Calculated Non-Adiabatic Flame Temperature Model: Prediction of Lower Flammability Limits of Hydrogen Mixtures

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1. Introduction

The lower flammability limit (LFL) of hydrogen is of considerable interest in the nuclear industry because of the potential hydrogen risk as a consequence of severe accidents [1]. Although many experimental studies have been conducted to determine LFL of various mixtures extensively, it is still difficult to identify the limits of all possible mixture conditions under a nuclear reactor severe accident. For this reason, a theoretical model for predicting LFL is needed to evaluate the hydrogen risk according to mixture conditions such as mixture compositions and different initial temperatures.

Through numerous studies, it was found that the calculated adiabatic flame temperature (CAFT) remains nearly constant regardless of the properties of limiting mixtures if fuel type is the same. However, this concept exhibits limited accuracy depending on the mixture condition. The limitation of the CAFT model deviates from the assumption on an adiabatic condition, whereas the heat loss mechanism suppresses the flame propagation in actual condition. Without considering the mechanism, underestimation of LFL occurred for some hydrogen mixtures.

Therefore, the objective of this study is to develop the calculated non-adiabatic flame temperature (CNAFT) model, which relaxes the assumption of adiabatic condition. The model facilitating prediction of the LFL of hydrogen mixtures assumes combustion in a non-adiabatic condition considering heat loss due to the radiative heat transfer. It is because the radiative heat transfer dominantly determines the total amount of the heat loss from reaction zone to environment. It is assumed that, if fuel type is the same, the CNAFT would remain constant regardless of the property of limiting mixtures.

2. Modeling

2.1 Radiative heat loss during flame propagation

The essential heat loss mechanisms considered to predict flammability limits are the convective and radiative heat transfer from the flame to the environment [2]. For continuous flame propagation, these heat losses as well as the heat supplied to the unburned gas must be satisfied through the reaction heat. However, convective heat loss can be ignored if the tube diameter is larger than a certain value. The radiative heat loss was considered dominant in the energy balance of the flame front [3].

The effects of radiative heat loss from the flame to the ambient environment can be classified as conduction of heat into the post-reaction zone, which is cooled via radiative heat loss $q_{rad,1}$ and radiative heat loss from the reaction zone itself, $q_{rad,2}$. First, it should be noted that heat conduction into the post-reaction zone is caused by the temperature gradient near the end of the reaction zone. In steady-state one-dimensional laminar flame propagation, the temperature distribution in the post-reaction zone can be defined as in **Equation (1),** where R is the radiative volumetric heat loss. Mayer noted that the transport term on the left of **Equation (1)** is much greater than the diffusion term over the range of mass flow rates in typical flame propagation [2]. Therefore, a peak temperature gradient under the influence of heat losses can be solved with the radiative heat loss as shown in **Equation (2)**. Finally, the heat loss rate from the reaction zone per unit area of the flame front due to conduction into the cooling post-reaction zone can be calculated using **Equation (3)**. The equation consists of several variables determined by the mixture properties. The thermal conductivity value used is the one at the flame front, while the density and specific heat are those of the unburned gas.

Second, the radiative heat loss rate from the reaction zone itself is calculated via integration, as shown in **Equation (4)**. Where R_r is the space-averaged radiative heat loss rate. However, Lakshmisha et al. proved that the fraction of $q_{rad,2}$ was very small compared to heat release rate for near lean flame. They numerically solved the equations for premixed flames considering detailed chemistry and variable properties [4]. As a result, most of the heat loss needed for calculating the peak temperature can be estimated only by considering the conduction of heat into the post-reaction zone, which is cooled via radiative heat loss $q_{rad,1}$.

