



Original Article

Improved prediction model for H₂/CO combustion risk using a calculated non-adiabatic flame temperature modelYeon Soo Kim ^a, Joongoo Jeon ^a, Chang Hyun Song ^a, Sung Joong Kim ^{a, b, *}^a Department of Nuclear Engineering, Hanyang University, Republic of Korea^b Institute of Nano Science & Technology, Hanyang University 222 Wangsimni-ro, Seongdong-gu, Seoul, 04763, Republic of Korea

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ABSTRACT

During severe nuclear power plant (NPP) accidents, a H₂/CO mixture can be generated in the reactor pressure vessel by core degradation and in the containment as well by molten corium-concrete interaction. In spite of its importance, a state-of-the-art methodology predicting H₂/CO combustion risk relies predominantly on empirical correlations. It is therefore necessary to develop a proper methodology for flammability evaluation of H₂/CO mixtures at ex-vessel phases characterized by three factors: CO concentration, high temperature, and diluents. The developed methodology adopted Le Chatelier's law and a calculated non-adiabatic flame temperature model. The methodology allows the consideration of the individual effect of the heat transfer characteristics of hydrogen and carbon monoxide on low flammability limit prediction. The accuracy of the developed model was verified using experimental data relevant to ex-vessel phase conditions. With the developed model, the prediction accuracy was improved substantially such that the maximum relative prediction error was approximately 25% while the existing methodology showed a 76% error. The developed methodology is expected to be applicable for flammability evaluation in chemical as well as NPP industries.

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1. Introduction

According to the International Atomic Energy Agency (IAEA) classification, a severe accident (SA) in a nuclear power plant (NPP) is defined as a potential accident involving fuel damage and consequential core meltdown [1]. When the SA occurs in conventional light water reactors (LWRs), fuel claddings made of zirconium alloy in uncovered regions react with high temperature steam. This reaction is accompanied by violent exothermic heat and hydrogen generation in the reactor pressure vessel (RPV). Because hydrogen gas is very diffusive, it can spread out quickly through the containment building. Under this circumstance, if the hydrogen is ignited by a potential ignition source, a dynamic pressure and

thermal load caused by the combustion may threaten the containment structural integrity [2].

Because the containment building is the last barrier preventing the release of radioactive material, reducing the hydrogen combustion risk is deemed an important safety precaution to cope with the SAs in NPPs. The Fukushima Daiichi NPP accident in 2011 already showed that the hydrogen combustion risk is no longer a hypothetical issue in nuclear safety. Many regulations and research studies on hydrogen combustion risk have been conducted actively. On the other hand, if the RPV fails so that the accident progresses to the ex-vessel phase, carbon monoxide and hydrogen are generated in the containment cavity through molten corium-concrete interaction (MCCI). Carbon monoxide is also a flammable gas, which raises the combustion risk when coexisting with hydrogen [3].

However, most of the previous studies and regulations have mainly focused on the hydrogen risk and paid relatively less attention to the risk posed by carbon monoxide. The Organization for Economic Cooperation and Development (OECD) highlighted the effect of carbon monoxide and noted that the H₂/CO mixture should be considered in accident scenarios involving ex-vessel phenomena [4]. Recently, the Institut de Radioprotection et de Surete Nucleaire (IRSN) in France announced a plan to develop a

Abbreviations: CAFT Calculated Adiabatic Flame Temperature, CNAFT Calculated Non-Adiabatic Flame Temperature; CFD Computational Fluid Dynamics, LFL Lower Flammability Limit; MCCI Molten Corium-Concrete Interaction, NPP Nuclear Power Plant; OPR1000 Optimized Power Reactor 1000, RPV Reactor Pressure Vessel; SA Severe Accident, SBO Station Black-Out; UFL Upper Flammability Limit, ISO International Standard Organization.

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Nomenclature

C	Molar concentration (mol/m^3)
\bar{c}_p	Average heat capacity at constant pressure ($\text{J}/\text{mol}\cdot\text{K}$)
D	Number of diluents in the gas mixture
E_a	Activation energy (J/mol)
ΔH_f^0	Standard formation enthalpy (J/mol)
H	Released enthalpy of the mixture (J)
i	Gas species in the gas mixture
j	Flammable gas species in the gas mixture
k	Inert gas species in the gas mixture
L	Flammability limit (vol%)
LFL	Lower flammability limit (vol%)
M	Number of gas species in the gas mixture
N	Number of fuels in the gas mixture
N_e	Nitrogen equivalency coefficient
n	Converted mole number $n_i = n_i / \sum_{\text{reactants}} n_i$ (mole)
p_i	Perturbation coefficient

$Q_{rad,1}$	Volumetric heat loss (J)
R	Gas constant ($8.314 \text{ J}/\text{mol}\cdot\text{K}$)
T_{CAFT}	Calculated adiabatic flame temperature (K)
$T_{CAFT,threshold}$	Threshold calculated adiabatic flame temperature (K)
T_f	Peak flame temperature (K)
$T_{f,threshold}$	Threshold peak flame temperature (K)
T_o	Initial temperature of gas mixture (K)
T_{ref}	Reference temperature (298 K)
UFL	Upper flammability limit (vol%)
\dot{w}	Reaction rate ($\text{kg}/\text{m}^3\cdot\text{s}$)
X	Gas concentration (vol%)
X_d	Concentration of diluent in gas mixture (vol%)
y_j	Volume fraction of flammable gas j in the multi-fuel

Greek letters

α	Thermal diffusivity (m^2/s)
π	CNAFT coefficient

methodology for combustion risk assessment of the H_2/CO mixture [5]. It is therefore clear that the combustion risk of the H_2/CO mixture needs to be considered as an imminent issue.

In general, the first step of the risk assessment methodology is flammability evaluation, which is conducted with a flammability limit [6]. The flammability limit is a limiting concentration of a flammable gas in a certain oxidizer, at which a flame can propagate. While a lower flammability limit (LFL) is a minimum concentration, an upper flammability limit (UFL) is a maximum concentration required for the flame to propagate. As the amount of combustible gas generated in NPP is limited, the LFL is mainly applied in flammability evaluation under SA [7–10].

The containment building at the ex-vessel accident phase is

characterized by three factors as shown in Fig. 1; the existence of carbon monoxide with hydrogen, high temperature, and diluents such as carbon dioxide and steam. As the LFL is as a function of these three factors, a methodology to estimate the LFL of the H_2/CO mixture diluted at a high temperature is required for the flammability evaluation at the ex-vessel accident phase. In the practical sense, several researchers tried to develop simple correlations to estimate the LFL of H_2/CO mixture based on their own experiments. However, the applicable range of the correlations is limited significantly [11–16].

