A Comparative Study of Flammability Limit Models for H_2/CO Mixture on the Applicability of Severe Accident Conditions

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1. Introduction

Through the Fukushima accident, it was proved that hydrogen released into containment building may cause explosion under severe accident (SA). After the accident, researches have been actively conducted to predict and mitigate the combustion risk. On the other hand, as the accident progresses to ex-vessel phase, carbon monoxide is generated in the containment by molten corium-concrete interaction (MCCI). Carbon monoxide is also flammable gas, which can increase the combustion risk when coexisting with hydrogen. However, most of the previous studies have mainly focused on hydrogen and paid relatively less attention to carbon monoxide.

If hydrogen and carbon monoxide coexist, it can increase the combustion risk because the concentration of combustible gas increases. On the contrary, there exist the various diluents at high temperature in containment building under SA like steam, carbon dioxide and nitrogen. These diluents can mitigate the combustion risk due to high specific capacity. In contrast, as the containment building sustains high temperature, less energy is required to heat the gas mixture, which makes combustion risk increase. Likewise, the flammability in containment building under SA is varying according to the fuel fraction, temperature and concentration of diluents. But, there is still lack of research to estimate the flammability of binary fuel mixture applicable to SA conditions. Consequently, importance of the methodology to predict the combustion risk of H_2/CO binary fuel mixture is becoming highlighted.

Therefore, the objective of this study is to confirm the most appropriate methodology applicable to SA. For this, the various method to assess flammability of H_2/CO mixture is explained. Next, the applicability of each method to SA condition is investigated through comparison with experimental value. The methods are introduced categorized into three part; MELCOR default option, empirical correlation and model based on theory. It is noted that every method has limit to apply in analysis on combustion risk under SA condition.

2. Methodology

Flammability limit is limiting concentration of a flammable gas in air where flame propagates. That is, if the concentration of flammable gas is within the flammable range, the combustion reaction occurs sustainably. Lower flammability limit (LFL) is the minimum concentration while upper flammability limit (UFL) is the maximum concentration. As the amount of combustible gas which can be generated in nuclear power plant is limiting, LFL is mainly applied in flammability evaluation under severe accident.

Because hydrogen and carbon monoxide coexist in the containment building at ex-vessel phase, the LFL of H_2/CO mixture should be obtained separately. In this section, the various method to predict the LFL of H_2/CO is described in three categories; MELCOR default option, empirical correlations and method based on the theory.

2.1. MELCOR default option

MELCOR default option predicts the LFL of H_2/CO fuel mixture with Le Chatelier's law simply like equation where y is the fraction of the flammable components in the mixture (1) [1]. The LFL of each gas can change according to the propagation direction. As the method only considers the relative fraction of flammable gas, The LFL is calculated as the same value regardless of initial temperature and diluents. It needs to be improved to reflect those effects.

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

2.2. Empirical correlations

The LFL of H_2/CO fuel mixture is as a function of various parameter such as the concentration of fuel fraction, diluents, initial temperature and pressure. Therefore, some researchers tried to develop empirical correlation based on their own experiments.

First, Karim et al. suggested the correlation for diluted binary fuel mixture by extending Le Chatelier's law through the experiment [2]. As described in the equation (2), the diluents are treated as the fuel whose LFL is infinite. As temperature effect was not considered, the predicted value is possibly overestimated. Although the dilution effect was included in the method, the heat capacity of the individual diluent was not included. In addition, the application range is limited. For example, the concentration ratio of nitrogen to hydrogen should be less than 15.3, which is out of range under SA [3]. Therefore, the method is difficult to apply to flammability evaluation under SA.

$$\frac{1}{LFL_{mix}} = \frac{y_{H_2}}{4.1} + \frac{y_{CO}}{12.5} + \frac{y_{diluents}}{\infty} \quad (2)$$

Second, Hustad et al. also modified Le Chatelier's law through temperature dependent correlation for each gas like the equation (3) [4]. Even if the temperature effect was included, the dilution effect was not considered. However, Hustad et al. conducted the experiment with the gas mixture including nitrogen as a diluent. Although the correlation does not contain the dilution term, it seems that the method can be applied to an analysis.

$$\frac{1}{LFL_{mix}} = \frac{y_{H_2}}{5(1-0.00129(T-25))} + \frac{y_{CO}}{15(1-0.00095(T-25))} \quad (3)$$

Third, Jaimes determined the correlation for specified H_2/CO fuel ratio based on the experiment. Jaimes' correlation is characterized by the pressure effect consideration compared with other methods. It is shown in Table I [5]. As the correlation was developed only for specific ratio of H_2/CO mixture, it can be applied only to the limited case. In addition, as Jaimes conducted the experiment without any diluent, it seems also inappropriate for SA.

