

REDIM-BASED MODEL REDUCTION OF THE DECOMPOSITION OF UREA-WATER-SOLUTION IN FILMS AND DROPLETS ECCOMAS CONGRESS 2022

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Abstract. Selective catalytic reduction (SCR) process with urea-water solution (UWS) is often used in automotive industry to decrease emissions of nitric oxides (NO_x) in the exhaust gas. In this process the urea from UWS decomposes to isocyanic acid and ammonia, where the latter is needed to increase the efficiency of the NO_x reduction on the catalyst surface.

Along with the advantages of using UWS several drawbacks reduce the performance of a SCR system. Incomplete decomposition of urea leads to a formation of residuals affecting the efficiency of the exhaust gas systems. Therefore, the complete decomposition of urea and homogeneous distribution of the resulting ammonia in front of the SCR catalyst represent main challenges in improving the SCR technology.

In order to investigate the process of the urea decomposition a detailed chemical kinetic mechanism in the liquid phase is employed. The results are compared with a commonly used approach to model urea decomposition as an evaporation with a following decomposition reaction in the gas phase. It is shown that by using such a mechanism, the decomposition of urea and the gas phase composition with the urea decomposition products can be described more accurately. However, implementing these mechanisms in computations (in CFD approaches) requires a large amount of computational (CPU) time and memory. The method of Reaction Diffusion Manifolds (REDIMs) is implemented for the reduction of the detailed chemical kinetics in the stage of urea decomposition such that the distribution of products of the urea decomposition can be captured accurately in the gas phase with only two reduced variables instead of the 7 gas phase species of the original model.

1 INTRODUCTION

The reduction of harmful emissions of pollutants of internal combustion engines continues to be an important topic in the industry. It has been shown e.g., in [1], that nitric oxides NO_x have toxic effects. In order to reduce the concentration of NO_x in exhaust gases, selective catalytic reduction (SCR) of nitric oxides in the exhaust treatment systems (de- NO_x process) has been suggested and used with ammonia as a reacting agent [6], which increases the efficiency of the catalytic process.

However, because ammonia is considered a hazardous material [5], harmless urea-water-solution (UWS), is used as a source for ammonia in the exhaust gas system [7]. Urea-water-solution is injected into the exhaust gas treatment system where it decomposes to ammonia, mixes with exhaust gas and reacts with NO_x on the catalyst surface. When using UWS several drawbacks might reduce the performance of a SCR system, namely, incomplete decomposition of urea might lead to formation of residuals affecting efficiency of the exhaust gas systems. Therefore, the complete decomposition of urea and homogeneous distribution of the resulting ammonia in front of the SCR catalyst represent main challenges in improving the SCR technology. For this several technical issues remain to be solved concerning the decomposition of UWS injected droplets, e.g. the formation of solid residuals, incomplete decomposition [8] and homogeneous distribution of the ammonia in the mixture coming to the surface of catalyst monolith [2].

In order to deal with the urea decomposition, originally, the so-called empirical model has been established [2], which describes the urea decomposition in the gas phase by using following three steps to describe the process:

- water evaporation;
- urea decomposition into ammonia and isocyanic acid;
- hydrolysis of isocyanic acid into ammonia and CO_2 .

The two main underlying assumptions behind this approach are presented in the following. First, urea decomposition is infinitely fast, and second, the process is diffusion controlled, meaning that evaporation governs the decomposition process. Hence this model will be referred to as an "evaporation model" in future. Recently a detailed chemical mechanism with 13 elementary steps for the decomposition of urea in the liquid phase has become available [16]. Using such mechanisms, the decomposition of urea can be described more accurately. This represents the first objective of the study, namely, to compare predictions of both models for typical conditions of the exhaust gas treatment systems.

Nowadays, CFD plays a very important role in the study of practical engineering scale systems. Hence, simulations of the decomposition of UWS can be useful to better understand the phenomena and to optimize after-treatment processes. Because the process is very complex, involving chemically reacting, multi-phase turbulent flows, a wide range of time-scales and spatial scales are relevant. Reduced models are required to describe the process and to enable CFD simulations with realistic computational effort. However, the developed detailed mechanisms often require a large amount of computational (CPU) time.