Therefore, the theoretical model is required to calculate the LFL under various conditions. Numerous theoretical approaches have been proposed to explain the flame propagation and extinction phenomena in terms of thermal theory, chemical kinetics, and preferential diffusion etc. Table 1 shows the pros and cons of the representative models. The theoretical models including the effect of chemical kinetics determine the LFL as the concentration at the balance between chain-branching and chain-terminating reactions under thermodynamic conditions. It is possible to calculate the LFL according to temperature, pressure and fuel/oxidizer composition with great accuracy in the kinetic method [17]. However, the lumped parameter code such as MELCOR does not calculate the radical concentration [16]. Although it is possible to calculate the radical concentration with utilization of CFD calculation, SA involves various phenomena of combustion as well as MCCI, FCI, DCH, to mention a few. So the calculation time with CFD could be ineffective for such environment. Therefore, kinetic models are difficult to apply for SA analysis in terms of the calculation cost. In case of the model for the preferential diffusion, it is possible to explain the cellular flame structure of hydrogen mixture, which appears at propagation [18]. But, the effect of temperature is minimal so that it is not appropriate for the SA analysis as well [13]. For the applicability of the theoretical model to SA analysis, calculated adiabatic flame temperature (CAFT) model has been developed to estimate the flammability limit using energy balance on adiabatic assumption. CAFT model is known to be particularly suitable for LFL, where a thermally controlled behavior is dominant [19]. Kilchuk compared the measurement and prediction results using the CAFT model [20]. Because the model assumes an adiabatic condition, the prediction showed lower accuracy and conservative results especially for a specific mixture. Although the conservatism is basic philosophy in SA analysis, reasonable logic should be preceded when actuating

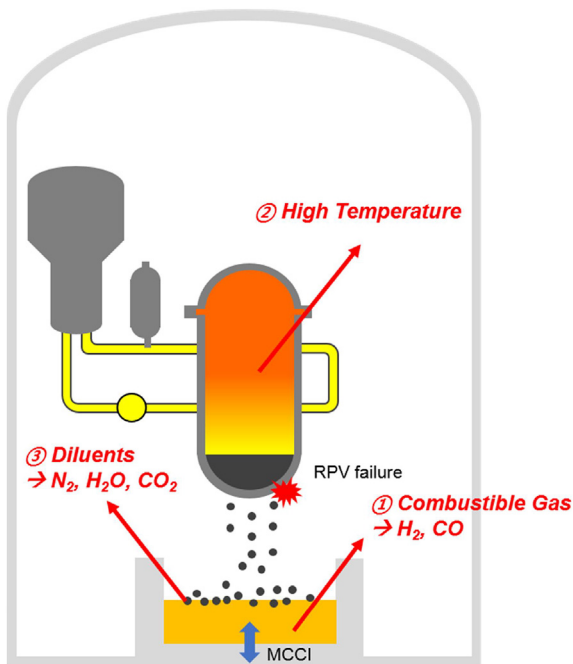


Fig. 1. Schematic view of containment building under SA involving ex-vessel phenomena.

Table 1
Comparison of the representative method based on theory about flame extinction.

	Consideration of thermodynamic condition	Accuracy of LFL prediction	Applicability for SA analysis
Thermal theory	High	Satisfactory	Possible
Chemical kinetics	High	High	Difficult
Preferential Diffusion	Low	Satisfactory	Difficult

mitigation strategy timely such as spray system [21,22].

Considering the foregoing discussion and state-of-the-art flammable gas combustion risk, the objective of this study is set to develop an improved methodology performing better accuracy for flammability evaluation of H₂/CO mixtures including heat loss under SA conditions. The developed methodology is based on Le Chatelier's law, which has been validated by many theoretical and experimental studies [13,15,23–27]. This law makes it possible to individually consider the heat transfer characteristics of hydrogen and carbon monoxide on the LFL prediction of H₂/CO mixtures. The method proposed and developed in this study incorporates the heat transfer mechanism of hydrogen through the recently developed calculated non-adiabatic flame temperature (CNAFT) model. Meanwhile, the combustion of carbon monoxide was treated with adiabatic assumption because carbon monoxide has lower heat diffusivity compared to hydrogen so that heat loss by conduction is negligible. To confirm the feasibility of the developed methodology, a principle used in other methodologies for H₂/CO mixtures was investigated. Finally, the LFL predicted by several methodologies including the proposed method was compared to the experimental results.

2. Development of the methodology

The flammability limit is a limit in the concentration of a flammable gas in a certain oxidizer where a flame can propagate. The flammability limit is a function of various factors such as fuel gas, temperature, pressure, gas composition, flame propagation direction, measuring system, ignition energy, buoyancy effect and residence time [11–14,20,23–26]. In the experimental aspect, it is determined in a rather simple and realistic condition such as oxidizer at a specific thermodynamic condition. The LFL is the minimum concentration for the flame propagation, while the UFL is the maximum. In other words, if the concentration of fuel gas satisfies Eq. (1), the combustion reaction occurs sustainably upon ignition.

$$LFL < X < UFL \quad (1)$$

The LFL is mainly applied in flammability evaluation under SA, because the amount of combustible gas generated in NPP is determined by the oxidation source of the in-core materials [7–10]. Additionally, as two flammable fuels coexist at the ex-vessel phase, the LFL of the binary fuel mixture, not the individual fuel, should be considered. Therefore, in this section, the existing methodologies to calculate the LFL of H₂/CO mixture are explained. Then a reliable methodology to improve the prediction accuracy is developed.

2.1. Le Chatelier's law

Le Chatelier suggested a law to predict the lower limit of the fuel mixture based on his own experiment [28]. The law is widely used to predict the flammability limit of fuel mixtures when the flammability limits and fractions of each fuel are known. The law has been recognized as a reliable prediction tool in many reports including OECD/NEA and ASTM reports, and even adopted in the MELCOR BUR package [4,16,29]. The numerical form of the law is

described as shown in Eq. (2), where L is the flammability limit, j is the flammable gas species, y_j is the fraction of the flammable species j in the gas mixture, and N is the number of flammable gases. With this law, the flammability limit of binary fuels can be calculated rather simply. The law was justified by many researchers through additional experiments [13,15,23–27]. Mashuga and Crowl proved the law in the thermodynamic aspect based on several assumptions described below [27].

$$\frac{1}{L_{mix}} = \sum_j^N \frac{y_j}{L_j} \quad (2)$$

- The heat capacities of the products are constant.
- The mole number of the gas is constant.
- The adiabatic temperature rise at the flammability limit is the same for all species.
- The combustion kinetics of the pure species is independent and unchanged by the presence of other combustion species.

Although the law was generally validated in many literature studies, its accuracy in the prediction of the UFL is relatively low [23]. Through the measured data, Kondo et al. indicated that the perturbation effect caused by fuel blend is not negligible in rich mixtures, contrary to the lean mixtures [15]. According to Wu et al. and Ma, when predicting the UFL of hydrocarbons, the consideration of chemical kinetics is imperative because it is difficult to estimate the combustion products owing to plausible incomplete combustion [30,31]. In addition, Vidal et al. and Bertolino et al. pointed out that the kinetics become more important for the UFL compositions while thermal behavior is more dominant for the LFL [19,26]. Wierzbka and Kilchuk suggested through their experimental data that radicals generated from hydrogen can contribute to the significant oxidation of carbon monoxide at UFL composition [24]. Likewise, the behavior in rich mixtures is against the last assumption of Mashuga and Crowl. Thus, it is unreasonable to apply Le Chatelier's law for the UFL. However, because the amount of combustible gas generated in NPP is determined by the oxidation source of the in-core materials, the LFL is mainly applied in flammability evaluation under SA [7–10]. Therefore, the main goal of the current study is to develop a reliable methodology to improve the prediction of the LFL of H₂/CO mixtures.

