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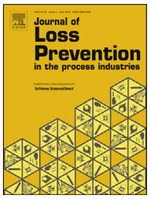

Numerical study of influence of initial pressures and temperatures on the lower flammability limits of oxygenated fuels in air

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ABSTRACT

An approach for predicting the lower flammability limits (LFL) of oxygenated fuel in air is presented. The lower flammability limits of methanol, ethanol, methyl formate and dimethyl ether in air are determined using calculated adiabatic flame temperature method at pressures up to 100 bar and temperatures up to 1000 K and the influence of initial pressure and temperature on lower flammability limit is discussed in the study. The results show that the predicted LFLs of mixtures decrease slightly with increasing pressure at high temperature. The predicted LFLs for a methanol-air mixture decrease by 0.24, 0.25, 0.25 vol% with the initial pressure from one to 100 bar at initial temperature of 800 K, 900 K and 1000 K. The variation in the LFLs is 0.11–0.12 vol% for ethanol-air, 0.18–0.19 vol% for methyl formate-air and 0.13–0.14 vol% for dimethyl ether-air at the same temperature and pressure conditions. Moreover, the LFLs of mixtures at 1000 K and 100 bar are much lower than those at atmospheric pressure and ambient temperature. The LFL values at high temperatures and pressures represent potentially greater danger of fires and explosions for these fuels.

1. Introduction

The oxygenated fuels as industrial materials and clean resources are widely used in industrial processes. Knowledge of the material safety properties is essential for handling and processing flammable substances, where the flammability limit is one of the most important factors for assessing the fire and explosion hazards. The flammability limits provide the range of fuel concentration, within which a combustible substance in air can ignite and burn. Therefore, it is important to know the flammability limit data to determine preventive measures to ensure the safety of industrial operation. The fuel concentration limit, often referred to as lower flammable limit (LFL), is the minimum concentration of fuel in air that will support flame propagation (Crowl and Louvar, 2011). The flammability limits are affected by a variety of factors including temperature, pressure, oxygen concentration, dilution, ignition energy, direction of flame propagation, etc. (Giurcan et al., 2015; Lian et al., 2010, 2012; Van den Schoor et al., 2008; Zlochower and Green, 2009). Flammability limits have been investigated experimentally and reported in scientific literature, where there has been a large array of experimental data on lower flammability limits for mixtures of gases and vapors with air at atmospheric pressure and ambient temperature (Brandes and Möller, 2003; Cashdollar et al., 2000; Coward and Jones, 1952). In practice, many industrial processes involve the mixing of combustible substances with oxidizing gases at elevated pressures and temperatures so that non-atmospheric conditions must be considered. However, experimenting with fuel-air mixtures is greatly difficult and troublesome, especially at elevated pressures and temperatures. Therefore, there is scant data for LFLs of combustible mixtures under non-ambient conditions. Moreover, some fuels will decompose at high temperature, so that the experimental determination of the LFL is unfeasible.

There are some prediction models established for assessing the flammability limits, (Albahri, 2013; Gharagheizi, 2009; Shimy, 1970), but these methods primarily provide possibilities for evaluating the flammability limits under ambient conditions. It has been reported that the LFL can be predicted using the adiabatic flame temperature (Shebeko et al., 2002; Vidal et al., 2006), where the adiabatic flame temperature is obtained from the empirical data, but no data currently exist for high temperatures and pressures.

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Therefore, the purpose of this work is to estimate the adiabatic flame temperatures for combustible mixtures under various conditions by means of an algebraic method, then to predict the LFLs of oxygenated fuels (methanol, ethanol, methyl formate and dimethyl ether) using adiabatic flame temperatures at pressures from 1 to 100 bar and temperatures from ambient to 1000 K. Furthermore, the influence of high temperatures and pressures on the LFLs for oxygenated fuel-air mixtures is also investigated in this work.

2. Methods

2.1. LFL prediction method

The flammability limit can be estimated as a function of the calculated adiabatic flame temperature (CAFT). According to Shebeko et al. (2002), the flammability limit is associated with a certain critical reaction temperature, which can be assumed to be equivalent to the adiabatic flame temperature at the LFL composition. The adiabatic flame temperature is the maximum temperature achieved due to combustion when the fuel composition is equal to the LFL. The CAFT approach is applied by assuming no heat losses, and that the mixture has reached chemical equilibrium. In addition, it is assumed that the combustion process occurs at constant pressure, and that the initial and final enthalpies remain constant. The methodology was described by Vidal et al. (2006), and the mathematical formula for the LFL can be represented as:

$$LFL = \frac{100}{1 + \nu_{a0}} \tag{1}$$

where ν_{a0} is the number of moles of air per mole of fuel in the mixture at the lower flammability limit. The approach is based on the premise that the LFL is primarily thermal in behavior and not highly dependent on kinetics (Crowl, 2003). Based on these assumptions, the energy balance is given by Eq. (2). For oxygenated fuel-air combustion, the final reaction temperature can be determined from thermal balance.

