Replacing coal with biomass holds great potential to reduce global CO2 emissions due to its closed carbon cycle. However, controlling harmful NO\_x emissions from solid biomass combustion is one of the major challenges, which necessitates complex and costly exhaust gas after-treatment systems. To analyze NO\_x formation pathways, it is crucial to accurately model the complex sub-processes and interactions 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.

This project investigated the formation pathways of NO\_x from solid pulverized biomass flames. We conducted several direct numerical simulations (DNS) of pulverized solid biomass combustion under different atmospheric conditions to compare the flame behavior and examine the effect on NO\_x formation pathways. As atmospheric conditions directly impact the combustion process, an optimized combustion strategy can be developed to minimize NO\_x formation from solid pulverized biomass flames.

To address the high computational cost associated with modeling solid biomass flames, we employed an existing simplified modeling approach to study the influence of the released volatile composition on NO\_x formation. The predictions of this simplified modeling approach were evaluated against the predictions of detailed DNS. Based on these comparisons, we proposed a modified formulation of the existing model that offers improved accuracy in predicting NO\_x formation. This enhanced method can be effectively integrated into reduced-order flamelet modeling frameworks for solid fuel combustion.

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 modeled in the Eulerian framework. The governing equations in the Euler-Lagrangian framework are solved using the in-house semi-implicit finite element solver CIAO.

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 to update the dispersed phase state, position, and source terms for the Eulerian equations.

This section presents the results of the parameter study to analyze the 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 NO\_x formation pathways within this project, but are not shown here for brevity. The analysis presented focuses on flames of pulverized Miscanthus biomass under a variety of atmospheric conditions, in order to evaluate the influence of these conditions on NO\_x production.

Figure~\ref{fig:ComparisonNOxOxidizer} shows the NO\_x mole fractions and gas temperature for three different atmospheres for Miscanthus. It can be seen that the global maximum of 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 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 NO\_x formation, which is highest in air due to the presence of thermal-\ce{NO\_x}.

Figure~\ref{fig:FlameJointT} presents the correlation between the NO\_x mole fraction and the gas phase temperature. As discussed previously, distinct high- and low-temperature zones are visible around the stoichiometric mixture fraction in Fig.~\ref{fig:FlameJointT}a. Moreover, the peak NO\_x production rate coincides with the maximum consumption rate of NFuel - the total nitrogen-containing volatiles released from the particles - in the high-temperature, fuel-rich region near the particles themselves. This highlights the critical role of fuel-bound nitrogen in the overall formation of NO\_x during biomass combustion.

Figure~\ref{fig:ROPA\_NOx\_Atm\_effect} presents an analysis of 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 NO\_x formation is evident in the role of \ce{N} and \ce{HNO} in \ce{NO} production. Under oxy-fuel conditions, the contribution of the \ce{N} radical to \ce{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 results in an overall higher production \ce{OH} radicals, which in turn enhances \ce{NO} production.

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 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 NO\_x formation predictions as shown in Fig.~\ref{fig:DVC\_FVC\_FVCN}.

A parameter study was performed to analyze the NO\_x formation pathways under different atmospheric conditions in biomass jet flames. Overall, lower 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.

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