Analysis of the injection of urea-water-solution for automotive SCR systems: spray/exhaust-gas-interaction

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Abstract

Selective Catalytic Reduction (SCR) is increasingly used to reach NOx emission levels which are unachievable in-cylinder. This technology sprays urea water solution (UWS) as reducing agent in exhaust system. This work focuses on evaporation and mixing modeling of the UWS using commercial CFD code ANSYS Fluent. A user subroutine is written to modify the rate determining multicomponent evaporation with two step urea vapor decomposition. The results are validated with experimental measurements. This numerical framework allows to simulate SCR system and to predict conversion efficiency and local distribution of the reducing agent.

Introduction

Emission norms are becoming tougher and therefore engine manufactures are exploring different ways to cut down tail pipe emissions. In recent years, lot of emphasis is on treating exhaust gases and SCR is becoming a preferred way to deal with NOx coming out from diesel engines [1]. In SCR system UWS is injected into the hot exhaust gases (See Fig1). Automotive SCR systems use a 32.5 % wt. solution of urea in water (also known AdBlue, Diesel Exhaust Fluid, or DEF). Injected liquid undergoes atomization, water vaporization and mixes with hot exhaust gases. At higher temperature urea undergoes thermolysis and hydrolysis to form ammonia and iso-cyanic acid described by eq 2 and 3 [2,3]. In presence of catalyst this ammonia reacts with NOx to produce CO2 and H2O [4,5].

Water vaporization from UWS spray,
$$(NH_2)_2CO_{(aq)} \rightarrow (NH_2)_2CO_{(s\,or\,l)} + 6.9H_2O_{(g)} \tag{1}$$
Urea thermolysis and formation of ammonia and iso-cyanic acid,
$$(NH_2)_2CO_{(s\,or\,l)} \rightarrow (NH_3)_{(g)} + HNCO_{(g)} \tag{2}$$
Hydrolysis of iso-cyanic acid.
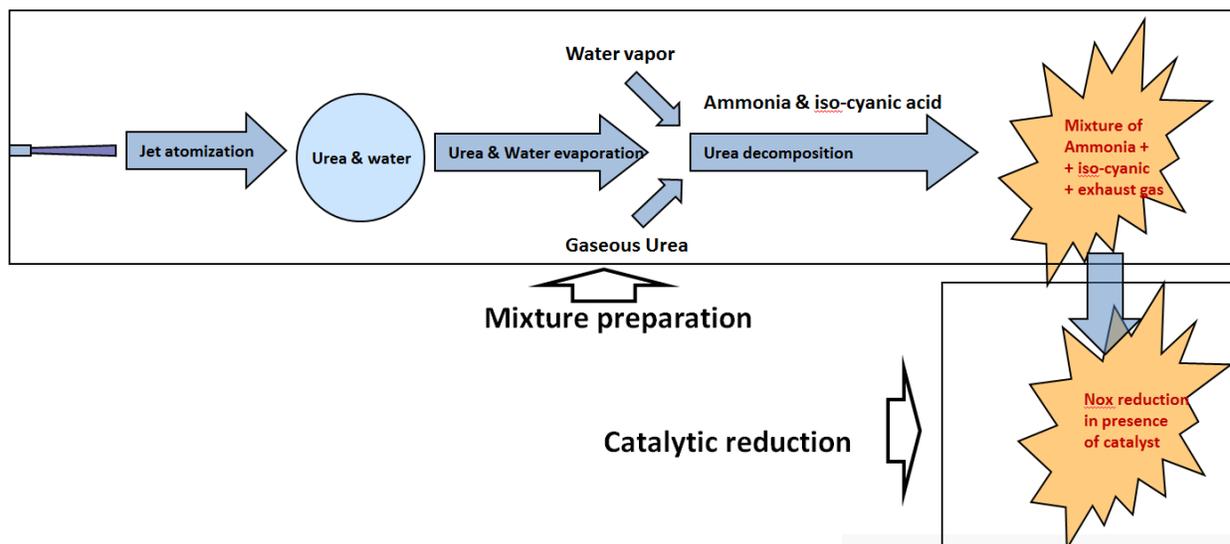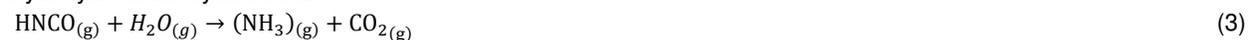$$HNCO_{(g)} + H_2O_{(g)} \rightarrow (NH_3)_{(g)} + CO_{2\,(g)} \tag{3}$$

Figure 1. Sketch showing mixture preparation and catalytic reduction process in SCR system.

