Study of conversion of ammonia from urea water solution droplets using CFD

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Abstract. This paper deals with the numerical analysis of the spray behaviour of urea water solution (UWS) droplets used in Selective catalytic reduction (SCR) process. The study uses the ANSYS-Fluent-14 as a basic framework for numerical simulations. The evaporation modelling is based on multi-component droplet evaporation approach along with the consideration of Stefan flow. The urea decomposition treated as direct thermolysis approach, where the modelling is based on the single kinetic rate approach by the proper fitting of pre-exponent. This developed model was used for spray simulation of UWS droplet evaporation to determine the urea to ammonia conversion efficiency. The obtained spray simulation results were compared with the available experimental data. The comparison shows the pre-exponent developed in the study is suitable for direct thermolysis approach to get promising results in determining the ammonia conversion efficiency.

1. Introduction
The Selective Catalytic Reduction (SCR) is the well-known technology in which nitrogen oxides in the diesel engine exhaust. The reduction of NO\textsubscript{x} is carried out with the aid of a reducing agent, mostly ammonia is used. The urea water solution (UWS) is mainly used to produce ammonia. The UWS is a solution that comprises urea and water. The ammonia (NH\textsubscript{3}) is produced by thermal and chemical decomposition urea by spraying UWS droplets in exhaust gas [1]. In ideal case urea fully converted into ammonia but in practice, unconverted urea remains in the duct. The general steps involved in UWS droplet heating are given below.

- Water evaporation from UWS solution.
- Thermolysis of urea leading the formation of ammonia NH\textsubscript{3} and isocyanic acid (HNCO).
- Hydrolysis of isocyanic acid (HNCO) leading the formation of ammonia NH\textsubscript{3} and CO\textsubscript{2}.

The Urea water solution injected into the hot exhaust, then it atomizes to fine droplets. The droplets undergo heating leads to temperature rise of droplet and this leads to evaporation of water. Due to higher vapour pressure of water compared to urea, rapid evaporation of water take place. This leads to further change in properties of UWS droplet such as mass fraction. From literatures studied we understood that for the multicomponent droplet modeling several approaches can be used for calculate the droplet dynamics. In Rapid mixing model (RM) approach assumes uniform temperature and species concentration. Hence droplet liquid properties same at a given instant of time for the droplets dynamics calculations. However, in Diffusion limit model (DL) assumes these properties are varied with time. The study of birchold [2] suggests that the rapid mixing model is sufficient for evaporation...
modeling, also it take less computational effect compared to the DL model. While the ramdan [3] report that the deviation between these two models is significant only at low temperatures. It also states that, at lowest temperature the DL model is better to capture droplet dynamics than the RM model. Vikas et al.[4] compared the evaporation rate of UWS droplet with that of water droplet, study shows a small decrease in the mass change but the trend follows the same pattern.

The evaporation of water from the droplet, resulting solid urea melts and starts to decompose thermally, which means thermolysis and hydrolysis of urea. There exist several suggestions regarding the exact temperature at which urea starts to thermally decompose. These studies indicate that different approaches can be used for the modeling of urea decomposition. Most of the studies proposed use Arrhenius type expression of urea decomposition modeling. The proposed model by strom et al. [5] states that after complete evaporation of water content present in the droplet, the remaining urea will not have any mass transfer with the surrounding gas phase until it is heated upto 425K. When it attains 425 K, the convective heat transfer take place from the gas phase to the droplet is used for vaporize urea without any sensible heat change within the droplet. However, the experiments results given by [6] pointed out that the notable decomposition of urea was observed to start at around 406K. The experiments on a single droplet by Wang et al.[7] conforming that the fast depletion of urea at temperatures above 423 K. Almost all of the above models is assumed that urea is evaporate from its solid phase and directly decompose into gaseous ammonia (NH₃) and isocyanic acid (HNCO). By the literature review, it is found that there is a scope for develop pre- exponent for Urea thermolysis to improve the prediction of variation in ammonia formation along the duct.

In the present study, develop an evaporation model for both UWS evaporation and urea decomposition. The developed model considers the urea decomposition is take place as direct decomposition process. The convective and diffusive species transport across the droplet is considered for heat and mass transfer modeling of UWS droplet evaporation. The urea decomposition process is modeled by using kinetic rate model. This study developed a Pre-exponent for Urea thermolysis modelling to improve the prediction of variation in ammonia formation along the duct. This study also made fine tuning of vapour pressure, diffusivity and specific heat values for urea and water from available experimental literatures. The numerical modeling is carried out by modify Inbuilt droplet evaporation and boiling laws with user defined functions (UDFs) developed in the present study. This developed model was used in UWS spray simulation modeling of UWS droplet evaporation to determine the urea to ammonia conversion efficiency.

