표면반응을 위한 OpenFOAM 기반 라이브러리 개발: 암모니아 개질

Danh Nam Nguyen*, 이재훈*, 서해원**, 안형준**, 유춘상*,†

Development of an OpenFOAM-based library for surface chemistry: An application for ammonia decomposition

Danh Nam Nguyen*, Jae Hun Lee*, Hae Won Seo**, Hyung Jun Ahn**, Chun Sang Yoo*,†

Recently, hydrogen (H₂) production has gained significant attention since H₂ has emerged as an effective and clean alternative to fossil fuels, especially in the power generation sector, to meet carbon neutrality by 2050 [1,2]. While many experimental studies on the H₂ production from catalytic ammonia (NH₃) decomposition have been conducted [2-5], the numerical investigation on this field is limited due to lacking sufficient computational fluid dynamics (CFD) package for public use to handle surface reactions occurring in catalytic processes. In that context, we developed a new surface chemistry library in OpenFOAM (OF) platform, a free and robust open-source CFD package [6], to provide a sufficient CFD tool for researchers working on this field and combustion community since there is no such library officially available in OF. The developed library can handle several types of typical surface reaction rate models consisting of the basic Arrhenius form, sticking coefficient, and surface coverage dependence models. It can be utilized for simulations of catalytic reacting flows at surfaces and through porous media using detailed microkinetic models. The developed library is validated through simulations of ammonia decomposition to produce hydrogen using Ru/MgO catalyst.

Typically, a surface mechanism may include I surface reactions that involve up to K chemical species in the system where the rate constant for the i-th reaction can be assumed to have Arrhenius temperature dependence (i.e., Arrhenius form). However, the rate expression for a surface reaction can be altered in several ways from the basic expression [7]. For some simple surface reaction mechanisms, it is convenient to specify the surface reaction rate in terms of a "sticking coefficient" (probability), rather than an actual reaction rate [7]. In some cases, there are experimental data indicating that the Arrhenius expression for the rate constant is modified by coverage (concentration) of some surface or bulk species. The details of these altered forms can be found in [7].

One of the key features of OF is its extensibility since it is written in C++ using object-oriented programming (OOP) technique. However, this extensibility must be satisfied with OOP characteristics. In other words, the newly added classes will interface with existing code through inheritance, polymorphism, and abstraction features.

In this work, the surface reaction rate constants must be in a general form to ensure the OOP characteristics in the code development. This is one of the keys for developing a framework to handle surface chemistry in OF. To do so, we introduce a general form (i.e., Arrhenius-like) for surface reaction rate constants of the i-th reaction given as:

$$k_i = A_i T^{\beta_i} \exp\left(-\frac{E_i}{RT}\right) \cdot S_i \cdot COV_i \cdot P_i \qquad (1)$$

where the pre-exponential factor A_i, the temperature exponent β_i, and the activation energy E_i are specified for each reaction as input to the program. R is the gas constant. S_i, COV_i, and P_i terms are representative for

* 울산과학기술원 기계공학과
** 포스코홀딩스 저탄소CCUS연구센터
† 연락저자, csyoo@unist.ac.kr

contribution of sticking coefficient reactions, coverage modifications rate constant reactions, and partial pressure dependent reactions (such as in Takahashi model [8]). They have the following forms depending on the type of reactions. Specifically, when it is a general surface reaction (i.e., in Arrhenius form):

$$S_i = 1, \ COV_i = 1, \ P_i = 1 \qquad (2)$$

If it is a sticking coefficient reaction:

$$S_i = \frac{\amalg_{i=1} \sigma_j^{v'_{ij}}}{\left(\Gamma_{tot}\right)^m} \sqrt{\frac{RT}{2\pi W_k}}, \quad COV_i = 1, \ P_i = 1 \quad (3)$$

where, W_k is the molecular weight of the gas-phase species, Γ_{tot} is the total surface site concentration summed over all surface phases, and m is the sum of all the stoichiometric coefficients of reactants that are surface species. The product term $\amalg_{i=1} \sigma_j^{v'_{ij}}$ is the product of site-species occupancies, raised to a power equal to the reaction order for that species, for all site species that are reactants. σ_j is the number of sites that the surface species occupies, and v_j is the reaction order for that species [7].

