PHENOMENOLOGICAL MODEL OF UREA WATER SOLUTION DOSAGE STRATEGY FOR UREA-SELECTIVE CATALYTIC REDUCTION SYSTEMS

Sadashiva Prabhu S.^{1,✉}, Nagaraj S. Nayak² and Kapilan Natesan³

¹Department of Mechanical and Manufacturing Engineering, Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, Karnataka, India-576104

² KBAT Technologies Private Limited, Pune, Maharashtra, India-411033

³ Department of Mechanical Engineering, Nitte Meenakshi Institute of Technology, P.B.No.6429, Yelahanka, Bangalore-560064

✉Corresponding Author: ss.prabhu97@gmail.com

ABSTRACT

Selective Catalytic Reduction (SCR) is the latest technology adopted to diesel engines of automobiles to transform NO_x. The required reducing agent (NH₃) is generated after engine exhaust by injecting Urea in the form of Urea Water Solution (UWS). There are some numerical methods with limited experimental details to estimate the behavior of UWS droplets in a heated environment, and some of them have been implemented into CFD codes. In the CFD codes, many numerical relationships are not validated for the evaporation of UWS droplets. In the SCR system of modern automobiles, the dosage strategy is based on DOE techniques. But, the theoretical method is required for UWS dosage during optimization of the SCR system. So, an integrated zero-dimensional model is required for dosage strategy during simulation studies so that exact dosage could be possible based on NO_x, flow rate, and temperature of exhaust gas to suit actual SCR situations. In the present work, a phenomenological model is developed based on theoretical correlations, experimental data generated by authors, and data from the literature.

Keywords: Phenomenological Modelling, UWS, SCR, Dosage, Evaporation, Catalyst.

RASĀYAN J. Chem., Vol. 14, No.4, 2021

INTRODUCTION

Oxides of nitrogen (NO_x) emitted from the exhaust of diesel engines can be reduced by the after-treatment method, Selective Catalytic Reduction (SCR). In this technique, Urea is used to generate the reducing agent ammonia (NH₃) and 32.5% aqueous urea solution is injected in the form of an atomized spray to hot exhaust gases. The UWS transforms into solid Urea and water vapor. Solid Urea undergoes thermolysis and produces NH₃ and Isocyanic acid (HNCO). HNCO further reacts with water vapor and gives CO₂ and NH₃.¹ The reduction of NO_x takes place over the catalyst through various favorable reactions.^{2,3} NH₃ slip to the environment to be avoided by the proper dosage of UWS. UWS conversion to NH₃ depends on several factors like temperature of the exhaust gas, residence time, type of spray, the droplet size of UWS, etc. Accordingly, the dosage strategy of UWS is to be tuned based on the factors associated with it.

The theoretical demand of NH₃ was proposed by Calatayud *et al.* and Ciardell *et al.*^{4,5} Subsequently, the UWS requirement was proposed by Tao *et al.*⁶ In the numerical model proposed by Lu *et al.*, engine speed, torque and temperature-related signals are sent to Dosing Control Unit through CAN-bus⁷ and required dosing is achieved. Once the SCR system is implemented in a diesel engine, the developed dosing control unit should be calibrated using DOE or with an emission map.

The SCR system has to work on varying engine load conditions, wherein temperature, the flow rate of exhaust gas, and NO_x contents vary. The required UWS dosage has to be optimized based on NO_x content and UWS decomposition characteristics. The stoichiometric urea requirements are calculated using chemical reactions which occur over the catalyst. The amount of NO_x conversion is based on the conversion efficiency of a particular catalyst. The probability of reactions occurring over the catalyst is related to

NO_2/NO_x ratio. Based on the efficiency of NO_x reduction over SCR catalyst, reducing agent NH_3 is calculated, and UWS dosing strategy is determined initially. However, when UWS is spray introduced into hot exhaust gases, vaporization of water from the droplet and subsequent urea decomposition plays a major role in the generation of NH_3 . When UWS droplet diameter is larger, the amount of evaporation reduces, and consequently, urea conversion reduces; thereby, the NH_3 mass fraction drops down. The droplet evaporation and urea decomposition both vary with temperature and residence time. So, the stoichiometric quantity of NH_3 generation from UWS cannot be attained at all conditions of exhaust gas. Therefore, the UWS requirement varies once again. So, the actual dosage strategy depends on the conversion efficiency at the catalyst, urea decomposition efficiency and percentage of evaporation UWS, etc. Some expressions found in the literature are not dealt with the evaporation of UWS and Urea conversion efficiencies. Further, many theoretical aspects were not incorporated in detail in them. In the present study of dosage modeling, major catalytic reactions based on NO_x/NH_3 ratio, UWS droplet evaporation and Urea conversion efficiencies are considered. A classical model which contributes to predicting the dosage strategy is given in the following sections in detail.