Typical approaches to cope with the complexity of chemical kinetics are automatic model reduction methods [17]. The method of Reaction Diffusion Manifold (REDIM) [14, 9] has

been developed for the reduction of the detailed chemical kinetics. In this work, as a second objective, the developed concept of REDIMs is further extended to describe reduced the gas phase chemical kinetics and mixture composition near the droplet / film surface. For this, the boundary conditions at the phase interface are modified and account for influence of chemical reactions in the liquid phase. By using these boundary conditions, the REDIM is developed and validated for a simple reference case suggested under typical SCR conditions.

The outline of the study is as following. First the physical model is described and two chemical mechanisms for the decomposition of urea are presented and compared. Next a reduced model to describe the processes in the gas phase in the vicinity to UWS droplets or films is constructed. It is adapted to more complex boundary conditions at the droplet and film surface for the relevant stages and processes (see e.g., Stein et al. [14]), which govern the main course of the urea decomposition. Then the developed reduced model is validated by comparing reduced and detailed model predictions.

2 PHYSICAL MODEL

The evaporation and decomposition of UWS in an ambient gas of constant uniform pressure is modelled and simulated. Two generic configurations are considered: a single spherical droplet and a planar wall film. Due to the symmetry a one-dimensional model can be formulated for both cases. In the scope of this work, the film geometry will be used, however the qualitative results will be similar for droplets. The gas around the film is assumed to be stagnant in any but the direction of the one-dimensional model, which is perpendicular to the surface of the film. In this way convective processes do not directly change the thermo-chemical system states, but only their spatial fields. This is indicated by the fact that the convection term is absent in the underlying equations in the Lagrangian coordinate frame used to integrate the detailed and reduced systems [10].

For the manifold based reduced models applied in this work (see e.g. [9] for details) this assumption is not important because even strong convective processes will not affect the REDIM system solution directly [3]. The REDIM represents the balance between diffusion and reaction processes, while the convection term describes the evolution along the tangent space of any low-dimensional manifold used to represent the reduced model, thus, it will be filtered out by the projection in the REDIM equation.

The resulting model system is separated into a liquid and gaseous phase where in each phase the conservation equations for mass, species and energy are solved [10, 12]. In the case of generic 1D symmetries, e.g., in the center of the spherical droplet and at the wall for the film, Neumann boundary conditions with zero gradients are applied. The Neumann boundary for the temperature at the wall assumes a thin wall, which heats up with the liquid phase.

Dirichlet boundary conditions for typical exhaust gas temperatures and compositions are applied for the far field. Both the liquid and gaseous phases are connected by an interface. UWS in the relevant temperature range behaves like an ideal mixture [11], while for the gas phase, a detailed transport model with non-equal diffusivities is employed [10].

The gas phase chemistry is described by a detailed mechanism for reactions between NO_x and NH_3 before they reach the catalyst [13]. For the interface and the liquid phase, two mechanisms are available which are explained in sections 2.1 and 2.2 respectively.

The spatial coordinates of the one-dimensional model are discretized by finite differences. To resolve the changing steep gradients close to the droplet, an adaptive non-equidistant grid is used together with a regridding procedure based on a grid function [10]. The resulting differential and algebraic equations system describes both phases. It is integrated by the linearly implicit extrapolation method LIMEX [4]. The complete model including both phases, the interface and boundary conditions and the discretization is implemented into the in-house code INSFLA. More details can be found in [9].

2.1 Decomposition modelled by an evaporation model

The evaporation model provides a simple way to describe the decomposition of urea to ammonia and isocyanic acid. It assumes, that liquid urea evaporates into gaseous urea, then decomposes rapidly in the gas phase:



Additionally, the gas phase chemistry also includes one one-step reaction for the hydrolysis of HNCO(g) as used by Birkhold et al. [2]:



The model, however, shows an unwanted coupling between the evaporation and decomposition reactions by reducing the urea concentration at the droplet surface leading to an increased evaporation rate [15]. To counter this, the vapour pressure curve and decomposition rate has to be adjusted to available experimental data to describe the evaporation process with respect to mass and energy balances.

2.2 Decomposition modelled by a liquid chemistry mechanism

The liquid chemistry mechanism is a detailed chemical mechanism describing all reactions in the liquid phase (homogeneous reactions) and at the phase boundary (heterogeneous reactions). It was developed by Tischner et al. [16] and consists of 5 homogeneous reactions and 8 heterogeneous reactions shown in Tab. 1. The full names, chemical formulas and phases of all species in the mechanism can be found in Tab. 2.

