Prediction of Burning Velocity for New Refrigerants by Developing Reaction Models Based on Graph Network Analysis

○Kenji TOYODA, Nobuaki NAGAO, Takahiro OHGOE, Hikaru MURAKAMI*, Takahiko HASHIMOTO*, and Akira HIWATA*

Green Transformation Divisions, Panasonic Holdings Corporation, Kadoma 1006, Kadoma-Shi, Osaka, 571-8506, Japan

* Heating & Ventilation A/C Company, Panasonic Corporation, Nojihigashi Minamikusatsu-Shi, Shiga, 525-0058, Japan

ABSTRACT

To preserve the Earth's environment, new refrigerant materials with low GWP are needed. Predicting laminar burning velocity (LBV) is important for assessing their safety. While LBV for hydrofluorocarbon refrigerants has been calculated using the NIST Fluorine model, mixing chemical species not included in the model (e.g., NH_3) requires quantum chemical calculations, which are resource intensive. This study proposes a method to add elementary reactions to the NIST Fluorine model based on graph network analysis, enabling rapid prediction of LBV for new refrigerants.

Keywords: Low GWP, Laminar Buring Velocity, Graph Network, Reaction Model

INTRODUCTION

To protect the global environment, there is a demand for refrigerants with low Global Warming Potential (GWP). In the development of refrigerant materials, safety must be ensured alongside cooling performance. One of the safety indicators is the safety group defined by the ASHRAE standard, which is primarily determined by the laminar burning velocity (LBV). As shown in Table 1, the maximum LBV (LBV_{max}) of R-32, a refrigerant commonly used in household packaged air conditioners, is approximately 7 cm/s, and it belongs to safety group A2L. However, its GWP is 675, necessitating alternatives with lower GWP. On the other hand, natural refrigerant R-290 has a low GWP, but it falls into safety group A3 and has a high LBV_{max}. Thus, the development of refrigerant materials that simultaneously achieve low GWP and low flammability is an urgent task.

In hydrofluorocarbon (HFC) refrigerants, the LBVs are calculated using the NIST Fluorine model [1], and comparisons with experimental data for various refrigerants have been reported. It is possible to predict LBV_{max} of HFC refrigerant materials using this model, although low flammability can sometimes complicate LBV calculations. For new chemical species (e.g., NH_3), it is necessary to develop a reaction model corresponding to the specific species. Developing such a reaction model requires high-precision quantum chemical calculations and combustion experiments, which are time-consuming. In this study, we propose a method to rapidly develop reaction models by adding elementary reaction data generated by the Reaction Mechanism Generator (RMG) [2] to the NIST Fluorine model, based on graph network analysis. We developed a reaction model for a refrigerant mixture of R-290 and R-717, and validated the proposed method by comparing it with previous studies [3-7]. Subsequently, we built a reaction model for a refrigerant mixture of R-152a [8], which is being researched as a substitute for R-134a, by adding R-717, and evaluated its potential by calculating its LBV.

TABEL 1: Properties of Refrigerants

Refrigerants	Chemical Formula	Boling Point (°C)	GWP	Safety Group
R-32	CH_2F_2	-51.7	675	A2L
R-290	C_3H_8	-42.1	3	A3
R-134a	$C_2H_2F_4$	-26.5	1300	A1
R-152a	$C_2H_4F_2$	-24.1	124	A2
R-717	NH_3	-33.4	0	B2L

METHODS

In this study, reaction models corresponding to new chemical species were constructed using graph network analysis, and LBV_{max} values of the new refrigerants were calculated using Chemkin [9]. The refrigerants considered in this study are R-290/R-717 and R-152a/R-717 mixtures. For the new chemical species, such as NH_3, or R-717, the reaction models were generated using RMG. RMG can automatically generate reaction models for user-specified reactants based on reliable elementary reaction database. However, the elementary reaction data generated by RMG can be extremely large in volume, which can increase the computational load for LBV calculations in Chemkin. To address this, only the most significant elementary reactions were extracted and added to the NIST Fluorine model. During this process, graph network analysis was employed to ensure the connectivity of reaction pathways. A graph network is a data structure that treats chemical species as nodes and reactions as edges. Figure 1 illustrates the reaction network for the case where R-152a, or CH_3-CHF_2, reacts with O_2 (gray nodes) within the NIST Fluorine model, producing CO_2, H_2O, and HF (dark gray nodes).

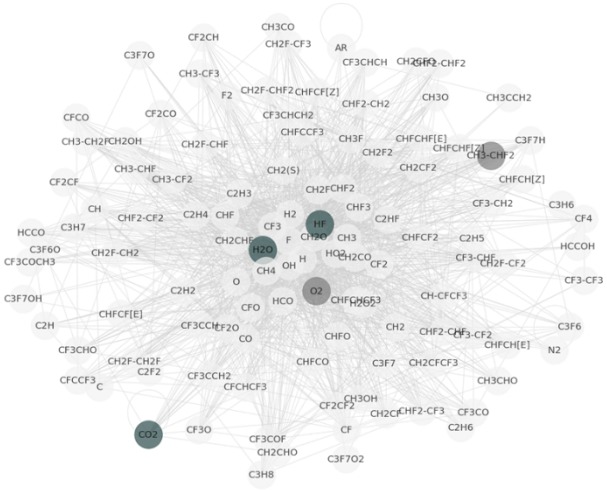

Fig.1 Graph Network of R152a Combustion Reaction

The elementary reaction data involving NH_3 were added to the NIST Fluorine model using graph network analysis. These NH_3-related elementary reactions were generated with RMG, and to reduce the computational load for LBV calculations, only the most significant elementary reactions were extracted and incorporated. Sensitivity analysis was performed using Cantera [10] to evaluate the sensitivity of the reactions relative to reactant quantities, allowing for ranking of the elementary reactions based on their importance. The calculation conditions for RMG and Cantera are summarized in Table 2.

