Numerical Investigations on the Molecular Reaction Model for Thermal Cracking of n-Decane at Supercritical Pressures

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ABSTRACT: The pyrolysis of endothermic hydrocarbon fuel plays a vital role in regenerative cooling channels. Based on previous experiments and mechanism models of n-decane, and considering the impact of the secondary reaction at high conversion, the present work establishes a cracking reaction model of n-decane containing 16 species and 26 reactions. One-dimensional plug flow reactor simulation verifies that the model has high accuracy in predicting species distribution. The high-accuracy model is applied to the computational fluid dynamics (CFD) simulation of the supercritical cracking heat transfer, and compared with the results of a one-step global model as the chemistry model. The results show that the high-accuracy model is more accurate in terms of fuel conversion, temperature, and product distribution. Furthermore, the reasons for the difference of the two chemistry models in the CFD simulation are analyzed from the perspective of chemical kinetics. The new model generates more products of small molecules due to the consideration of secondary reactions. However, for the one-step model, it mainly cracked into large molecules even at high conversion. The product distribution affects the chemical endotherm and then the fuel temperature, which in turn affects the reaction rate and finally the conversion of the fuel. In addition, pyrolysis affects the properties of the fuel, which in turn affects the convective heat transfer. Among the several influencing factors of heat transfer, the correction factor of isobaric specific heat, which is the ratio of the specific heat of fluid to the average specific heat, can well reflect the changing trend of the convective heat transfer coefficient. The present work demonstrates the important role of the kinetic model in the simulation of the supercritical cracking heat transfer process, and the corresponding methods can be used in the design of regenerative cooling systems.

1. INTRODUCTION

The combustor of a supersonic aircraft has an extremely harsh thermal environment.1−4 The regenerative cooling method is one of the best cooling technologies for rescuing this problem.5,6 The coolant flows through cooling channels to cool the combustor walls before it is pumped into the combustion chamber.7,8 Endothermic hydrocarbon fuels with high density and heat sink capacity due to endothermic reactions of the fuels, such as JP-7, JP-8, JP-10, and RP-3, are applied as the primary coolant.9−11 Moreover, the endothermic cracking process of n-decane, as a representative component and model fuel,12 has attracted much attention from researchers.13,14 During the cooling process, fuels undergo heat transfer coupled with thermal cracking and turbulent flow in a supercritical pressure state (4 MPa or higher).15 To accurately determine the supercritical cracking heat transfer performance of fuels in cooling channels, it is necessary to study the interaction of flow and chemical reactions.

Computational fluid dynamics (CFD) simulation is an effective tool to pore over this coupling process. To explore the impact of pyrolysis on heat transfer and flow characteristics, the chemical reaction mechanism is indispensable in CFD simulation. However, due to the limitation of the number of computations, most numerical simulation studies on the cracking process of hydrocarbon fuels including aviation kerosene, n-dodecane, and n-decane use global mechanism models, and the secondary reactions are not always considered in the existing literature.

Ward et al.16,17 developed a one-step global model of 19 species for n-decane pyrolysis based on proportional product distribution (PPD). This model was applied to numerous studies.18−26 Tao et al.24 used this model to study the effect of n-decane thermal cracking under supercritical conditions on heat transfer characteristics and flow resistance and suggested that cracking can enhance heat transfer and improve heat transfer deterioration. Feng et al.25 established a numerical
model with the PPD chemical model to analyze the effect of turbulence on pyrolysis. Their result indicated that with increasing turbulence intensity, the radial distribution of conversion is more uniform. Lei et al. also applied this model to study the effect factors of convective heat transfer and then modified the Dittus—Boelter correlation, which is suitable for conversion less than 23% of rectangular tubes. According to the experimental measurements from Ward,16,17 Ruan et al. proposed a global pyrolytic reaction model with 18 species for n-decane, which was employed in CFD simulation. A pyrolysis mechanism model of aviation kerosene RP-3 with two reactions proposed by Jiao et al.33 was used in CFD simulation to study the cracking effect on heat transfer in the different regions through two aspects including heat absorption and fuel properties. The traditional global mechanism as a practical solution for CFD simulation does not require a large number of computations, while accurately predicting fuel thermal cracking behavior, heat transfer, and flow characteristics under mildly-cracked conditions of low conversion. There is a big deviation in the prediction of the flow field at high fuel conversion as a result of secondary reactions.13,14,17,34 To consider the impact of the secondary reactions in the framework of one global reaction, the DGR model was constructed for n-decane, with the stoichiometric coefficients related to the conversion and pressure. Because the format of DGR is different from the commonly used mechanism, it is necessary to configure complex user-defined functions (UDFs) when implemented in CFD simulation. Therefore, some researchers used skeletal mechanisms in CFD applications to break the limitations that