$$\rho_u c_p S_u \frac{dT}{dx} - \frac{d}{dx} k \frac{dT}{dx} = -R(T) \tag{1}$$

$$\left(\frac{dT}{dx}\right)_{x=x_f} = -\frac{R(T_f)}{\rho_u c_p S_u(T_f)} \tag{2}$$

$$q_{rad,1} = -k_f \left(\frac{dT}{dx}\right)_{x=x_f} = k_f \frac{R(T_f)}{\rho_u c_p S_u(T_f)} \tag{3}$$

$$q_{rad,2} = \int_0^\delta R_r dx \tag{4}$$

2.2 CNAFT coefficient

As shown in **Equation (5)**, the magnitude of the radiative heat loss rate can be determined using the thermal diffusivity, flame speed, and volumetric heat loss rate. The laminar flame speed of the limiting mixtures is independent of the mixture properties and its finite value can be calculated from the results presented by Davies and Taylor [5]. Their observations were derived from experimental results, which proved that an upward propagating flame at the limit of flammability has properties in common with a rising Taylor bubble of hot gas [6]. On the other hand, according to a previously proposed optically thin radiation model, volumetric heat loss rate is determined by the threshold peak temperature and the presence of radiating species [3]. Because the threshold peak temperatures of the limiting mixtures were assumed to be invariable, the volumetric heat loss rate was considered to be constant with the exception of mixtures containing the radiating species. Consequently, it was experimentally and theoretically suggested that radiative heat loss rate $q_{rad,1}$ can be determined using a linear function of thermal diffusivity.

Henceforth we determined that the amount of heat loss rate during flame propagation can be estimated through the radiative heat loss rate $q_{rad,1}$. Therefore, in this study, **Equation (6)** is proposed to calculate the value of CNAFT to build an LFL prediction model considering radiative heat transfer. This equation assumes combustion in a non-adiabatic condition while considering heat loss due to radiative heat transfer. Thermal diffusivity is divided by the molar concentration C to predict heat loss in mole units. This parameter was defined as a CNAFT coefficient, π, which can be calculated as the mean value of the physical properties of each gas component of the mixture.

$$q_{rad,1} = k_f \frac{R(T_f)}{\rho_u c_p S_u(T_f)} = \frac{\alpha R(T_f)}{S_u(T_f)} \sim \alpha \qquad (5)$$

$$\sum n_i [\Delta H_{f,i}^0]_{reactants}$$
$$- \sum n_i [\Delta H_{f,i}^0 + \bar{c}_{p,i}(T_{CNAFT} - T_{ref})]_{products} = Q_{rad,1} \sim \alpha/C \quad (6)$$

The mechanistically derived **Equation (5)**, which considers that radiative heat loss and the linearly proportional CNAFT coefficient, was validated using the experimental results by Terpstra [3]. To validate this linearity, a constant CNAFT for hydrogen mixtures was required, and this temperature was selected to be the CAFT for the H₂-air mixture at 20 °C. Because a smaller coefficient indicates a lower amount of radiative heat loss, the difference between the CAFT and CNAFT would be the smallest of the mixtures. Thus, the heat loss magnitude of each mixture was inversely estimated based on a CNAFT of 581 K using **Equation (6)**. The thermal conductivity used for calculating the coefficient was also substituted with a corresponding value at this temperature. **Figure 1** shows the calculated radiative heat loss for each mixture based on their initial mole

number before the reaction. The amount of heat loss not being applied to the standard H₂-air mixture at 20 °C increases with the coefficient. A proportional relationship between the two variables was confirmed as shown in **Equation (7)**, which indicates that both variables have a strong linear relationship.