TABLE2: RMG and Cantera Conditions

Refrigerants	Reactant	Kinetic Models	Temperature (K)	Pressure (bar)	Target Species for Sensitivity
R-290/R-717	C_3H_8, NH_3, O_2	GRI-Mech3.0-N	2200	1.0	C_3H_8
R-152a/R-717	$C_2H_4F_2$, NH_3, O_2	NIST Fluorine, GRI-Mech3.0-N	2200	1.0	$C_2H_4F_2$

The reactants were the refrigerant components and oxygen. For the reaction models used in RMG, GRI-Mech 3.0-N was employed for the R-290/R-717 mixture, while NIST Fluorine and GRI-Mech 3.0-N were used for the R-152a/R-717 mixture. The temperature was set to 2200 K, corresponding to the ignition temperature in LBV calculations for pure R-290 and R-152a, and the pressure was fixed at 1 bar. The species subjected to sensitivity analysis using Cantera [10] were C_3H_8 and $C_2H_4F_2$ for the R-290/R-717 and R-152a/R-717 mixtures, respectively. The top-ranked elementary reactions based on their absolute sensitivity coefficient were incorporated into the NIST Fluorine model through graph network analysis, ensuring that the reaction pathways connecting the starting node of the new chemical species NH_3 to the end node of the product nitric oxide (NO) were maintained.

Based on the reaction models built through graph network analysis, LBVs were calculated using the Chemkin PREMIX module. The initial temperature was set to 300 K, and the pressure to 1 atm. The fuel was the respective refrigerant mixture (R-290/R-717 or R-152a/R-717), and the oxidizer was air (N_2 79%, O_2 21%). The volume concentrations of NH_3 (x_{NH3}) were varied at 0%, 20%, and 50% to examine the dependence of LBV on x_{NH3} concentration. Multi-component transport calculations were performed considering the Soret effect. The effect of radiative heat loss was neglected in this analysis.

RESULTS AND DISCUSSION

R-290/R-717 MIXTURE

The results for the R-290/R-717 mixture refrigerant are presented. Figure 2 shows the dependence of LBV on the equivalence ratio (Eq). The LBV reaches its maximum near an Eq of 1.1, and as the NH_3 concentration (x_{NH3}) increases, the LBV_{max} decreases. Table 1 summarizes the dependence of LBV_{max} on x_{NH3}. Compared to experimental values, the calculated LBV slightly overestimates, but it is in good agreement with the GRI-Mech 3.0 model [11]. Besides, we confirmed NO as a combustion product of NH_3.

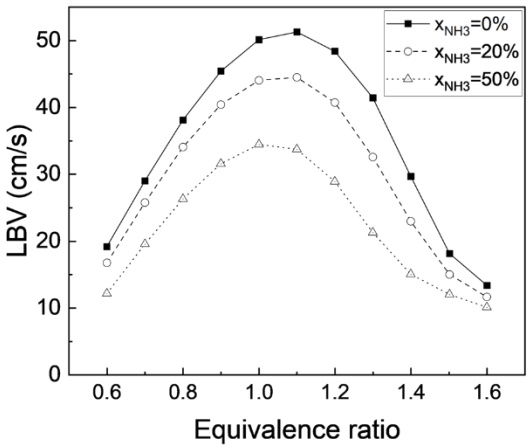

Fig.2 LBV of R-290/R-717 as a Function of Equivalence Ratio.

TABLE3: LBV_{max} (cm/s) of R-290/R-717 Mixture with Varying NH_3 Concentration

x_{NH3} (%)	This Study	GRI-Mech3.0	Expt.
0	51.3	51.5	42.5 [3]
20	44.5	44.9	34.0 [4]
50	34.5	34.0	28.5 [4]

To investigate how NH_3 influences the combustion reactions of C_3H_8, the peak molar fractions of radicals relevant to combustion, such as H, OH, O, as well as NH_2 and NH radicals associated with NH_3, were plotted (Fig. 3). As x_{NH3} increases, the molar fractions of H, OH, and O radicals decrease, with H radicals showing a significant reduction from 0.01 to 0.006. Conversely, the molar fractions of NH_2 and NH radicals slightly increase. These results are consistent with those reported by Z. Wang et al. [4]. Furthermore, the changes in these radical concentrations reflect that the oxidation of NH_3 primarily proceeds through H, OH, and O radicals [6].

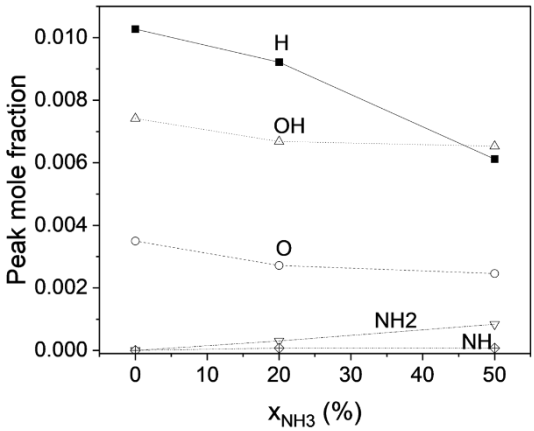

Fig.3 Peak Mole Fraction of H, OH, O, NH_2 and NH radicals with Varying NH_3 Concentration in R-290/R-717 mixture.