UWS Dosage Modelling

UWS dosage modeling is accomplished in stages, namely, identifying catalytic reactions, generation of NH_3 from UWS, determination of evaporation efficiency through the evaporation model and thermal decomposition of urea decomposition. Each stage is dealt with separately following sections. A few of the assumptions made while arriving at required expressions are i) UWS droplets are spherical, uniform size and, completely mix with hot air and do not settle iii) Solid urea decomposition after the evaporation of water from UWS iii) Catalytic reactions based on NO_2/NO_x ratio iv) Evaporation efficiency is based on global evaporation history.

Catalytic Reactions

The reduction of NO_x is based on several catalytic reactions, and the occurrence of those reactions is based on NO_2/NH_x ratio. The major reactions that occur over the catalyst during the conversion of NO_x into N_2 are as follows.^{2, 8}

The subsequent NH_3 requirement for the above reactions is based on the probability of occurrence of those reactions. Based on NO_2/NO_x ratio, the possible reactions are given in the following cases, and the NH_3 requirement is calculated accordingly based on the molar fraction of NO and NO_2 . The molecular weights of NH_3 , NO , and NO_2 are taken as 17, 30, and 46, respectively, for required calculations. The detailed calculations of NH_3 requirement based on NO_x in the exhaust for two different cases of NO_2/NO_x ratios are as detailed in Appendix-II.

NH_3 Generation from UWS

As discussed earlier, UWS droplets evaporate in a heated environment, and the Urea decomposes into NH_3 and HNCO . HNCO undergoes hydrolysis and generates NH_3 . So, the actual NH_3 generation is based on the efficiency of evaporation, efficiencies of thermolysis, and hydrolysis processes. Based on the factors involved in NH_3 formation from UWS spray, the NH_3 generated can be expressed as a function of stage efficiencies of evaporation, thermolysis, and hydrolysis. A simple NH_3 conversion factor comprising these efficiencies is multiplied by stoichiometric NH_3 to find actual NH_3 . So, it is written in the form,

Actual NH_3 generated = Stoichiometric $\text{NH}_3 \times \text{NH}_3$ Conversion Factor

NH_3 Conversion Factor = $f(\text{evaporation efficiency, thermolysis efficiency, hydrolysis efficiency})$

Usually, it is considered as:

$$\text{NH}_3 \text{ Conversion Factor} = \{\eta_{\text{evap}} \times (\eta_{\text{therm}} + \eta_{\text{hyd}})\} \quad (4)$$

To determine UWS evaporation efficiency, the temperature, droplet size, and residence time are considered major variables and efficiency of urea decomposition can be evaluated using pre-determined rate equations.^{9,10} Hydrolysis is a slow reaction that requires a catalyst if the residence time is less in SCR mixing pipe. The hydrolysis reaction is considered to occur by two pathways, namely catalytic and non-catalytic. Catalytic hydrolysis is considered with rate equation of hydrolysis reaction whereas non-catalytic hydrolysis by experimental methods relating to residence time. Each of the above efficiencies is calculated by respective mathematical models as described in the following sections. Accordingly, the NH_3 conversion factor is calculated using the relation mentioned above.

Determination of Efficiency of Evaporation (η_{evap})

The residence time is an important parameter that relates to the efficiency of evaporation. It is the time required to fill the SCR mixing chamber with the incoming exhaust gas, and it is evaluated as $t_r = \text{Volume of the SCR mixing chamber (m}^3\text{) / Volume flow rate of exhaust gas (m}^3\text{/sec)}$. The required residence time for evaporation of UWS droplets is based on their droplet sizes. Another important factor that determines the rate of evaporation and evaporation efficiency is the temperature of the exhaust gas. There are some additional factors like UWS flow rate, injection methods, heat transfer coefficient, etc. However, we consider the most influencing factors like residence time, temperature, and droplet size in our modeling. Modeling of both evaporation of water and urea thermolysis are explained in the following sections in detail.

UWS Evaporation Model

In this evaporation model, a spherical liquid droplet in a hot exhaust gas atmosphere is considered, which provides a convection environment to the droplet. The heat transfer due to convection leads to an increase in droplet temperature till its boiling point (T_e), and drop temperature is considered to be constant afterward, and water evaporation is considered to initiate from this point. The mass flow rate from the droplet during the evaporation of the droplet is expressed in the following form considering energy balance during the evaporation process⁹.

$$L \frac{dm_d}{dt} = -\phi_c \quad (5)$$

ϕ_c is the heat flux due to convection, m_d – a mass of the droplet and L is the latent heat of evaporation and convection heat transfer ‘ h ’ can be obtained through Nusselt number (Nu) as,

$$h = \frac{Nu \lambda_g}{D_d}, \text{ where } \lambda_g \text{ is the thermal conductivity of the gas, } D_d \text{ droplet diameter.}^9 \text{ Assuming the uniform}$$

temperature in the droplet and is equal to T_e . The convection heat flux ϕ_c can be expressed as,

$$\phi_c = \pi D_d^2 \frac{Nu \lambda_g}{D_d} (T_a - T_e) \quad (6)$$

where T_a is the temperature of surrounding gas, assuming uniform temperature throughout the droplet and equal to T_e ⁹. The linear form of evolution of droplet size is given by D^2 -law,

$$D_d^2(t) = -\beta_e t + D_d^{02} \quad (7)$$

D_d^0 = initial drop diameter $D_d(t)$ - drop diameter after time interval ‘ t ’, β_e - evaporation rate which is obtained as,

$$\beta_e = \frac{4 \lambda_g}{L \rho_w} Nu (T_a - T_e) \quad (8)$$

Birkhold *et al.*¹⁰ used Nusselt number to evaluate UWS drop evaporation in the following form.