To estimate the LFL of the H₂/CO mixture, Le Chatelier's law shown in Eq. (2) was specified to Eq. (3). It is inferred that the LFL of each gas should be calculated accurately to evaluate the flammability of the H₂/CO binary mixture. Hong et al. also confirmed the applicability of Le Chatelier's law for the H₂/CO mixture based on the four facts described below [32].

- The combustion heat per mole of H₂ and CO is similar.
- H₂ and CO require 1 mol oxygen to oxidize 2 mol gas.
- H₂ and CO have similar combustion completeness including lean mixture after ignition.
- The flammability limit of the H₂/CO mixture is approximated by combining each LFL simply.

$$\frac{1}{L_{mix}} = \frac{y_{H_2}}{L_{H_2}} + \frac{y_{CO}}{L_{CO}} \quad (3)$$

2.2. State-of-the-art models

Several researchers tried to develop empirical correlations based on Le Chatelier's law [11–15]. The MELCOR code, which is used for nuclear regulation, includes a simple model for flammability evaluation. The MELCOR default model calculates the LFL of the H₂/CO fuel mixture through Le Chatelier's law as shown in Eq. (4), where y is the fraction of the flammable components in the mixture [16]. The LFL of each gas is determined experimentally under normal temperature and pressure conditions. On the other hand, Kondo et al. introduced a physical term based on measurements at 35 °C as shown in Eq. (5), where p_i is the coefficient of perturbation meaning the disturbance degree of combustion reaction owing to the other coexisting fuel gas [15]. Despite the additional consideration of the fuel blend effect, the perturbation term becomes nearly zero for the lean mixture. Kondo et al.'s correlation then becomes exactly similar to the MELCOR default model. However, because these methods consider the relative fraction of flammable gas only, the calculated LFL value is independent of initial temperature and diluents. Therefore, it needs to be improved to reflect SA conditions for practical application.

$$\frac{1}{LFL_{mix}} = \frac{y_{H_2}}{4.1} + \frac{y_{CO}}{12.5} \quad (4)$$

$$\frac{1}{LFL_{mix}} = \sum_j^N \frac{y_j}{LFL_j} [1 + p_j(1 - y_j)] \quad (5)$$

Hustad and Sønju modified Le Chatelier's law to estimate the LFL of the H₂/CO mixture with temperature dependent equations for each gas as shown in Eq. (6) [12]. Temperature dependent equations were devised separately through experiments for the upward propagation flame of each gas. As shown in the correlation, the term related to the dilution effect was not included. However, Hustad and Sønju's experiment was conducted with the gas mixture, including nitrogen as a diluent. Thus, the method partially considers the dilution effects.

$$\frac{1}{LFL_{mix}} = \frac{y_{H_2}}{5[1 - 0.00129(T_o - 25)]} + \frac{y_{CO}}{15[1 - 0.00095(T_o - 25)]} \quad (6)$$

Moreover, there are several methods that consider the dilution effects. Karim et al. suggested a correlation for the diluted binary fuel mixture by extending Le Chatelier's law through the experiment [11]. As described in Eq. (7), the diluents are treated as the combustible gas whose LFL is infinite. Although the dilution effect was included in the equation, the individual characteristics of each diluent were not considered. In addition, the applicable range is limited. For example, the concentration ratio of nitrogen to hydrogen should be less than 15:3. Schröder and Molnarne proposed a method with a wide applicable range [33], which was adopted for the ISO Standard 10,156 [34]. The method also considers the individual dilution capacities of the diluents in the gas mixture with the coefficient of nitrogen equivalency calculated by the measured data [33,35]. The coefficient of nitrogen equivalency was determined by scaling the non-nitrogen diluents equivalent to the nitrogen, whose dilution capacity is different from that of the nitrogen. The method is expressed as Eq. (8), where M is the

number of components in the gas mixture, j is the individual pure component in the gas mixture, and N_e is the coefficient of nitrogen equivalency [36]. However, because the coefficient was determined under normal temperature and pressure, it is inapplicable for the ex-vessel phase application because the temperature is not considered.

$$\frac{1}{LFL_{mix}} = \frac{y_{H_2}}{4.1} + \frac{y_{CO}}{12.5} + \frac{y_k}{\infty} \quad (7)$$

$$\frac{1}{LFL_{mix}} = \sum_i^M \frac{y_i}{LFL_i} - \sum_k^D (N_{e,k} - 1)y_k \quad (8)$$

There also exists a correlation considering more than two parameters simultaneously without adopting Le Chatelier's law. James determined the correlation as a function of initial temperature and pressure for specific H₂/CO fuel ratios as shown in Table 2 [13]. James's correlation is characterized by the pressure effect term unlike other methods. However, the gas mixture used in the experiment did not contain any diluents so that the correlation was inapplicable for assessing the dilution effect. In addition, the correlation was developed only for specific fuel ratios of the H₂/CO mixture. Because the gas composition in the containment building at the ex-vessel phase varies significantly, the correlation cannot be applicable for the SA analysis in the current study. Grune et al. developed the flammability criteria shown in Eq. (9) based on experimental data from the H₂/CO-air-H₂O/CO₂ mixture [14]. If the left-hand side term is larger than 4, the mixture can be classified as flammable. This criterion judges the flammability of the H₂/CO fuel mixture considering conditions with oxygen depletion as well. Although it can distinguish the flammability of the H₂/CO mixture, the LFL at various conditions could not be obtained owing to the lack of a test matrix. For this reason, it is insufficient for use in the SA analysis.

$$[X_{O_2} - 3] \cdot [(X_{H_2} + X_{CO}) - 10] > 4 \quad (9)$$

2.3. Development of methodology

Le Chatelier's law was originally developed for the mixture in pure air under normal temperature and pressure [11,12]. SA conditions include high temperature and high concentration of diluents, however, it requires additional modification [31,35,37]. Therefore, Eq. (3) was modified into Eq. (10) to account for the SA condition by introducing terms dependent on temperature and diluent concentration.

$$\frac{1}{LFL_{mix}(T_o, X_d)} = \frac{y_{H_2}}{LFL_{H_2}(T_o, X_d)} + \frac{y_{CO}}{LFL_{CO}(T_o, X_d)} \quad (10)$$

Based on the relevant observation and analysis, a consensus was reached that the effect of heat behavior during flame propagation is most dominant in determining the LFL [15,19,30,31]. The CAFT model was developed and is widely used to predict the LFL based on thermal theory. It predicts the LFL by mechanically estimating the peak flame temperature, assuming adiabatic condition (no heat loss) during flame propagation. The peak flame temperature T_f determines the chemical reaction rate \dot{w} as given in Eq. (11), the Arrhenius equation [38]. If the peak flame temperature is greater than a certain value called the threshold peak flame temperature $T_{f,threshold}$, it is inferred that the flame can propagate sustainably. Because estimating T_f and $T_{f,threshold}$ is challenging, however, adiabatic flame temperature T_{CAFT} and threshold adiabatic flame

Table 2
Jaimes's correlation for H₂/CO mixture as a function of temperature and pressure.