However because of low residence time and lower operating temperature, an automotive SCR system poses additional performance challenges. Complete evaporation, decomposition and uniform reductant mixing upstream of the catalyst is very crucial for optimum NOx reduction, catalyst utilization, lower ammonia slip and hence overall SCR system performance. CFD is widely used [6,7] for optimizing mixing process but use of simple approximate methods such as approximating UWS spray with water-spray is common. This is because of complex multicomponent evaporation/boiling of UWS and urea decomposition. This paper shows the modeling of UWS injection, atomization, evaporation, urea decomposition and its validation against experimental data.

Details of the present model

The commercial CFD code ANSYS Fluent (version R15) is used as the basic framework for the present work. ANSYS Fluent is a general purpose, finite volume solver and can solve unsteady, turbulent, compressible, reacting multi-phase flow problems using unstructured grids [8]. While the exhaust gas phase is modeled using Eulerian Fluid flow solver, Lagrangian Discrete-Phase-Model (DPM) is used for modeling the UWS spray. Multi-component UWS droplets are represented by discrete parcels that are collections of statistically similar drops.These parcels are then tracked using the DPM model. Two-way coupling of mass, momentum and energy between liquid and gas phases is considered. Inbuilt droplet evaporation, boiling laws are modified using user defined functions (UDFs) developed in the present study.

UWS material properties

The UWS liquid properties except the density are computed as the mass weighted value of the properties of each component:

$$\varphi_p = \sum_i x_i \varphi_i \tag{4}$$

where φ_p represents the properties and x_i is the mass fraction of component i in the liquid mixture. The density is computed as the volume-weighted value of the densities of each component:

$$\rho_p = \sum_i y_i \rho_i \tag{5}$$

where ρ_p is density and y_i is the volume fraction of component i in the liquid mixture. Urea properties are used from a UWS producers catalog and listed in table 1. The properties of the liquid mixture are used for spray atomization and evaporation calculations. The evaporation and decomposition models for individual droplets are discussed below.

Table 1 Thermophysical properties of urea

Property	Value
Density	$1280 \ kg/m^3$
Specific Heat	$2375 \ ^j/_{kg-k}$
Vaporization temperature	$420K$
Boiling Temperature	$483K$

Heat and mass transfer calculation

The droplet temperature and drop diameter changes with the evaporation of water or the decomposition of urea. The rate of droplet temperature change is determined by the energy balance

$$\rho_p V_p c_p \frac{dT_p}{dt} - \rho_p A_p \Delta H_p \frac{dR_p}{dt} = A_p Q_p \tag{6}$$

where ρ_p, c_p, and ΔH_p are the density, specific heat, and latent heat of evaporation of the droplet, respectively, V_p and A_p are the volume and surface area of the droplet, T_p and R_p are the temperature and radius of the droplet, respectively. Q_p is the rate of heat conduction to the droplet surface per unit area, which is calculated by the Ranz-Marshall correlation. The rate of droplet diameter change is computed from the change of the droplet mass:

$$\frac{dD_p}{dt} = \left(\frac{6}{\pi} \frac{1}{\rho_p} \frac{dm_p}{dt} \right)^{\frac{1}{3}} \tag{7}$$

where m_p and D_p are the mass and diameter of the droplet, respectively. The rate of change of the droplet mass is determined by the water evaporation and/or the urea decomposition.