$$Nu = \frac{\ln(1 + B_T)}{B_T} Nu_0 \text{ where } B_T = \frac{c_{p,vap} (T_a - T_e)}{L} \text{ where } B_T \text{ is the Spalding Number related to heat transfer}$$

and $c_{p,vap}$ is the vapor specific heat capacity.

ρ_w -liquid water density and Nusselt number (Nu_0) corresponds to droplet diameter, and relative velocity of the droplet in the hot gas is given by,

$$Nu_0 = 2.0 + 0.552 Re_d^{\frac{1}{2}} Pr^{\frac{1}{3}} \quad (9)$$

where Reynolds Number Re_d is calculated based on droplet diameter and Prandtl number Pr is obtained based on the property of exhaust gas.⁹ The quantity $0.552 Re_d^{\frac{1}{2}} Pr^{\frac{1}{3}}$ is added to consider turbulence aspects along with convection. In our modeling, the expression containing the Nusselt number is used for the evaporation rate from a droplet, and it can be expressed as,

$$\beta_e = \frac{4\lambda_G}{\rho_w c_{p,vap}} \ln(1 + B_T) Nu_0 \quad (10)$$

The density of UWS is given by $\rho_{UWS} = (1 - C_u)\rho_w + C_u\rho_u$

The diameter of the droplet ' D_d ' after complete evaporation of water after time interval ' t_e ' is evaluated using the relation,

$$\rho_u \frac{\pi D_d^3}{6} = C_u \rho_{UWS} \frac{\pi D_0^3}{6} \text{ along with the equation of } \rho_{UWS}$$

and Eq.-7 results,

$$D_d^2(t) = (C_u(C_u + (1 - C_u)\frac{\rho_w}{\rho_u}))^{\frac{2}{3}} D_0^2 \quad (11)$$

The time of evaporation ' t_e ' can be evaluated as,

$$t_e = \left\{ 1 - (C_u(C_u + (1 - C_u)\frac{\rho_w}{\rho_u}))^{\frac{2}{3}} \right\} \frac{D_0^2}{\beta_e} = \frac{1}{\beta_e} 0.58 D_0^2 \quad (12)$$

In SCR mixing pipe, the rate of flow for which $t_r > t_e$ the evaporation efficiency is considered as 100%. For the case, $t_r < t_e$ the evaporation efficiency is to be determined as,

$$\eta_{evp} = \frac{\frac{4}{3}\pi \left\{ \frac{D_0^3}{8} - \frac{(D_0^2 - \beta t_r)^{\frac{3}{2}}}{8} \right\} \rho_{uws} \times 100}{\frac{4}{3}\pi \left\{ \frac{D_0^3}{8} \right\} \rho_{uws}} = \frac{D_0^3 - (D_0^2 - \beta t_r)^{\frac{3}{2}} \times 100}{D_0^3} \quad (13)$$

EXPERIMENTAL

For validation, evaporation efficiency obtained numerically from the Eq.-13 is done from the experiments conducted in a hot air test bench for different flow rates at a fixed rate of UWS injection. Instead of single droplet evaporation, the global evaporation history of a spray of UWS is considered. In the hot air test bench, droplets are made to pass over metal foil (circular shape), as shown in Fig.-1a. The UWS droplets which are not evaporated and decomposed are collected in the metal foil. The amount of UWS injection for a particular duration (4sec) is taken as W_0 . The initial weight of the film is taken as W_1 gms, and the weight of the foil after 4 seconds of the collection is taken as W_2 gms. The difference of weights ($W_2 - W_1$) accounts for the weight of water not evaporated plus the weight of undecomposed Urea. The film is made to dry in the open air, and the weight is measured again as W_3 . All W_1 , W_2 , and W_3 are obtained from the digital weighing machine with accuracy ± 10 mg. Now the weight difference of weights ($W_2 - W_3$) accounts for the amount of water evaporated from foil. In other words, the quantity ($W_2 - W_3$) is the amount of water which not evaporated from the original UWS quantity W_0 . This quantity is measured for a fixed rate of injection of UWS 10ml/min, and the water content in the injected quantity of UWS is equal to 0.833gms ($m_0 = \text{flow}$

rate of UWS $\times$ water mass fraction (Y_{water}) in UWS (0.675) $\times$ duration of injection (4 seconds)). The percentage of evaporation is evaluated as,

$$\% \text{ Evaporation} = \frac{(m_0 - (W_2 - W_3)) \times 100}{m_0} \quad (14)$$