$LFL_{mix} = [a \cdot T + b] \cdot P + c \cdot T + d; T = [^{\circ}C], P = [bar]$				
H ₂ /CO	$a \times 10^4$	$b \times 10^1$	$c \times 10^3$	d
20/80	4.3714	1.6857	-12.14	10.282
40/60	-1.7143	1.5629	-6.7543	7.8609
60/40	0.28571	1.1429	-7.0457	6.4371

temperature $T_{CAFT,threshold}$ are used to determine the possibility of flame propagation instead. In developing the CAFT model, it was assumed that T_f and $T_{f,threshold}$ are proportional to T_{CAFT} and $T_{CAFT,threshold}$, respectively. Although each flammable gas has its own threshold adiabatic flame temperature, the value is constant regardless of the initial temperature and gas composition at the lean limit concentration [12,19,20,27,37,39–41]. Terpstra, Karim et al. and Hustad and Sønju determined the threshold value as the adiabatic flame temperature when the initial temperature of the fuel is room temperature [12,37,41]. They calculated $T_{CAFT,threshold}$ for hydrogen was 618–638 K while for carbon monoxide 1491–1583 K in the literature. In other words, the LFL is defined as the concentration of combustible gas, at which the adiabatic flame temperature becomes threshold temperature. Through this, the LFL of each gas can be calculated using the energy equation even when the mixture gas composition or initial temperature vary. Under a constant pressure condition, the LFL can be estimated through Eq. (12) in the CAFT model. Eq. (12) is also expressed in Eq. (13). According to literature, the CAFT model showed satisfactory accuracy for almost every fuel gas including carbon monoxide [34].

$$\dot{w} \sim \exp(-E_a/RT_f) \quad (11)$$

$$\left[\sum_i H_{i,react} \right]_{T_o} = \left[\sum_i H_{i,prod} \right]_{T_{CAFT}} \quad (12)$$

$$0 = \sum n_i \left[\bar{c}_{p,i} (T_o - T_{ref}) + \Delta H_{f,i}^0 \right]_{react} - \sum n_i \left[\bar{c}_{p,i} (T_{CAFT} - T_{ref}) + \Delta H_{f,i}^0 \right]_{prod} \quad (13)$$

However, because the CAFT model assumes an adiabatic condition, it bears critical limitations for specific mixture conditions. First, the accuracy of the CAFT model reduces for the mixture at a high temperature. This is because the model does not reflect the heat loss dominant at higher temperatures [42]. Second, the CAFT model also shows poor accuracy for the mixture containing radiating species as a diluent [43]. This is caused by radiative heat loss by the radiating species, which makes it more difficult for flame temperatures to reach the threshold value. Finally, the model also shows unsatisfactory accuracy in the determination of large heat diffusivity for the hydrogen mixture [37,39,40]. The gas mixture in the containment building under SA conditions not only maintains high temperature but also contains a significant fraction of steam and hydrogen. Because these conditions are far from adiabatic, an additional consideration should be made to increase the prediction accuracy.

To address the low prediction accuracy of the CAFT model, many researchers tried to improve the model by considering the heat loss mechanism. According to Mayer's study, three kinds of heat loss mechanisms are reported to occur as shown in Fig. 2; convective heat loss from the reaction zone to the cold wall, radiative heat loss from the reaction zone itself, and conductive heat loss into the post-reaction zone cooled by the radiative heat loss [42]. Liaw and Chen considered the radiative heat loss from the flame to the ambient

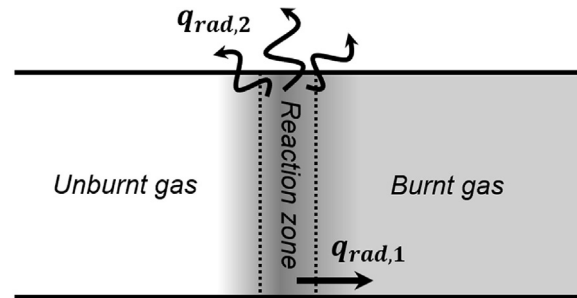


Fig. 2. Heat loss during flame propagation [39].

region in the CAFT model [39]. On the other hand, Zhao et al. introduced convective heat loss as well as radiative heat loss [26]. Although heat loss was included in the aforementioned studies, the calculated heat loss was negligible resulting in unsatisfactory accuracy as well. Shih, Ha et al. and Holborn and Battersby pointed out that the conductive heat loss from the reaction zone to the post-reaction zone should be considered as shown in Fig. 2 [44–46].

By considering the heat loss mechanism during flame propagation, Jeon et al. developed a CNAFT model which could predict the LFL of gas mixtures [40]. The model considered conductive heat loss through Eqs. (14) and (15). Using theoretical studies and computational verification [47], they found that the $Q_{rad,1}$ term in Eqs. (14) and (15) was strongly proportional to thermal diffusivity divided by molar concentration, defined as the CNAFT coefficient as shown in Eq. (16). The heat loss was estimated using the CNAFT coefficient so that the LFL of the gas mixture at high temperatures could be calculated with improved accuracy. They also confirmed that the CNAFT model could predict the LFL of hydrogen mixtures containing steam from the radiating species through the optically thin approximation of the thermal radiation rate. More details about the model can be found in Ref. [40,47]. It is noted that heat diffusivity of carbon monoxide is approximately 3.6 times smaller compared to hydrogen as summarized in Table 3. Heat diffusivity of fuel gas determines heat loss amount as shown in Eq. (16). It implies that the heat loss effect can be ignored in predicting the LFL of carbon monoxide mixtures. Fig. 3 compares the amount of radiative heat loss by hydrogen and carbon monoxide as a function of initial temperature. It is analyzed that the heat loss of carbon monoxide is relatively low compared to hydrogen especially at higher temperature. Therefore, LFL_{CO} was calculated based on adiabatic assumptions (CAFT model), while the LFL_{H_2} was predicted using the CNAFT model.

Table 3
Comparison of heat diffusivity for hydrogen and carbon monoxide as a function of temperature.