A mixture having a high coefficient requires more combustion heat to compensate for its higher radiative heat loss than other mixtures. Given that the heat generated by combustion of a near lean H₂-air mixture is 11.38 kJ/mole, this difference in the amount of heat loss must be considered.

$$Q_{rad,1}(\pi) = 0.246(\pi - \pi_{air,20°C}), \pi = \frac{\alpha}{C}[10^3 \cdot \frac{cm^5}{mol \cdot sec}] \qquad (7)$$
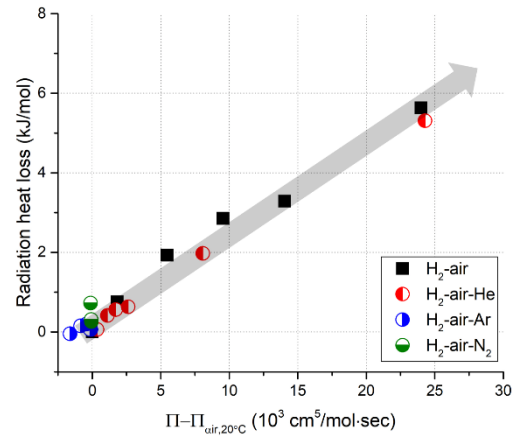

Figure 1. Linear relationship between the CNAFT coefficient and radiative heat loss.

2.3 Consideration of steam effect

Unlike other diluents in Figure 1, the steam classified as the radiating species causes the radiative heat loss of the gas itself. This steam effect should be considered because hydrogen mixtures generated during the accident usually has high steam concentration. If the amount of heat loss of H₂-ar-steam during flame propagation is not properly predicted, the value of LFL can be underestimated. The effect can be explained by the optically thin approximation. Since the flame thickness at the flammability limits was very small, the assumption of optically thin conditions is justified by referring to the Hottel's charts. Therefore, the volumetric radiative heat loss can be calculated by **Equation (8)** [7]. Where σ is the Stefan-Boltzmann constant, T_0 is the ambient temperature, p_{steam} is the partial pressure of steam and a_{steam} is the Planck's mean absorption coefficient of steam. It should be noted that, in the case of a mixture containing steam, the volumetric rate increases proportionally as the partial pressure of steam increases. In other words, the volumetric rate cannot be assumed to be constant as in a mixture without steam. Therefore, the total amount of radiative heat loss during flame propagation of a mixture with steam under isobaric condition can be estimated by **Equation (9)**. The value of steam concentration at the flame front during

propagation $X_{steam,flame\ front}$ according to the mixture conditions is necessary for the calculation.

The reference concentration $X_{steam,ref}$ is the steam concentration at the flame front during flame propagation in mixtures without steam. Even if there is no steam in the initial mixture, steam can be produced through the combustion process As with mixtures that initially contain steam, the steam concentration at flame front is one of the parameters to determine the amount of radiative heat loss in mixtures without steam. However, it was deduced that the variation of the steam concentration was negligible in other diluent types by confirming the proportional relationship between the CNAFT coefficient and the amount of heat loss. It is because the difference of initial hydrogen concentration between the limiting mixtures is sufficiently.

$$R = 4\sigma(T_f^4 - T_0^4)p_{steam}a_{steam} \qquad (8)$$

$$Q_{rad,1}(\pi) = 0.246(\pi - \pi_{air,20°C}) \cdot \frac{X_{steam,flame\ front}}{X_{steam,ref}} \qquad (9)$$

A detailed mechanism of elementary reactions involving hydrogen combustion can provide reasonable predictions of steam concentration during flame propagation. Fernandez-Gasliteo showed, for hydrogen-air mixtures that are very fuel lean, the 7-steps shown in **Table 1** suffice to describe accurately progress of combustion. All chemical intermediates are small enough to assume a steady state approximation, while the main reactants obey the overall irreversible reaction $2H_2 + O_2 \rightarrow 2H_2O$. This small concentration of radical causes the direct recombination reactions to become very slow compared with reaction 4f. For this reason, the 7-steps including three reversible shuffle reactions 1-3 and the irreversible recombination 4f can accurately predict the variation of the steam concentration during combustion process [2].