Fig.-1: (a) Exhaust Pipe and Metal Foil, (b) Schematic Experimental Setup

RESULTS AND DISCUSSION

The results of experimental values from Eq.-14 for various flow conditions are compared with numerical results obtained from Eq.-13, and good agreement is observed at all temperatures, except with some deviation at 150°C (Fig.-2a to d). At 150°C, experimental values were found superior to numerical values. The experimental values do not account for the weight of UWS droplets that settle by gravity and adhere to walls of the pipe which are of significant quantities at 150°C. This leads to a decrease in quantity $W_2 - W_3$. So, the efficiency of evaporation shows a higher value as per Eq.-14. As numerical values are based on evaporation and decomposition of single droplets wherein gravity effects and wall effects are ignored.

Note: If the residence time $t_r > t_e$ evaporation of UWS is complete, the percentage of evaporation is assumed to be 100%. However, for shorter residence times, the evaporation amount is calculated based on mass corresponding to the volume difference of the droplet. The final volume is obtained based on the diameter, which is calculated using D^2 -law.

Fig.-2: Comparison of Experimental and Numerical Percentage of Evaporation at (a) 150°C (b) 175°C (c) 200°C and (d) 300°C

Thermal Decomposition Efficiency of Urea

Thermal decomposition of Urea takes place by heat addition from the hot exhaust gas. The rate constant in the exponential form can be obtained as:

$$k = Ae^{\frac{E_a}{RT}} \quad (15)$$

Where k is the rate constant, E_a is the activation energy, A is the frequency factor, R is the gas constant, and T is the temperature. As mentioned earlier, NH_3 formation from urea decomposition follows two steps,

(i) Decomposition urea (Thermolysis) into NH_3 and HNCO occurs by the reaction,

(ii) Conversion of isocyanic acid into NH_3 (Hydrolysis of HNCO) occurs by the reaction,

In the following section, the urea thermolysis process and efficiency of urea thermolysis in a hot gas environment are discussed.

Estimation of urea thermolysis efficiency

We consider a fast reaction for the conversion of gaseous Urea to NH_3 and HNCO , which is proposed by Rota *et al.*¹¹, for which rate constant is in the form,

$$k = A \left[\frac{T}{T_0} \right]^n e^{\frac{E_a}{RT}} \quad (18)$$

Where A - is the frequency factor 12700s^{-1} , E_a -is the activation energy (15540 J/mol), T - is the gas temperature, T_0 - is a reference temperature, and 'n' is a dimensionless number often it is taken as zero.¹¹

¹² The rate of decomposition of Urea is given as,

$$\frac{dC_u}{dt} = -kC_u \quad (19)$$

Where C_u is the urea concentration in mol/m^3 and 't' is time in seconds. The time available for urea decomposition can be estimated as the difference between residence time and evaporation time ($t_r - t_e$). For the evaluation of the amount of urea decomposition, the Eq. (19) is rearranged and integrated as below for concentration limits C_1 to C_2 and time limits 0 to $(t_r - t_e)$.

$$\int_{C_1}^{C_2} \frac{dC_u}{C_u} = -k \int_0^{t_r - t_e} dt \Rightarrow \log [C_2] - \log [C_1] = -k (t_r - t_e) \Rightarrow \frac{C_2}{C_1} = e^{-k(t_r - t_e)}$$

Then the thermolysis efficiency reduces to a form,

$$\eta_{\text{the}} = \frac{C_1 - C_2}{C_1} = 1 - e^{-k(t_r - t_e)} \quad (20)$$

Note: The C_1 and C_2 can be in any units in Eq.20. We assume thermolysis efficiency as 99% to determine the minimum time required for thermolysis.

$$\frac{C_1 - C_2}{C_1} = 1 - e^{-kt_{\text{ther}}} = 0.99 \Rightarrow 0.01 = e^{-kt_{\text{ther}}} \quad \text{where } t_{\text{ther}} = \text{thermolysis time}$$

If $t_r - t_e > t_{\text{ther}}$, then it infers that urea thermolysis is 100% and if $t_r - t_e < t_{\text{ther}}$, then the percentage of thermolysis is calculated using Eq.-20.