As illustrated in Figure 1 the water component is first released from the liquid mixture by vaporization. The effect of the convective flow of the evaporating material from the droplet surface to the bulk gas phase (Stefan Flow) becomes important. Following expression has been adopted following the work of Miller [9] and Sazhin [10]:

$$\frac{dm_p}{dt} = k_c A_p \rho_\infty \ln(1 + B_m) \tag{8}$$

$$B_m = \frac{Y_{i,s} - Y_{i,\infty}}{1 - Y_{i,s}} \tag{9}$$

where, k_c, $Y_{i,s}$ and $Y_{i,\infty}$ are the mass transfer coefficient, vapor mass fraction at the surface, and vapor mass fraction in the bulk, respectively

$$Sh = \frac{k_c \, D_p}{D_{i,m}} = 2.0 + 0.6 Re^{1/2} Sc^{1/3} \tag{10}$$

$D_{i,m}$ is the diffusion coefficient of the water vapor in the ambient. It is calculated at film averaged temperature, Re and Sc are the Reynolds and Schmidt numbers, respectively.

Urea decomposition model
As illustrated in Figure 1 after water vaporization remaining urea starts decomposing. Though Eq. (2) is a rather simplistic, single step description of the decomposition of urea, formation of polymeric compounds including biuret, cyanuric acid, ammelide, ammeline and melamine are observed during urea decomposition reaction [11]. Urea starts melting at 133 °C [12] with vigorous decomposition starting at approximately 140 °C. However, there is considerable uncertainty in the paths and rates of these reactions in an SCR system [13]. Therefore, following some previous studies [13], thermolysis is considered to be a single step process with melting of urea followed by a fast decomposition reaction in the boundary layer of the melt. Mass transfer during thermolysis is calculated by the single kinetic rate Arrhenius type model:

$$\frac{dm_u}{dt} = -\pi D_d A e^{(-E_a/RT_d)} \tag{11}$$

Where m_u is mass of urea and $A = 0.42 kg/sm$ and $= E_a 6.9 \times 10^4 \, J/mol$.

Model validation
The numerical model discussed above is used for reproducing experimental work done by Kim et al. [14]. Kim's experimental set-up is shown in Fig. 2. Automotive exhaust conditions are created using a hot generator. Gases produced from generator were directed through a duct, and urea-water solution with 40 % wt. urea was injected at the center of this tube at an injection pressure of 2 bar. The corresponding spray velocity was 10.6 m/s and the urea flow rate was 18 cc/min. Injection produced a hollow cone type spray structure with cone angle of 70°. The injected drop-size was reported to follow a Rossin-Rammler distribution with a mean diameter of 44 microns and spread parameter of 3.2657. Ammonia concentration was measured at three monitoring planes using FTIR and measurements from six points were used to compute an average ammonia concentration on a plane. The data was collected for different gas temperatures and gas flow rates.
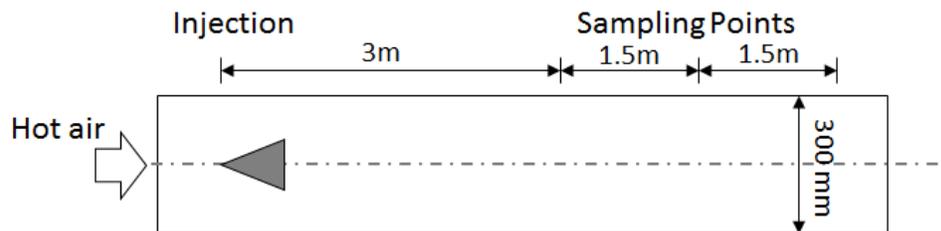
Figure 2. Sketch showing Kim et. al. [14] experimental setup.