Note that there is a difference between homogeneous and heterogeneous reactions, particularly that heterogeneous reactions relate to the surface area A_{ref} , instead of the volume. For this reason, the heterogeneous reaction rates have to be transformed into volume specific reaction rates:

$$\dot{r}_k^{\text{surf.}} = \dot{r}_k \frac{A_{ref}}{VF}. \quad (3)$$

Otherwise, the reaction rates are determined using the extended Arrhenius equation:

$$\dot{r}_k = A_k T^{\beta_k} \exp\left(\frac{E_{a,k}}{RT}\right) \prod_{i=1}^{n_s} c_i^{\mu_{i,k}}. \quad (4)$$

Table 1: Liquid chemistry mechanism

Homogeneous reactions				
urea(l)	+	HNCO(l)	\rightleftharpoons	biu(s)
urea(l)	+	HNCO(l)	\rightleftharpoons	biu(l)
biu(l)	+	HNCO(l)	\rightleftharpoons	triu(s)
triu(s)			\rightarrow	cya(s) + NH ₃
triu(s)			\rightarrow	ammd(s) + H ₂ O(g)
Heterogeneous reactions				
2 ureal(l)			\rightarrow	biu(l) + NH ₃
biu(l)	+	urea(l)	\rightarrow	triu(s) + NH ₃
cya(s)			\rightarrow	cya(g)
urea(g)			\rightleftharpoons	urea(l)
HNCO (g)			\rightleftharpoons	HNCO (l)
urea(l)			\rightleftharpoons	urea(s)
biu(l)			\rightleftharpoons	biu(s)
ammd(s)			\rightleftharpoons	ammd(g)

2.3 Comparison of evaporation and liquid chemistry mechanisms

Figures 1 show comparisons of the species mass flow rates at the film surface for the initial and boundary conditions in Tab. 3. On the left figure one can see only few species (4) present in the simplified evaporation model, while the right figure shows a wider spectrum of species formed and released from the liquid into the gas phase. Although the overall mass flows described by the two models match quite well due to appropriate fitting of the vapour pressure curves one can clearly see significant differences in the distribution over time as well as distribution over the species. Because the evaporation model is based on brutto reactions instead of the elementary reactions, the gas composition produced by the evaporation model oversimplifies the process. Also, the evaporation model underestimates the overall decomposition time (see Fig. 1 on the

Table 2: Species in liquid chemistry mechanism

Short name	Species name	Chemical formula	Phases
H ₂ O	water	H ₂ O	g, l
urea	urea	CO(NH ₂) ₂	g, l, s
NH ₃	ammonia	NH ₃	g
HNCO	isocyanic acid	HNCO	g, l
cya	cyanuric acid	C ₃ H ₃ N ₃ O ₃	g, s
biu	biuret	C ₂ H ₅ N ₃ O ₂	l, s
triu	triuret	C ₃ H ₆ N ₄ O ₃	s
ammd	ammelide	C ₃ H ₄ N ₄ O ₂	g, s

right, the film lifetime according to the evaporation model is marked with a dashed black line). For the boundary and initial conditions, the film has a much longer life-time.

Table 3: Initial and boundary conditions of the reference case

Far field boundary conditions	
T_∞	673 K
$n_{\text{H}_2\text{O}}$	0.1 mol/kg
n_{N_2}	0.7 mol/kg
n_{O_2}	0.1 mol/kg
n_{CO_2}	0.1 mol/kg
Film initial conditions	
T_0	300.1 K
$n_{\text{urea(s)}, 0}$	0.266 mol/kg
$n_{\text{H}_2\text{O}, 0}$	0.734 mol/kg

Moreover, one can observe the traces (gaseous ammeline mass flow rate is increasing) of the residual formation process, which is forming in longer time scales. Thus, this is completely neglected by the evaporation model. Secondly, the evaporation model overestimates the ammonia-, while significantly underestimating the isocyanic acid mass flow rates. This additionally confirms the fact that in order to quantitatively describe the composition of the exhaust gas and residual formation one needs to increase the model complexity and to account for the liquid phase reactions.