Conversion of Isocyanic acid into NH_3 (Hydrolysis Reaction)

Catalytic Conversion

HNCO , which is formed during the thermolysis process, will undergo hydrolysis and gives NH_3 . The hydrolysis of Isocyanic acid is a slower reaction compared to thermolysis. Usually, it occurs over the catalyst. However, it occurs with higher residence time and at elevated temperatures of the exhaust gas without the catalyst. The rate of reaction over the catalyst for the hydrolysis reaction is given by the following formula³,

$$\frac{dC_{\text{HNCO}}}{dt} = C_{\text{HNCO}} \times 2.5 \times 10^5 e^{\frac{-62220}{RT}} \quad (21)$$

$$\frac{dC_{\text{HNCO}}}{C_{\text{HNCO}}} = 2.5 \times 10^5 e^{\frac{-62220}{RT}} dt$$

$$= kt \quad \text{if } k = 2.5 \times 10^5 e^{\frac{-62220}{RT}}$$

Where C-molar concentration in mol/m^3 , R-universal gas constant in J/mol K. T-temperature in K and t is time in secs. It is assumed that hydrolysis reaction occurs in the time interval after evaporation and thermolysis times have been elapsed. So, integrate for the limits C_1 to C_2 for HNCO and 0 to $t_r - (t_e + t_{\text{ther}})$ for 't', and we get the final expression as given below:

$$\eta_{\text{hyd}} = \frac{C_1 - C_2}{C_1} = 1 - e^{-k(t_r - (t_e + t_{\text{ther}}))} \quad (22)$$

Note: The above method of determination of conversion efficiency is valid if the hydrolysis takes place over the catalyst.

Non-Catalytic Conversion of Isocyanic acid into NH_3 (Hydrolysis Reaction)

Here, unlike the previous method, the NH_3 is generated by hydrolysis at elevated temperatures and increased residence time. The experimental results of Kim *et al.*¹³ which have been used by few authors to compare their simulated results^{10,14}. Same results are used here to obtain the rate of hydrolysis in which no catalyst is used and authors opine experimental values obtained are due to both thermolysis and hydrolysis reactions. From the plots of conversion efficiency vs. residence time (Figs.-3a to c, Fig.-4 a to e), the conversion efficiency (η) can be expressed in the form of a straight-line equation, $\eta = C_1 t + C_2$ by curve fitting.

The conversion efficiency is equal to C_2 when $t=0$. As the thermolysis reaction is very fast, the time required for thermolysis is very small. In such cases, when $t_{\text{ther}} \sim 0$, the constant C_2 can be considered as η_{ther} , and the remaining part of the equation can be considered as $\eta_{\text{hyd}} = C_1 t$. For the SCR system with residence t_r , the time available for hydrolysis is $t_r - (t_{\text{ther}} + t_e)$, and it can be substituted in place of 't'. Then the efficiency of hydrolysis is expressed as, $\eta_{\text{hyd}} = C_1 [t_r - (t_{\text{ther}} + t_e)]$.

Fig.-3: Conversion Efficiency of Urea at Different Flow Rates and at Temperature of 400°C with respect to Residence Time at (a) 10.3 m/sec (b) 8.3 m/sec and (c) 6 m/sec^{10,13,14}

Fig.-4: Conversion Efficiency of Urea at Different Flow Rates and Temperature with respect to Residence Time for conditions (a) 350°C-10.8 m/sec (b) 350°C-9.1 m/sec (c) 350°C- 6.4 m/sec (d) 300°C-9 m/sec and (e) 300°C-6.6 m/sec^{10,13,14}

Evaluation of Constant C_1

Assuming there is no hydrolysis catalyst in SCR mixing pipe, C_1 is evaluated using experimental data obtained from Kim *et al.*¹³. In any SCR system, evaporation and thermolysis both occur in a very short time for the droplet sizes ranging from 20-200 μm . The first stage of urea decomposition (thermolysis) gives nearly 30-50% of total NH_3 . The obtained from experiments of Kim *et al.* indicate conversion efficiency for residence times up to 0.8 sec for all temperature ranges¹³. As thermolysis time is very short, the variation

of conversion efficiency after 0.1 sec is only due to the hydrolysis effect. Hence, the variation of the NH_3 concentration after 0.1 secs indicates the variation of conversion efficiency due to hydrolysis alone. The nature of graphs of experimental data is linear in the form $\eta = C_1 t + C_2$. With appropriate curve fitting, the constant C_1 is approximated as 35-45 depending on the temperature range.

UWS Dosage Calculation

We know that, Actual NH_3 generated = Stoichiometric $\text{NH}_3 \times \text{NH}_3$ conversion factor

$$\text{Stoichiometric } \text{NH}_3 = \frac{34}{60} \times 0.325 \times m_{\text{uws}} \quad (\text{Eq.-3. of Appendix})$$

$$(\text{NH}_3) \text{ conversion factor} = \eta_{\text{evap}} \times (\eta_{\text{therm}} + \eta_{\text{hyd}})$$

Actual NH_3 generated from UWS = NH_3 generated (stoichiometric) $\times$ (NH_3) conversion factor

$$\Rightarrow \text{Actual } \text{NH}_3 \text{ generated from UWS} = \text{Stoichiometric } \text{NH}_3 \times (\eta_{\text{evap}} \times (\eta_{\text{ther}} + \eta_{\text{hyd}})) \quad (23)$$

We can conclude that NH_3 required for catalytic conversion of NO_x should be equal to NH_3 generated from UWS, and in such cases, Eq. (4) and Eq. (23) can be equated and it can be written as,