Table 1. Kinetic Model for the Thermal Cracking of n-Decane

| reaction | $E_a$ (kcal/mol) | $A$ (s$^{-1}$) | source |
|----------|------------------|-------------|--------|
| $C_{10}H_{22} =$ | | | |
| $>0.41SH_2 + 0.2CH_4 + 0.39C_2H_4 + 0.3C_3H_8 + 0.37C_4H_{10} + 0.16C_6H_{14}$ | 59.35 | 6.21E + 15 | “ |
| $>0.1C_6H_8 + 0.04C_6H_{10} + 0.04C_8H_{12} + 0.005C_{10}H_{14}$ | | | |
| $C_2H_4 < \rightarrow >C_2H_2 + H_2$ | 65.21 | 4.65E + 13 | 17 |
| $2C_2H_4 \rightarrow >C_4H_6 + CH_4$ | 50.25 | 3.75E + 12 | “ |
| $C_2H_4 + >C_2H_2 + CH_4$ | 41.26 | (1.03E + 12)$^b$ | 17 |
| $C_2H_4 + >C_2H_2 + >C_2H_2 + CH_4$ | 60.43 | (7.08E + 13)$^b$ | 17 |
| $C_2H_4 < \rightarrow >C_2H_2 + H_2$ | 50.60 | 4.69E + 10 | 17 |
| $C_3H_6 < \rightarrow >C_3H_2 + H_2$ | 51.29 | 5.89E + 10 | 17 |
| $C_4H_6 < \rightarrow >C_4H_2 + CH_2$ | 59.06 | (2.54E + 13)$^b$ | 41 |
| $C_3H_5 < \rightarrow >C_3H_2 + CH_3$ | 54.49 | 1.42E + 13 | “ |
| $2C_4H_6 < \rightarrow >3C_4H_2$ | 59.39 | 7.39E + 11 | 41 |
| $C_2H_4 + >C_2H_2 + CH_4$ | 55.80 | 7.28E + 16 | “ |
| $C_2H_4 + >C_2H_2 + >C_2H_2 + CH_4$ | 56.20 | (1.00E + 16)$^b$ | 41 |
| $C_3H_6 < \rightarrow >C_3H_2 + H_2$ | 59.64 | 7.00E + 12 | 17 |
| $C_2H_4 < \rightarrow >C_2H_2 + H_2$ | 62.06 | 1.64E + 12 | 17 |
| $C_3H_6 < \rightarrow >C_3H_2 + H_2$ | 70.68 | 7.00E + 14 | 17 |
| $C_4H_6 < \rightarrow >C_4H_2 + CH_2$ | 61.31 | 4.10E + 14 | “ |
| $C_3H_5 < \rightarrow >C_3H_2 + CH_3$ | 50.00 | 1.00E + 10 | 17 |
| $C_4H_6 < \rightarrow >C_4H_2 + H_2$ | 53.56 | 1.11E + 11 | “ |
| $C_2H_4 + >C_2H_2 + >C_2H_2 + H_2$ | 36.90 | 9.74E + 13$^b$ | “ |
| $C_2H_4 + >C_2H_2 + >C_2H_2 + 2H_2$ | 52.20 | (1.36E+15)$^b$ | 41 |
| $C_3H_5 < \rightarrow >C_3H_2 + H_2$ | 36.60 | 1.08E + 14$^b$ | “ |
| $C_4H_6 < \rightarrow >C_4H_2 + H_2$ | 55.07 | 2.35E + 12 | “ |
| $C_5H_{12} + H_2 \rightarrow >C_5H_4 + >C_2H_4 + C_2H_2$ | 55.07 | 4.00E + 12 | “ |
| $C_2H_4 + >C_2H_2 + >C_2H_2 + 2H_2$ | 57.07 | 9.10E + 12 | “ |
| $C_3H_6 < \rightarrow >C_3H_2 + 2CH_2$ | 59.64 | 7.00E + 16 | “ |
| $C_4H_{10} =$ | | | |
| $>0.094H_2 + 0.2CH_4 + 0.4C_2H_4 + 0.2C_6H_8 + 0.4C_4H_{10} + 0.1C_8H_{12}$ | 44.08 | 1.80E + 13 | “ |
| $+ 0.2C_6H_8 + 0.04C_6H_{10} + 0.04C_8H_{12} + 0.198C_{10}H_{14}$ | | | |

*aKinetic parameters rederived by authors. *bUnits: m$^3$/(mol·s)*. 
global mechanisms cannot be used for high fuel conversion. Xu et al.\textsuperscript{35} used a molecular kinetic model\textsuperscript{36,37} for aviation kerosene, including 18 species and 24 reactions in the numerical study of fuel cracking and heat transfer. Zhao et al.\textsuperscript{38} also utilized this cracking mechanism to study the pressure numerical study of fuel cracking and heat transfer. Li et al.\textsuperscript{39} applied improved kinetics of the aviation kerosene HF-1\textsuperscript{35} in a CFD model to the coupling mechanism of heat transfer and thermal cracking. The results pointed out that increasing heat flux leads to local heat transfer deterioration. However, when the framework mechanism model is applied to numerical simulations, there are still few studies to analyze the mechanism performance from the perspective of chemical kinetics. Therefore, it is necessary to develop a cracking mechanism model under high conversion and then apply it to numerical simulations to reveal the interaction between flow and chemical reaction.

The focus of the present work is to conduct a comprehensive study on the cracking heat transfer process of n-decane under supercritical pressure to reveal the interaction between flow and chemical reaction. Based on previous experimental data and mechanism models, a high-accuracy multi-step cracking reaction model is established and incorporated into a CFD model. Compared with the one-step model, the multi-step mechanism better describes the reaction flow process. Furthermore, the reasons for the difference in the convective heat transfer coefficient prediction of the two reaction models in the CFD simulation are analyzed from heat absorption capacity and thermophysical properties. Among the several influencing factors of heat transfer, the correction factor of isobaric specific heat can well reflect the changing trend of the convective heat transfer coefficient. The present work demonstrates the important role of the mechanism model in the simulation of the supercritical cracking heat transfer process, and provides guidance for the selection of the chemical reaction model in CFD simulation.