Simulation results

Figure 3 shows the comparison of conversion efficiency for two different gas velocities. The predicted conversion efficiencies are in good agreement with Kim's [14] experiments. Figure 4 and Figure 5 show the comparison at higher gas temperature 350 deg C and 400 deg C respectively. Simulation predictions shows a good match and this builds the confidence in model. All numerical simulations were without any tuning. Figure 6 and Figure 7 show the NH3 mass fraction and gas temperature contours for different gas velocities at 350 deg C inlet gas temperature. At lower gas velocity NH3 mass fraction is higher which is due to higher residence time as well as lower gas mass flux.
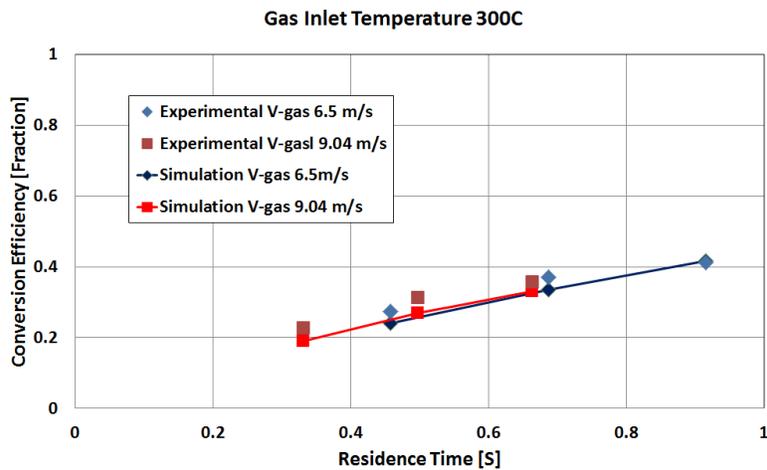
Gas Inlet Temperature 300C

Figure 3. Comparison of urea conversion efficiency against experimental data [14], Gas inlet temperature = 300 deg C.

Gas Inlet Temperature 350C

Figure 4. Comparison of urea conversion efficiency against experimental data [14], Gas inlet temperature = 350 deg C.
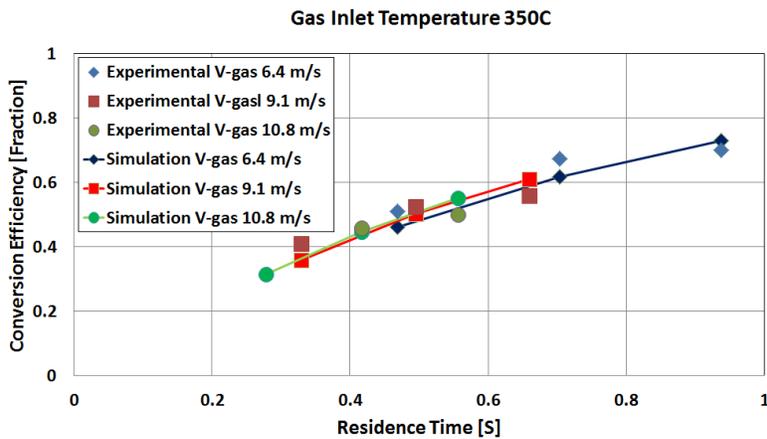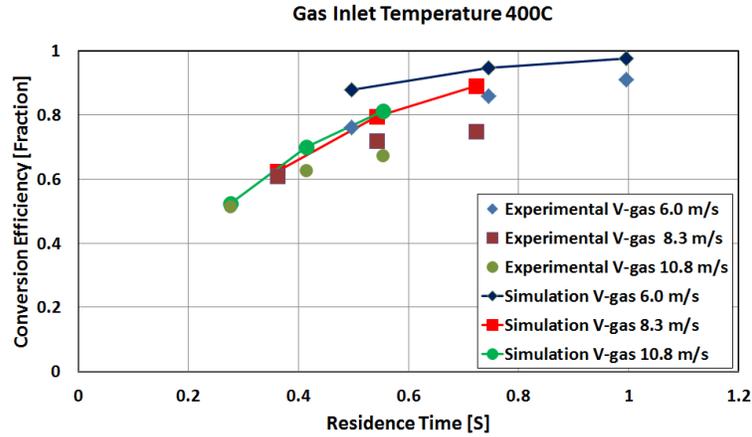
Gas Inlet Temperature 400C

