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Benjamin, S.F. and Roberts, C.A.

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appropriate for Light-Duty Vehicles under Steady State and Transient Conditions. © 2009

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Significance of droplet size when injecting aqueous urea into a Selective Catalytic Reduction after-treatment system in a light-duty Diesel exhaust

S. F. Benjamin and C. A. Roberts

Automotive Engineering Applied Research Group, Faculty of Engineering and Computing, Coventry University, UK

ABSTRACT

Application of SCR catalyst technology in a light-duty Diesel exhaust system requires injection of a reductant. Aqueous urea is injected with a spray unit directly into the exhaust upstream of an SCR catalyst. Ideally, the aqueous urea droplets must first evaporate and break down to ammonia and HCNO before reaching the catalyst. Multiple chemical reactions then occur on the catalyst reducing NO_x. Droplet size is thus critical in this process. Laser PDPA measurements have been made in the laboratory of the diameter of water droplets from a commercially available urea spray unit in hot air flow to characterise the spray. These measurements have shown significant numbers of droplets with diameters greater than 120 microns. Measurements have also been made with a typical mixer unit downstream of the spray unit and the effect of this on the droplet size distribution is reported. A simple model of the warm up and evaporation of an aqueous urea droplet convecting in a Diesel exhaust has been developed. This can be run as a single droplet simulation programme but could be incorporated into a full CFD model. The latter is required for designing SCR injection systems without recourse to testing. The model is valid for the early part of the evaporation process where it is assumed that water leaves the aqueous urea droplet and also for the later stage where the urea leaves the droplet prior to breaking down by thermolysis. The model has been tested against data available in the literature. The effect of initial droplet size, droplet injection temperature and velocity, and of the exhaust temperature, vapour pressure and flow rate under typical operating conditions are demonstrated. The implications of the model are that the urea droplets must be very small, less than 50 microns, if they are to evaporate in the short distance between the injector and the catalyst in a typical light duty Diesel exhaust system.

NOTATION

A_C	cross-sectional area of liquid droplet	(m ²)
A_O	surface area of liquid droplet	(m ²)
C_D	coefficient of drag for sphere	
C_p	specific heat at constant pressure	(J/kg K)

D_V	diffusion coefficient of water vapour in air-water vapour film	(m^2/s)
h	coefficient of heat transfer in film in absence of mass transfer	$(J/m^2 s K)$
k	thermal conductivity	$(J/m^2 s K)$
k_G	mass transfer coefficient	$(kg/m^2 s Pa)$
M	molecular weight	(kg/mol)
$M\%$	mass of droplet relative to that at injection	
m	mass of liquid droplet	(kg)
m_U	mass of urea component in droplet	(kg)
m_W	mass of water component in droplet	(kg)
$MolF$	mol fraction of water in aqueous urea solution	
N_{NU}	Nusselt number for heat transfer	
$N_{NU'}$	Nusselt number for mass transfer (Sherwood number)	
N_{PR}	Prandtl number $[C_{PM} \cdot \mu_M / k_M]$	
N_{RE}	Reynolds number $[2r \cdot U \cdot \rho_M / \mu_M]$	
N_{SC}	Schmidt number $[\mu_M / \rho_M \cdot D_V]$	
P_T	total pressure	$(Pa \text{ (abs)})$
P_A	average partial pressure of air in film, $[P_T - (P_{VL} + P_{VB})/2]$	$(Pa \text{ (abs)})$
P_{VB}	partial pressure of water vapour at outer edge of film, i.e background vapour pressure	$(Pa \text{ (abs)})$
P_{VL}	partial pressure of water vapour at aqueous urea droplet surface at temperature T_L	$(Pa \text{ (abs)})$
P_{VW}	partial pressure of water vapour above pure water	$(Pa \text{ (abs)})$
Q	total heat transfer from air to droplet	(J/s)
Q_L	sensible heat transfer received by droplet	(J/s)
Q_S	heat carried away from droplet by diffusing vapour	(J/s)
Q_V	heat received at droplet surface	(J/s)
Q_A	heat of vapourisation	(J/s)
R	universal gas constant (8.3145)	$(J/mol / K)$
r	radius of droplet	(m)
R_{PPT}	computed rate of urea precipitation (crystallisation)	(kg/s)
T	temperature	(K)
t	time	(s)
U	droplet velocity relative to exhaust gas, $[U_D - U_{EXH}]$	(m/s)
U_D	droplet velocity	(m/s)
U_{EXH}	velocity of exhaust gas	(m/s)
V_{INJ}	injection velocity	(m/s)
V_U	volume of urea component in droplet	(m^3)
V_W	volume of water component in droplet	(m^3)
w	rate at which water vapour leaves droplet	(kg/s)
w_U	rate at which urea leaves droplet	(kg/s)
z	droplet penetration	(m)
x	factor $(w C_{PV} + w_U C_{PUG}) / h A_D$	
λ_W	latent heat of vapourisation of water	(J/kg)
λ_U	enthalpy of melting plus latent heat of vapourisation of urea	(J/kg)
μ	viscosity	$(kg/m s)$
ρ	density	(kg/m^3)
Δt	time interval	(s)
ΔU	relative velocity increment	(m/s)
ΔT_{L_i}	incremental temperature change in droplet at time step i	(K)

subscript

A	air
B	background (exhaust)
i	time step
L	liquid
M	mixture
V	water vapour

W	water
U	crystalline or solid urea
UG	urea in gaseous phase

1 INTRODUCTION

Selective Catalytic Reduction (SCR) provides an effective means of reducing NO_x emissions from Diesel engines through reaction with ammonia on a catalyst, usually vanadium or zeolite **(1)**. The process normally involves injecting aqueous urea (32.5% w/w) as a spray some distance upstream of a catalytic coated monolith. Droplets evaporate in the hot exhaust stream leaving a residue of solid urea that either sublimates or melts and vapourises before breaking down by thermolysis into gaseous products (isocyanic acid and ammonia) at temperatures in excess of 406K for subsequent reaction with NO_x within the monolith.

For optimum performance completion of droplet evaporation should be achieved at the front face of the monolith. Maximum conversion efficiency is then realised provided the flow field along with the gaseous bi-products are uniformly distributed at the front face of the monolith. In practice this is difficult to achieve due to packaging constraints. Critical to system design are the injector's characteristics and its positioning within the exhaust assembly. Depending on type, Sauter mean diameters up to 150 microns might be expected, with smaller droplets, near 10 microns, associated with air-assisted injectors **(2)**. Furthermore, for any particular injector, the droplet size distribution includes the presence of some larger droplets. Although fewer in number, they may contribute a significant volume flux. Thus the droplets injected into an exhaust by a spray can range from a few microns to several hundred microns in diameter.