2. CHEMICAL KINETIC MODEL

2.1. Model Construction. In previous work, Wang et al.\textsuperscript{40} proposed a descriptive chemical kinetic model for n-decane thermal cracking based on their experimental results of product distributions.\textsuperscript{41} The model contains one primary reaction and 21 secondary reactions to describe the product distributions from low to high conversion of n-decane. However, in the descriptive model, the non-aromatic main products with more than four carbons and the aromatic species are lumped as C5+ and CnH2n+6.\textsuperscript{42} The present kinetic model, hereafter referred to as a multi-step model, was derived from the experimental results, it does not consider the coking process that should occur when the fuel temperature is above 700 °C.

The corresponding structures to the species involved in the primary reaction are given in the Supporting information. The pre-exponential factor is 6.209 × 10\textsuperscript{15} s\textsuperscript{-1}, and the activation energy is 59.35 kcal/mol. Table 1 shows the kinetic model of n-decane cracking. The kinetic parameters of partial secondary reactions come from the literature\textsuperscript{44-46} in Arrhenius form. Moreover, the pre-exponential factor and activation energy of some secondary reactions have been adjusted to improve the predictions of the model on species distribution of typical cracking products including methane, ethane, ethylene, propylene, benzene, and toluene-based on the simulation results of the Chemkin program.\textsuperscript{47} The adjusted reactions were labeled in Table 1. The present kinetic model, hereafter referred to as a multi-step model, was derived from the experimental results, it does not consider the coking process that should occur when the fuel temperature is above 700 °C.

2.2. Model Validation. The model validation has been conducted against the pyrolysis experiments\textsuperscript{41} from low conversion to high conversion of n-decane in an electrical heating tube under a pressure of 4 MPa and temperature range of 480–740 °C. Table 2 shows the three experimental operating conditions from run1 to run3. According to the fuel temperature distribution of the heating tube obtained from the experiments as shown in Figure 1, a one-dimensional plug flow reactor (PFR) was used to simulate the reaction process using the Chemkin program.\textsuperscript{47}

The experimental data used in this paper are from the work of Wang et al.\textsuperscript{41} Wang et al. carried out experiments in a two-stage fuel heating and cracking system. The detailed local

Table 2. Three Operation Conditions in PFR Experiments

| run no. | q\textsubscript{in} (g/s) | p (MPa) | L (m) | T\textsubscript{out} (°C) |
|---------|----------------|---------|-------|----------------|
| 1       | 1.00           | 4.0     | 0.55  | 719.6          |
| 2       | 1.00           | 4.0     | 0.50  | 728.7          |
| 3       | 1.00           | 4.0     | 0.46  | 740.1          |

Figure 1. Fuel temperatures along the test tube reactor. The data from ref 41.
The chemical compositions and temperatures of the reactor tube were obtained by the electric heating tube method. The tube (2 mm inner diameter) was placed horizontally and heated by resistive heating. Consistent with the actual working conditions in the engine’s cooling channel, the pressure was set to 4.0 MPa, and the mass flow rate was 1.00 g/s. The pyrolysis experiments were conducted from low conversion to high conversion of n-decane. A detailed description of the experimental system can be found in the previous work of Lei et al.22 The fluid temperatures were measured using a thermocouple with an accuracy of ±0.5%. The relative uncertainty of the measured mass flow rate of the inlet fuel was less than 0.1%, and the uncertainties of the measured mass fraction for all species were less than 2.5%.

Figure 2 shows the comparisons between simulated and experimental yields of typical cracked products of n-decane along the test tube reactor. Methane, ethane, ethylene, and propylene are the gas-phase products with higher yields. Benzene and toluene are important products of the secondary reaction.41 Therefore, these six products were selected as components for comparison of the errors between simulations and experiments. As shown in Figure 2, the predicted yields of methane, ethane, and ethylene are consistent with the experimental values in a wide range. When the conversion exceeds 70%, the predicted values of methane and ethane are slightly lower than experiments and the maximum relative error is within 15%. The predicted values of ethylene under run1 and run2 conditions are only slightly lower than the experiment at 0.45–0.55 m. Under run3 conditions, when the cracking rate of n-decane is greater than 65%, the maximum relative error reaches 24%. The simulated values of propylene under the three operating conditions are all greater than the experimental values, indicating that the reaction kinetics related to the formation of propylene may be greatly overestimated. The yields of benzene and toluene obtained by the simulation are in good agreement with the experimental results under the operating conditions of run2 and run3, and both are higher than the experimental values under the operating conditions of run1. The deviation of some points should be ascribed to the uncertainty of the cracking experiment of n-decane and the analysis uncertainty of the complex components, and to the kinetic model with limited components and reactions.

