–air mixtures was developed. The method approximates k_{FL}^{av} by means of correlations. For the total set of experimental data, it was found that, for dilution with N_2 and CO_2 respectively: (a) at the LFL the Average of the relative errors (AARE) were 4.02% and 7.01%, the squared correlation coefficients (R^2) were 0.9833 and 0.9660; and (b) at the UFL the AAREs were 3.91% and 5.57%, the R^2 were 0.9920 and 0.9792.

At the Fuel Inertization Point (FIP) there is an inert concentration above which the mixture is non-flammable. A method was developed to determine the diluent mole fraction in the combustible–inert mixture at the FIP. The AAREs of 0.82% and 1.95% were obtained for dilution with N_2 and CO_2, respectively.

1. Introduction

The study of flammability limits is relevant to several industrial processes due to safety conditions. The theoretical aspects of the flammability limits (FL) are still being developed. However, their practical implications are very well stablished, and they have to be considered for any combustion application.

The present work deals with the FL of combustible–diluent–air mixtures. In the scope of the studies on flammability limits, it is considered as a diluent any inert species that once added to a combustible–air mixture reduces its flammability. Examples of such species are nitrogen (N_2), carbon dioxide (CO_2), water vapor (H_2O) and Helium (He), among others.

A combustible–diluent–air mixture is flammable when the combustible concentration is within the flammability limits. The lower flammability limit (LFL), for a fixed diluent concentration, is the lowest combustible concentration in the combustible–diluent–air mixture which sustains flame propagation. The upper flammability limit (UFL), for a fixed diluent concentration, is the highest combustible concentration in the combustible–diluent–air mixture which sustains flame propagation. In the case where no inert is present, its fixed concentration would be zero. This applies in general to any combustible–oxidant mixture. For instance, Pfahl et al. [1] determined the FLs of some combustibles using N_2O as oxidant. The earlier works by Zabetakis [2], Coward and Jones [3], and the reviews by Lovachev [4], Macek [5] and Coronado et al. [6] provide insight into this matter.

The FLs of a combustible–air mixture depend on the initial temperature and pressure conditions [7–11]. Also, there are different standard test methods to determine the FL [12]. These methods produce slightly different results for the LFL and sometimes they produce different results for the UFL of some combustibles. For example, Coward and Jones [3] report different values of the UFL of ethylene–air mixtures.

Several methods to calculate the FL of combustible–air mixtures at reference conditions have been developed and validated [13–19]. Although there are some approximations to the determination of the FL of combustible–diluent–air mixtures, there is still room for improvement.

The knowledge of the FL of combustible–diluent–air mixtures can be useful for several combustion applications, for example, Bade Shresta and Karim [20] have studied the performance of internal combustion

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Nomenclature

FL	flammability limit, %
g^0	specific Gibbs free energy at standard pressure in mole basis, kJ/mol
ΔG_T^0	standard state Gibbs function change, kJ/mol
$\bar{h}_i$	specific absolute enthalpy of species i in mole basis, kJ/mol
$\Delta\bar{h}_i$	specific sensible enthalpy of species i in mole basis, kJ/mol
$\bar{h}_{f,i}^0$	formation enthalpy of species i in mole basis at standard pressure, kJ/mol
H_C	heat of combustion of 1 mol of the combustible, kJ
K_{eq}	equilibrium constant for the water–gas homogeneous reaction
k_{FL}	factor which relates the FL of a combustible–air mixture to that of a combustible–inert–air mixture. It can be determined at the LFL and UFL.
k_{FL}^{av}	average value of k_{FL} determined for a particular combustible–inert–air system. It can be determined at the LFL and UFL.
LHV	lower heating value, kJ/g
M_d	representation of the diluent's molecule
n_i	number of moles of species i, mol
n_T	total number of moles of gaseous species in the products, mol
P_{air}	percentage of air in the combustible–diluent–air mixture, %
P_d	percentage of diluent in the combustible–diluent–air mixture,%
R	Universal gas constant, kJ/mol-K
R^2	squared correlation coefficient
s	specific entropy, kJ/mol-K
S	sample standard deviation
T	temperature, K
v_{air}^{FL}	number of moles of oxygen at the flammability limit, mol
v_{air}^{LFL}	number of moles of oxygen at the lower flammability limit, mol
v_{air}^{UFL}	number of moles of oxygen at the upper flammability limit, mol
v_{air}^{FIP}	number of moles of oxygen at the Fuel Inertization Point, mol
v_{air}^{s}	stoichiometric Number of moles of oxygen for y_F moles of combustible, mol
$v_{air,1}^{s}$	stoichiometric Number of moles of oxygen for 1 mol of combustible, mol
x_C	number of moles of carbon in the combustible, mol
x_H	number of moles of monoatomic hydrogen in the combustible, mol
x_O	number of moles of monoatomic oxygen in the combustible, mol
y_d	diluent mole fraction in the combustible–diluent mixture
y_F	combustible mole fraction in the combustible–diluent mixture
θ_d	ratio of adiabatic flame temperatures at LOC and at LFL
ϕ	equivalence ratio

Subscripts and Superscripts

air	air
av	average value
d	variable related to the combustible–diluent–air mixture
F	variable related to the combustible
LFL	variable at the lower flammability limit
FIP	variable at the fuel inertization point
P	products of the combustion process
R	reactants of the combustion process
UFL	variable at the upper flammability limit

Abbreviations

ARE	absolute value of the relative error,%
AARE	average of the absolute values of the relative errors of a set of data,%
FIP	Fuel Inertization Point
FL	flammability limit
LFL	lower flammability limit
UFL	upper flammability limit

engines operating with methane diluted with CO_2 and N_2. Also, the addition of diluents to combustible–air mixtures can reduce NOx emissions in spark ignition engines [21,22] and in diesel engines [23]. The diluents can decrease the constant volume peak combustion pressure and the mass burning rate of a combustible–air mixture as was shown by Zhang et al. [24] for the case of methanol.

The present article deals with the effect on the FL of diluent species as nitrogen and carbon dioxide. The objective is to develop two methods:

a) An empirical method for the determination of the FL of combustible–diluent–air mixtures at reference temperature and atmospheric pressure. This method can be used to determine the variation of the FL with different diluent concentrations.
b) A method to determine the diluent concentration at the fuel inertization point. This method can be used to assess the maximum diluent concentration for which the mixture is still flammable in air.

2. Overview of the effect of diluent species on the flammability limits

This section is divided in two sub-sections. On the first of these sub-sections some definitions, relevant to the present study, are provided together with the mathematical relations among the variables which appear on the study. On the second sub-section, the mathematical relations which can be applied to quantify the effect of the diluents on the FL are introduced.

2.1. Definitions and basic relations

In the present work, the term combustible is used to denote a species which can be flammable in the presence of an oxidant. A diluent could be any species which behaves as an inert in the combustion process. The diluents studied in the present work are N_2 or CO_2. The oxidant is air considered to be formed by 3.76 mol of N_2 per 1 mol of O_2. Which is a simplified composition of the atmospheric air when other species as argon or carbon dioxide are not considered, leaving 79% of N_2 and 21% of O_2.

Three different mixtures are defined before further development:

a) **Combustible–air mixtures:** These are mixtures containing only the combustible and air without the presence of any diluent. Furthermore, in Sections 3 and 4 the FL of these mixtures are considered known quantities. Its lower flammability limit is denoted by LFL_A and its upper flammability limit by UFL_A.
b) **Combustible–diluent mixtures:** These are mixtures formed by the