For any injector it is important that wall wetting be avoided. Droplets in contact with cold surfaces can form deposits **(3)**. This can lead to fouling of the injector itself and possible malfunction and the formation of deposits (e.g. melamine) on the walls of the exhaust following impingement. Both result in inefficient utilisation of the reductant. Deposits on the monolith have also been reported and this could cause premature deactivation of the catalyst.

Wall wetting in the vicinity of the injector can be minimised by aligning the injector with the main flow. This can be achieved by injecting at a bend within the exhaust system. Alternatively, mixing units or plates **(4)** are often positioned just downstream of the injector. These serve to redirect the spray along the direction of the main exhaust stream, and if well-designed will also act to boil off the proportion of the spray mass flux that impinges to form a liquid film. They reduce the size of the droplets by impaction and improve the uniformity of the spray across the exhaust pipe. Inevitably some droplets will reach the monolith and either vaporise therein or indeed pass through it **(5)**. The latter scenario is undesirable as it results in ammonia and/or urea "slip" through the exhaust system.

Clearly predicting the fate of droplets within the exhaust assembly is of interest. Computational fluid dynamics (CFD) has been used to predict droplet behaviour **(2, 6)**. Such models are quite comprehensive but can be difficult to implement. Simulations are computationally intensive as many droplet "parcels" need to be tracked due to the statistical nature of the process. The ultimate aim of this research is to develop and validate a full CFD model to facilitate the design of SCR exhaust systems without the need for testing; an important objective is the development of a single droplet model. Such a model provides a relatively quick method for evaluating droplet behaviour as a function of engine operating condition and droplet characteristics. As a stand-alone model this informs the development of

requirements for injector and mixer systems for a particular engine/exhaust system. The same model can be incorporated later into full CFD simulations. Laser PDPA measurements of water droplets injected into a hot air flow stream with and without a mixer are included in this research paper to illustrate the range of droplet sizes encountered in practical exhausts.

This paper describes a simple model of the warm up and evaporation of an aqueous urea droplet injected into a Diesel engine exhaust. It permits the evaluation of factors affecting droplet behaviour, namely: initial droplet size, injection temperature and velocity, exhaust temperature, vapour pressure and flow rate. The model is based on one derived by El Wakil et al **(7)** for liquid fuel injection into air. It describes the transient heat, mass and momentum transfer processes and droplet behaviour as equilibrium is approached. Conditions in an exhaust are somewhat different to those explored by El Wakil et al., who assumed a zero background vapour pressure. With injection temperatures of ~ 20 deg $^{\circ}\text{C}$ condensation of exhaust water vapour on to droplets can occur initially before evaporation proceeds. The model accounts for this and for increasing urea concentration as water subsequently leaves the droplet. The model extends to the point where all the water has been driven off, leaving a urea droplet or particle, and beyond this to the final stage where urea leaves the droplet and is available for break down by thermolysis into ammonia and isocyanic acid. This has been modelled by including a urea decomposition rate based on an Arrhenius expression from Birkhold et al. **(8)**. The model output is compared with data from Wang et al. **(9)**, who have investigated the evaporation of stationary aqueous urea droplets, although with diameters just below 1 mm these were larger droplets than those characteristically generated by SCR urea spray units. The full single droplet model and solution procedure are described in detail in this paper and some results are presented that are pertinent to conditions prevailing in a typical Diesel exhaust.

2 MEASURED DROPLET SIZES

Phase Doppler Particle Anemometry can be used to measure the velocity and diameter of droplets from a spray injection system. Fig. 1 shows measured droplet volume distributions for four different locations in the duct exit plane when a spray was spraying obliquely into the duct from an angled side branch. When the mixer is not present, large droplets are apparent with a significant proportion of the volume of the spray at diameters of 150 microns or above, particularly at locations below the centre of the duct. When the mixer is present, there is still a small number of larger droplets, but the peak of the volume distribution is now between 50 and 80 microns, dependent upon location. There is scatter in Fig. 1 because data rates are low and the total number of data points collected was between 3,000 and 8,000, which is quite low for PDPA measurements. Nevertheless, the measurements indicate the range of droplet sizes encountered with spray systems. They also show that even with a mixer present, droplets with diameters above 80 microns represent a significant fraction of the volume in parts of the spray field.

3 MODEL DESCRIPTION

The model follows that described by El Wakil et al. **(7)**, but is modified for spray droplets of 32.5% w/w aqueous urea solution. Such urea solutions are sometimes known by trade names, for example Adblue or Bluetec. The droplet is considered to be a mixture of urea and water with total mass ($m_w + m_u$) and with density ρ_L . The model has been extended to include background water vapour content, which will be greater than zero in a typical Diesel exhaust stream. The flow is assumed one-dimensional, with the injector aligned with the main flow. In the analysis that

follows the droplet is assumed to be spherical and its interaction with other droplets is ignored.

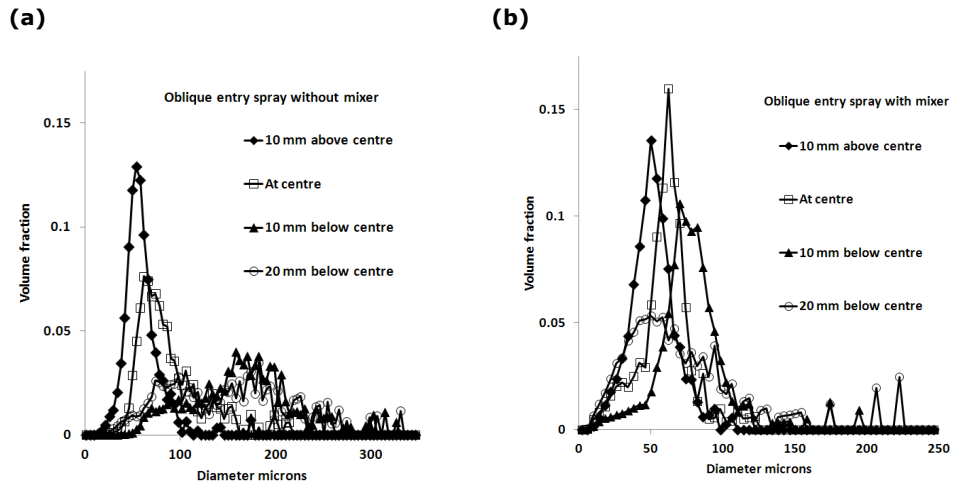


Figure 1: Droplet volume distributions measured with PDPA system; (a) without and (b) with a mixer composed of static angled plates.