The simulation results of fuel density and corresponding residence time are compared with experimental results as shown in Figure 3. As the heating distance increases, the fuel density drops from 95.2 to 17.0 kg/m³ in the experiment, while the simulated value decreases from 84.5 to 17.0 kg/m³. The relative error of 13% is obtained at the entrance, which should be attributed to estimating the thermophysical properties of the fuel with the ideal gas equation of state, which is different from the real fuel properties. The results show that the
residence time increases rapidly at the beginning attributed to the relatively high density of the unreacted n-decane, and then the residence time gradually increases because the fuel density decreases sharply resulting from the heating, phase transition, and thermal cracking of n-decane. Finally, the maximum calculated fuel residence time of 0.075 s is obtained at the exit of run1. Overall, the developed multi-step kinetic model has high accuracy in predicting the typical product yields, density, and residence time. After the above validation from chemical kinetics, the developed model can be used in the following numerical simulations.

2.3. One-Step Kinetic Model for Comparison. The one-step global model proposed by Ward\textsuperscript{17} was used for comparative study in the following part of the numerical simulation. The one-step model with 19 species is expressed as follows

\[
\begin{align*}
\text{C}_{10}\text{H}_{22} & \rightarrow 0.151\text{H}_2 + 0.143\text{CH}_4 + 0.256\text{C}_2\text{H}_4 \\
& + 0.126\text{C}_6\text{H}_8 + 0.230\text{C}_7\text{H}_8 + 0.180\text{C}_8\text{H}_8 \\
& + 0.196\text{C}_{10}\text{H}_4 + 0.102\text{C}_{10}\text{H}_{10} + 0.171\text{C}_{12}\text{H}_{10} \\
& + 0.124\text{C}_{12}\text{H}_{12} + 0.195\text{C}_{14}\text{H}_{12} + 0.089\text{C}_{16}\text{H}_{14} \\
& + 0.169\text{C}_{16}\text{H}_{14} + 0.072\text{C}_{18}\text{H}_{16} + 0.152\text{C}_{18}\text{H}_{18} \\
& + 0.012\text{C}_{18}\text{H}_{18} + 0.053\text{C}_2\text{H}_4 + 0.003\text{C}_6\text{H}_{10} \\
\end{align*}
\]

(2)

Its pre-exponential factor is $1.6 \times 10^{15}$ s$^{-1}$, and the activation energy is 63 kcal/mol. The corresponding chemical names of the species involved in the model are included in the Supporting information. The one-step global model is widely used for low fuel conversion, so it can be used to compare the performance of the multi-step model and the one-step model in the front section of the reaction tube. Under the condition of high fuel conversion, the comparison of the two reaction models can illustrate the effect of the secondary reactions on fuel cracking.

3. CFD MODEL

3.1. Computational Model and Mesh. Based on experimental conditions,\textsuperscript{41} a two-dimensional axisymmetric model of the horizontal circular tube was established for the CFD simulation, as shown in Figure 4. The radius was 1 mm, and the length of the uniformly heated section was 550 mm. At the inlet, an adiabatic section of 150 mm was adopted with the purpose of the complete development of the flow. While at the outlet, an adiabatic section of 150 mm was also included to avoid the outflow boundary effects. There are detailed fuel conversion, fluid temperature, and species distribution along the electrical heating tube reactor for operation condition 1, so these conditions were selected as boundary conditions of numerical simulations. The mass flow rate was set as 1 g/s, operating pressure was 4 MPa, inlet temperature was 753 K, the wall heat flux was 640 kW/m$^2$, and gravitational acceleration was 9.8 m/s$^2$. To verify the reasonability of the two-dimensional axisymmetric model, three-dimensional simulations are performed for the same operating conditions, and the comparisons are given in Figures S1–S3 of the SI. The slight temperature difference demonstrate that the flow can be considered as axisymmetric under the present conditions.

The mesh independence was first studied to ensure the accuracy of the mesh before conducting a detailed numerical study. The axial and radial direction mesh size was determined as $850 \times 40$. To ensure the wall $y^+$ is less than 1, the first layer mesh height was 0.001 mm, and the mesh growth rate was 1.2.

3.2. Governing Equations and Solution Method. For the two-dimensional (2D) axisymmetric geometry, the equations for conservation of continuity, momentum, energy, and species could be written as follows\textsuperscript{48}

\[
\frac{\partial}{\partial x}(\rho \nu_x) + \frac{\partial}{\partial r}(\rho \nu_r) + \frac{\rho v}{r} = 0
\]

(3)

\[
\frac{1}{r} \frac{\partial}{\partial x} (r \rho \nu_x) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho \nu_r) = -\frac{\partial p}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} \left[ \mu \left( \frac{\partial \nu_x}{\partial x} + \frac{\partial \nu_r}{\partial r} \right) \right]
\]

(4)
\[
\frac{1}{r} \frac{\partial}{\partial x} (r \rho \nu v_x) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho \nu v_r) = -\frac{\partial p}{\partial r} + \frac{1}{r} \frac{\partial}{\partial x} \left[ \rho \left( \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} \right) \right] \\
+ \frac{1}{r} \frac{\partial}{\partial r} \left[ \frac{\partial}{\partial r} \left( 2 \rho \left( \frac{\partial v_x}{\partial r} - \frac{2}{3} \nabla \cdot \vec{v} \right) \right) \right] - 2 \mu \frac{v_y}{r^2} + \frac{2 \mu}{3} r \left( \nabla \cdot \vec{v} \right) + \rho g 
\]