Figure 2 shows the verification of our computation by a typical time history obtained ignition above crossover temperature for a stoichiometric H$_2$-air mixture with San Diego mechanism obtained from Ref. [8]. It was identified that the 7-step chemistry provide a sufficiently accurate results in the temporal evolution of hydrogen mole fraction. Although the temperature change shows a slight difference, it is clear that this difference will be further reduced in lean conditions. It means that the steam concentration at flame front during propagation of hydrogen lean flame can be predicted by this simplified chemistry.

As a result, **Figure 3** shows the temporal evolution of hydrogen and steam concentration for each limiting mixture during homogenous ignition above crossover temperature. When the steam concentration is zero, the LFL is 3.9% and it burns completely in a very short time. This complete combustion in the hydrogen lean condition without steam was identified not only in this homogeneous ignition simulation, but also in a computation of steady planar deflagration obtained with

COSILAB code [9]. In the case of the limiting mixture with a steam concentration of 20%, the initial hydrogen concentration 5.31% is also completely burned. This aspect is equally founded in the other two cases, and the steam concentration after ignition is very close to the sum of initial hydrogen and steam concentration. In conclusion, the calculation of steam concentration during flame propagation under each limiting mixture condition can be substituted by a complete combustion approach.

Table 1. 7-step mechanism with Arrhenius form [8]

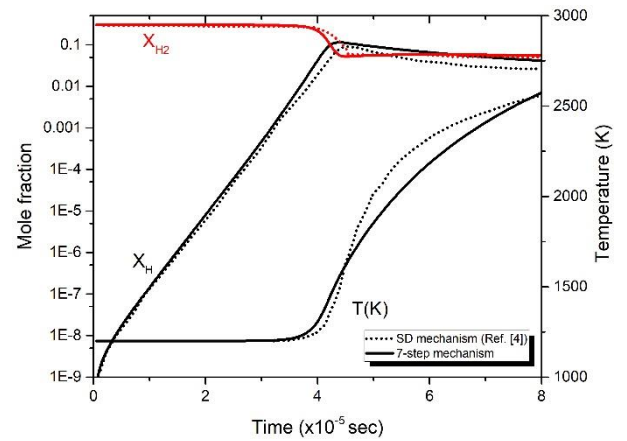| Reaction		A^a	n	$T_a[K]$
1. $H + O_2 \leftrightarrow OH + O$		3.52e+16	-0.7	8590
2. $H_2 + O \leftrightarrow OH + H$		5.06e+04	2.67	3166
3. $H_2 + OH \leftrightarrow H_2O + H$		1.17e+09	1.3	1829
4f. $H + O_2 + M \rightarrow HO_2 + M^*$	k_0	5.75e+19	-1.4	0
	k_α	4.65e+12	0.44	0
5f. $HO_2 + H \rightarrow OH + OH$		7.08e+13	0	148
6f. $HO_2 + H \rightarrow H_2 + O_2$		1.66e+13	0	414
7f. $HO_2 + OH \rightarrow HO_2 + O_2$		2.89e+13	0	-250

Figure 2. Code validation for 7-step mechanism in at constant adiabatic pressure and T_i=1200K
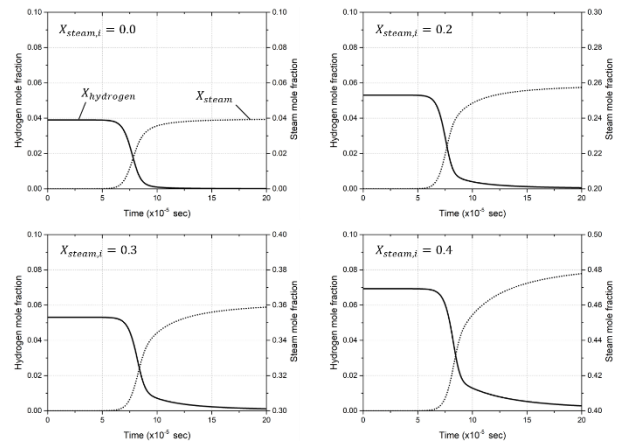

Figure 3. Temporal evolution of mole fraction for each limiting H2-air-steam mixture with 7-step mechanism

In conclusion, the CNAFT coefficient can be used to estimate radiative heat transfer based on mixture properties. Variables such as initial temperature, diluent type, and diluent composition ratio affect these mixture properties. By knowing the thermal diffusivity of a mixture for which the LFL is not known experimentally, the amount of heat loss in the CNAFT model can be estimated. Finally, the hydrogen concentration at which the CNAFT reaches 581 K considering the estimated heat loss is the LFL value predicted by the CNAFT model.