3.1 Heat transfer

Fig. 2 shows the heat balance near the surface of a liquid droplet. The heat transfer from the exhaust stream Q is equivalent to the net effect of the following four energy transfer processes. Q_v represents the transferred heat arriving at the liquid surface. Q_L is the sensible heat transferred into the droplet. Q_λ is the latent heat of evaporation of water and/or urea. Q_s represents heat that is transferred away from the droplet because water vapour is removed by convective mass transfer.

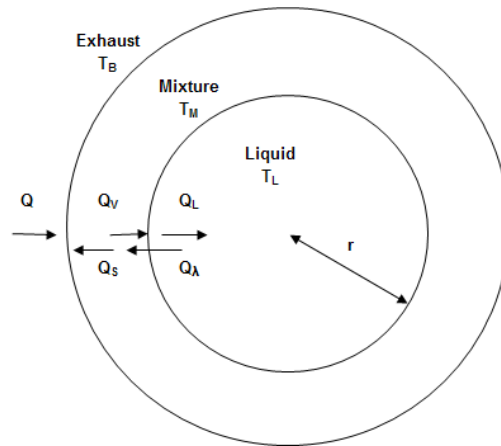


Figure 2: Heat balance within a droplet.

Hence under quasi steady state conditions:

$$Q_V = Q_L + Q_\lambda \quad [1]$$

$$Q_V = Q - Q_S \quad [2]$$

From **(7)**

$$Q_V = h \cdot A_o \cdot (T_B - T_L) \cdot (x / (e^x - 1)) \quad [3]$$

$$Q_V = Q \cdot x / (e^x - 1) \quad [4]$$

For an aqueous urea droplet

$$x = (w C_{PV} + w_U C_{PUG}) / h A_o \quad [5]$$

The factor $x / (e^x - 1)$ in equ. [4] represents the fraction of the heat transfer Q from the exhaust that arrives at the surface of the liquid droplet. This either provides sensible heat to the droplet Q_L and/or heat of evaporation, Q_λ , which is $w\lambda$ for water plus $w_U\lambda_U$ for urea.

The heat transfer coefficient, h is that derived by Ranz and Marshall **(10)** for spherical droplets.

$$N_{Nu} = h \cdot 2r / k_M = 2.0 + 0.6 \cdot (N_{Pr})^{1/3} (N_{Re})^{1/2} \quad [6]$$

Under equilibrium conditions Q_L is zero, and hence from equ. [1]

$$Q_V = Q_\lambda \quad [7]$$

3.2 Mass transfer

Mass transfer of water to or from the droplet is described using the expression of Bird et al. **(11)**:

$$w = A_o \cdot k_G \cdot P_T \cdot \ln[(P_T - P_{BL}) / (P_T - P_{VL})] \quad [8]$$

with mass transfer coefficient k_G **(7)** derived from equ. [9]

$$N_{Nu'} = 2r \cdot P_A \cdot k_G / D_V \cdot \rho_M = 2.0 + 0.6 (N_{Sc})^{1/3} (N_{Re})^{1/2} \quad [9]$$

Mass transfer of urea is described **(8)** by

$$w_U = \pi D \cdot 0.42 \exp(-69,000.0 / RT) \quad [10]$$

3.3 Momentum transfer

The drag on the droplet **(7)** with cross sectional area A_c is given as

$$m \cdot \Delta U / \Delta t = -C_D \cdot A_c \cdot \rho_M \cdot U^2 / 2 \quad [11]$$

where C_D is given **(12)** by equ. [12]

$$C_D = (24 / N_{Re}) [1 + (0.197 N_{Re}^{0.63}) + 0.00026 N_{Re}^{1.38}] \quad [12]$$

3.4 Solution procedure

The equations were solved using explicit time-marching coded into a Fortran programme. From equ. [11] at time step i the velocity deficit for the droplet is

$$\Delta U_i = -\Delta t[(3/8)C_{D, \rho_M} U^2 / \rho_L r]_i \quad [13]$$

Hence at $i + 1$ the droplet velocity relative to the exhaust is

$$U_{i+1} = U_i + \Delta U_i \quad [14]$$

The droplet mass at i is given by

$$m_i = [(4/3)\pi r^3 \rho_L]_i \quad [15]$$

Hence at $i + 1$ using equations [8] and [10]

$$m_{W i+1} = m_{W i} - w_i \Delta t \quad [16]$$

$$m_{U i+1} = m_{U i} - w_{U i} \Delta t \quad [17]$$

$$m_{i+1} = m_{W i+1} + m_{U i+1} \quad [18]$$

Using equs. [1] to [6] enables the change in droplet temperature to be found from equ. [19]

$$\Delta T_{L i} = \Delta t.[Q_L / (m \cdot C_{PL})]_i \quad [19]$$

Thus the droplet temperature at $i + 1$ is

$$T_{L i+1} = T_{L i} + \Delta T_{L i} \quad [20]$$

and the new droplet radius becomes

$$r_{i+1} = [m_{i+1} / (4\pi \rho_L)]^{1/3} \quad [21]$$

Penetration of the droplet along the exhaust is given by

$$z_i = \sum (U_i + U_{EXH}) \cdot \Delta t \quad [22]$$

Values for the following quantities are specified as data input to the model:

Droplets

r_0 initial radius
 T_L initial temperature at injection
 V_{INJ} injection velocity

Exhaust gas

U_{EXH} velocity
 T_B temperature
 P_T pressure
 P_{VB} background water vapour pressure

The simulation can be terminated by a criterion in the programme such as the mass of the droplet having fallen to a few % of the initial value.

3.5 Droplet properties for use in model

Vapour film (mixture) properties are evaluated at the logarithmic film temperature, T_M , for an average water vapour concentration, $(P_{VL}+P_B)/2$. At the later stages of the simulation, the effect of gaseous urea on the vapour film properties has been neglected as reliable property values for gaseous urea are unavailable. This could, however, be incorporated easily into the model when such data become available, and if a urea vapour mass diffusion model were to be used in place of equ. [10]. Air, water vapour, water and urea properties that have been used in the model are given in detail in the Appendix to this paper, but some assumptions made when specifying suitable values are outlined below. Table 1 summarises the model.

3.5.1 Density of aqueous urea solution

The solution is assumed to be a mixture of solid urea and water. Its density is calculated as a function of temperature from the total mass of urea plus water and the total volume. The expansion coefficient for solid urea crystal (**13**) implies that the volume change for solid urea up to its melting point can be neglected, so that the solid urea density value at ambient temperature is valid. This method for estimating density in the model is applicable to the droplet until its disappearance. Shinoda (**14**) indicates that the volume change on mixing to form a solution is dependent upon molecular shape and cannot be predicted accurately by simple theory. He states that where there is mutual solubility the volume change is very small. Only if heat of mixing is large, will it be large. The pragmatic assumption here is that the volume change can be neglected.