(5)

\[
\frac{\partial}{\partial x} (\rho \nu h) + \frac{\partial}{\partial r} (\rho \nu h) = \frac{\partial}{\partial x} \left( \frac{\lambda}{c} \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial r} \left( \frac{\lambda}{c} \frac{\partial T}{\partial r} \right) - \frac{\rho \nu h}{r} + \frac{\lambda}{c} \frac{\partial T}{\partial r} + S_h \nabla \cdot \vec{v} \]

(6)

\[
\frac{\partial}{\partial x} (\rho \nu Y_i) + \frac{\partial}{\partial r} (\rho \nu Y_i) = \frac{\partial}{\partial x} \left( \frac{j_i}{\rho} \right) + \frac{\partial}{\partial r} \left( \frac{j_i}{\rho} \right) - \rho \nu Y_i r + \frac{j_i}{r} + R_i 
\]

(7)

where

\[
\nabla \cdot \vec{v} = \frac{\partial v_x}{\partial x} + \frac{\partial v_y}{\partial y} + \frac{v_x}{r} 
\]

(8)

And \(x\) is the axial coordinate, \(r\) is the radial coordinate, \(v_x\) is the axial velocity and \(v_y\) is the radial velocity, \(S_h\) is the energy source representing the heat of the chemical reaction, \(Y_i\) is the mass fraction of species \(i\), \(j_i\) is the diffusion flux of species \(i\), and \(R_i\) is the net rate of production of species \(i\).

The turbulence kinetic energy \(k\) and its rate of dissipation \(\epsilon\), were obtained from the following transport equations

\[
\frac{\partial}{\partial x} (\rho \nu \nu k) + \frac{\partial}{\partial r} (\rho \nu \nu k) = \frac{\partial}{\partial x} \left[ \mu + \frac{\mu_t}{\sigma_k} \frac{\partial k}{\partial x} \right] + \frac{\mu_t}{\sigma_k} \frac{\partial}{\partial r} \left[ \mu + \frac{\mu_t}{\sigma_k} \frac{\partial k}{\partial r} \right] - \frac{\rho \nu k}{r} \\
+ 1 r \left[ \mu + \frac{\mu_t}{\sigma_k} \right] \frac{\partial k}{\partial r} + C_\varepsilon \frac{\nu \nu \epsilon}{k} - C_\varepsilon \frac{\nu \nu \epsilon^2}{k} 
\]

(9)

\[
\frac{\partial}{\partial x} (\rho \nu \nu \epsilon) + \frac{\partial}{\partial r} (\rho \nu \nu \epsilon) = \frac{\partial}{\partial x} \left[ \mu + \frac{\mu_t}{\sigma_\epsilon} \frac{\partial \epsilon}{\partial x} \right] + \frac{\mu_t}{\sigma_\epsilon} \frac{\partial}{\partial r} \left[ \mu + \frac{\mu_t}{\sigma_\epsilon} \frac{\partial \epsilon}{\partial r} \right] - \frac{\rho \nu \epsilon}{r} \\
+ 1 r \left[ \mu + \frac{\mu_t}{\sigma_\epsilon} \right] \frac{\partial \epsilon}{\partial r} + C_{\varepsilon 1} \frac{\nu \nu \epsilon}{k} - C_{\varepsilon 2} \frac{\nu \nu \epsilon^2}{k} 
\]

(10)

The turbulent viscosity \(\mu_t\) was computed as follows

\[
\mu_t = \rho C_{\mu_t} \frac{k^2}{\varepsilon} 
\]

(11)

where \(G_k\) represents the generation of turbulence kinetic energy due to the average velocity gradients and \(C_{\mu_t}\), \(C_{\varepsilon 1}\), \(C_{\varepsilon 2}\), \(\sigma_k\), and \(\sigma_\epsilon\) are constant, and they were 0.09, 1.44, 1.92, 1.0, and 1.3, respectively.

The steady-state conservation equations were solved using commercial software ANSYS Fluent 14.5. The standard \(k-\varepsilon\) model was employed to simulate the turbulent flow. The “enhanced wall treatment” was used for the near-wall treatment. The Eddy-dissipation concept (EDC) model was utilized to consider the interaction between turbulence and chemical reactions. The SIMPLEC algorithm was adopted for the coupling of pressure–velocity, and the second-order upwind scheme was utilized for the discretization of the convection terms. The convergence criterion was that the residuals of the continuity, energy, and other equations were less than \(10^{-3}\), \(10^{-6}\), and \(10^{-6}\), respectively. The difference in mass flow rate between the inlet and outlet was less than \(10^{-3}\), the outlet temperature and velocity were stable.

3.3. Fluid Properties. The thermophysical properties of the fuel are calculated based on the method of Li et al.\(^5^9\) The specific heat, and enthalpy and entropy of n-decane, and its cracked products were provided by thermodynamic data, as listed in Table S3. Table S4 lists the transport data of thermal conductivity and viscosity of species. According to Super-trapp,\(^50\) the linear interpolation of density with respect to temperature was obtained. Correspondingly, the density, specific heat, thermal conductivity, and viscosity of the mixture were calculated by the volume-weighted mixing law, mixing law, mass-weighted mixing law, and mass-weighted mixing law, respectively.