Temperature [K]	273	293	373	473	573	673
α_{H_2} [cm ² /s]	0.668	0.756	1.153	1.747	2.444	3.238
α_{CO} [cm ² /s]	–	0.208	0.315	0.475	0.662	0.875
α_{H_2}/α_{CO}	–	3.63	3.66	3.68	3.69	3.70

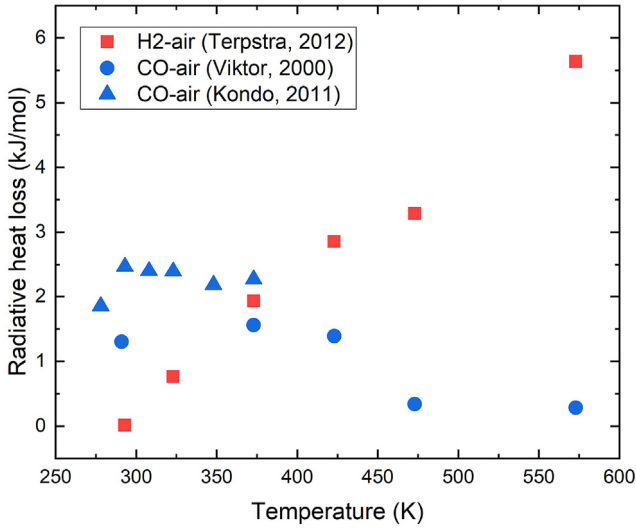


Fig. 3. Radiative heat loss according to the initial temperature and fuel gas.

$$\left[\sum_i H_{i,react} \right]_{T_0} = \left[\sum_i H_{i,prod} \right]_{T_f} + Q_{rad,1} \quad (14)$$

$$Q_{rad,1} = \sum n_i \left[\bar{c}_{p,i} (T_0 - T_{ref}) + \Delta H_{f,i}^0 \right]_{react} - \sum n_i \left[\bar{c}_{p,i} (T_f - T_{ref}) + \Delta H_{f,i}^0 \right]_{prod} \quad (15)$$

$$Q_{rad,1} \sim \frac{\alpha}{C} = \pi \quad (16)$$

In addition to the CNAFT model, the role of the heat loss mechanism was explained by investigating flame physics through elaborate numerical analysis. Zhou and Shoshin identified that hydrocarbons having a smaller diffusivity have a local minimum heat release rate at the flame tip, where their extinction starts. Thus, heat loss to the post reaction zone was no longer the main heat transfer mechanism [48]. These negligible heat loss effects on the LFL have been confirmed in several previous studies [37,39,49]. Similarly, Karim et al. insisted that carbon monoxide or methane is less affected by heat loss than hydrogen based on the analytically calculated dimensionless heat loss [37]. Liaw and Chen compared the previously measured LFL of flammable gas with the LFL calculated by the CAFT model [39]. In their calculation, almost all flammable gases including carbon monoxide showed an acceptable average deviation of about 0.22 vol% between the experiment and prediction results. However, the four times or larger average deviation between the prediction and measurement results was confirmed to be about 0.94 vol% especially for hydrogen mixtures. They insisted that the inhomogeneous distribution caused by the diffusion of low-density hydrogen at the flame front was the main reason for the large deviation. The diffusion effect of hydrogen on flame structures was also reported by Ma [31]. The effects of these flame structures are interesting topics worth investigating and require high-fidelity computational fluid dynamics (CFD) simulation. Therefore, it is left as a separate topic for future study.

In summary, the methodology to predict the LFL of the H₂/CO mixture at the ex-vessel phase was developed in this study. The ex-vessel phase includes three distinctive characteristics important for predicting the LFL as shown in Fig. 1: carbon monoxide, high temperature, and the diluent. Le Chatelier's law was applied to

include the effect of carbon monoxide in the binary fuel mixture. The LFL of each gas was estimated with energy balance assuming non-adiabatic conditions based on the peak flame temperature theory. The threshold temperature for hydrogen is adopted as 610 K considering heat loss [40] while the threshold temperature for carbon monoxide is adopted as 1491 K. Because the energy balance equation contains the temperature, heat capacity, and mole fraction terms of each gas species, the effect of the temperature and diluents can be considered in the methodology [50].

3. Verification and validation of the methodology

In the foregoing discussion, various correlations to predict the LFL of the H₂/CO mixture were investigated and their development background and major limitations were explained. The MELCOR default option and Hustad and Sønju's correlation applicable for SA conditions were selected among them and compared with the developed method. The LFL of the H₂/CO mixture predicted by each method is compared to the LFL predicted using the developed model for verification by each factor; y_{CO} , T_0 , and X_d . Through the comparison, the efficacy of the developed methodology is discussed hereafter.

Figs. 4–6 present the dependence of LFL on the CO fraction in the H₂/CO mixture in air under atmospheric pressure. For comparison, the initial conditions for the undiluted mixture were fixed at 100, 150 and 200 °C. Because the LFL of carbon monoxide is larger than hydrogen, the value of LFL for H₂/CO mixture increases with the increasing CO fraction in the mixture. The increasing trend appears clearly with the steep curve toward the end because all the methods adopted Le Chatelier's law. Predictions by the MELCOR code and Hustad and Sønju showed a larger LFL than the measured values in Figs. 4 and 5 with maximum relative errors of 33.2% and 40.9%, respectively. On the contrary, the prediction by the current model exhibits significant improvement by showing a maximum error of 9.23% relative to the measured data by Van den Schoor et al. A similar trend is observed in Fig. 5, where the LFL prediction by the current model agrees well with the measured LFL by Kilchuk. In Fig. 6, unlike the LFL data shown in Figs. 4 and 5 for 100 and 150 °C, respectively, the prediction by the current model for 200 °C shows relatively poor agreement with the LFL measured by Jaimes and Hustad and Sønju. Comparing with the LFL measured by Van den Schoor et al. however, the current model shows reasonable

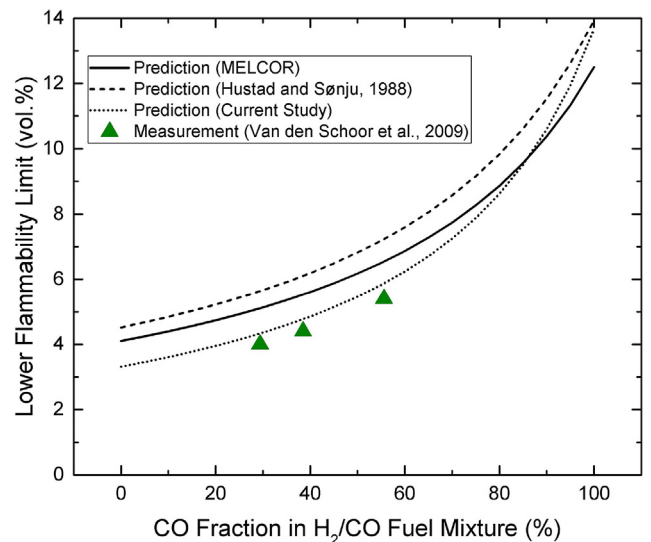


Fig. 4. LFL as a function of CO fraction in the H₂/CO mixture in air at 1 bar and 100 °C.