Table 1 Summary of model

Temperature	State of droplet	Enthalpy
$T \ll 100 \text{ }^\circ\text{C}$	Aqueous urea solution, initially 32.5 % w/w	Water vapourisation takes heat from the droplet.
$T < 100 \text{ }^\circ\text{C}$	After water vapour has left droplet, solid urea precipitate and saturated aqueous urea solution co-exist.	Crystallisation or precipitation of urea out from solution is exothermic.
$100^\circ\text{C} < T < 132.7^\circ\text{C}$	Particle of solid or crystalline urea; urea sublimates from solid urea.	Sublimation of urea direct to the gaseous state takes heat from the particle.
$T \geq 132.7 \text{ }^\circ\text{C}$	Partially molten urea particle; urea evaporates from molten urea; gaseous urea decomposes away from the particle.	Transformation of the particle from the solid to the liquid state is endothermic. Transformation of molten urea to its gaseous state is also endothermic.

3.5.2 Specific heat of aqueous urea solution

The data of Gucker and Ayres (**15**) are used as the basis for the values used in the model, but apply only to aqueous urea solutions less than 60% w/w. The urea solution in the droplet will become more concentrated than 60%w/w as the water is driven off and the droplet temperature rises. The difference between the Gucker and Ayres data (**15**) and values based on a weighted average of the urea and water specific heats is acceptably small. The weighted average additionally provides an estimate for the specific heat value at higher concentrations. It also remains appropriate if the urea precipitates out when the concentration becomes very high and the droplet becomes a mix of solid urea plus saturated solution. A fit to the Ruehrwein and Huffman data (**16**) is used for the specific heat of the solid urea component.

3.5.3 Latent heat of water vapourisation from solution

The latent heat for vapourisation of pure water is used, even though the water will be evaporating from a moderately concentrated or saturated solution at the later stages of evaporation in the model. This assumption is pragmatic in the absence of relevant data. Othmer (17) states that "the latent heat of water evaporated from sodium chloride solution changes little with increase in concentration of the salt solution; thus there is only a negligible amount of heat of solution to be considered in addition to the latent heat of water itself". For the purposes of single droplet modelling, it is assumed that the same is true for urea solution.

The latent heat of vapourisation of water is in the region of 43 kJ/mol of water, over the range 300 to 370 K (18). The heat of solution of urea in water is about +12.6 kJ/mol of urea for a saturated solution (19). Urea dissolving in water cools the mixture/solution, so as water evaporates from a saturated solution, if urea comes out of solution, this will tend to warm the mixture/solution. This can be added into the droplet model as a urea crystallisation sub-model. Its effect is, however, very small as discussed later.

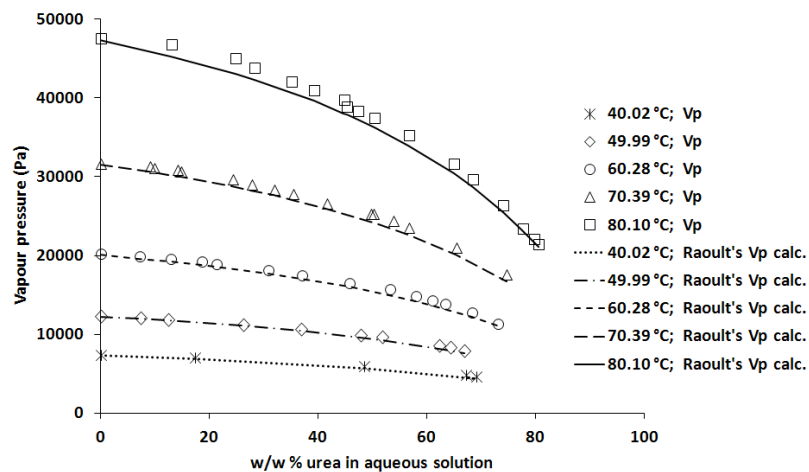


Figure 3: Measured vapour pressures over aqueous urea solution from (20) compared with calculated values based on Raoult's law for five temperatures in the range from 40 to 80 °C.

3.5.4 Latent heat of vapourisation of urea from drop or particle

Birkhold et al. (8) represent the heat of urea decomposition (+185.5 kJ/mol) as a vapourisation enthalpy of +87.4 kJ/mol, which cools the liquid drop or solid particle as urea converts to the gaseous state, and a decomposition enthalpy of +98.1 kJ/mol, which cools the gases produced. The model here focuses on the droplet, so the value 87.4 kJ/mol (1,456,667 J/kg urea), plus a small addition of 14.5 kJ/mol (241,667 J/kg urea) to account for melting, (8) and Miller and Ditmar (1934), referenced in (21), can be used as the latent heat for the process of converting urea from the solid to the gaseous state. Thus 1,698,333 J/kg urea is used in the single drop model as the energy requirement to transform the urea into the gaseous state.

3.5.5 Partial pressure of water vapour above the surface of the droplet

Fig. 3 shows vapour pressure data from Perman & Lovett (20) compared with values calculated from the Raoult's law approximation where the vapour pressure for water is multiplied by the mol fraction of water in the solution. Water vapour pressure as a function of temperature is given in the Appendix. The agreement in Fig. 3 is good and supports the use of the Raoult's law approximation in the single droplet model.

3.5.6 Partial pressure of urea vapour above surface of droplet

The need to specify the partial pressure due to vapourisation of the urea itself, and to have values for the properties of gaseous urea, is circumvented by Birkhold et al. (8), who give a decomposition rate for urea as a function of temperature $T(K)$ based on an Arrhenius expression. This is equ. [10] above where the pre-exponential factor is 0.42 kg/s/m, and the activation energy is 69,000 J/mol. This equation can be assumed to describe both the rate at which the urea is transformed from the solid to the gaseous state and also the rate at which it subsequently decomposes into isocyanic acid and ammonia.

3.5.7 Specific heat of gaseous urea

A value for C_{PUG} is required for equ. [5]. The authors are not aware of a reliable value for this so the approximation for the minimum value for a polyatomic gas, C_p is $4R$ J/mol/K, is used, where R is the universal gas constant. The model is not highly sensitive to this value but is more sensitive to the latent heat of vapourisation, as discussed in the next section.