Table I: Jaimes' correlation for H_2/CO mixture as a function of temperature and pressure [5]

$LFL_{mix} = [a \cdot T + b] \cdot P + c \cdot T + d$; T = [℃], P = [bar]				
H2/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

On the other hand, Grune et al. developed the flammability criteria like the equation (4) [6]. If the left-handed side term is larger than 0, the mixture can be classified as flammable. It can judge the flammability of H_2/CO fuel mixture considering even the oxygen depletion. Though the criteria can distinguish the flammability of H_2/CO mixture, it cannot calculate the LFL accurately. For this reason, it is insufficient to be used for the analysis.

$$[O_2(\%) - 3] \cdot [(H_2(\%) + CO(\%)) - 10] - 4 > 0 \quad (4)$$

2.3. CAFT model

There exists a theory-based methodology to estimate the LFL of H_2/CO mixture diluted at high temperature. CAFT (Calculated Adiabatic Flame Temperature) model is widely used model to estimate the LFL using thermodynamic 1st law, assuming adiabatic condition like the equation (5). Using the CAFT model, the LFL of H_2/CO mixture according to diluents and temperature can be calculated. More detailed explanation of CAFT model is described in reference [7]. Unlike the methods explained above, the effect of diluents and temperature is modelled. For this reason, it was expected to be the most suitable method for SA.

$$\left[\sum_i H_{i,reactant}\right]_{To} = \left[\sum_i H_{i,product}\right]_{Tf} \quad (5)$$

3. Result and Discussion

The LFL of H_2/CO mixture predicted applying three of the methodologies mentioned above is compared with the value experimentally measured in this part. The selected methods are MELCOR default option, Hustad's correlation and CAFT model, whose application range is relatively wide. The comparison results are explained categorized into three part, which characterize the SA at ex-vessel phase; carbon monoxide, diluents and temperature. Through the result, the applicability to SA is discussed.

3.1. The effect of carbon monoxide

Figure 1 shows a comparison between the experimentally measured LFL and the value predicted by three methods mentioned above according to the CO fraction in the H_2/CO fuel mixture. For comparison, the experimental value was selected only for the undiluted mixture at 200℃.

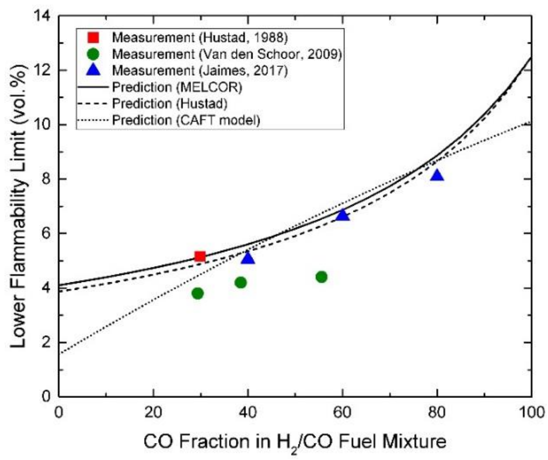

Fig. 1. Comparison of the measured and predicted LFL as function of CO fraction in the fuel mixture [4, 5, 8]

The experimental value increases as the volume fraction of CO in the mixture increases. It is because the carbon monoxide has larger LFL than that of hydrogen. The prediction applying the methodologies reflects the trends. In case of MELCOR and Hustad's correlation, it shows similar trends in curve as both methods apply Le Chatelier's law. Especially, the LFL of hydrogen and carbon monoxide was estimated as 3.87 vol.% and 12.5 vol.% each at 200℃ by Hustad's correlation. Otherwise MELCOR predicts the LFL of hydrogen and carbon monoxide as 4.1 vol.% and 12.5 vol.% regardless of temperature. For this reason, Hustad's correlation shows more similar prediction value with the MELCOR default option.

The predicted value seems nearly same from 40% to 80% regardless of the methods. However, the CAFT model predicts the LFL of H_2/CO mixture as lower value than the others in the range less than 20% and more than 90%. But in our preliminary risk analysis using MELCOR code, the volume fraction of carbon monoxide of combustible gas exists in the range from 30% to 90%.

3.2. The effect of initial temperature

A comparison between the experimental LFL and those calculated by three methods is shown in figure 2 according to the initial temperature. For direct comparison, the experimental value was selected only for undiluted H_2/CO-air mixture. The concentration ratio of carbon monoxide to hydrogen is selected as 75:25.

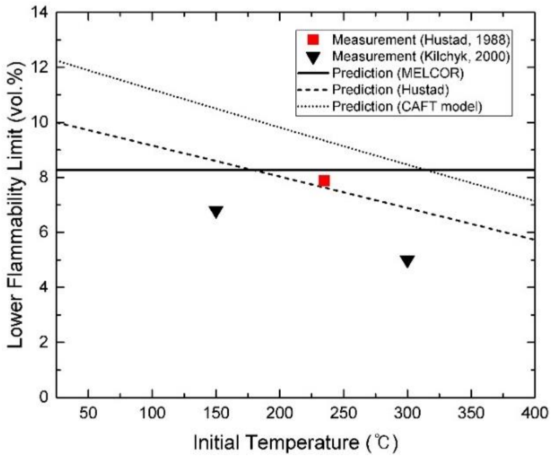

Fig. 2. Comparison of the measured and predicted LFL as function of initial temperature [4, 7]

The experimentally determined value decrease as the initial temperature increases. It is because less energy is required at higher temperature to heat up the mixture to threshold temperature for flame propagation.