To examine the impact of elementary reactions involving NH_3 on LBV, sensitivity analysis was performed. Figure 4 shows the dependence of the top-ranking elementary reactions, those with the largest absolute sensitivity values, on x_{NH3}. The sensitivity of the radical branching reaction H + O2 <=> O + OH was the highest, and the sensitivity coefficients of nitrogen-involving elementary reactions were smaller compared to hydrocarbon reactions. It was confirmed that nitrogen-involving reactions do not directly affect LBV. Instead, the increase in NH_3 suppresses combustion progression by scavenging H radicals, leading to a reduction in LBV [7].

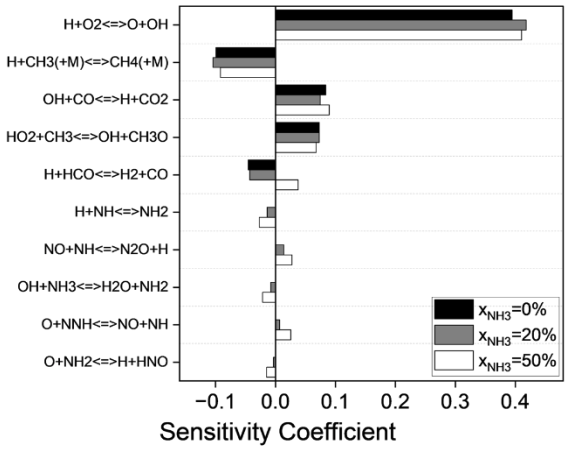

Fig.4 Sensitivity Analysis for LBV of R-290/R-717 mixture with Varying NH_3 Concentration.

These results show that the proposed method demonstrates reliable predictions of LBV_{max} through its graph network analysis-based reaction model.

R-152a/R-717 MIXUTURE

The calculation results for the R-152a/R-717 mixture refrigerant are presented. Figure 5 shows the dependence of LBV on Eq. LBV reaches its maximum near an Eq of 1.1, and as x_{NH3} increases, LBV_{max}

decreases. Specifically, at x_{NH3} = 0%, 20%, and 50%, LBV_{max} values are 24.4, 22.1, and 17.6 cm/s, respectively. It has been reported [12] that the LBV_{max} of a 50:50 molar mixture of R-152a and R-1234yf is approximately 14 cm/s, indicating that the R-152a/R-717 mixture has a slightly higher LBV_{max}. Besides, we confirmed NO as a combustion product of NH_3.

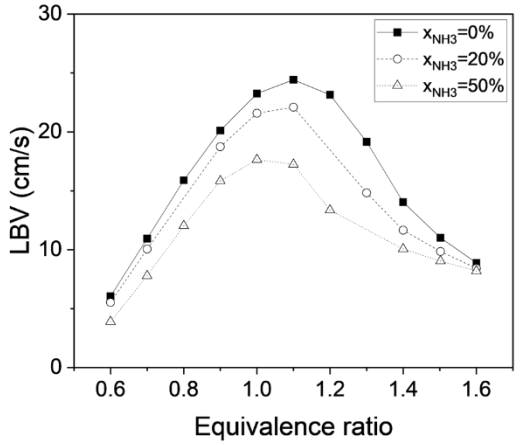

Fig.5 LBV of R-152a/R-717 as a Function of Equivalence Ratio.

To examine how NH_3 influences the combustion reaction of $C_2H_4F_2$, or R-152a, the peak molar fractions of radicals critical to combustion, such as H, OH, O, as well as NH_2 and NH related to NH_3, were plotted (Fig. 6). As x_{NH3} increases, the molar fractions of H and O radicals decrease, while OH remains nearly unchanged, and NH_2 and NH radicals increase. Notably, H radicals decrease significantly from about 0.004 to 0.002, while NH_2 radicals increase markedly up to 0.002. Compared to the R-290/R-717 mixture, the amount of H, OH, and O radicals decreases due to the formation of F radicals generated from R-152a, which suppresses NH_3 oxidation. Under this suppression, NH_2 is thought to be regenerated through reactions with H radicals, leading to an increase in NH_2 radicals and a decrease in H radicals.

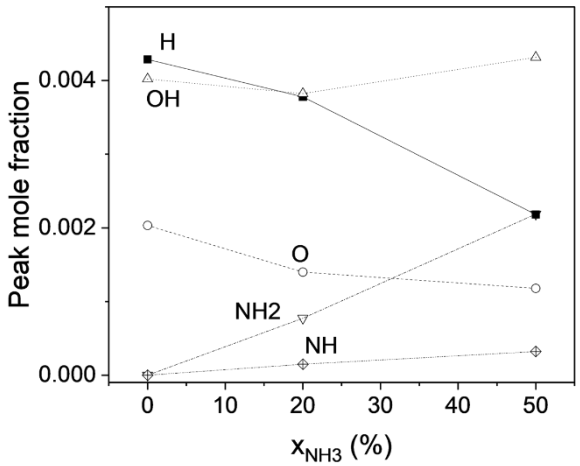

Fig.6 Peak Mole Fraction of H, OH, O, NH_2 and NH radicals with Varying NH_3 Concentration in R-152a/R-717 mixture.

Sensitivity analysis was performed to investigate how elementary reactions involving NH_3 affect LBV. Figure 7 shows the dependence of the top-ranking elementary reactions, those with the highest absolute sensitivity values, and nitrogen-involving reactions on x_{NH3}. Like the R-290/R-717 mixture, the highest absolute sensitivity was observed for the radical branching reaction H + O2 <=> O + OH. However, unlike the R-290/R-717 case, the sensitivity coefficient of the H + NH <=> NH2 reaction, related to NH_2 regeneration, is comparable to that of HFC elementary reactions. This suggests that the suppression of NH_3 oxidation enhances the contribution of NH_2 regeneration reactions.