4 RESULTS AND DISCUSSION

The model can be run for pure water droplets and a comparison has been performed for the data from Table 3 of Part II of the Ranz and Marshall papers (10). In that experiment, the drops were stationary and hot air flowed past them at velocities up to 1.84 m/s. This was achieved in the model described here by adjusting the differential between injection and exhaust velocities to the air velocity stated in (10) and by setting the drag coefficient in the model, equ. [12], to zero. The model and data were in full agreement, as would be expected. Data for stationary aqueous urea droplets in hot gaseous surrounding are given in (9). In an attempt to model this set of data using the simple model described in this paper it was necessary to set equal injection and exhaust velocities to simulate a stationary droplet not experiencing air flow. In (9) and in Fig. 4 the data are plotted as D^2/Do^2 against t/Do^2 in s/mm² units. The droplets are just under 1 mm diameter so the values on the abscissa approximate to real time in seconds.

A spherical 32.5% w/w urea solution droplet shrinks to a value for the D^2/Do^2 ratio of about 0.415 when all the water has left the droplet. In the experiment in (9), the droplet of exterior diameter just below 1 mm is suspended around a 0.275 to 0.3 mm bead. This raises the D^2/Do^2 ratio that corresponds to the disappearance of all water to almost 0.44. Inspection of the originally plotted data as it is shown in (9) indicates a change in the character of the plots at D^2/Do^2 about 0.55. This data is represented as lines with symbols in Fig. 4. Assuming that by this stage of the evaporation process only water has been driven off from the droplet, a ratio of 0.55 corresponds to a highly concentrated mixture of approximately 1 mol of water per 1 mol of urea. The evaporation mechanism will change at this stage since this mixture will not behave like a solution of urea in water; the urea may precipitate out with the water then being driven off more readily. This has been included in the single droplet model as a crystallisation sub-model, the details of which are given in the Appendix. Comparison of the model predictions in Fig. 4a with Fig. 4b shows a

subtle change in the gradient of the curve when D^2/Do^2 is about 0.55 in Fig. 4b; this can be discerned for the lines at temperatures ≥ 523 K, most easily at 673K, but it is a very small change. The authors of (9) discuss the observation of “microexplosions”, which can occur when water is trapped inside a urea crust shell that heats more rapidly. An attempt has been made (22) to model urea crust formation, and demonstrated a small effect at high ambient temperature, but was only able to model crust formation at low ambient temperature by use of a modification to the mass reduction coefficient. The simple model described in this paper here does not attempt to simulate “microexplosions” that may follow crust formation, but nevertheless has the ability to model the data from (9). The droplet initial temperatures are not specified in (9) but it is indicated that they are at ambient room temperature. This has been assumed to be 291K in the simulations here.

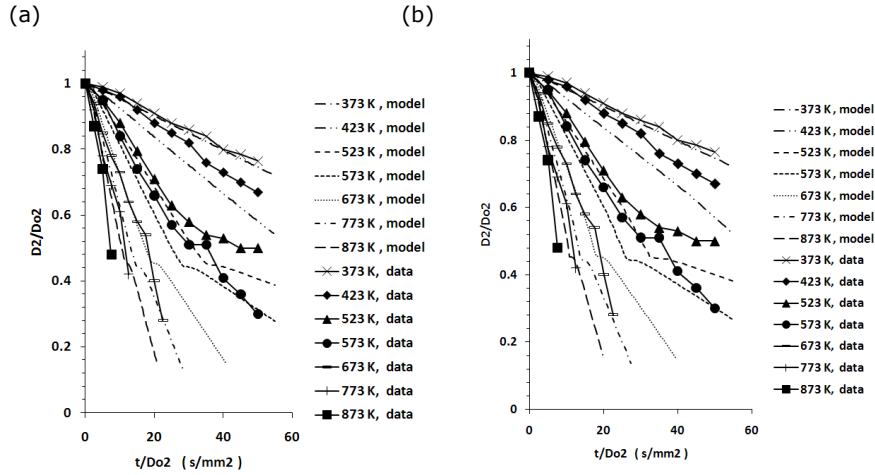


Figure 4: Predictions from single droplet model compared with data from (9); (a) simple droplet model (b) droplet model with urea crystallisation sub-model.

It was necessary to lower the activation energy by 25% in equ. [10] from (8) describing the urea transfer to the gaseous state; this improved the agreement between data and model at temperatures above 523 K, notably 673 K and 773 K. The change in the nature of the curves in Fig. 4 between 523 K and 573 K is qualitatively well predicted by the single droplet model. The limiting Sherwood and Nusselt numbers in equs. [6] and [9] were reduced from 2.0 down to 1.54 in the model to allow for the non-spherical shape of the droplets (23), which corresponded to a long axis to short axis ratio of about 1.5 in (9). The steep gradient seen in Fig. 4 for 673, 773 and 873 K after all the water has left the droplet is sensitive to the value used for the latent heat of evaporation of urea in the model, and best agreement with the data is obtained if the decomposition enthalpy is excluded, as discussed above. The model is less sensitive to the specific heat of urea gas, required by equ. [5], and doubling the value from 4R J/mol/K causes a negligible change in gradient. Overall, Fig. 4 shows that the model spans the data fairly well across the range 373 K to 873 K, although agreement is not exact. With large droplets near 1 mm diameter as used in (9) it is possible that there is some internal resistance in the liquid and that the droplet temperature is non-uniform; this is not accounted for in the model. Also, there may be some heat flux through the bead and fibre in the experimental set up (9).

It was considered that the model predictions and data were close enough over a wide temperature range to make the model useful for predicting and examining the outcome for a droplet when injected into a typical Diesel exhaust. The simple model without the crystallisation sub-model was used for this. Fig. 5 presents model output for 10 and 50 micron spherical droplets. An exhaust flow rate of 32 g/s has been chosen, typical of a passenger Diesel vehicle operating at around 1500 rpm. With an exhaust gas temperature of 560K this results in a gas velocity of 26 m/s for a typical exhaust system. It is assumed that the exhaust contains 5% water vapour and droplets are injected at 291K with a velocity of 22 m/s in the direction of the main flow. The injector would not normally be expected to be placed more than about 1m upstream of the SCR catalyst. Initially water vapour condenses on the droplet because P_{VB} is greater than the surface vapour pressure, P_{VL} . This results in a negative value of Q_{λ} and a small increase in droplet mass. As the droplet heats up, P_{VL} increases and evaporation begins as the vapour flux is reversed. An equilibrium state occurs where $Q_L = 0$ and droplet temperature becomes constant. Comparison of Fig. 5a with 5b shows that the larger droplet travels a significantly greater distance to attain the velocity of the exhaust. The warm up period for the 10 micron droplet is short compared with the time spent in the equilibrium state, but almost complete evaporation of water has occurred by about 0.05m. At this distance the 50 micron droplet has only just attained equilibrium. Droplet temperature control by evaporation of water diminishes at about 0.06 m for the 10 micron droplet and 1.5 m for the 50 micron droplet. At this point, Q_L peaks and Q_{λ} dips as the droplet changes from a drop of concentrated urea solution to a urea particle. Between these two states is a time period or distance where the particle warms up but does not evaporate significantly. More rapid heating of the urea particle occurs after all water has been driven off, but the rate of decrease of droplet mass declines. The droplet temperature is held constant and low by water evaporation in the early evaporation stage, but is held at a constant higher temperature higher when urea sublimates or melts and vapourises in the later stage.