However, the LFL predicted with MELCOR is fixed at constant value as the temperature term is not included. On the other hand, the value predicted by Hustad's correlation and CAFT model reflect descending trends. Throughout the result, it is inferred that MELCOR is not proper for SA.

3.3. The effect of diluents

At ex-vessel phase, three kinds of diluents exist possibly in containment building; steam, nitrogen and carbon dioxide. Although carbon dioxide exists in the containment building, its concentration is very small about 3 vol.% [3]. In addition, the experimental data for comparison is not enough. For this reason, the effect of steam and nitrogen was discussed in this part.

Figure 3 shows a comparison between the measured value and the value predicted by three methods according to the steam concentration in the gas mixture. For comparison, the experimental value was selected only for H_2/CO-air-H_2O mixture. The concentration ratio of carbon monoxide to hydrogen is selected as 94:6. The initial value was fixed at 150℃.

As the MELCOR default option and Hustad's correlation do not consider the dilution effect, the prediction value remains constant regardless of the steam concentration. In case of CAFT model, the prediction changes with very small fluctuation However, the experimental value increase with a larger inclination as the steam concentration increases. Since steam is radiating species, the radiative heat loss is relatively large. It leads large deviation between the measurement and prediction with CAFT model [9]. As the steam occupies maximum 80 vol.% in gas mixture under SA, the methods should be improved for application.

Figure 4 shows a comparison between the measured value and the value predicted by three methods according to the nitrogen concentration in the gas mixture. If nitrogen is additionally included in the gas mixture, it is treated as diluent which is distinguished from the nitrogen in air. For comparison, the experimental value was selected only for H_2/CO-air-N_2 mixture at 100℃. The concentration ratio of carbon monoxide to hydrogen is selected as 30:70.

The experimental value maintains at constant value. It is judged that the similar heat capacity of air and nitrogen leads to the constantly measured LFL. As mentioned above, the MELCOR default option and Hustad's correlation do not consider the effect of diluents. It causes the constant predicted value regardless of the nitrogen concentration. Although the dilution effect was modelled in the CAFT model, the predicted value changes little like the experimental value. It is judged that the CAFT model reflects the physical phenomena for gas mixture containing nitrogen.

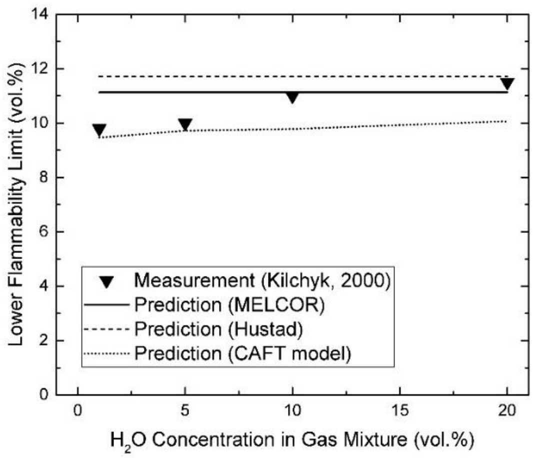

Fig. 3. Comparison of the measured and predicted LFL as function of steam concentration in the fuel mixture [7]

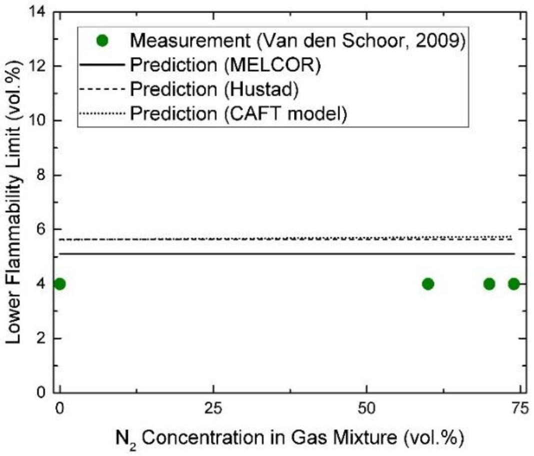

Fig. 4. Comparison of the measured and predicted LFL as function of nitrogen concentration in the fuel mixture [8]

4. Conclusions

In this paper, the various methodologies to estimate the LFL of H_2/CO fuel mixture are explained. The LFL predicted by each method is compared with the experimentally measured LFL. Through the comparison, the applicability of the methodologies to SA is investigated. As a result, the CAFT model is expected to be the most appropriate for an analysis for SA, if improved. The major things to improve are summarized as below.

(1) The prediction with CAFT model shows the satisfactory accuracy in the CO fraction range under SA, from 30% to 90%. Throughout the result, it is judged that the improvement according to the CO fraction is not required.

(2) Although CAFT model includes the temperature term, the deviation between prediction and measurement is not reasonable. It seems that the threshold temperature decrease effect due to heat loss should be modelled.

(3) In case of the gas mixture containing radiating species especially steam, the radiative heat loss should be additionally modelled.

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