If it is a coverage modification of rate constant reaction:

$$S_i = 1 \ , \ P_i = 1,$$

$$COV_i = \prod_{k=K_s^f\left(N_s^f\right)}^{K_s^l\left(N_s^l\right)} 10^{\eta_{ki}[Z_k(n)]} \ [Z_k(n)]^{\mu_{ki}} \exp\left(-\frac{\varepsilon_{ki}[Z_k(n)]}{RT}\right) \quad (4)$$

where η_{ki}, μ_{ki} and ε_{ki} are three coverage parameters for species k in the reaction i-th. The product in Eq. 4 over only those surface species that are specified as contributing to the coverage modification. Note that, the surface site fractions Z_k appear in the equation rather than molar concentrations for surface species [7].

If it is partial pressure dependent reaction (i.e., Takahashi reaction [8]):

$$S_i = 1, \ COV_i = 1, \ P_i = \frac{1}{\sum_{j=1}^{N_g}[c_j]} \qquad (5)$$

where C_j is the concentration of gas phase species.

By utilizing the proposed form, the implementation of surface reaction rate models in OF becomes feasible and straightforward, leveraging the foundational structure of the *chemistryModels* library. Consequently, a new library named *catalystModels* has been developed. This library can be used for simulations of catalytic processes where the reactive flows take place on catalytic surfaces or within porous media.

To validate the newly developed library, we conduct two-dimensional (2-D) axisymmetric simulations of ammonia decomposition within a tubular channel featuring a reacting surface using Ru/MgO catalyst in OF. This setup is inspired by a previous study on ammonia decomposition in a fixed bed reactor configuration [9]. However, in this test case, the porous media is not included to simplify the problem, and the heated wall is changed to be catalytic wall compared to those in [9]. The details of computational domain and boundary conditions are depicted in Fig. 1. The calculation of surface chemistry is evaluated by a simplified version of the modified Takahashi micro kinetics [10] such that the partial pressure terms in the reaction rate equations are neglected. The details of the modified Takahashi surface chemical mechanism can be found in [10]. Simulations with the same configuration and boundary conditions performed using ANSYS Fluent [11] are served as the benchmark data in this case.
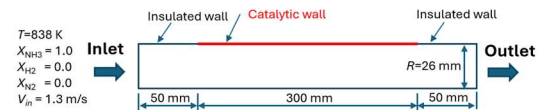

Figure 1. The configuration of a tubular reactor for ammonia decomposition.

The isocontours of temperature and NH₃ mass fraction predicted by OF using the

developed library and the benchmark data obtained from ANSYS Fluent are shown in Fig. 2 for qualitative comparison. Overall, the figure indicates that the developed library in OF can be utilized to predict reasonably well the behavior of reactive flows including reacting surfaces in comparison to the benchmark data. Specifically, it can be observed that species fluxes are generated from the reacting wall, implying that surface reactions are taking place. In addition, temperature at the reacting wall and near that surface are decreased compared to that in the central exist, reflecting an endothermic process of the ammonia decomposition where heat is absorbed from the surrounding.
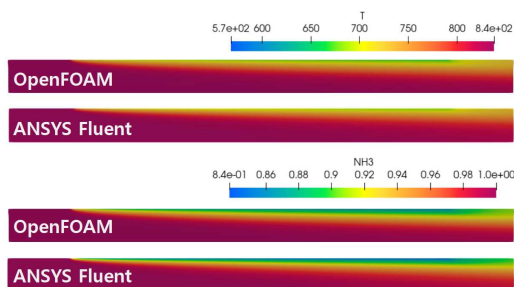

Figure 2. The distribution of the temperature(top) and ammonia mass fraction (bottom) over the whole domain.

