VAPORIZATION OF MULTICOMPONENT FUEL DROPLETS NUMERICAL AND EXPERIMENTAL EVALUATION

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Abstract
This paper outlines two different droplet models which account for multicomponent evaporation – one model assumes a discrete mixture of individual species and the other model applies a continuous distribution function to describe the microphysics of mixture evaporation. Both models are used to investigate several blends consisting either of two or four different n-alkane compounds. The results are discussed along with experimental data to figure out the accuracy and the restrictions of the numerical models.
The experimental technique applied for this purpose is based on a vertical stream of monodisperse droplets. Sampling from this droplet stream allows to measure both – instantaneous droplet mass and instantaneous liquid composition.

Introduction
A fundamental task for the improvement of gasoline engines is to broaden the understanding of the physical processes involved in spray evaporation. Since commercial gasoline is a complex blend comprising nearly 200 different hydrocarbon compounds, there is a great interest in modeling multicomponent evaporation. The objective of this work is to discuss two different modeling approaches and compare the computational results to experimental data.
The first model originates in the work of Abramzon and Sirignano [1]. Commonly this model is known as 'Effective Diffusion Model'. Since it considers individual species rather than a homogenous blend, it is called 'Discrete Multicomponent Model' in this study. The second model is based on the ideas of continuous thermodynamics. According to this theory the molecular composition of the fuel is described by a continuous distribution function of the molecular weight [2,3]. Correspondingly, the model is called 'Continuous Multicomponent Model' here. For practical purpose it is useful to focus on the moments of the molecular distribution rather than on the distribution itself. Then thermophysical properties like the vapor pressure can directly be related to the moments of the molecular distribution.
Both models contain approximations and assumptions. These assumptions are necessary to proceed from first principles of thermodynamics to equations governing the behavior of multicomponent droplets. Particularly in case of the continuous multicomponent model, which is a very versatile approach, it is interesting to ask how accurately it agrees with reality. For that reason specific computational results are compared to experimental data.

Discrete multicomponent model
The discrete multicomponent model is based on the pure-liquid evaporation model in Ref. [1]. According to this approach the gas phase surrounding the droplet surface is considered as a one dimensional film of constant thickness (film theory). Heat and mass transfer between the droplet and the ambient gas take place in this film. Inside the film the gas is considered to be an ideal mixture of fuel vapour and inert air. Its thermophysical properties are estimated according to the 1/3-rule of Sparrow and Gregg [6]. Furthermore quasi-steady phase equilibrium is assumed. Separate consideration of all components contained in the mixture provides the governing equations for heat and mass transfer throughout the droplet surface:

$$\dot{m} = 2\pi\rho_g D_{im} r_d Sh\, ln\left(\frac{Y_{g,i,\infty} - \varepsilon_i}{Y_{g,i,surf} - \varepsilon_i}\right) \qquad \dot{Q} = (T_{g,surf} - T_{g,\infty})\sum_i^n \dot{m} c_{p,g,i}\left[\exp\left(\left(\sum_i^n \dot{m}_i c_{p,g,i}\right)\Big/\left(4\pi\lambda_g r_d\right)\right) - 1\right]^{-1}$$

Here ε_i denotes the fractional rate of evaporation, which is defined as $\varepsilon_i = \dot{m}_i / \dot{m}$. $Y_{g,i}$ is the mass fraction of component i and r_d is the droplet radius. In terms of molar fraction X_i the vapour concentrations at the droplet surface equate from Raoults law:

$$X_{g,i,surf} = X_{l,i,drop}\left(p_{vapor,i} / p_\infty\right)$$

Inside the droplet heat conduction and diffusive mass transfer are treated by one dimensional transport equations. Convective fluxes on the other hand are modeled by additional factors calculated from the droplets Peclet-number. Each fuel compound has to be considered by a separate mass transfer equation. Together with the

equations derived from the film theory this yields a set of parabolic differential equations. All equations are solved in a coupled fashion. In our work this is achieved by Crank-Nicholson discretisation and an efficient tridiagonal matrix algorithm. Further information about the physical model can be found e.g. in [1,6].

Continuous multicomponent model

A major drawback of the discrete component model is that each mixture compound requires a separate transport equation and separate thermophysical equations. So with a large number of hydrocarbon compounds the computational effort is tremendous and constrains the ability to model complex mixtures like commercial gasoline. To overcome this problem Tamim and Hallett [2] suggested to apply continuous thermodynamics. According to this idea the mixture composition is represented by a continuous distribution function of the molecular weight I . Thus the mass fractions y_i of all species can be written as:

$$y_i = f(I)\,dI \qquad \text{where } f \text{ satisfies} \qquad \int_0^\infty f(I)\,dI = 1.0$$

Based on this transformation a detailed derivation of the continuous model equations can be found in Ref. [2]. The first step of this derivation is to substitute the mass fractions of the heat and mass transfer equations. Subsequently these equations are remodeled by a mathematical procedure in order to obtain a representation which contains different order moments of the distribution rather than the distribution function itself. The continuous multicomponent model can therefore also be classified as a 'method of moments'. Computationally this is very advantageous. To account for hydrocarbon mixtures Tamim and Hallett [2] propose to apply a Γ-distribution.

$$f(I) = \frac{(I-\gamma)^{\alpha-1}}{\beta^{\alpha}\Gamma(\alpha)} exp\left(-\left(\frac{I-\gamma}{\beta}\right)\right)$$

In case of gasoline the Γ-distribution yields very reasonable results. Ref. [3] demonstrates the good agreement of the experimental and the computational boiling curve of gasoline. But since the multicomponent model is based on the same physical principles as the discrete model, it is also interesting to figure out the suitability for a mixture comprising only a few different hydrocarbon compounds. In particular such an investigation reveals the characteristic features of the continuous thermodynamics approach.