$$\sum_i H_{R,i}(T_i, P) = \sum_j H_{P,j}(T_{ad}, P) \tag{2}$$

where $H_{R,i}$ is the absolute enthalpy of the reactant and H_{Pj} is the absolute enthalpy of the product; T_i and T_{ad} are the initial temperature and the adiabatic flame temperature. Methanol, ethanol, methyl formate and dimethyl ether are considered as reactants in the combustion. The products are composed of CO, CO_2, H_2O(v), N_2, O_2, H_2, NO, OH, O, H and N. The absolute enthalpy and the enthalpy of formation are related as follows:

$$H(T, P) = \Delta H_f(T_i, P) + \overline{C}_P(T - T_i) \tag{3}$$

where $\overline{C}_P$ is the average constant pressure heat capacity from initial temperature to the final temperature. For oxygenated fuel$C_nH_mO_l$, the enthalpy of formation can be obtained from Eq. (4).

$$\Delta H_f(T_i, P) = \Delta H_f(T_o, P) + \left\{ \overline{C}_P[C_nH_mO_l] - n\overline{C}_P[C] - \frac{m}{2}\overline{C}_P[H_2] - \frac{l}{2}\overline{C}_P[O_2] \right\}(T_i - T_o) \tag{4}$$

where T_o is the reference temperature. The adiabatic flame temperature can be determined by Eq. (2) using a computer code, and the equilibrium compositions of the combustion products can be obtained by a minimization of the overall Gibbs free energy (Melhem, 1997). It should be pointed out that an iterative procedure is applied to these calculations by the compiled programs. When the adiabatic flame temperature under various initial conditions is determined, the LFL can be predicted by Eq. (1).

For real gases, the thermodynamic parameters should be determined as a function of temperature and pressure. However, the properties are cumbersome to measure, and rare data at high temperature and pressure can be obtained from database, including heat capacity, entropy, enthalpy, Gibbs free energy, etc. Therefore, the thermodynamic parameters should be estimated, especially reasonable values for heat capacity and enthalpy under elevated temperatures and pressures.

2.2. Thermodynamic model

2.2.1. Heat capacity

Some methods have been presented for estimating the heat capacity of real gas. The Lee-Kesler method (Poling et al., 2001) was used to predict heat capacity by the corresponding states principle and the graph or data sheet was applied as an assistant tool. The virial equation of state was applied to single-phase gas systems to estimate the thermodynamic parameters. Some values of the virial coefficients for linear 1- alkanols and alkyl ethers were reported by Tsonopoulos and Dymond (1997), but uncertainties in virial coefficients could affect the results. The Peng-Robinson (PR) cubic equation of state was applied to determine the thermodynamic properties for real gas by Poling et al. (2001), the departure function is represented as,

$$\frac{C_P}{R} = \frac{C_P^{ig}}{R} - 1 - \frac{T}{R}\int_V^{\infty}\left[\left(\frac{\partial^2 P}{\partial T^2}\right)_V\right]_T dV - \frac{T}{R}\left(\frac{\partial P}{\partial T}\right)_V^2 \Bigg/ \left(\frac{\partial P}{\partial V}\right)_T \tag{5}$$

where, C_P and C_P^{ig} are the constant pressure heat capacity of real gas and ideal gas respectively.

Smith et al. (2001) provided a general form of a cubic equation of state to illustrate the pressure-volume-temperature relationships for pure gases,

$$p = \frac{RT}{V - b} - \frac{a(T)}{(V + \varepsilon b) + (V + \delta b)} \tag{6}$$

The parameters vary with type of equation of state. For the PR cubic equation of state, $\varepsilon = 1 - \sqrt{2}$ and$\delta = 1 + \sqrt{2}$,

$$a(T) = 0.45724\alpha(T_r)R^2T_c^2 \Big/ P_c \tag{7}$$

$$b = 0.07779RT_c/P_c \tag{8}$$

whereP_c and T_c are the critical pressure and temperature respectively, $\alpha(T_r)$ is found from the following Eqs. (9) and (10),

$$\alpha(T_r) = \left[1 + m\left(1 - T_r^{1/2}\right)\right]^2 \tag{9}$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{10}$$

where $T_r = T/T_c$ is the reduced temperature andω is the acentric factor. The heat capacities of a real gas at different pressures and temperatures can be obtained through the PR cubic equation of state using the computer program in this work. The values of P_c, T_c and ω for different gases are taken from chemical and physics database (Lide, 2009).

In our previous work, we determined the constant pressure heat capacities (C_P) of gases at elevated conditions by the departure