2. Methodology
In this study, the UWS droplet evaporation process considered to be quasi-steady. The droplet internal flow circulation and the radiative heat transfer were not considered. The evaporation model is based on the convection- diffusion approach by consider the effect of stefan flow and non-unity lewis number assumption. The heat and mass transfer processes in the gas phase near the droplet surfaces determine the amount of heat transferred to the droplet liquid phase. The internal circulation regarding the droplet characteristics is not considered in this study. The droplet physical properties are taken from the reference [8]. The vapour pressure values for urea and water taken from the reference [9].

2.1. Governing Equations
In the case of evaporation modelling, the calculation of heat and mass transfer at the surface of the droplet requires knowledge about mole fraction and component concentration at the surface. In this region, both liquid and gaseous phases are in thermal equilibrium. Hence, for the calculation of these quantities, Raoults law is used. The rate of mass transfer is determined by using the relation shown in Equation (1).

\[
\frac{d m_r}{d t} = -\pi D_f \rho_g \bar{u}_g S_h \ln(1 + B_m)
\]  

(1)
Where, the splashing mass transfer coefficient and Schmidt number is calculated as given by following equations (2) and (3) respectively.

\[ B_m = \frac{V_{ls} - V_{lg}}{1 - V_{ls}} \]  
(2)

\[ Sh_c = 2 + 0.6 \text{Re}^{\frac{1}{3}} \text{Sc}^{\frac{1}{3}} \]  
(3)

The rate of droplet temperature change is determined by the energy balance as shown in equation (4).

\[ \frac{dT_p}{dt} = -\frac{\dot{m}_{\text{vap}}}{m_p C_p} \left( \frac{C_{P_{\text{vap}}} (T_g - T_p) - \Delta H_{\text{vap}}}}{B_T} \right) \]  
(4)

Where, the splashing heat transfer number is calculated as given in following expressions.

\[ B_T = (1 + B_m)^\phi \]  
(5)

\[ \phi = \left( \frac{Sh_c}{Nu_c} \right) \left( \frac{C_{P_{\text{vap}}} \left( \frac{1}{C_{P_{\text{g,mix}}} \left( \frac{1}{Le_{\text{g,mix}}} \right)} \right) \right) \]  
(6)

The rate of droplet diameter change is computed from the change of the droplet mass as shown in Equation (7).

\[ \frac{dB_p}{dt} = \left( \frac{6}{\pi \rho_p} \frac{dm_p}{dt} \right) \]  
(7)

The urea decomposition process is modelled as volumetric reaction in the gaseous phase. For the description of the decomposition an Arrhenius expression is used and is shown in Equation (8). The activation energy constant for this reaction is taken from the study [10]. The pre-exponent is obtained by trial and error to match reasonably with the experimental data.

\[ A = 0.451 \text{ kg/ms} \]  

\[ E_a = 6.7 \times 10^4 \text{ J/mol} \]

2.2. Numerical Simulation Details

The numerical simulation study is carried by using the commercial CFD code ANSYS-Fluent. This study considers the single UWS droplet evaporation in a hot stream air flowing through a pipe. The Eulerian-Lagrangian approach available in ANSYS-Fluent is used as the basic framework for UWS spray simulation in the present study. The exhaust gas is considered as the continuous phase and the UWS droplets are considered as the discrete phase. In addition to solve transport equations for the continuous phase, we can simulate discrete second phase in a Lagrangian frame. The coupling between discrete phase and the continuous phase flow is made with two way coupling method. The droplet trajectories are computed in a Lagrangian frame using the Discrete Phase Model (DPM). The heat and mass exchange is modelled by using convection-diffusion approach. The urea decomposition is modelled by using single kinetic rate devolatilisation model. The urea decomposition is consider as volumetric reactions occurring in the gaseous phase, which is defined by using laminar finite-rate interactions between turbulence and chemistry the model constant is fitted to experimental value through repeated simulation. The developed heat and mass transfer model for UWS droplet evaporation including vapour pressure expressions can be implemented through user-defined C code.