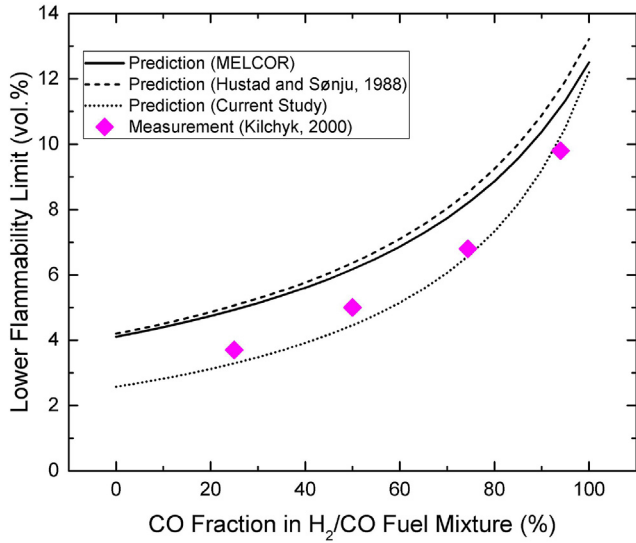


Fig. 5. LFL as a function of CO fraction in the H₂/CO mixture in air at 1 bar and 150 °C.

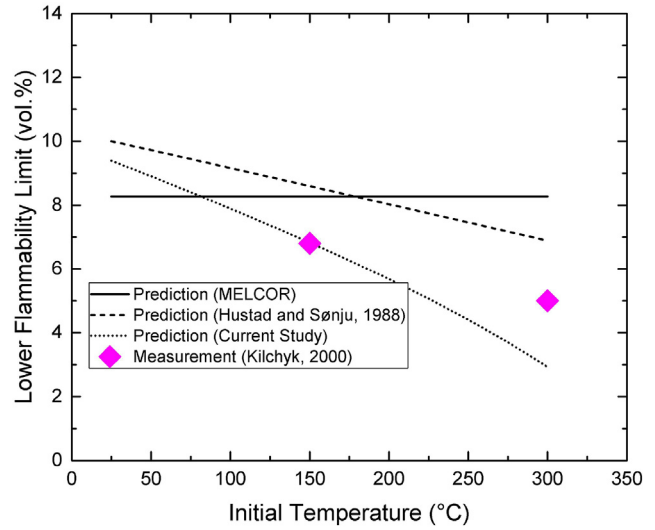


Fig. 7. LFL as a function of initial temperature in the H₂/CO mixture with y_{CO} of 70% in air at 1 bar.

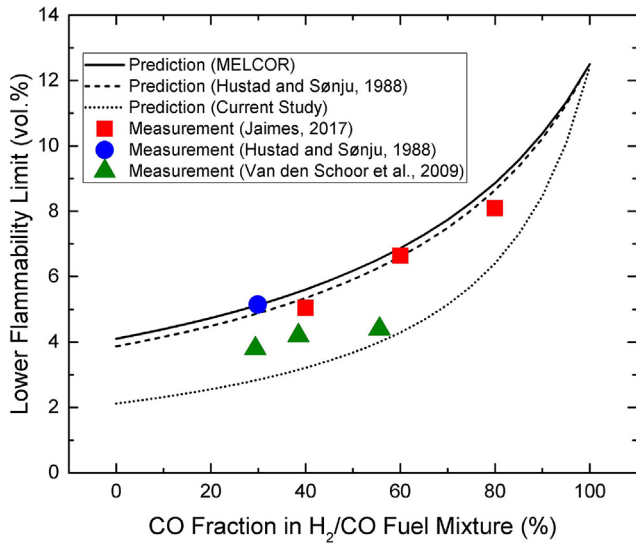


Fig. 6. LFL as a function of CO fraction in the H₂/CO mixture in air at 1 bar and 200 °C.

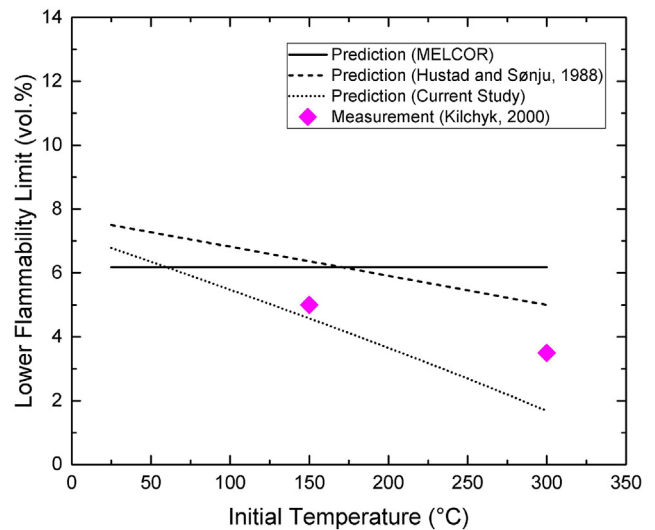


Fig. 8. LFL as a function of initial temperature in the H₂/CO mixture with a fuel ratio of 50:50 in air at 1 bar.

prediction accuracy compared to those of the MELCOR code and Hustad and Sønju's model.

It is inferred that these errors may be caused by the experimental procedures. There are two representative methods to determine the flammability limit experimentally. The first method uses flame visualization. When a flame propagates with a specific length in the test tube, the concentration of fuel gas is defined as the flammability limit. Hustad and Sønju, Kilchyk, and Van den Schoor et al. conducted the experiment with flame visualization. However, Hustad and Sønju defined the standard length as 1.8 m, while the others chose 1.0 m. Because the longer propagation length requires greater concentration, the current model underestimates the LFL compared to Hustad and Sønju's data. On the other hand, the second method measures the increase in pressure caused by combustion. Wang et al., Grune et al. and Jaimes determined the LFL by considering the increase in pressure. Wang et al. and Grune et al. obtained LFLs with 3% and 5% increase in pressure, respectively. However, Smedt et al. argued that the criterion involving a 7% increase in pressure is too high to measure the LFL

[51]. Because the gas mixture contains more fuel gas, the pressure loads increase when ignited. This is why the current model underestimates Jaimes's data.