For quantitative assessment, Fig. 3 shows the one-dimensional (1-D) profiles of temperature and NH_3 mass fraction along the radial direction at the outlet of the domain together with the benchmark data. It is seen that the predicted profiles closely resemble those of the benchmark data. However, in proximity to the reacting wall, the temperature predicted by OF is marginally underestimated compared to ANSYS Fluent. This deviation originates from differences between two platforms in how to evaluate the convective and diffusive mass fluxes of gas phase species at the catalytic surface. In ANSYS Fluent, these fluxes are evaluated by using diffusion velocity based on fully multicomponent mixture model, while those are evaluated based on unity Schmidt and Lewis number assumptions in OF.
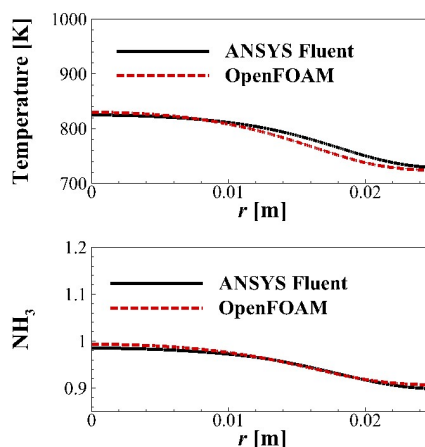

Figure 3. The 1-D profile along the radial direction of predicted temperature (top) and mass fraction of NH_3 (bottom) at outlet of the domain in comparison with benchmark data (ANSYS Fluent). Black lines are data obtained by ANSYS Fluent. Red dashed lines are data obtained by OF.

For further validation including porous media model, we perform simulations of 2-D axisymmetric fixed bed catalytic reactor for ammonia decomposition using the developed library with a configuration as depicted in Fig.4. In this configuration, Ru/MgO catalyst [9] is utilized. This test case has been conducted computationally by Takahashi et al. [9]. Detailed descriptions of the test case can be found in [9]. It is of importance to note that the computational domain is the same as in simulations for reacting surface cases as discussed above. However, it includes porous media zone as modeling for fixed bed reactor. The computational domain also consists of 41,600 structured elements with the uniform grid size of 0.5 mm in both axial and radial directions. Simulations are conducted in steady state mode with different inlet temperature conditions [9] in which the surface chemistry is calculated based on the modified Takahashi micro kinetic model [10].

Heat transfer models play a critical role in the simulation of the catalytic fixed bed reactor. In the present work, all sufficient heat transfer models as mentioned in [9] have also been

implemented in OF. The details of heat transfer models can be found in [9].
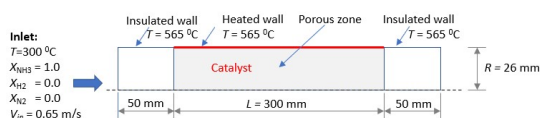

Figure 4. The configuration of a fixed bed reactor for ammonia decomposition [9].

Figure 5 demonstrates the predicted conversion rates of ammonia to hydrogen within the fixed bed reactor using Ru/MgO catalyst at various inlet temperatures in comparison to benchmark data by Takahashi et al. [9] and a previous study by Nguyen et al. [10]. Overall, the results from the present study exhibit good agreement with the benchmark data [9] and the previous study [10], indicating that the developed library can be utilized for simulations of a fixed bed reactor using detailed surface chemical mechanisms. Specifically, the NH_3 conversion rates predicted by OF closely align with the benchmark data when inlet temperatures exceed 350^oC. However, for inlet temperatures below 350^oC, the NH_3 conversion rates are slightly underestimated. We conjecture that these discrepancies likely originate from differences in the adopted microkinetic model and the CFD framework between our study and the one by previous works [9, 10].
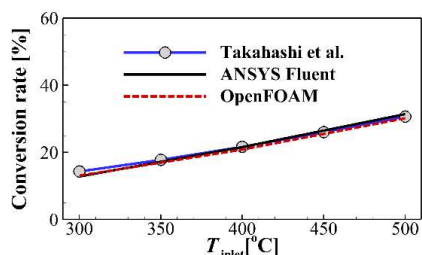

Figure 5. The validation for different inlet temperatures. Blue line with symbols is benchmark data from [9]. Black line is data by from [10] using ANSYS Fluent. The red dashed line is data obtained using OF.

Acknowledgements

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