Steady state numerical simulations are conducted for the validation spray analysis of urea water solution. The turbulence model used in the study is realizable k-epsilon model with wall treatment based on standard wall function method. The lower order implicit and higher order Runge-Kutta methods are adopted for capturing droplet trajectories. The pressure velocity coupling is solved by
using coupled scheme. The second order upwind scheme is used for solving momentum, turbulence and species transport equations. The residual convergence criterion for continuity momentum turbulence equations 1e-3 and for species energy equations is 1e-6. Urea water solution spray simulation is conducted using the computational domain shown in Figure 2, which have similar dimensions as of kim et al [10] shown in figure 1. 124993 hexahedral cells are used for geometry meshing with minimum orthogonal quality of 0.8149. No significant changes in the species concentration are observed in the Eulerian domain with further mesh refinement.

![Figure 1. Sketch of kim’s experimental setup.](image1.png)  
![Figure 2. The flow domain developed for the present study.](image2.png)

The hot air is introduced into the duct at different velocities and temperatures as shown in Table (1). The cone type injection is used for the injection of UWS droplets. The injection parameters are given in table (2).

| Table 1. Different cases of Ambient Air Temperatures and Air Velocities used in the study. |
|----------------------------------|------------------|
| Air Temperature (K) | Air Velocity (m/s) |
| 573 | 6.6 |
| 623 | 9.1 |
| 673 | 10.8 |

| Table 2. Spray Parameters and Droplet Characteristics used in the DPM injection setup. |
|----------------------------------|------------------|
| Parameters | Magnitude |
| Cone angle (degree) | 70 |
| Spread parameter | 3.27 |
| Mass flow rate (kg/s) | .00033 |
| Velocity of droplets (m/s) | 10.6 |
| Minimum diameter (m) | $5 \times 10^{-6}$ |
| Mean diameter (m) | $4.4 \times 10^{-5}$ |
| Number of diameters | 10 |
| Number of particle streams | 6 |
3. Results and Discussions
The ideal urea conversion is different with respect to the different flow rate and ambient conditions. The simulated results of the ammonia production are converted to the ammonia conversion efficiency. The ammonia conversion efficiency is defined as the ratio of the actual ammonia formed in the duct to the ideal possible ammonia conversion from the injected amount of urea. The conversion efficiency of ammonia depends upon the temperature of the exhaust gas and residence time. The residence time has the meaning that, how much time the urea conversion reaction occurs within the domain. The residence time is the function of flow velocity Vikas et al.[11]. For the purpose of the validation, this study measure the values of ammonia content present at each sampling points A, B and C. The ammonia conversion efficiency obtained in this study is compared with experimental data [10]. The efficiency versus residence time plots for the ambient conditions of 573 K, 623 K and 673 K are shown in Figure 3, Figure 4, and Figure 5 respectively.

![Figure 3. Ambient Temperature 573K](image3)

![Figure 4. Ambient Temperature 623K](image4)

![Figure 5. Ambient Temperature 673K](image5)
The results show generous agreements with the experimental data [10]. The obtained results show that the ammonia conversion efficiency increases initially (A to B) and then shows a reduction (B to C) along the flow direction. It can also see that the conversion efficiency increases with increase in exhaust temperature. This is because higher evaporation rate of UWS droplets at higher temperatures, which leads to higher conversion of ammonia from UWS.

Figure 6 shows the temperature distribution in the duct for 673 K. In addition, the urea thermolysis reaction also causes temperature drop in the hot air, since during the direct thermolysis approach this heat is extracted from the surroundings at the droplet surface. The ammonia mass fraction contours in the duct at 623K obtained in the study is shown in Figure 7. This shows that the thermolysis reaction is active at a location downstream of the injection point. This is due to the time lag required for the initiation of urea evaporation.

![Figure 6. Temperature distribution contour](image)

![Figure 7. Mass fraction contour of ammonia.](image)

4. Conclusion
This study develops a UWS evaporation model based on multi-component droplet evaporation approach along with the consideration of Stefan flow. The direct thermolysis approach is considered for the urea depletion process, where the modeling is based on single kinetic rate approach by proper fitting of pre-exponent. The overall comparison shows results show a reasonable match with the experimental data. This shows the predicted pre-exponent is more suitable to get promising results for the spray simulations of urea-water solution of the direct thermolysis approach to determine the ammonia conversion efficiency.
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