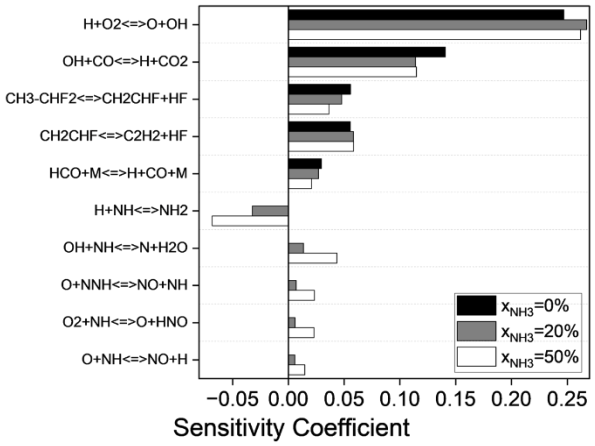

Fig.7 Sensitivity Analysis for LBV of R-152a/R-717 mixture with Varying NH_3 Concentration.

Using the reaction model built through graph network analysis, the LBV_{max} of the R-152a/R-717 mixture refrigerant was calculated, predicting a slightly higher value than that of the R-152a/R-1234yf mixture. Additionally, the reduction in LBV_{max} due to NH_3 addition is attributed to the suppression of NH_3 oxidation, which promotes NH_2 regeneration.

In summary, the proposed graph network analysis-based reaction modeling method enables reliable prediction of LBV_{max} for refrigerant materials involving new chemical species. It also provides insights into how compositional changes influence combustion reaction mechanisms.

CONCLUSIONS

In this study, elementary reaction data involving new chemical species were generated using RMG, and the top-ranked reactions based on sensitivity analysis were incorporated into the NIST Fluorine model using graph network analysis to develop reaction models. Using these models, the LBVs were calculated, and it was confirmed that the results for the R-290/R-717 mixture closely matched those obtained with the

conventional model. Subsequently, a reaction model was built for a refrigerant mixture of R-152a and R-717, which has a relatively low GWP and belongs to safety group A2, and the LBV_{max} was calculated. When 50% of NH_3 was added, the LBV_{max} decreased to 17.6 cm/s. The addition of NH_3 reduces both GWP and flammability, indicating the potential for using R-152a/R-717 mixtures as refrigerants. Overall, the proposed method demonstrated in this study is expected to contribute to the development of new refrigerant materials and their mixture compositions.

NOMENCLATURE

LBV : Laminar burning velocity, $cm \cdot s^{-1}$
LBV_{max} : Maximum value of LBV, $cm \cdot s^{-1}$
x_{NH3} : NH_3 concentration, %
Eq : Equivalence ratio

REFERENCES

[1] V. I. Babushok, D. R. Burgess Jr., D. Kim, M. Hegetschweiler, and G. T. Linteris, "Modeling of Combustion of Fluorine-Containing Refrigerants", NIST Technical Note TN 2170, National Institute of Standards and Technology, Gaithersburg, MD, (2021).

[2] M. Liu, A. Grinberg, D. Matthew, S. Johnson, M. J. Goldman, A. Jocher, A. M. Payne, C. A. Grambow, K. Han, N. W. Yee, E. J. Mazeau, K. Blondal, R. H. West, C. F. Goldsmith, and W. H. Green, " Reaction Mechanism Generator v3.0: Advances in Automatic Mechanism Generation", J. Chem. Inf. Model. 61(6) 2686-2696 (2021).

[3] C. Chen, Z. Wang, Z. Yu, X. Han, Y. He, Y. Zhu, and A. A. Konnov, "Experimental and kinetic modeling study of laminar burning velocity enhancement by ozone additive in NH3+O2+N2 and NH3+CH4/C2H6/C3H8+air flames", Proceedings of the Combustion Institute 39(4) 4237-4246 (2023).

[4] Z. Wang, C. Ji, D. Wang, T. Zhang, Y. Zhai, and S. Wang, "Experimental and numerical study on laminar burning velocity and premixed combustion characteristics of NH3/C3H8/air mixtures", Fuel, 331(2) 125936 (2023).

[5] J. Liu, D. Liu, L. Dai, C. Zou, Q. Lin, and C. Peng, "The effects of C/N cross-reactions on the NH3/C3H8 combustion: A shock-tube and modeling study", Combustion and Flame, 270, 113716 (2024).

[6] G. Yin, B. Xiao, J. You, H. Zhan, E. Hu, and Z. Huang, "Experimental and kinetic modeling study on propane enhancing the laminar flame speeds of ammonia", Fuel Processing Technology, 247, 107779 (2023).

[7] D. Wang, Z. Wang, T. Zhang, Y. Zhai, R. Hou, Z.-Y. Tian, C. Ji, "A comparative study on the laminar C1–C4 n-alkane/NH3 premixed flame", Fuel 324, 124732 (2022).

[8] G. A. Longo, C. Zilio, and G. Righetti, "Condensation of the low GWP refrigerant HFC152a inside a Brazed Plate Heat Exchanger", Experimental Thermal and Fluid Science, 68, 509-515 (2015).

[9] ANSYS Chemkin-Pro: Release 2022 R1. ANSYS, Inc., Canonsburg.

[10] D. G. Goodwin, H. K. Moffat, I. Schoegl, R. L. Speth, and B. W. Weber, "Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes", https://www.cantera.org, 2024. Version 3.1.0.

[11] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner, Jr., V. V. Lissianski, and Z. Qin, http://www.me.berkeley.edu/gri_mech/.

[12] D. K. Kim, V. I. Babushok, M. J. Hegetschweiler and G. T. Linteris, "Flame Propagation in Blends of R-152a, R-134a, and R-1234yf with Air." Combustion Science and Technology 196(18) 5107–5127 (2023).