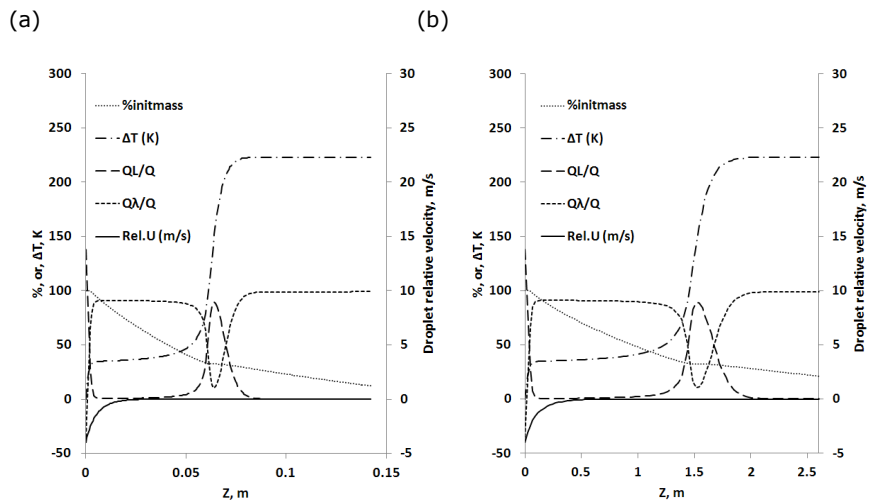


Figure 5: Normalised heat fluxes, droplet mass, droplet relative velocity and temperature rise with distance from injector for droplet sizes (a) 10 micron and (b) 50 micron. Droplet initial temperature 291K; exhaust temperature 560K.

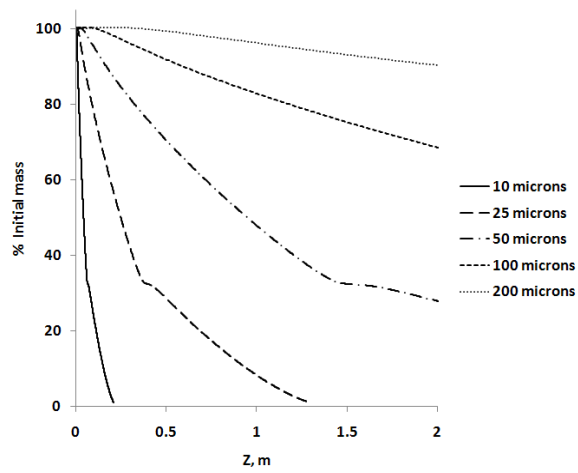


Figure 6: Droplet relative mass with distance from injector. Droplet initial temperature 291 K; exhaust temperature 560 K.

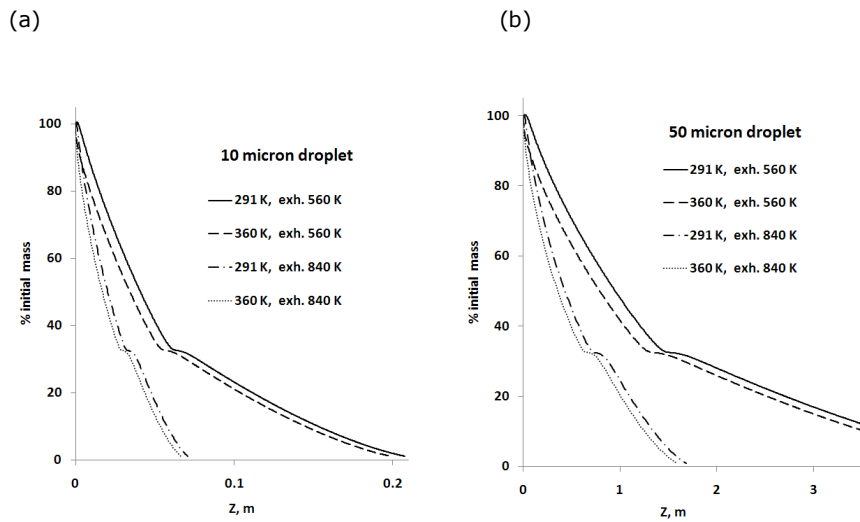


Figure 7: Droplet relative mass with distance from injector as a function of injection temperature (291K and 360K) and exhaust temperature (560K and 840K) for droplet size (a) 10 micron (b) 50 micron.

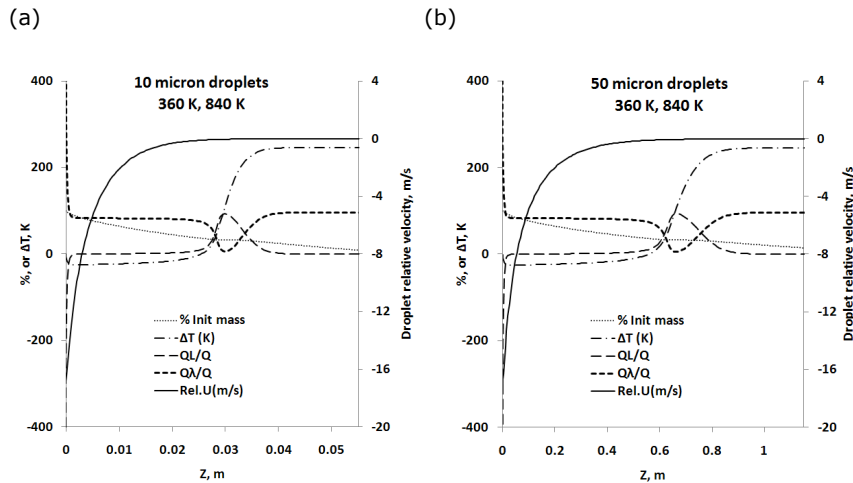


Figure 8: Normalised heat fluxes, droplet mass, droplet relative velocity and temperature rise with distance from injector for injection temperature 360K and exhaust temperature 840K and for droplet sizes (a) 10 micron (b) 50 micron.