3.4. Parameter Definition for Analysis. The conversion of n-decane was defined as

\[
\epsilon_{n-\text{decane}} = (1 - Y_{\text{C}_{10}H_{22}}) \times 100\% 
\]

(12)

where the mass fraction of n-decane \(Y_{\text{C}_{10}H_{22}}\) was computed as follows

\[
Y_{\text{C}_{10}H_{22}} = \frac{\int \rho \nu Y_{\text{C}_{10}H_{22}} \mathrm{d}A}{\int \rho \nu \mathrm{d}A} 
\]

(13)

The definition of heat transfer coefficient \(h\), Nusselt number \(Nu\), Reynolds number \(Re\), Prandtl number \(Pr\), and correction factor for specific heat \(C_p,\text{ave}/C_p,\text{f}\) used to analyze the effect of convective heat transfer were as follows

\[
h = \frac{q_w}{T_w - T_f} 
\]

(14)

\[
Nu = \frac{hd}{\lambda} 
\]

(15)

\[
Re = \frac{\rho v d}{\mu} 
\]

(16)

\[
Pr = \frac{C_{\nu,\mu}}{\lambda} 
\]

(17)

\[
C_{p,\text{ave}}/C_p,\text{f} = (H_w - H_f)/(T_w - T_f)/C_p,\text{f} 
\]

(18)

where \(q_w\) is the wall heat flux, \(T_w\) is the wall temperature, \(d\) is the diameter, \(\lambda\) is the thermal conductivity, \(\rho\) is the density, \(\mu\) is the dynamic viscosity, \(C_{p,\text{ave}}\) is the specific heat of fluid, \(C_p,\text{f}\) is the average specific heat, \(H_w\) is the enthalpy of the wall temperature, and \(H_f\) is the enthalpy of the fluid temperature. Fluid temperature \(T_f\) was computed as follows

\[
T_f = \frac{\int A C_p \nu \nu T \mathrm{d}A}{\int A C_p \nu \nu \mathrm{d}A} 
\]

(19)

The total heat absorbed by fuel \(Q_{\text{total}}\) consists of sensible heat sink and chemical heat absorption.\(^5^1\) The total heat absorption is calculated from the difference between the absolute enthalpy of the fuel at the inlet of the tube (\(H_{\text{abs, inlet}}\)
and the absolute enthalpy of the mixture at any tube length \( l \) \( (H_{\text{abs}, l}) \), as shown by eq 20

\[
Q_{\text{total}, l} = H_{\text{abs}, l} - H_{\text{abs, inlet}} \tag{20}
\]

where \( H_{\text{abs, inlet}} \) is the sum of the formation enthalpy of n-decane and the sensible enthalpy of inlet temperature \( (T_{\text{inlet}}) \), the formula is as follows

\[
H_{\text{abs, inlet}} = H_{\text{f,n-decane}}(T_{\text{ref}}) + H_{\text{sen}}(T_{\text{inlet}}) \tag{21}
\]

The sensible heat sink \( Q_{\text{sen}, l} \) can be calculated by the temperature integration of specific heat of the pyrolysis fuel. The chemical heat sink \( Q_{\text{chem}, l} \) was obtained based on the difference of \( Q_{\text{total}, l} \) and \( Q_{\text{sen}, l} \).

4. RESULTS AND DISCUSSION

Although the simulation conditions are the same, the results of the flow field are different for the multi-step kinetic model and one-step kinetic model, which indicates the importance of the mechanism in the CFD simulation. The simulation results of the two models are discussed in the following sections.

4.1. Fuel Conversion and Temperature. Figure 5a illustrates the results of n-decane conversion. Compared with the one-step model, the conversion predicted by the multi-step kinetic model is more consistent with the experimental data. The occurrence of pyrolysis in the multi-step model is earlier than the one-step model. More specifically, the multi-step model begins to crack at about 190 mm, where the conversion is 0.78%, while the one-step model begins to crack at about 290 mm, where the conversion is 0.56%. This phenomenon is related to the reaction rate constant. Figure 6 shows the rate constant \( K \) of the primary reaction of the two models. The inlet temperature of the two models is the same at 753 K, but the \( K \) of the multi-step model is larger than that of the one-step model, so the multi-step model cracks earlier, which leads to a greater conversion in the front section of the tube. Then, at 250 and 350 mm for the multi-step model and the one-step model, the slopes of the conversion indicate that the reaction rate of n-decane has become larger, which suggests that the fuel enters the severe cracking zone. Eventually, the conversion of the multi-step model is lower than that of the one-step model. The conversion at the exit of the multi-step model is 86.65%, and the relative error from the experiment is 1.1%. In contrast, n-decane in the one-step model has completely cracked at 690 mm. Compared with the experimental data, the relative error at the exit is 16.7%. This is related to the temperature as shown in Figure 5b, the temperature of the multi-step model is much lower than that of the one-step model, which leads to a smaller reaction rate. Consequently, the conversion of the multi-step model is lower than that of the one-step model.

Figure 5b presents the results of the fuel temperature \( T_f \). Compared with the one-step model, the temperature predicted by the multi-step mechanism model is more consistent with the experimental data. And the temperature of the multi-step model is much lower than that of the one-step model, which is related to the heat absorption capacity of n-decane. Before about 190 mm, the multi-step model has not cracked, and its variation tendency of temperature is generally in agreement with the one-step model. But after that, the two models show obvious discrepancies due to the occurrence of different pyrolysis reactions. Figure 7 gives the chemical endotherm due to pyrolysis of n-decane as the difference value between the total heat absorption capacity and sensible heat sink. As exhibited in Figure 7, the heat absorption capacity provided by chemical reactions of the multi-step model is always larger than that of the one-step model in the entire reaction zone.