グラフネットワーク解析に基づいた反応モデル構築による新冷媒の燃焼速度予測

Prediction of Burning Velocity for New Refrigerants by Developing Reaction Models Based on Graph Network Analysis

豊田健治・長尾宣明・大越孝洋　パナソニックホールディングス(株)
村上光・橋元任彦・鶸田晃　パナソニック(株)

◯ Kenji Toyoda, Nobuaki Nagao, Takahiro Ohgoe, Hikaru Murakami*, Takahiko Hashimoto*, and Akira Hiwata*
Green Transformation Divisions, Panasonic Holdings Corporation, Kadoma 1006, Kadoma-Shi, Osaka, 571-8506, Japan
* Heating & Ventilation A/C Company, Panasonic Corporation, Nojihigashi Minamikusatsu-Shi, Shiga, 525-0058, Japan

To preserve the Earth's environment, new refrigerant materials with low GWP are needed. Predicting laminar burning velocity (LBV) is important for assessing their safety. While LBV for hydrofluorocarbon refrigerants has been calculated using the NIST Fluorine model, mixing chemical species not included in the model (e.g., NH_3) requires quantum chemical calculations, which are resource-intensive. This study proposes a method to add elementary reactions to the NIST Fluorine model based on graph network analysis, enabling rapid prediction of LBV for new refrigerants.

Key Word: Low GWP, Laminar Buring Velocity, Graph Network, Reaction Model

背景・目的

地球環境の保全のため、地球温暖化係数(GWP)の低い冷媒が求められている。冷媒材料の開発においては冷凍能力の他に安全性も確保しなければならない。安全指標の一つとして、 ASHARAE 規格の安全性グループがあり、主に層流燃焼速度(LBV)で決定される。表 1 に示すように、家庭用やパッケージエアコンで一般的に使用されている冷媒 R-32 の LBV の最大値(LBV_{max})は約 7 (cm/s)、安全性グループは A2L であるが、GWP が 675 であり、低 GWP への代替が求められている。一方、自然冷媒である R-290 の GWP は低いが、安全性グループが A3 で LBV_{max} が高い。このように、低 GWP と低燃焼性を両立する冷媒材料の開発が急務である。

フッ素炭化水素(HFC)系の冷媒では、NIST Fluorine モデル[1]を用いて LBV が計算されており、さまざまな冷媒の実験値との比較が報告されている。このモデルをもとに、HFC の冷媒材料の LBV_{max} の予測が可能である。ただし、燃焼性が低いと LBV 計算が困難な場合がある。新しい化学種(例 : NH_3)においては、その化学種に対応した反応モデルを構築しなければならない。新たな反応モデルを構築するには、高精度な量子化学計算や燃焼実験が必要であり、時間を要する。そこで本研究では、Reaction Mechanism Generator (RMG)[2]で生成された素反応データをグラフネットワーク解析にもとづいて、NIST Fluorine モデルに追加することで、高速に反応モデルを構築する手法を提案する。R-290 に R-717 を混合した冷媒の反応モデルを構築し、先行研究例[3-7]と比較することで、本研究の手法の妥当性を検証した。次に、R-134a 代替として研究開発されている R-152a[8]に R-717 を混合した冷媒の反応モデルを構築し、LBV を計算することでその利用可能性について検討した。

TABEL 1: Properties of Refrigerants

Refrigerants	Chemical Formula	Boling Point (°C)	GWP	Safety Group
R-32	CH_2F_2	-51.7	675	A2L
R-290	C_3H_8	-42.1	3	A3
R-134a	$C_2H_2F_4$	-26.5	1300	A1
R-152a	$C_2H_4F_2$	-24.1	124	A2
R-717	NH_3	-33.4	0	B2L

方法

本研究では、グラフネットワーク解析を用いて、新しい化学種に対応した反応モデルを構築し、Chemkin[9]を用いて新冷媒の LBV_{max} を計算した。本研究で計算した冷媒は、R-290/R-717、R-152a/R-717 の混合冷媒である。ここで、新しい化学種である R-717 の NH_3 が関与する反応モデルは、RMG を用いて生成する。RMG は、信頼性のある素反応データベースに基づいて、ユーザが指定した反応物に対する反応モデルを自動的に生成することができる。ただし、RMG で生成される反応モデルの素反応データは非常に大量になる場合があり、それにより Chemkin での LBV の計算負荷が高くなってしまう。そこで、重要度の高い素反応データのみを抽出し、NIST Fluorine モデルに追加することを試みた。ここで、素反応データの追加は、反応経路の接続を確保するため、グラフネットワーク解析に基づいて実行した。グラフネットワークとは、化学種をノード、反応をエッジとして取り扱うデータ構造である。図 1 に、NIST Fluorine モデルにおける R-152a を燃料としたときの反応モデルのグラフネットワークを示す。R-152a である CH_3-CHF_2 と O_2(灰色のノード)が反応して、CO_2, H_2O, HF(暗灰色のノード)が生成される。

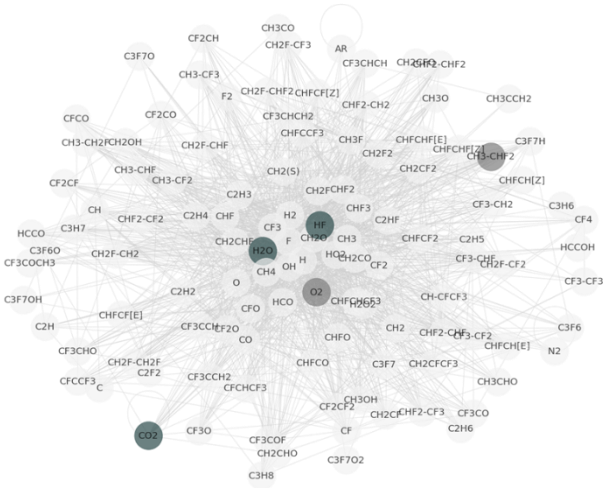

Fig.1 Graph Network of R152a Combustion Reaction

この NIST Fluorine モデルに、グラフネットワーク解析を用いて NH_3 が関与する素反応データを追加する。NH_3 が関与する素反応データは、RMG を用いて生成し、LBV の計算負荷を軽減するために、重要な素反応を抽出して追加する。Cantera[10]を用いて反応物の量に対する感度解析を行い、素反応の重要度に関してランキング化を行い、ランク上位を抽出する。表 2 に、RMG と Cantera の計算条件を示す。

