Replacing coal with biomass holds great potential to reduce global~\ce{CO2} emissions due to its closed carbon cycle. However, controlling harmful~\ce{NO\_x} emissions from solid biomass combustion is one of the major challenges, which necessitates complex and costly exhaust gas after-treatment systems. To understand and analyze~\ce{NO\_x} formation pathways, it is essential to accurate model the complex sub-processes of the solid particles and the gas phase. High-fidelity simulations can generate datasets that are fundamental for analyzing these formation pathways, providing insights that are beyond the reach of experimental techniques.

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This project aimed to investigate the formation pathways of~\ce{NO\_x} from pulverized solid biomass flames. We conducted several direct numerical simulations (DNS) of pulverized solid biomass combustion under different atmospheric conditions, compared the flames to each other, and analyzed the~\ce{NO\_x} formation pathways.

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In order to reduce the overall computational cost of modeling solid biomass flames, an existing simplified volatile release approach is applied and compared to the detailed release model. Additionally, to improve the accuracy of~\ce{NO\_x} formation predictions, we enhanced the simplified release model with a new formulation and applied and compared it to our simulations.

The thermochemical conversion of solid fuels involves mass, momentum and energy transfer between the particles and the gas phase. To model these interactions, the Euler-Lagrangian approach is employed, where the solid particles are described in the Lagrangian framework using a point-particle assumption and the gas phase is modelled in the Eulerian framework. The governing equations in the Euler-Lagrangian framework are solved using the in-house semi-implicit finite element solver CIAO.

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Second order accuracy in space and time is used to solve the Eulerian equations. The scalar transport is solved using the WENO5 scheme for the convective and a second order central difference scheme for the diffusive terms. Species mass fractions and temperature are solved using Strang splitting for scalar equations. A backward differential formula from the CVODE solver is used to integrate the chemical subsystem. To advance the particles in time, a two stage Runge-Kutta solver with second order accuracy is used, updating the dispersed phase state, position and source terms for the Eulerian equations.

This section presents the results of the parameter study to analyze the~\ce{NO\_x} formation pathways using DNS. Note that additional simulations with different biomass types have also been performed to validate the particle and gas phase model and to analyze the~\ce{NO\_x} formation pathways within this project, but are not shown here for brevity. The pulverized biomass flames for miscanthus were analyzed under different atmospheres.

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Figure~\ref{fig:ComparisonNOxOxidizer} shows the~\ce{NO\_x} mole fractions and gas temperature for three different atmospheres for miscanthus. It can be seen that the global maximum of~\ce{NO\_x} mole fractions occurs at the flame tip in all investigated atmospheres in weaker temperature regions due to a longer residence time, while the local maximum of~\ce{NO\_x} occurs around the stoichiometric conditions in high temperature regions. Comparing the flames to each other, it can be seen that the oxidizer conditions have a significant effect on the flame topology and the overall~\ce{NO\_x} formation, which is highest in air due to the presence of thermal-\ce{NO\_x}.

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Figure~\ref{fig:ROPA\_NOx\_Atm\_effect} presents an analysis of~\ce{NO\_x} formation pathways through a rate of production analysis (ROPA) of all nitrogen element fluxes, integrated across both the entire numerical domain and simulation time to provide a comprehensive overview. The influence of atmospheric conditions on~\ce{NO\_x} formation is evident in the roles of~\ce{N} and~\ce{HNO} in~\ce{NO} production. Under oxy-fuel conditions, the contribution of the N radical to NO formation decreases, while the influence of~\ce{HNO} becomes more significant, causing a shift in the dominant formation pathways. Additionally, an increase in oxygen content in the oxidizer composition leads to a higher overall production of~\ce{OH} radicals, which in turn enhances~\ce{NO} production.

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An existing modeling approach assumes a fixed volatile composition (FVC) release with reduced computational cost compared to the detailed dynamic volatile composition (DVC) release model. Figure~\ref{fig:DVC\_FVC\_FVCN} shows a good agreement for gas-phase temperature prediction, while the~\ce{NO\_x} mole fraction field cannot be captured by the FVC model. Assuming a separate release of the N-containing volatiles from the other volatiles (FVC-N), due to the different release time scales of the N-containing volatiles, leads to a significant improvement in~\ce{NO\_x} formation predictions as shown in Fig.~\ref{fig:DVC\_FVC\_FVCN}.

A parameter study was performed to analyze the~\ce{NO\_x} formation pathways under different atmospheric conditions in biomass jet flames. Overall, lower~\ce{NO\_x} emissions were observed under oxy-fuel conditions, where~\ce{HNO} is the major direct precursor of NO, while the N-radical is the most dominant direct precursor of~\ce{NO} in air.

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Finally, a modification of the FVC model using a separate release of N-containing volatiles is able to capture the~\ce{NO\_x} formations of the DVC model. These model assumptions lead to a significant improvement in the reduced-order modeling of~\ce{NO\_x} formation in solid pulverized biomass flames.

Comparison between~\ce{NO\_x} mole fractions and gas temperature in different atmospheres around the statistically steady-state. Particles are colored by the particle temperature. Stoichiometric mixture fractions for each flame are visualized by black isolines.

Effect of different atmospheres on the ROPA of~\ce{NO} integrated over the entire computational domain and simulation time. The extended Zeldovich reactions are marked with X.

Comparison between the DVC, FVC, and FVC-N modeling assumptions for the~\ce{NO\_x} mole fractions and the gas-phase temperature in the miscanthus jet flame in air. Particles are colored by the particle temperature and stoichiometric mixture fractions are visualized by black isolines.