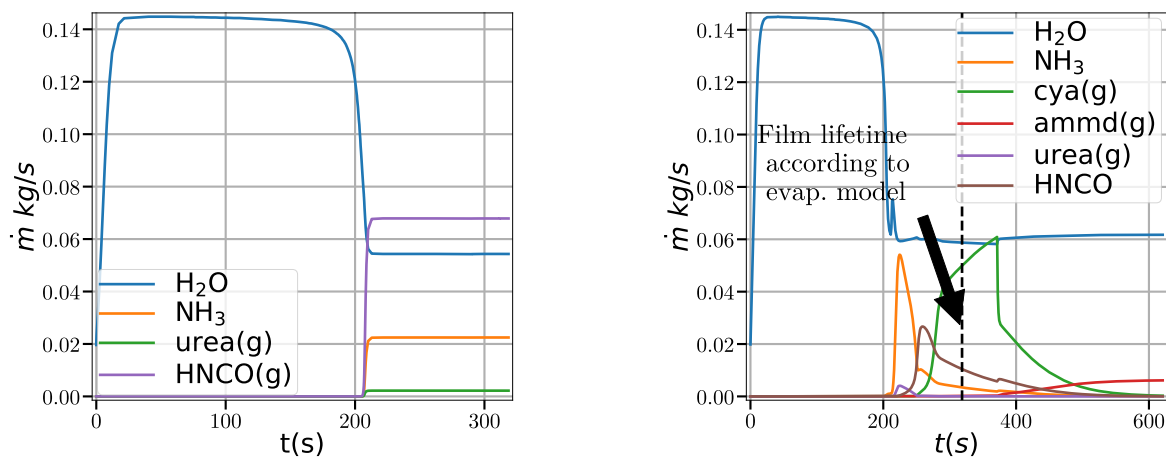


Figure 1: Mass flows from the film as predicted by the evaporation (left) and liquid chemistry (right) models.

3 REDIM CONSTRUCTION: UREA DECOMPOSITION

The main phase of the decomposition of the urea begins when water has almost completely evaporated (see e.g., [14]) and urea melts. In this stage the transport and chemistry in the gas phase needs to be treated in a coupled way. Because of this a reduced kinetic model that accounts for this coupling is required.

The REDIM method was especially designed for this case. The general behavior of the droplet or wall film in this stage is similar to the water evaporation phase such that if one is interested in the gas phase composition, then the REDIM method can provide a reduced description for the gas phase transport and chemistry and relies on the conditions at the liquid surface [14]. This model has been validated in an earlier work for the droplet cases with the evaporation model implemented and detailed chemical kinetics of the gas phase [13].

The REDIM method is a manifold based reduction concept. Accordingly, rate limiting processes are considered and only taken into account to define the overall dimension of the reduced model. These govern the system states being confined / constrained to a low dimensional manifold. Hence, the state vector $\psi = (h, p, w_1/M_1, \dots, w_n/M_n)$, where h is the specific enthalpy, p the pressure, n the number of species and w_i the mass fraction for species i , M_i the molar mass of species i can be given as a function of the reduced coordinates $\theta = (\theta_1, \dots, \theta_m)$, where m is the number of reduced coordinates. In this manner, the problem of model reduction is reformulated as a problem of finding such an appropriate manifold.

Once the reduced manifold is constructed local coordinates representing the manifold are required to implement and to represent the reduced model. During the urea decomposition phase we have found that two degrees of freedom are needed to describe the system. The first degree of freedom can be attributed via given local coordinate e.g., θ_1 to the heat transport (energy balance) towards the liquid surface. The second one θ_2 can be attributed to the decomposition of urea, i.e. a variable governing the progress of chemical reactions. These two degrees of freedom fully address the completed chemical and transport processes.

To construct a REDIM an initial guess for the manifold and spatial gradients are required [9]. These are usually taken from detailed reference computations of the two phase problem such that the transient system solution can be used to define boundary conditions for the gas phase. These fully account for the influence and urea decomposition product mass flows of the liquid phase chemical reactions. The REDIM is adapted to the complex boundary conditions at the phase boundary, namely, the mass flow rates, as predicted by the detailed liquid chemistry mechanism, were implemented at the boundary. The initial guess has to be unambiguous with respect to the two parametrization variables and the detailed results are interpolated on a grid based on these variables.