TABLE2: RMG and Cantera Conditions

Refrigerants	Reactant	Kinetic Models	Temperature (K)	Pressure (bar)	Target Species for Sensitivity
R-290/R-717	C_3H_8, NH_3, O_2	GRI-Mech3.0-N	2200	1.0	C_3H_8
R-152a/R-717	$C_2H_4F_2$, NH_3, O_2	NIST Fluorine, GRI-Mech3.0-N	2200	1.0	$C_2H_4F_2$

反応物は、冷媒の構成物と酸素である。RMG で使用した反応モデルは、R-290/R-717 の混合冷媒の場合は GRI-Mech3.0-N、R-152a/R-717 の混合冷媒の場合は NIST Fluroine と GRI-Mech3.0-N とした。温度は R-290 および R-152a 単体の LBV での到達温度 2200 (K)とし、圧力は 1 (bar)とした。Cantera の感度解析の対象の化学種は、R-290/R-717 と R-152/R-717 の混合冷媒の系それぞれにおいて、C_3H_8 と $C_2H_4F_2$ とした。新しい化学種である NH_3 を開始ノードとして、生成物である一酸化窒素 NO の終了ノードまでの経路が接続されるように、グラフネットワーク解析を用いて感度の絶対値の上位の素反応を NIST Fluorine に追加した。

グラフネットワーク解析によって構築した反応モデルに基づいて、Chemkin PREMIX モジュールを使用して LBV を計算した。初期温度は 300 (K)、圧力は 1 (atm)とし、燃料は R-290/R-717、R-152a/R-717 の混合冷媒、酸化剤は空気(N_2 79%, O_2 21%)とした。ここで、R-717 である NH_3 の体積濃度(x_{NH3})を 0, 20, 50%に変化させ、x_{NH3}依存性を調べた。輸送については Soret 効果を考慮し Multi-component transport を用いて計算した。なお、輻射効果は無視した。

結果・考察

まず、R-290/R-717 混合冷媒の計算結果について示す。図 2 は、LBV の当量比 Eq 依存性である。当量比 Eq が 1.1 付近で LBV が最大となり、x_{NH3} が増加するにしたがって、LBV_{max} が減少する。表 1 に、LBV_{max} のx_{NH3}依存性をまとめた。実験値に比べ、やや過大評価するが、既存モデル GRI-Mech3.0[11]とほぼ同じであることを確認した。なお、NH_3 の燃焼生成物として NO を確認している。

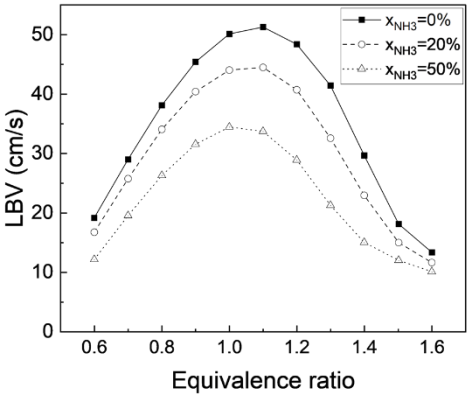

Fig.2 LBV of R-290/R-717 as a Function of Equivalence Ratio.

TABLE3: LBV_{max} (cm/s) of R-290/R-717 Mixture with Varying NH_3 Concentration

x_{NH3} (%)	This Study	GRI-Mech3.0	Expt.
0	51.3	51.5	42.5 [3]
20	44.5	44.9	34.0 [4]
50	34.5	34.0	28.5 [4]

NH_3 が C_3H_8 燃焼反応にどのように影響するかを調べるため、燃焼反応で重要となるラジカル H, OH, O および NH_3 に関連するラジカル NH_2, NH のピークモル分率をプロットした(図 3)。x_{NH3}が増加するにしたがって、H, OH, O ラジカルが減少、特に H ラジカルは 0.01 から 0.006 まで大幅に減少する。一方、NH_2, NH ラジカルはやや増加する。この結果は、Z. Wang らが報告している結果 [4]と一

致している。また、これらのラジカル量の変化は NH_3 の酸化が H, OH, O ラジカルによって主に進行していることを反映している [6]。

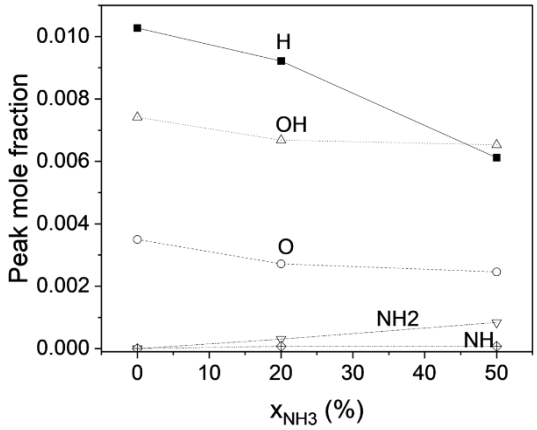

Fig.3 Peak Mole Fraction of H, OH, O, NH_2 and NH radicals with Varying NH_3 Concentration in R-290/R-717 mixture.