Fig. 6 shows the effect of droplet size for the same conditions as Fig. 5. Clearly, droplets much larger than 10 micron would not be expected to evaporate before reaching the catalyst in a typical exhaust. Even a 25 micron droplet, although the water has all evaporated before 0.5 m, has not reached zero mass at 1.0 m. Figs. 7 and 8 show the effect of exhaust and injection temperatures for 10 and 50 micron droplets. Fig. 7a shows that increasing injection temperature from 291K to 360K causes a modest increase in evaporation rates. Increasing the gas temperature (for the same mass flow rate) results in a more significant reduction in evaporation time. Fig. 7b shows similar behaviour for the 50 micron droplet. For this larger droplet, even at high exhaust gas temperature, droplet impingement on an SCR placed less than 1.5m from the injector would not be avoided. It should be recalled that the measured droplets, Fig. 1, showed a large proportion of the spray with diameters greater than 50 microns. Fig. 8 shows droplets rapidly cooling to their equilibrium temperature, ΔT being negative, due to the enhanced vapour flux at the droplet surface where the vapour pressure is initially high. At about 0.03 m for the 10 micron droplet and 0.6 m for the 50 micron droplet, temperature control by evaporation of water ceases and the urea particle temperature rises rapidly.

Fig. 9 shows conversion of the urea for two cases: low temperature exhaust, 560 K and 26 m/s, and high temperature exhaust, 840 K and 39 m/s. Droplets are injected at 291 K and 22 m/s. Fig. 9b shows that in the hot exhaust, conversion of 50 microns droplets is less than 50 % at 1 metre. Thus droplets of this size are unlikely to convert in the gas stream in an automotive exhaust where the distance between the spray and catalyst will be much less than 1 m. It is very clear that droplets with diameter much less than 25 microns are required if the droplets are to break down in the gas stream within 0.3 m, which is the likely path length of a droplet between the injector and the monolith in a typical Diesel exhaust. Larger droplets may, however, convert within a well-designed mixer placed between the spray and the monolith, or in the SCR catalyst monolith.

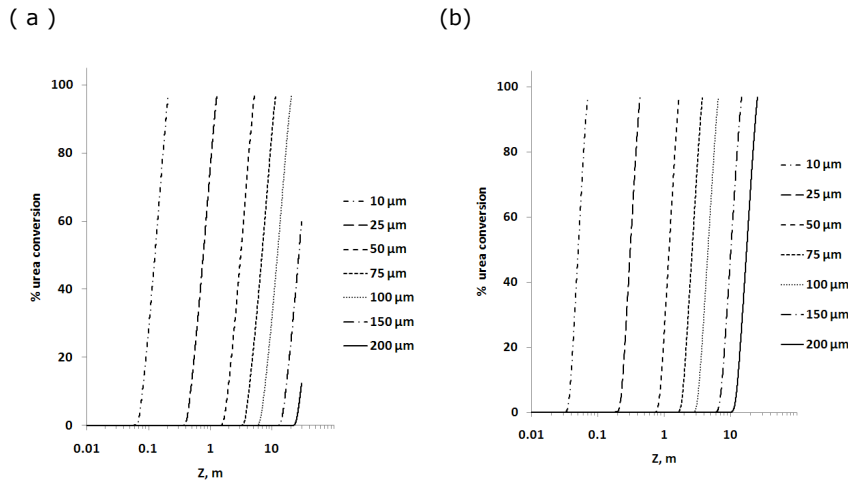


Figure 9: Conversion of urea from 291 K droplet injected at 22 m/s into exhaust with 5% background water vapour pressure for (a) 560 K exhaust at 26 m/s (b) 840 K exhaust at 39 m/s.

5. CONCLUSIONS

A simple model of the warm up and evaporation of an aqueous urea droplet injected into a Diesel exhaust has been developed and coded into a Fortran programme. It permits the evaluation of factors affecting droplet behaviour namely; initial droplet size, injection temperature and velocity, exhaust temperature, background vapour pressure in the exhaust and flow rate. It describes the transient heat, mass and momentum transfer processes and the droplet behaviour as equilibrium is established as the water evaporates. The phase of rapid heating that follows the loss of all water from the solution is also described, and finally the higher temperature equilibrium that is reached when the urea undergoes gasification. The model has been compared with some data from the literature for stationary urea droplets and found to give a moderate description. The model can be used to provide insight into the effect of injection and exhaust parameters on droplet size as it approaches the catalyst. This in turn offers guidance on the specification of injector requirements and shows that mixers are almost certainly required in a Diesel exhaust after-treatment SCR system. The model is useful as a stand-alone tool but can be incorporated into a full CFD model for evaluating SCR systems without recourse to testing.

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APPENDIX

Fluid properties for air, water vapour and aqueous urea solution and for the water vapour/air mixture in the film around the droplet were evaluated as follows, with temperature T (K). Heat of vapourisation for water leaving an Adblue droplet was assumed the same as for water. Throughout this appendix, notation is used so that, for example, 9.2E-11 represents 9.2×10^{-11} . Fig. A1 at the end of this appendix shows values for some of the parameters.

A1.1 Vapour pressures

The partial pressure of water vapour above pure water is from **(18)** and is shown in Fig. A1. Raoult's law is used to find the pressure above the liquid droplet.

$$P_{vW} \text{ (pa)} = 1000 \exp[-7.342973 \ln T - 7276.391/T + 67.02455 + 0.4161914E-05T^2]$$

$$P_{vL} \text{ (pa)} = [\text{MolF}] p_{vW} = p_{vW} (m_w/M_w) / [m_u/M_u + m_w/M_w]$$

A1.2 Latent heats of vapourisation

Latent heat for water is from **(24)** and shown in Fig. A1. The latent heat for urea is from **(8)** plus an addition to account for melting from **(21)**.

$$\lambda_w \text{ (J/kg)} = 2810050 - 220.225T - 3.39409T^2$$

$$\lambda_u = [87.4 + 14.5] \text{ (kJ/mol)} = 1698333 \text{ (J/kg)}$$

A1.3 Properties of air/water vapour film

$$T_M = (T_B - T_L) / \ln(T_B/T_L)$$

$$k_M = [1 - (P_{vL} + P_{vB})/2P_T]k_A + (P_{vL} + P_{vB})/2P_T \cdot k_v$$

$$\mu_M = [1 - (P_{vL} + P_{vB})/2P_T]\mu_A + (P_{vL} + P_{vB})/2P_T \cdot \mu_v$$

$$M_M = [(1 - (P_{vL} + P_{vB})/2P_T)M_A + (P_{vL} + P_{vB})/2P_T \cdot M_v]$$

$$\rho_M = (P_T M_M / RT_M)$$

$$C_{pM} = [\{1 - (P_{vL} + P_{vB})/2P_T\}M_A \cdot C_{pA}/M_M] + [(P_{vL} + P_{vB})/2P_T \cdot M_v \cdot C_{pV}/M_M]$$