The REDIM equation [9] is then integrated until a stationary solution is found, which can be seen in different projections in Fig. 2. As a result a REDIM manifold is obtained, which allows to recover the thermodynamic state and other relevant data from the parametrization variables θ_i , e.g. $\psi = \psi(\theta)$, $T = T(\theta)$, etc.

The data for reduced model simulations is then stored in tabulated form. It includes the parameterization, the transformation rules between reduced and detailed variables and the source and transport terms in reduced coordinates for each point. Following this strategy, 2D REDIMs were generated for a few exemplary boundary conditions (composition of exhaust gas, pressure,

etc.) for droplets and wall films, but the method can be applied to any other boundary condition. In case of a 2D REDIM there are only two variables necessary to fully describe the conditions in the gas phase, which originally required seven variables.

After the REDIM is calculated and tabulated the REDIM-reduced solution is obtained by solving Equation 5 for the new state variable $\boldsymbol{\theta} = (\theta_1, \theta_2)^\top$

$$\frac{\partial \boldsymbol{\theta}}{\partial t} = \boldsymbol{\Psi}_\theta^+ \mathbf{F} - v \text{grad}(\boldsymbol{\theta}) + \frac{1}{\rho} \boldsymbol{\Psi}_\theta^+ \text{div}(\mathbf{D} \cdot \boldsymbol{\Psi}_\theta \text{grad}(\boldsymbol{\theta})) \quad (5)$$

To integrate the equation, $\boldsymbol{\Psi}_\theta^+$, $\boldsymbol{\Psi}_\theta^+ \mathbf{F}$ and $\mathbf{D} \boldsymbol{\Psi}_\theta$ have to be known, also the the states $\boldsymbol{\Psi}(\boldsymbol{\theta})$ to reconstruct the original states from θ_1 and θ_2 .

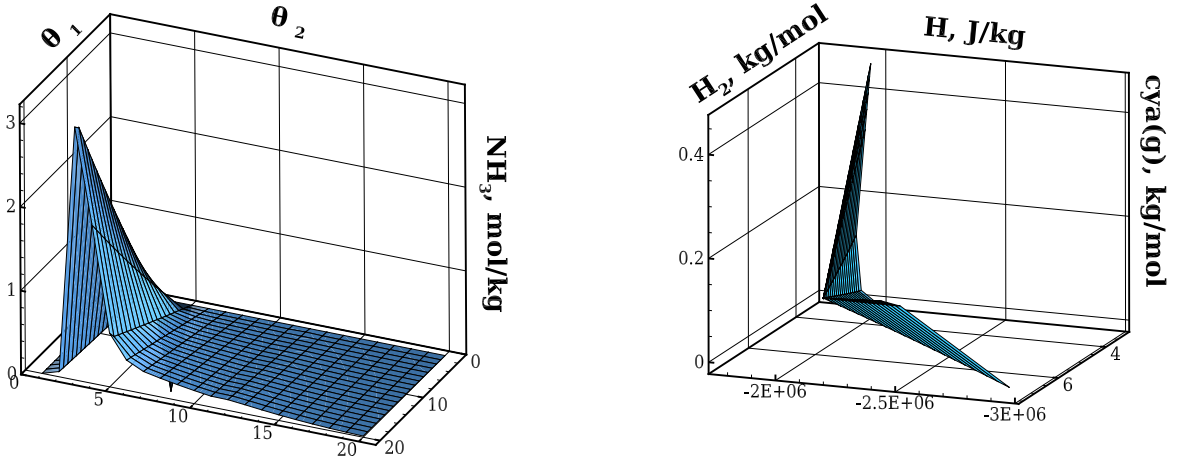


Figure 2: REDIM for the wall film in different projections in state space.

4 VALIDATION

In this section the predicted specific mole fractions of different species during urea decomposition of the REDIM-reduced model (See Equation 5) and the detailed mechanism are compared. The specific mole fractions of ammonia (Fig. 3) and cyanuric acid (Fig. 4) are compared at a fixed times (10 s, 100 s, 200 s and 300s after the start of urea decomposition stage) over the distance of the wall (in the gas phase, from current film height to the end of the computational domain), as well as at fixed distances from the wall ($5 \cdot 10^{-4}$ m, $7.5 \cdot 10^{-4}$ m and $1 \cdot 10^{-3}$ m), over time. Figures 3 and 4 show that the considered profiles or trajectories are barely distinguishable.