NH_3 濃度に対する素反応が LBV にどの影響するのかを調べるために、LBV に対する感度解析を行った。感度の絶対値が大きい上位の素反応、窒素が含まれる上位の素反応のx_{NH3}依存性を図 4 に示す。ラジカル分岐反応である H + O2 <=> O + OH の感度の絶対値が一番大きく、窒素が含まれる素反応の感度の絶対値は炭化水素の素反応に比べて小さい。窒素が含まれる素反応が LBV に直接的に影響を与えるのではなく、NH_3 の増加により H ラジカルを補足することで、燃焼の進行が抑制され LBV が減少すること [7]が確認された。

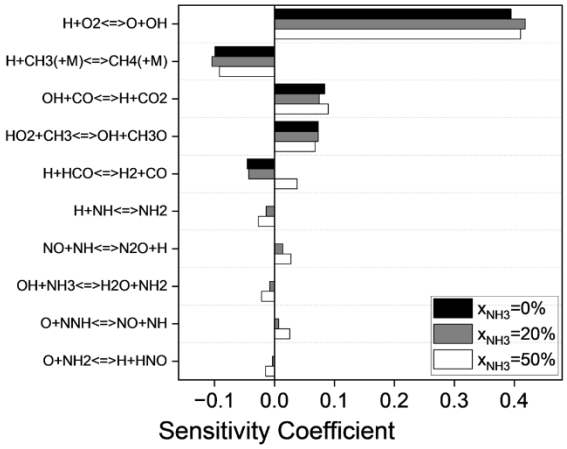

Fig.4 Sensitivity Analysis for LBV of R-290/R-717 mixture with Varying NH_3 Concentration.

これらの結果から、本研究で提案したグラフネットワーク解析の手法によって構築した反応モデルによる LBV_{max} の予測は妥当性があると判断した。

次に、R-152a/R-717 の混合冷媒の計算結果について示す。図 5 は、LBV の当量比 Eq 依存性である。当量比 Eq が 1.1 付近で LBV が最大となり、x_{NH3}が増加するにしたがって、LBV_{max} が減少する。x_{NH3}=0, 20, 50%で、LBV_{max} が 24.4, 22.1, 17.6 (cm/s) となる。R-152a/R-1234yf (モル分率 50 : 50)の混合冷媒の LBV_{max} は約 14 (cm/s)であることが報告 [12] されており、R152a/R-717 の混合冷媒はそれよりやや大きい。なお、NH_3 の燃焼生成物として NO を確認している。

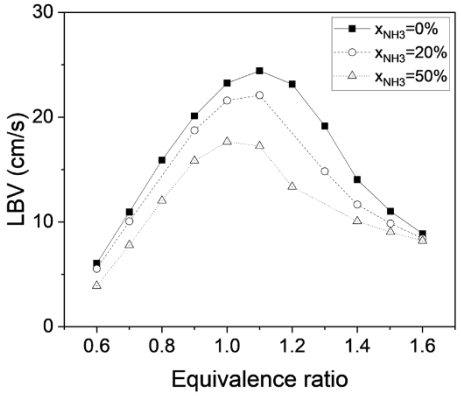

Fig.5 LBV of R-152a/R-717 as a Function of Equivalence Ratio.

NH_3 が R-152a である $C_2H_4F_2$ 燃焼反応にどのように影響するかを調べるため、燃焼反応で重要となるラジカル H, OH, O および NH_3 に関連するラジカル NH_2, NH のピークモル分率をプロットした(図 6)。x_{NH3}が増加するにしたがって、H, O ラジカルが減少する一方、OH はほぼ変わらず、NH_2, NH ラジカルは増加する。特に H ラジカルは約 0.004 から約 0.002 まで大幅に減少し、NH_2 は 0.002 まで大幅に増加する。R-290/R-717 混合冷媒に比べて、R-152a から発生する F ラジカルにより H, OH, O ラジカルの量が減少しており、NH_3 の酸化の進行が抑制される。NH_3 酸化の抑制下において、NH と H の反応により NH_2 が再生成されること

で、NH_2 ラジカルが増加、H ラジカルが減少すると考えられる。

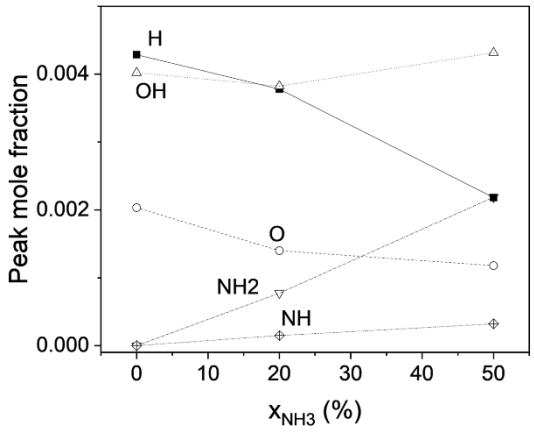

Fig.6 Peak Mole Fraction of H, OH, O, NH_2 and NH radicals with Varying NH_3 Concentration in R-152a/R-717 mixture.