![Figure 5. Comparison of numerical simulation results between the two different kinetic models. (a) Conversion \( \varepsilon_{\text{n-decane}} \) and (b) fuel temperature \( T_f \). Experimental data from ref 41.](https://example.com/fig5.png)

![Figure 6. Rate constants of the primary reaction of the multi-step model and the one-step model.](https://example.com/fig6.png)

![Figure 7. Heat absorption capacities of n-decane.](https://example.com/fig7.png)
Accordingly, the temperature change rate of the multi-step model is smaller than that of the one-step model, which results in a lower temperature. In the front section about 190 mm of the reaction tube, the multi-step model enters the slow cracking state earlier than the one-step model. The heat absorption capacity mainly contains a sensible heat sink in this region, consequently, the temperature increases rapidly for the two models. After about 250 mm, the reaction of the multi-step model is violent with more chemical endotherm, which reduces the change rate in temperature. At the exit, the chemical endotherm of the multi-step model and the one-step model are 1.46 and 0.87 MJ/kg, respectively, accounting for 40 and 25.6% of the total value. The fuel heats up to 988.1 and 1141 K at the exit, respectively, and the relative errors from the experiment are 0.47 and 15%.

4.2. Product Distributions. The differences in chemical heat sink as described above come from the different products predicted by the two reaction models. Therefore, it is necessary to analyze the distribution of cracked products from the level of the reaction mechanism. Figure 8 depicts the yield of 6 typical products along the flow direction. For the simulation results based on the one-step model, the species yield is zero in the front part of the tube since no cracking reaction takes place. Although the conversion of n-decane becomes higher in the later stage, it mainly cracks into large molecules, some small molecules, and no aromatic hydrocarbons due to the absence of secondary reactions. Finally, at the exit of the reactor tube, the three most abundant products of the one-step model are 1-hexene, 1-heptene, and 1-octene, and their mass fractions are 11.52, 11.65, and 11.98%, respectively. In contrast, there are more products of small molecules for the simulation results with the multi-step model, such as ethylene, 1-propene, and 1-butene, with mass fractions of 12.99, 18.36, and 12.55%, respectively. Additionally, the contribution of large molecules to the heat absorption is small, and the formation of small molecules results in more chemical heat sink, which are responsible for the reason why the chemical heat sink of the one-step model is less than the multi-step model. As shown in Figure 8, as the cracking progresses for the multi-step model, aromatic hydrocarbon (C_{6}H_{6}, C_{7}H_{8}), and the species (CH_{4}, C_{2}H_{6}, C_{2}H_{4}) with one and two carbon atoms are gradually lower than the experimental measurements, and the species (C_{3}H_{6}) with three carbon atoms are slightly higher than the experiment. At the exit, the relative errors of CH_{4}, C_{2}H_{6}, C_{2}H_{4}, C_{3}H_{6}, C_{6}H_{6}, and C_{7}H_{8} of the multi-step model are 29.74, 23.18, 24.37, 12.64, 5.04, and 0.47%.
from the one-dimensional laminar process of hydrocarbon fuels. CFD simulation gives more accurate results on the pyrolysis coupling between turbulence and chemical reactions in the Nu is the criterion number to represent calculation of convective heat transfer in this section. Discussion of the performance of the two kinetic models in the cracking flow and reactions occur within small scales. This is different from the one-dimensional laminar flow simulation in which reactions can occur in the entire grid. The consideration of the coupling between turbulence and chemical reactions in the CFD simulation gives more accurate results on the pyrolysis process of hydrocarbon fuels.

4.3. Convective Heat Transfer. The present work discusses the performance of the two kinetic models in the calculation of convective heat transfer in this section. Convective heat transfer coefficient \( h \) is a crucial parameter to estimate the heat transfer efficiency, while Nusselt number \( Nu \) is the criterion number to represent \( h \). In the process of cracking flow, the main influencing factors of heat transfer include heat absorption capacity through pyrolysis, the fluid physical properties depicted by \( Pr \), the fluid flow state depicted by \( Re \), and the correction factor of isobaric-specific heat \( (C_{p,ave}/C_p) \). The chemical endotherm is beneficial for heat transfer. From the convective heat transfer correlation proposed by Jackson and Hall (J−H correlation) (22), it is known that \( Pr, Re, \) and \( C_{p,ave}/C_p \) are all positively correlated with \( Nu \).

\[
Nu_{-H} = 0.021Re^{0.82}Pr^{0.5} \left( \frac{\rho_c}{\rho_f} \right)^{0.3} \left( \frac{C_{p,ave}}{C_p} \right)^n
\]  

(22)