Figs. 7 and 8 display the LFL as a function of initial temperature in the H₂/CO mixture in atmospheric pressure. The concentration ratio of carbon monoxide to hydrogen was fixed as 75:25 and 50:50. For direct comparison, the experimental value was selected only for the undiluted H₂/CO mixture. As presented in Figs. 7 and 8, the LFL decreases as the initial temperature increases. This is because less energy is required at a higher temperature to heat up the mixture up to the threshold temperature for flame propagation [41]. Hustad and Sønju's correlation and the current model effectively reflect the descending trends. Each maximum relative error between the measurement and prediction results was estimated to be 27.3% and 8.4% at 150 °C. Although the descending trend appears in Hustad and Sønju's correlation with increasing initial temperature, it shows a slight difference in the measurements. A more reasonable

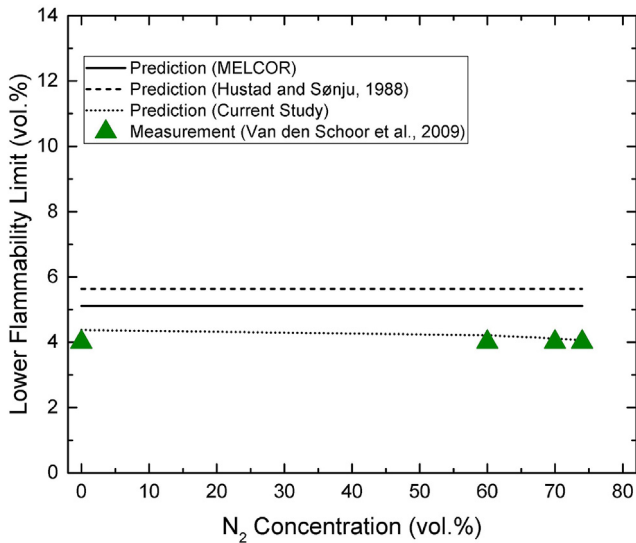


Fig. 9. LFL as a function of nitrogen concentration in the H₂/CO mixture with a fuel ratio of 70:30 in air at 1 bar.

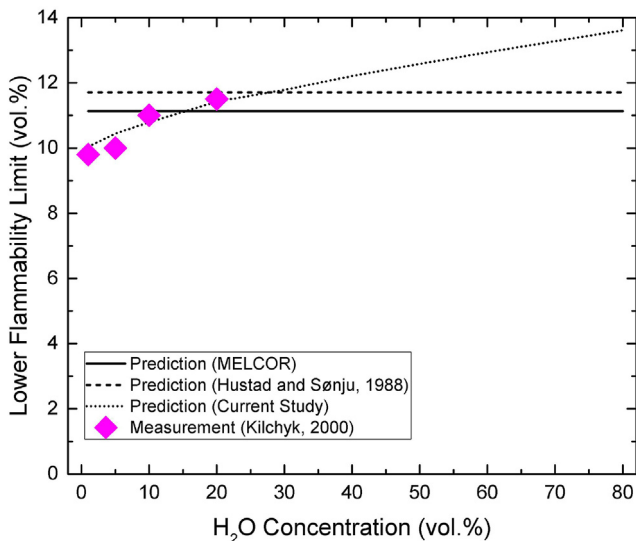


Fig. 10. LFL as a function of steam concentration in the H₂/CO mixture with a fuel ratio of 6:94 in air at 1 bar.

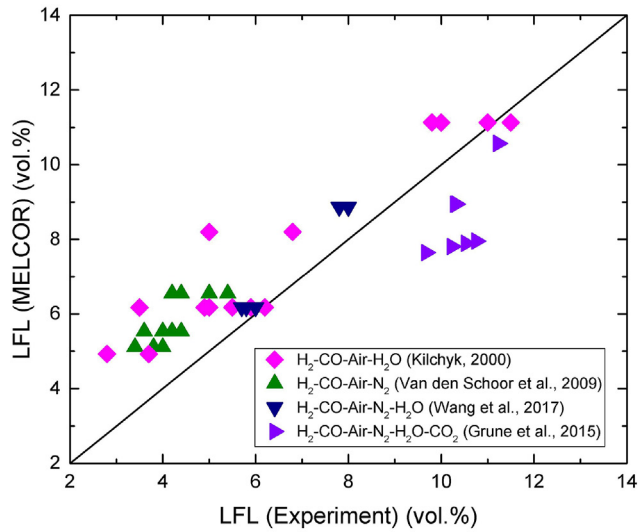
prediction was obtained when the developed methodology was applied. Meanwhile, the LFL predicted using the MELCOR code is at a constant value because the temperature effect was not implemented; this yielded a maximum error of 23.5%. Throughout the results, it is inferred that the MELCOR default model is unable to consider typical SA conditions. On the other hand, at 300 °C, all the prediction methods showed unsatisfactory agreement with the experimental data. However, it is unlikely that the SA condition will include temperature conditions greater than 173 °C, according to a MELCOR simulation under an unmitigated station black-out (SBO) scenario [52]. Thus, the current method is expected to be applicable for the SA analysis effectively.

At the ex-vessel phase, three kinds of diluents are likely to coexist in the containment building: nitrogen, steam, and carbon dioxide. Because the amount of experimental data for carbon dioxide are insufficient for comparison, the effects of steam and nitrogen are mainly discussed. Fig. 9 presents the LFL as a function of the nitrogen concentration in the H₂/CO mixture. If nitrogen is included in the gas mixture, it is treated as a diluent, which is distinguished from the nitrogen in air. For comparison, the experimental value was selected only for the H₂/CO-air-N₂ mixture. The concentration ratio of H₂ to CO is selected as 70:30 at 100 °C with a pressure of 1 bar. As shown in Fig. 9, the experimental value remains almost constant in spite of nitrogen addition. This could be caused by the similar heat capacities of air and nitrogen. The predicted LFL also shows an invariant trend in all three prediction methods. The prediction results by the MELCOR default option and Hustad and Sønju's correlation are reasonable because they do not include the dilution term. However, Hustad and Sønju developed a correlation based on their own experiment, which was conducted by including nitrogen as a diluent. Nevertheless, Hustad and Sønju's prediction showed an error of approximately 40.9% while the MELCOR prediction resulted in an error of 27.7% compared to the measured value. On the other hand, the current model predicted little change similar to that observed in case of the experimental value. It is inferred that the current model reflects the dilution effect properly by adding nitrogen to the H₂/CO mixture. In addition, the current model predicts the LFL with significantly improved accuracy within a maximum error of 9.23%.

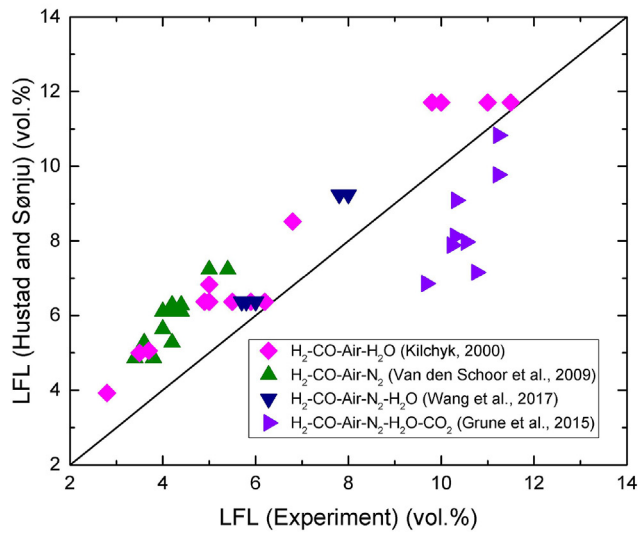
Fig. 10 compares the LFL with respect to the steam concentration in the gas mixture. The mixture condition was selected only for the H₂/CO-air-H₂O mixture at 150 °C and pressure at 1 bar. The concentration ratio of carbon monoxide to hydrogen was fixed at 94:6. As described in Fig. 10, the LFL of the H₂/CO mixture increases as steam is added to the mixture. Steam exhibits a larger heat capacity than air. Additionally, the heat loss of the steam is higher than that of nitrogen because steam is a radiating species. Owing to the participated heat loss, it is difficult to increase the flame temperature up to the threshold temperature. Thus, the LFL decreases with

Table 4
Summary of experimental information.