A1.4 Properties of air

Thermal conductivity for air and specific heat for air are fitted to data from **(25)** and shown in Fig. A1. Viscosity for air is fitted to data from **(24)** and shown in Fig. A1.

$$k_A \text{ (J/(m K s))} = \exp(1.7902 - (31.007/\ln T))$$

$$C_{pA} \text{ (J/(kg K))} = 1014.57 - 0.157358T + 4.81789E-04T^2 - 1.95751E-07T^3$$

$$\mu_A \text{ (kg/(m s))} = \exp(-6.205 - (26.794/\ln T))$$

A1.5 Properties of water vapour

Thermal conductivity, specific heat and viscosity for water vapour are from **(18)** and shown in Fig. A1. Diffusion coefficient for water vapour is from **(26,27)**.

$$k_v \text{ (J/(m K s))} = 0.007341 - 1.013E-05T + 1.801E-07T^2 - 9.100001E-11T^3$$

$$C_{pV} \text{ (J/(kgK))} = (33.76336 - 5.945958E-03T + 2.235754E-05T^2 - 9.962009E-09T^3 + 1.097487E-12T^4)(1000/18.0152)$$

$$\mu_v \text{ (kg/(m s))} = -3.189E-06 + 4.145E-08T - 8.272E-13T^2$$

$$D_v \text{ (m}^2\text{/s)} = 0.22E-04(101325/P_T)(T/273.15)^{1.75}, \text{ where } P_T \text{ (Pa)}$$

A1.6 Properties of drop components and of aqueous urea droplet mixture

The expression for C_{PU} was fitted to data from **(15)** and is shown in Fig. A1. The expression for C_{PW} is from **(18)** and is shown in Fig. A1. The expression for ρ_W was fitted to data from **(24)** and the value for ρ_U was also from **(24)**.

$$C_{PU} \text{ (J/(kg K))} = 4.5993T + 181.67$$

$$C_{PW} = (50.81069 + 0.2129361T - 6.309691E-04T^2 + 6.483055E-07 T^3)(1000/18.0152)$$

$$C_{PL} \text{ (J/(kg K))} = (m_W C_{PW} + m_U C_{PU}) / (m_W + m_U)$$

$$\rho_W = 1.55789E-05T^3 - 1.86761E-02T^2 + 6.73586T + 235.992$$

$$\rho_U = 1323 \text{ kg/m}^3$$

$$\rho_L = (m_U + m_W) / (V_U + V_W)$$

A1.7 Urea precipitation (crystallisation) sub-model

Droplet composition at each time step was compared with a saturation curve fitted to data from **(28)**:

$$[(m_W/M_W) / (m_U/M_U)]_{\text{saturation}} = 4.86387 \exp(-0.0223528 (T - 273.15))$$

P_{VL} based on Raoult's law for a saturated solution was used when the mixture was more concentrated, as it was assumed that the droplet was then a mixture of solid urea plus saturated solution.

$$Q_\lambda = w_\lambda + w_U \lambda_U - 210000 R_{PPT}$$

Heat of solution for urea in water is + 12.6 kJ/mol **(19)**, i.e. 210000 J/kg

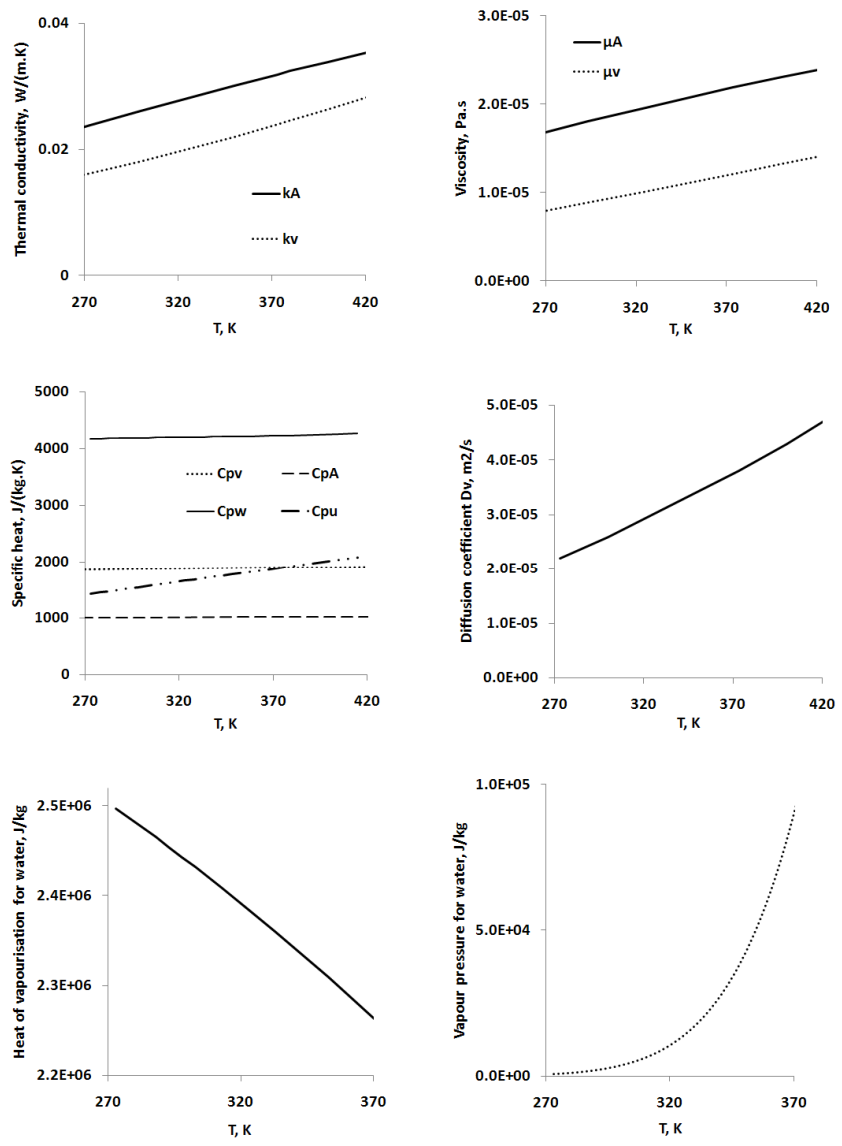


Figure A1: Values for parameters.