Actual NH_3 required for reduction of NO_x = Actual NH_3 generated from UWS

$$\Rightarrow K \frac{17 \times [X] \times M_{\text{ex}} \times 1000}{29 \times 3600} = (\text{NH}_3) \text{ generated (stoichiometric)} \times \eta_{\text{evp}} \times (\eta_{\text{ther}} + \eta_{\text{hyd}})$$

$$\Rightarrow K \frac{17 \times [X] \times M_{\text{ex}} \times 1000}{29 \times 3600} = \frac{34}{60} \times 0.325 \times m_{\text{uws}} \times (\eta_{\text{evap}} \times (\eta_{\text{ther}} + \eta_{\text{hyd}})) \quad (24)$$

$$\text{where (i) } K=1 \text{ if } x=\text{NO}_2/\text{NO}_x < 0.5 \text{ (ii) } K = \left\{ \frac{2}{3} + \frac{2}{3} x \right\} \text{ if } x = \text{NO}_2/\text{NO}_x > 0.5$$

$[X]$ – NO_x in PPM, M_{ex} – exhaust gas in kg/hr, m_{uws} – flow rate of UWS in g/sec

From the above equation, m_{uws} is calculated as a function of NO_x and mass flow rate. The effect of temperature, residence time, and droplet size are accounted in terms like η_{evap} , η_{ther} , and η_{hyd} .

As a summary, the expression obtained in Eq.-24 gives a complete dosage strategy considering many variables such as the mass of the exhaust gases, NO_x content, the efficiency of evaporation, thermolysis and hydrolysis efficiencies. The numerical results of evaporation of UWS droplets were found in-line with experimental values. Numerical methods are followed for thermolysis of Urea and hydrolysis of HNCO over catalyst. Further non-catalytic conversion of Urea was also considered.

CONCLUSION

In the phenomenological model developed, the UWS dosage strategy is based on variables like temperature, residence time, droplet diameter, amount of NO_x present, and the mass flow rate of exhaust gas. To establish by classical or other methods NH_3 requirement based on NO_x content, exhaust temperature, and flow rate so that the reducing agent is correctly dosed in the simulation for parametric studies. The model includes stage efficiencies of evaporation, urea decomposition, and catalytic conversion. The model enables us to do a UWS dosage strategy for simulation studies of SCR systems based on the above variables, and the same can be utilized for actual transient engine cycles as a complementary approach to other conventional DOE methods. Among dosage modeling obtained in literature, many theoretical aspects especially evaporation and thermolysis based on residence, are not incorporated in detail. Some numerical code developed can provide NH_3 distribution and conversion efficiency for a particular case. The developed phenomenological model accounts for many theoretical aspects related to evaporation and urea decomposition in addition. Further, for transient load conditions with varying flow rates and NO_x in real-time scenarios, the developed model can be used to get a dosage of UWS accurately.

ACKNOWLEDGEMENT

The authors would like to thank the Manipal Institute of Technology Manipal for their support in writing this paper.

APPENDIX-I

Thermolysis of Urea

Writing molecular weights,

60 17 43

For 1 mole of Urea

1 17/60 43/60

Then, Isocyanic acid may hydrolyze to give NH_3 and CO_2

Writing molecular weights

43 18 44 17

For 1 mole

1 18/43 44/43 17/43

If 43/60 mole of HNCO is available, then

43/60 17/43 × 43/60 = 17/60 mole

Total NH_3 by both thermolysis and hydrolysis = 17/60 + 17/60 = 34/60 mole (3)Flow rate of NO_x (kg/sec) = Mass flow rate exhaust gas × mass fraction of NO_x in exhaust gas
$$M_{\text{NO}_x} = M_{\text{exh}} \text{ (kg/hr)} \times (\text{volume fraction of } \text{NO}_x \times \text{Molecular wt. of } \text{NO}_x) / \text{Molecular wt. of exhaust gas}$$

$$M_{\text{NO}_x} = M_{\text{ex}} \frac{[X] \{ (1-x)30 + x46 \}}{29} \text{ kg/hr of } \text{NO}_x$$

$$= M_{\text{ex}} \frac{[X] \{ (1-x)30 + x46 \}}{29 \times 3600} \times 1000 \text{ gm/sec of } \text{NO}_x$$

APPENDIX-II

Case-1: $\text{NO}_2/\text{NO}_x < 0.5$

If exhaust gas contains 1 mole of NO_x , then the fraction of NO_2 is 'x' mole, and the fraction of NO is '1-x' mole. Mathematically,

$$\text{NO}_x = \text{NO} + \text{NO}_2 = 1, \text{NO}_2/\text{NO}_x = x, \text{NO}/\text{NO}_x = 1-x$$

If $\text{NO}_2 < \text{NO}$ ($\text{NO}_2/\text{NO}_x < 0.5$), then it is assumed that NO_2 will be completely consumed first during a *fast SCR reaction*. Considering *fast SCR reaction*,

(according to NH_3 : NO: NO_2 ratio)

If the exhaust gas contains 'x' mole NO_2 if it is completely utilized, then the 2:1:1 ratio turns to 2x: x: x as given below. The consumption of NO during *fast SCR reaction* is 'x' mole.