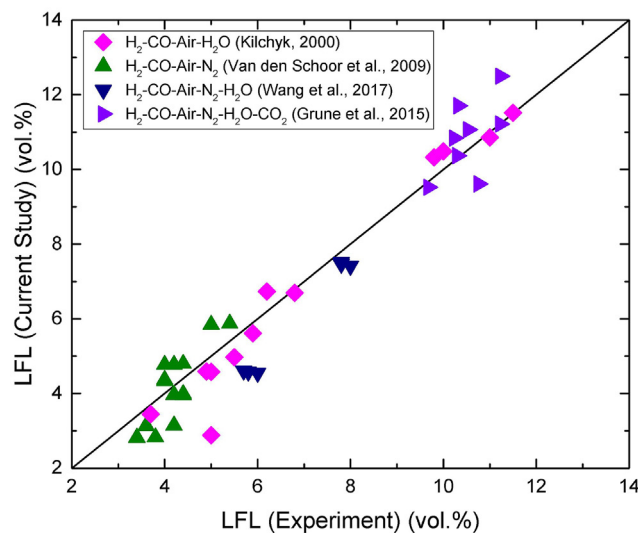
Researcher	Mixture	Y_{CO}	T_i (°C)	X_d (vol. %)
Kilchyk [12]	H ₂ /CO-air	25.6	150–300	0
	H ₂ /CO-air	50	150–300	0
	H ₂ /CO-air	75	150–300	0
	H ₂ /CO-air-H ₂ O	50	150	0–20
Van de Schoor et al. [15]	H ₂ /CO-air-H ₂ O	94	150	0–20
	H ₂ /CO-air-N ₂	55.6	100–200	0–79
	H ₂ /CO-air-N ₂	38.5	100–200	0–79
	H ₂ /CO-air-N ₂	29.4	100–200	0–79
Wang et al. [51]	H ₂ /CO-O ₂ -N ₂	50	150	60–80
	H ₂ /CO-O ₂ -N ₂	80	150	60–80
Grune et al. [11]	H ₂ /CO-O ₂ -N ₂ /H ₂ O/CO ₂	70–90	170	64–67
	H ₂ /CO-O ₂ -N ₂ /H ₂ O/CO ₂	70–90	250	64–67



(a)



(b)



(c)

increasing steam concentration. The heat loss participation caused relatively large errors of 19.5% and 13.6%, respectively, between the measurement and prediction results using the MELCOR and Hustad and Sønju models. Under 30 vol % of steam, however, the current model predicted the measured value accurately, while considering the heat loss, with a maximum relative error of 5.4%.

Additionally, the current model was validated by comparing its results with the experimental data adopted from the literature [20,23,26,53]. Major experimental information such as the test vessel geometry, test method, and mixture condition were investigated. The mixture composition, CO fraction, initial temperature, and diluent fraction are summarized in Table 4. Fig. 11-*ac* compare the experimental data based on Table 4 and the predicted values by the MELCOR default model, Hustad and Sønju, and current model. As mentioned above, the MELCOR default model calculates the LFL of the H₂/CO mixture with CO fraction only. The same value was predicted regardless of different initial conditions, and the maximum error was estimated at about 76%. Although Hustad and Sønju's correlation reflects the temperature condition, it also predicted the same LFL for several experimental data regardless of the diluent concentration. As a result, the results from MELCOR and Hustad and Sønju's model showed a large deviation from the measured results. For the current model, however, different LFLs were predicted with respect to initial conditions which caused a significant reduction in deviations from the experimental data. As a result, the maximum relative prediction error was lowered to 25%. Therefore, the accuracy of the current model was improved substantially by considering the real participating factors such as the initial temperature and diluents concentration.

On the other hand, carbon dioxide acting as a diluent is generated during the ex-vessel phase. For Grune et al.'s data representing the gas mixture containing carbon dioxide as a diluent, the MELCOR and Hustad and Sønju models showed maximum errors of 26% and 33%, respectively. When CO₂ is included in the gas mixture, the default option in MELCOR underestimates the LFL. So if the flammability is evaluated at the ex-vessel phase, it is highly likely that the combustion risk can be overestimated. Meanwhile, the current model estimated the LFL within a 13% error. By involving CO and CO₂ in the gas mixture, the current model was confirmed to predict the LFL with much improved accuracy for the representative gas mixture at the ex-vessel phase.

4. Conclusion

In this study, we developed a methodology to predict the LFL of H₂/CO mixtures based on Le Chatelier's law and the CNAFT model. The CNAFT model considers the heat transfer characteristics of hydrogen by mechanistic combustion analysis. Additionally, the accuracy of the current method was verified using experimental data representing SA conditions involving ex-vessel phenomena. It was noted that the maximum relative prediction error by the current method was reduced to 25% whereas as much as 76% was yielded by the MELCOR code. Major findings and future work can be summarized as follows.

- (1) A methodology to predict the LFL of H₂/CO mixtures at the ex-vessel phase was suggested based on Le Chatelier's law. Heat transfer characteristics of H₂ and CO can be individually reflected on the LFL prediction with CNAFT and CAFT models.

Fig. 11. Comparison of measurement and prediction by (a) MELCOR default option (b) Hustad and Sønju correlation, and (c) the developed model.

The CO fraction, initial temperature, and diluent concentration typical for the ex-vessel condition were thermodynamically considered in the LFL prediction.

- (2) Various methodologies to predict the LFL of the H₂/CO mixture were investigated. Hustad and Sønju's correlation and the default option in MELCOR were selected for comparison. They were compared with the CNAFT model with respect to three parameters; y_{CO} , T_0 and X_d . In the results, the current model showed a similar trend as the other methodologies. However, in the case of the gas mixture containing steam at a high temperature, only the current model showed a good agreement with the experimental values. Therefore, it is concluded that the method is applicable to the combustion risk analysis of SAs involving ex-vessel phenomena.
- (3) It is insisted that an inherent diffusivity of hydrogen results in a large heat loss. The flame with large diffusivity is known to exhibit a unique flame structure. Therefore, for future work the flame structures of H₂ and CO need to be compared by robust CFD simulations to further validate the current method.
- (4) The suggested methodology cannot consider the effect of pressure on the LFL of H₂/CO mixtures. It is necessary to improve the methodology to evaluate the flammability of H₂/CO mixture under the pressure conditions of containment by introducing an empirical factor.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.net.2020.07.040>.

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