For a better comparison of model predictions, the relative error of ammonia mole fraction over time and distance from the wall is calculated:

$$\text{rel. err.}(t, r) = \frac{|n_{\text{NH}_3, \text{det}}(t, r) - n_{\text{NH}_3, \text{red}}(t, r)|}{|n_{\text{NH}_3, \text{det}}(t, r)|} \quad (6)$$

If the value of n_{NH_3} is unknown at specific times or distances from the wall (the solution is discrete) linear interpolation is used.

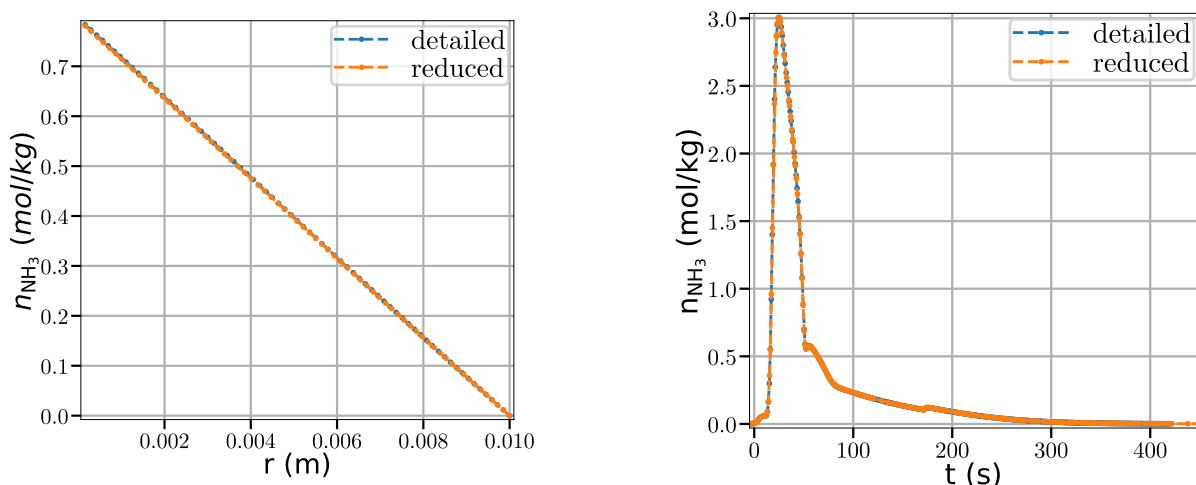


Figure 3: Comparison of reduced and detailed results for specific ammonia mole fraction during urea decomposition.

The relative error over the distance to the wall for different times, as well as the relative error over time at fixed distances from the wall can be seen in Fig. 5. It is striking, that at lower times the relative error is the highest, by approximately one order of magnitude. The reason for this is that the mole-fraction of the considered species at these time-steps, which is also in the denominator of the relative error, are very small, leading to higher relative errors.

In summary, because of the negligible differences in species mole fractions, the proposed reduced model provides an accurate approximation of the problem.

5 CONCLUSION AND OUTLOOK

Problems of incomplete decomposition and non-homogeneous distribution of the decomposition products of urea were in the focus of the present study. These are important because they can reduce the efficiency and life time of exhaust gas treatment systems.

The detailed chemical kinetic mechanism in the liquid phase suggested in [16] was used to improve the model of the decomposition. The results show that by using the detailed model both the decomposition of urea as well as formation of the residuals can be described more accurately.

In order to cope with the complexity of the liquid chemistry model the method of Reaction Diffusion Manifolds (REDIMs) was modified and implemented for the reduction of the detailed chemical kinetics. The suggested tabulation based approach was modified to capture the complex boundary conditions, which take into account the release of urea decomposition products from the liquid phase. The detailed and reduced (tabulated) models were compared for a typical set of initial and boundary conditions. It was shown that the distribution of the products of the urea decomposition can be captured accurately ($\text{rel. err}_{\text{NH}_3} \leq 2.5 \cdot 10^{-3}$ for $t \geq 300$ s). Only two reduced variables instead of 7 gas phase species of the original model were required to reach the accuracy reported. In this way, the problem of homogenisation and distribution of urea decomposition products can be modelled in a more reliable and reduced manner.