3. Results and Discussion

As a result, the amount of total radiative heat loss for the H_2-air-steam mixtures for CNAFT model can be finally calculated by **Equation (10)**. By the knowing initial condition of a mixture for which the LFL is not known experimentally including CNAFT coefficient and initial mole fraction, the amount of heat loss in the CNAFT model can be estimated.

The reference steam concentration, which was neglected to predict the heat loss of mixtures without steam, was determined by sensitivity analysis. Because the mixtures without steam produce steam concentration at flame front as hydrogen combustion proceeds, the reference concentration will be in the range of 3-6% for limiting mixtures. Therefore, the sensitivity analysis was performed to obtain the optimum value of reference concentration in the CNAFT model based on the range. It was confirmed that the average prediction accuracy was the highest when the reference concentration was set to 5%. Although this approach for averaged reference temperature may cause non-negligible errors, this empirical derivation was considered to essential for predicting the LFL in a H_2-air-steam mixture.

Finally, the hydrogen concentration at which the CNAFT reaches 581 K considering the estimated heat loss is the LFL value predicted by the CNAFT model.

$$Q_{rad,1}(\pi) = 0.246\big(\pi - \pi_{air,20°C}\big) \cdot \frac{X_{H_2,in} + X_{steam,in}}{X_{steam,ref}} \qquad (10)$$

Figure 4 shows the accuracy of the CNAFT model based on various upward flame propagation experiments. These mixtures have various initial conditions such as the type of diluent, diluent concentration and initial temperature. The range of initial temperature is from room temperature up to 300 °C. In conclusion, the model shows good agreement with experimental results regardless of the initial conditions. The relative error between the predicted values and experimental results does not exceed 13 % with the exception of the H_2-air-He mixture tested by Kumar (He: 40 vol%, T_i: 100 °C). This error occurs because the CNAFT coefficient is very high compared to other mixtures because the helium concentration and the initial temperature are high at the same time.
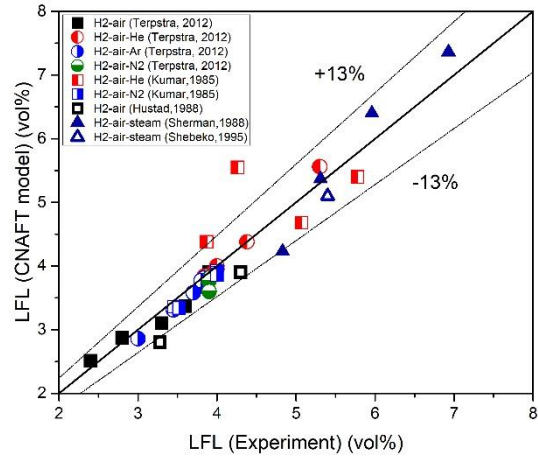

Figure 4. Prediction of the LFL using the CNAFT model

4. Conclusions

In this study, a CNAFT model was developed to predict the LFL of hydrogen mixtures based on the heat transfer mechanisms during laminar flame propagation. Agreement with experimental results on H_2-air-diluent mixtures was identified to be reasonable. We confirmed that considering radiative heat loss is essential for estimating the peak flame temperature for various mixture conditions. Since the CNAFT model can predict the LFL of the H_2-air-steam mixtures, we expect this model can be used for prediction of flammability in severe accident analysis.

ACKNOWLEDGEMENT

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