2x x x

Remaining NO after *fast SCR reaction* = (Amount of NO before *fast SCR reaction*) - (Amount of NO consumed during *fast SCR reaction*) = (1-x)-x = 1-2x moles

Assuming remaining NO of (1-2x) moles reacts with NH₃ as per *standard SCR reaction* (Eq.2) and writing the reaction and number of moles of reactant species we get,

4 4 ÷4 results

1 1

If (1-2x) moles of NO are utilized completely, then the molar proportion of NH₃: NO is 1-2x 1-2x

The NH₃ required for 1 mole of NO_x considering both *fast and standard SCR reactions* is calculated as,

Total NH₃ required = NH₃ consumption during *fast SCR reaction* + NH₃ consumption during *standard SCR reaction* $\Rightarrow 2x + 1 - 2x = 1$ mole.

According to this, 1 mole NO_x requires 1 mole of NH₃ for complete conversion of NO_x if NO₂/NO_x ratio is less than 0.5. In other words, 1 PPM of NO_x requires 1PPM of NH₃ for complete conversion.

We know that if 'x' is NO₂/NO_x ratio, 1 mole of NO_x is equivalent to [(1-x) (30) + (x)46] g. Then, [(1-x)(30) + (x)46] g NO_x requires -17g of NH₃

So, NH₃ required for the conversion 1 g of NO_x is $\frac{17}{(1-x)30 + x46}$ g

If the exhaust gas flow rate is M_{ex} (kg/hr) and if it contains [X] PPM of NO_x, then the flow rate of NO_x is obtained as $M_{\text{NO}_x} = \frac{[X] \{(1-x)30 + x46\}}{29 \times 3600} M_{\text{ex}} 1000$ g/sec of NO_x (Appendix -Eq. (4))

Note: Constituents of exhaust gases can be taken as that of air as it contains other constituents in lesser percentages. So, the molecular weight 29 is considered for exhaust gases. If the mass flow rate of exhaust gas is M_{ex} [kg/hr] and if it contains [X] PPM of NO_x then, NH₃ required is obtained as,

$$M_{\text{NH}_3} = \frac{17}{\{(1-x)30 + x46\}} \frac{[X] \{(1-x)30 + x46\}}{29 \times 3600} M_{\text{ex}} 1000 = \frac{17 \times [X] M_{\text{ex}} \times 1000}{29 \times 3600} \text{ g/sec.}$$

Case2: NO₂/NO_x > 0.5

When NO₂/NO_x > 0.5, then NO < NO₂, and it is assumed that NO is completely consumed first during *fast SCR reaction* and remaining NO₂ will take part in *slow SCR reaction*. The maximum possible consumption of NO is '1-x' mole. So, we consider (1-x) moles of NO to take part in a *fast SCR reaction*. Considering *fast SCR reaction* and writing the number of moles of reacting species we get,

2 1 1

for '1-x' moles of NO, the ratio changes to

2(1-x) 1-x 1-x

Remaining NO₂ after *fast SCR reaction* = (Amount of NO₂ before *fast SCR reaction*) - (Amount of NO₂ consumed during *fast SCR reaction*) = x - (1-x) = 2x - 1. So, the NH₃ required for one mole of NO_x is 2x - 1 moles

if a *fast SCR reaction* occurs. Considering *slow SCR reaction* and writing the number of moles of species we get,

$$8 \qquad 6 \qquad \div 6$$

$$8/6 \qquad 1$$

For $(2x-1)$ moles of NO_2 , the proportion becomes $4/3(2x-1): 2x-1$

Total NH_3 required = NH_3 consumption during *fast SCR reaction* + NH_3 consumption during *slow SCR reaction*.

For 1 mole NO_x , the total NH_3 required is $2(1-x) + [4/3(2x-1)]$ mole = $\left\{ \frac{2}{3} + \frac{2}{3}x \right\}$ moles

One mole of NO_x requires $\left\{ \frac{2}{3} + \frac{2}{3}x \right\}$ moles NH_3 . So, 1 PPM of NO_x requires $\left\{ \frac{2}{3} + \frac{2}{3}x \right\}$ PPM of NH_3 .

We know that 1 mole of NO_x is equivalent to $[(1-x)(30) + (x)46]$ g.