Figure 9a presents the simulation results of \( h \). In the front section of the tube, \( h \) predicted by the multi-step model and one-step model increase steadily to 5802 W/(m²·K) at 410 mm and 4614 W/(m²·K) at 370 mm, respectively. The conversion of n-decane calculated by the multi-step model in the front section of the tube is greater than that by the one-step model, resulting in more chemical endotherms, which is beneficial for heat transfer. As displayed in Figure 9b, the \( C_{p,ave}/C_p \) of the multi-step model is larger and more conducive to heat transfer than the one-step model. The \( Pr \) shown in Figure 9c reveals the changes in fuel properties caused by cracking. The multi-step model predicts that the conversion at 410 mm has reached 33%. Therefore, the gradually decreasing \( Pr \) is not conducive to heat transfer. On the simulation results using the one-step model, the obvious cracking starts at 350 mm with the conversion of 6%, so the \( Pr \) hardly changes in the front section of the tube. As demonstrated in Figure 9c, the \( Re \) values of the two models both decrease gradually, which is not advantageous to heat transfer. Among the above four influencing factors, the chemical endotherm and the increasing \( C_{p,ave}/C_p \) are dominant over the influence of decreasing \( Pr \) and \( Re \). Finally, \( h \) increases steadily in the front section of the tube, and the prediction of the multi-step model is greater than that of the one-step model. In the end section of the tube, the variation trend of \( h \) is different from that of the front. The increased rate of \( h \) predicted by the multi-step model becomes slow, and the one-step model does not increase but slightly decreases. For the multi-step model, as the reaction progresses, \( Pr \) and \( Re \) are reduced gradually, and they drop to 0.9355 and 25 726 at the exit, respectively. The simulation results of \( C_{p,ave}/C_p \) show a fluctuation trend, which makes \( h \) to fluctuate from 410 mm, increasing slightly. For the one-step model, \( Pr \) and \( Re \) decrease to 0.9568 and 26 717 at the exit. Due to the increase in the chemical endotherm caused by the violent cleavage reaction, \( C_{p,ave}/C_p \) decreases sharply from the position of 370 mm to the exit. Under the combined action of the four influencing factors, \( h \) appears an inflection point at the position of 370 mm of the tube.
As illustrated in Figure 9a, the simulation results of $Nu$ based on different kinetic models are distinct. The $Nu$ of the multi-step model is always greater than that of the one-step model. The correlation of (22) is further studied and developed by others.\textsuperscript{55,56} Based on the vertical tube experiment, Zhang\textsuperscript{57} proposed a correlation suitable for forced convection heat transfer of RP-3. Lei\textsuperscript{58} developed a n-decane correlation suitable for its conversion less than 23%. Figure 10 exhibits the comparison of $Nu$ between the J–H correlation and the simulation results. It can be seen that the correlation does not elucidate the trend of $Nu$ well, and the numerical results are larger than the correlation. The maximum relative errors of $Nu$ between the correlation and the two models reach 31 and 13%, respectively. For the one-step model, the changes in the chemical endotherm, $Pr$ and $C_{p,ave}/C_{p,f}$ induced by the cracking reactions are smaller than that of the multi-step model. Consequently, the results predicted by the one-step model are slightly close to the results of J–H correlation. From the above discussion, the chemical endotherm and the changes in physical properties attributed to fuel cracking play an essential role in the convective heat transfer process, especially the parameter of $C_{p,ave}/C_{p,f}$ which can well reflect the changing trend of the $h$. The coincidence of key inflection points for these two variables illustrates the conclusion.

5. CONCLUSIONS

The present work performs numerical investigations on the kinetic models for n-decane pyrolysis in a horizontal tube under supercritical conditions. Considering the high conversion of n-decane, a multi-step chemical model including secondary reactions is developed and applied in the CFD simulations in comparison with the corresponding results of the one-step global model. After careful analysis and comparison, the main summaries are as follows:

1. The multi-step model with high accuracy gives better prediction results on temperature, conversion, and product distributions. Compared with the experimental data and the simulation results of the multi-step model, the one-step model demonstrated a lower conversion of n-decane in the initial section of the tube, which is contributing to its slower rate constant than that of the primary reaction of the multi-step model. In the entire reaction zone, the chemical endotherm of the multi-step model is larger than that of the one-step model. Accordingly, the temperature change rate of the multi-step model is smaller than that of the one-step model, which results in lower temperature and conversion at the back section of the reactor tube. Moreover, from the yield of typical six products along the flow direction, one can see that the multi-step model generates more products of small molecules due to the consideration of secondary reactions. However, for the one-step model, it mainly cracked into large molecules even at high conversion. Overall, the multi-step model reproduces the flow field well even at high conversion.

2. On the correlations of convective heat transfer, the existing correlations are limited to the cases of relatively low conversion of fuels. In the supercritical cracking heating transfer process, the chemical endotherm and the changes in physical properties attributed to fuel cracking play an essential role in the convective heat transfer process, especially the parameters of $C_{p,ave}/C_{p,f}$. While the chemical endotherm and fluid properties are directly determined by the pyrolysis products, which are related to the kinetic models. Consequently, the choice of the chemical kinetic model is extremely imperative to pore over the cracking heat transfer process. As shown in Sections 4.1 and 4.2, the multi-step model with high accuracy gives better prediction results on temperature, conversion, and product distributions, which is more conducive to the study of the heat transfer process with thermal cracking and then construct the corresponding correlation of supercritical hydrocarbon fuels.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01178.

Species involved in the two chemical kinetic models, the thermodynamic file, the transport property file, comparison of the yields of all products obtained based on the two chemical kinetic models and experimental results at the exit of the reactor tube, the verification of the constructed two-dimensional axisymmetric model, conversion of n-decane obtained from the two-dimensional simulation and one-dimensional simulation with the multi-step reaction model (PDF)

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Notes
The authors declare no competing financial interest.

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