Figure 5. Comparison of urea conversion efficiency against experimental data [14], Gas inlet temperature = 400 deg C.
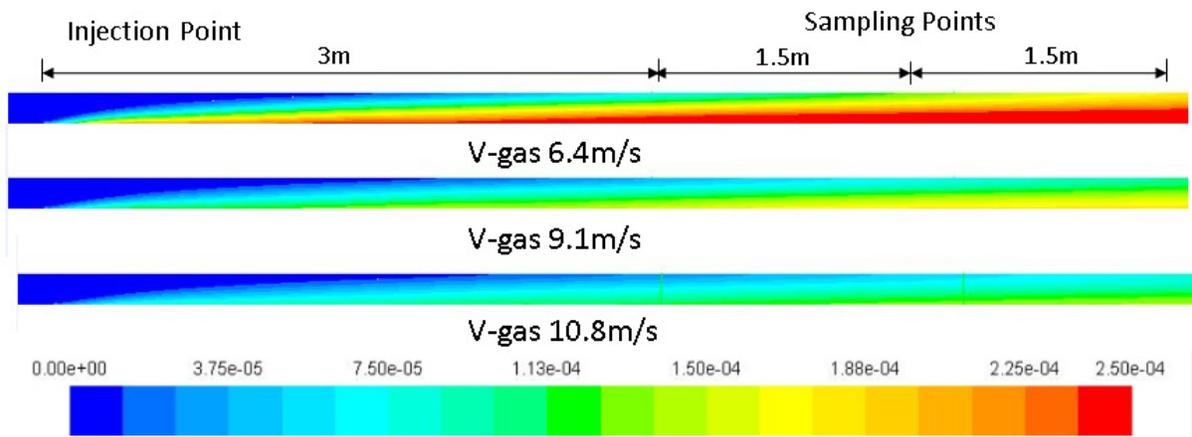

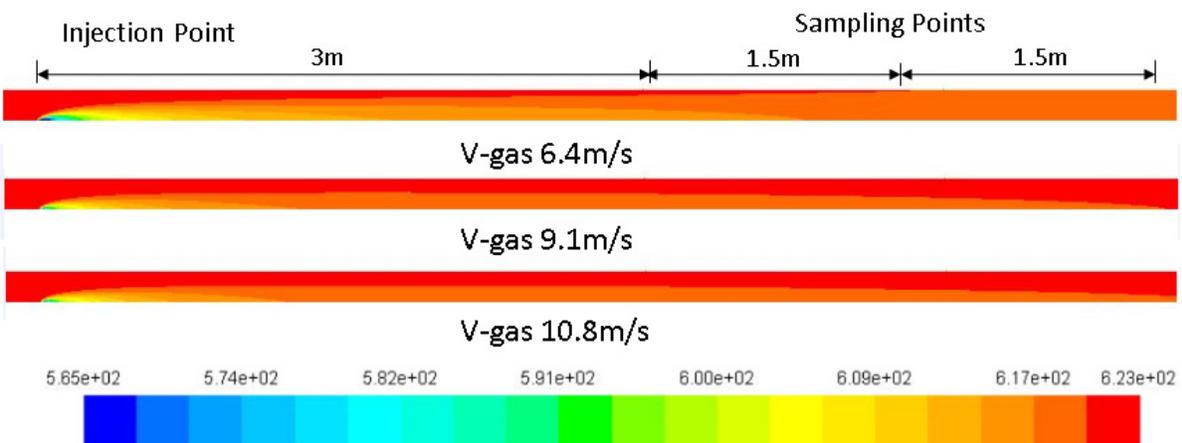**Figure 6.** NH3 mass fraction at different gas velocities, gas inlet temperature = 350 deg C.

Figure 7. Gas temperature (in Kelvin) at different gas velocities, gas inlet temperature = 350 deg C.

Conclusion

Numerical model has been developed to describe key mixture preparation processes which includes water vaporization, urea thermolysis and isocyanic acid hydrolysis in gas-phase that occur upstream of the catalyst. Multi-

component UWS spray is modeled using ANSYS Fluent and separate laws are defined for the heat and mass interaction between individual components and the gas phase. Urea decomposition is modeled by a kinetic rate model. Material property data and correlations reported in literature are used in the model development. Predictions from model have been compared with experimental data available in literature for various gas temperatures and velocities. Results show good agreement.

Spray wall interaction is also important in SCR application. Present study will be extended further to investigate the spray wall interaction taking place in SCR and appropriate model development to capture these phenomena.

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