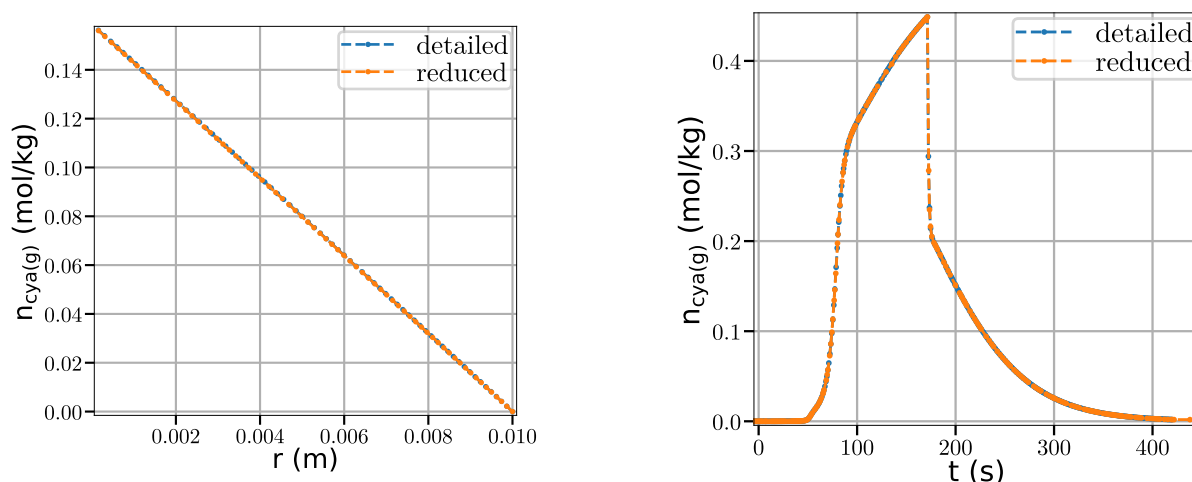


Figure 4: Comparison of reduced and detailed results for specific cyanuric acid mole fraction during urea decomposition.

Acknowledgments

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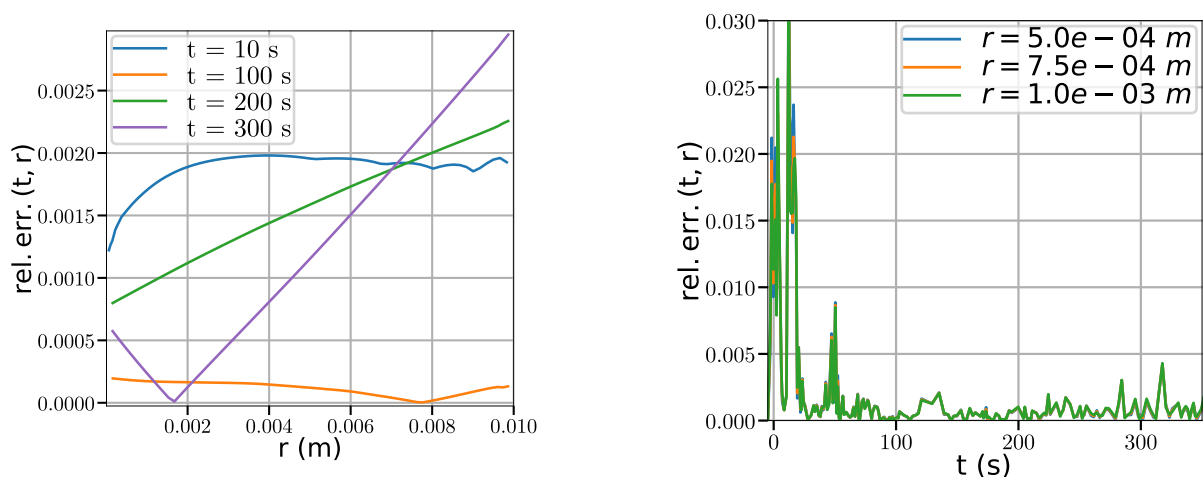


Figure 5: Comparison of relative error of ammonia mole fraction during urea decomposition at a fixed time over the distance from the wall and at a fixed distance from the wall over time.

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