NH_3 濃度に対する素反応が LBV にどの影響するのかを調べるために、LBV に対する感度解析を行った。感度の絶対値が大きい上位の素反応、窒素が含まれる上位の素反応のx_{NH3}依存性を図 7 に示す。R-290/R-717 の混合冷媒の場合と同様に、ラジカル分岐反応である H + O2 <=> O + OH の感度の絶対値が一番大きい。一方、R-290/R-717 の混合冷媒の場合と異なり、H + NH <=> NH2 の NH_2 再生成に関する感度の絶対値が HFC 系の素反応の値に近くなる。NH_3 の酸化の抑制により、NH_2 再生成の反応の寄与が大きくなったと考えられる。

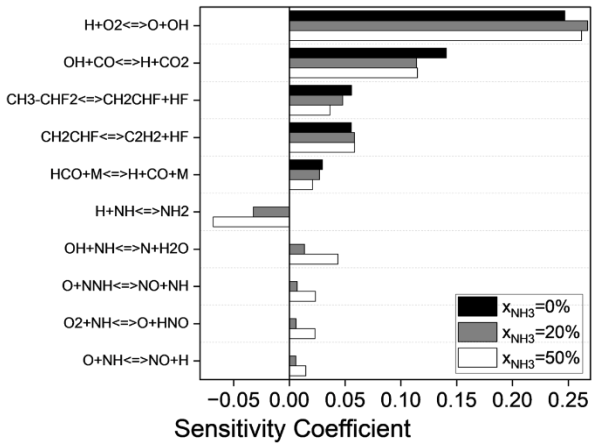

Fig.7 Sensitivity Analysis for LBV of R-152a/R-717 mixture with Varying NH_3 Concentration.

グラフネットワーク解析を用いて構築した反応モデルにより、R-152a/R-717 の混合冷媒の LBV_{max} を計算し、R-152a/R-1234yf の混合冷媒よりやや大きいと予測した。また、NH_3 の添加による LBV_{max} の低減の要因として、NH_3 酸化の抑制によって NH_2 再生成が寄与していると考えられる。

以上より、本研究で提案したグラフネットワーク解析を用いた反応モデルの構築手法により、新しい化学種に対応した冷媒材料の LBV_{max} を予測することが可能となり、また組成変化による燃焼反応機構への影響についても考察が可能となる。

まとめ・今後の展望

本研究では、新しい化学種が関与する素反応データを RMG によって生成し、感度解析でランキング化した上位の素反応データを、グラフネットワーク解析を用いて、NIST Fluorine モデルに追加することで反応モデルを構築した。構築した反応モデルに基づいて、層流燃焼速度を計算し、R-290/R-717 の混合冷媒で従来モデルとほぼ一致したことを確認した。次に、比較的低い GWP で A2 の R-152a に R-717 を混合した冷媒の反応モデルを構築し、LBV_{max} を計算した。NH_3 を 50%添加すると、17.6 (cm/s)まで低下した。NH_3 添加により GWP や燃焼性が低減するため、R-152/R-717 の混合冷媒の利用可能性も考えられる。このように、本研究で提案した手法は、新しい冷媒及びその混合組成の開発に貢献できると期待される。

参考文献

1）V. I. Babushok, D. R. Burgess Jr., D. Kim, M. Hegetschweiler, and G. T. Linteris, “Modeling of Combustion of Fluorine-Containing Refrigerants”, NIST Technical Note TN 2170, National Institute of Standards and Technology, Gaithersburg, MD, (2021).

2）M. Liu, A. Grinberg, D. Matthew, S. Johnson, M. J. Goldman, A. Jocher, A. M. Payne, C. A. Grambow, K. Han, N. W. Yee, E. J. Mazeau, K. Blondal, R. H. West, C. F. Goldsmith, and W. H. Green, ”Reaction Mechanism Generator v3.0: Advances in Automatic Mechanism Generation”, J. Chem. Inf. Model. **61**(6) 2686-2696 (2021).

3）C. Chen, Z. Wang, Z. Yu, X. Han, Y. He, Y. Zhu, and A. A. Konnov, “Experimental and kinetic modeling study of laminar burning velocity enhancement by ozone additive in NH3+O2+N2 and NH3+CH4/C2H6/C3H8+air flames”, Proceedings of the Combustion Institute **39**(4) 4237-4246 (2023).

4）Z. Wang, C. Ji, D. Wang, T. Zhang, Y. Zhai, and S. Wang, “Experimental and numerical study on laminar burning velocity and premixed combustion characteristics of NH3/C3H8/air mixtures”, Fuel, 331(2) 125936 (2023).

5）J. Liu, D. Liu, L. Dai, C. Zou, Q. Lin, and C. Peng, “The effects of C/N cross-reactions on the NH3/C3H8 combustion: A shock-tube and modeling study”, Combustion and Flame, 270, 113716 (2024).

6）G. Yin, B. Xiao, J. You, H. Zhan, E. Hu, and Z. Huang, “Experimental and kinetic modeling study on propane enhancing the laminar flame speeds of ammonia”, Fuel Processing Technology, 247, 107779 (2023).

7）D. Wang, Z. Wang, T. Zhang, Y. Zhai, R. Hou, Z.-Y. Tian, C. Ji, “A comparative study on the laminar C1–C4 n-alkane/NH3 premixed flame”, Fuel 324, 124732 (2022).

8） G. A. Longo, C. Zilio, and G. Righetti, “Condensation of the low GWP refrigerant HFC152a inside a Brazed Plate Heat Exchanger”, Experimental Thermal and Fluid Science, 68, 509-515 (2015).

9） ANSYS Chemkin-Pro: Release 2022 R1. ANSYS, Inc., Canonsburg.

10）D. G. Goodwin, H. K. Moffat, I. Schoegl, R. L. Speth, and B. W. Weber, “Cantera: An object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes”, https://www.cantera.org, 2024. Version 3.1.0.

11）G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. Gardiner, Jr., V. V. Lissianski, and Z. Qin, http://www.me.berkeley.edu/gri_mech/.

12） D. K. Kim, V. I. Babushok, M. J. Hegetschweiler and G. T. Linteris, “Flame Propagation in Blends of R-152a, R-134a, and R-1234yf with Air.” Combustion Science and Technology **196**(18) 5107–5127 (2023).