So, $(1-x)(30) + (x)46$ g of NO_x requires $\left\{ \frac{2}{3} + \frac{2}{3}x \right\} \times 17$ g of NH_3

$$1 \text{ g of } \text{NO}_x \text{ requires } \frac{\left\{ \frac{2}{3} + \frac{2}{3}x \right\} 17}{(1-x)30 + x46} \text{ g of } \text{NH}_3$$

If the exhaust gas contains $[X]$ PPM of NO_x , then NH_3 required will be $\left\{ \frac{2}{3} + \frac{2}{3}x \right\} [X]$ PPM

As mentioned earlier, if the exhaust gas flow rate is M_{ex} kg/hr and if it contains $[X]$ PPM of NO_x , then the flow rate of NO_x is obtained as,

$$M_{\text{NO}_x} = \frac{[X]\{(1-x)30 + x46\}}{29 \times 3600} M_{\text{ex}} \times 1000 \text{ g/sec of } \text{NO}_x \quad (\text{Appendix-Eq. (4)})$$

NH_3 requirement for the above mass flow rate of NO_x is obtained as,

$$M_{\text{NH}_3} = \frac{\left\{ \frac{2}{3} + \frac{2}{3}x \right\} 17}{\{(1-x)30 + x46\}} \frac{[X]\{(1-x)30 + x46\}}{29 \times 3600} M_{\text{ex}} 1000 = \left\{ \frac{2}{3} + \frac{2}{3}x \right\} \frac{17 \times [X] M_{\text{ex}} \times 1000}{29 \times 3600}$$

In general, we can write,

$$M_{\text{NH}_3} = K \frac{17 \times [X] M_{\text{ex}} \times 1000}{29 \times 3600} \quad (4)$$

where (i) $K=1$ if $\text{NO}_2/\text{NO}_x < 0.5$

(ii) $K = \left\{ \frac{2}{3} + \frac{2}{3}x \right\}$ if $\text{NO}_2/\text{NO}_x > 0.5$

REFERENCES

1. M. Koebel, E. O. Strutz, *Industrial & Engineering Chemistry Research*, **42(10)**, 2093(2003), <https://doi.org/10.1021/ie020950o>
2. M. Koebel, Martin Elsener and M. Kleemann, *Catalysis Today*, **59(3-4)**, 335(2000), [https://doi.org/10.1016/S0920-5861\(00\)00299-6](https://doi.org/10.1016/S0920-5861(00)00299-6)
3. D. S. Yim, S. J. Kim, J. H. Bai, K. I. Nam, Y. S. Mok, J. W. Lee, B. K. Cho, S. H. Oh, *Industrial & Engineering Chemistry Research*, **43(16)**, 4856(2004), <https://doi.org/10.1021/ie034052j>
4. M. Calatayud, B. Mguig and C. Minot, *Surface Science Reports*, **55(6-8)**, 169(2004),

- <https://doi.org/10.1016/j.surfrep.2004.05.002>
5. C. Ciardell, *Applied Catalysis B: Environmental*, **70(1-4)**, 80(2007), <https://doi.org/10.1016/j.apcatb.2005.10.041>
 6. H. Tao, (2009) Ph.D. Dissertation, Wuhan University of Technology, China.
 7. L. Lü and L. Wang, *International Journal of Automotive Technology*, **14(1)**, 13(2013), <https://doi.org/10.1007/s12239-013-0002-6>
 8. M. Koebel, M. Elsener, G. Madia, *Industrial & Engineering Chemistry Research*, **40**, 52(2001), <https://doi.org/10.1021/ie000551y>
 9. Sébastien Grout, Jean-Bernard Blaisot, Karine Pajot, Giovanni Osbat. *Fuel*, **106**, 166(2013), <https://doi.org/10.1016/j.fuel.2012.09.022>
 10. F. Birkhold, U. Meingast, P. Wassermann, and O. Deutschmann, *Applied Catalysis B: Environmental*, **70**, 119(2007), <https://doi.org/10.1016/j.apcatb.2005.12.035>
 11. R. Rota, D. Antos, E. F. Zanoelo and M. Morbidelli, *Chemical Engineering Science*, **57**, 27(2002), [https://doi.org/10.1016/S0009-2509\(01\)00367-0](https://doi.org/10.1016/S0009-2509(01)00367-0)
 12. H. Aoki, T. Fujiwara, Y. Morozumi, and M. Takatoshi, Measurement of urea thermal decomposition reaction rate for NO selective non-catalytic reduction, in Proceedings of the Fifth International Conference on Technologies and Combustion for a Clean Environment, pp. 115–118, Lisbon, Portugal, 1999.
 13. J.Y.Kim, S.H.Ryu, J.S.Ha, Numerical prediction on the characteristics of spray-induced mixing and thermal decomposition of urea solution in SCR system, in: Proc.2004 Fall Technical Conference of the ASME Internal Combustion Engine Division, Long Beach. ICEF2004-0889 <https://doi.org/10.1115/ICEF2004-0889>
 14. Jakov Baleta, Hrvoje Mikulcic, Milan Vujanovic, Zvonimir Petranovic, Neven Duic Numerical simulation of urea based selective non-catalytic reduction deNO_x process for industrial applications. *Energy Conversion and Management*, **125**, 59(2016), <https://doi.org/10.1016/j.enconman.2016.01.062>

[RJC-6427/2021]