A very crucial point for modeling droplet evaporation is the calculation of the thermophysical properties. Unlike the discrete model which applies separate property correlations for each compound, the continuous model requires a generalized form which allows to calculate the properties as a function of molecular weight. To obtain such equations the property data of the discrete model was compiled by multivariate regression. With respect to the model comparison the examples in Figure 1 shows that this guarantees an equivalent thermophysical basis.

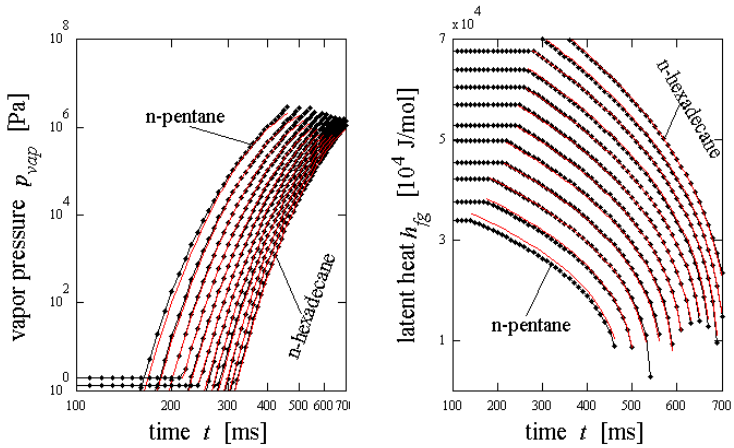

Figure 1 Vapor pressure and latent heat of vaporization for n-alkanes compounds
—●— discrete multicomponent model ▬ continuous multicomponent model

Experimental technique

To judge the suitability of both models, multicomponent evaporation is addressed from an experimental point of view. The investigation applied for this purpose is very straightforward. It is based on a steady stream of uniformly spaced droplets which is aligned in vertical direction (Fig 2). The droplet stream is released from a vibrating orifice droplet generator. Its working principle is to discharge a cylindrical laminar liquid jet from a calibrated orifice and simultaneously exert a hydrodynamic instability. This is done by means of an oscillating piezo-stack. Provided the excitation frequency and the liquid feed rate are chosen properly, this results in a monodispersed and uniformly spaced droplet stream (Rayleigh theory). For a detailed description of the operating characteristics refer to [4]

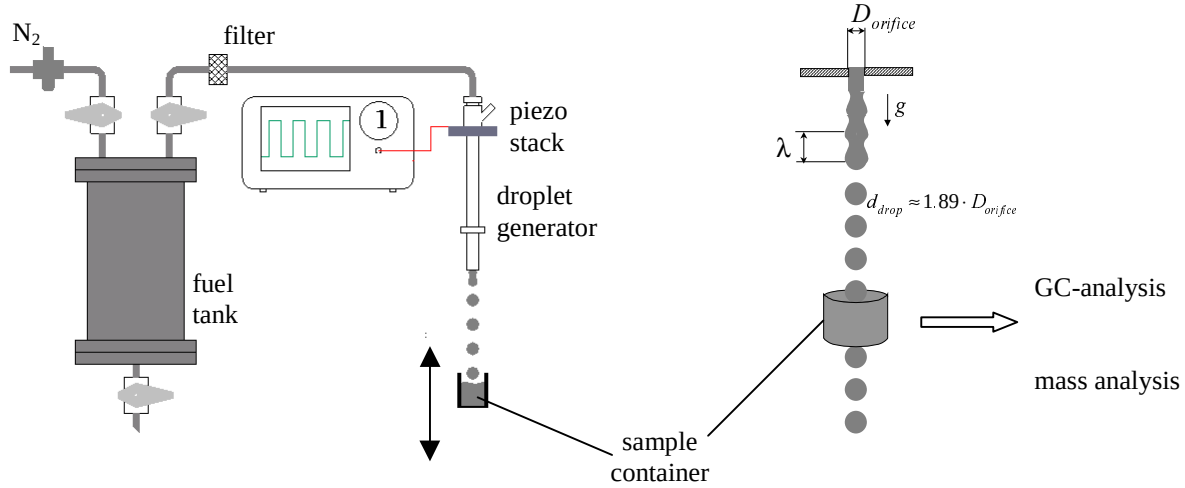

Figure 2: Schematic view of experimental setup

Since all droplets are discharged with equal characteristics and are subject to the same ambient conditions, sampling at different vertical positions allows to reveal the temporal evolution of the evaporation process. The samples are analyzed in two ways. On the one hand the mass is compared to the mass discharged at the generators orifice to obtain the rate of evaporation. On the other hand the samples are analyzed by gas chromatography (GC). This provides quantitative information on the instantaneous fuel composition and reveals how the mixture composition is gradually shifting towards low volatile compounds due to evaporation. Although the basic idea of this measurement technique is simple, it is rather beneficial for studying multicomponent evaporation. The reason is that it supplies quantitative information on two droplet properties simultaneously – droplet mass and liquid composition. Especially the latter one is a key parameter for multicomponent evaporation. It is decisive for nearly all thermophysical properties including vapor pressure, heat of vaporization and mass diffusivity. As a result the droplet composition along with the droplets mass is a convincing criterion for the evaluation of the theoretical models.
Since the goal of this work is to investigate both – the discrete multicomponent model as well as the continuous multicomponent model – it is reasonable to constrain the number of species for the purpose of model evaluation For that reason different blend levels of binary and quaternary n-alkane mixtures are chosen in this study. For an overview see table 1.

Blend No.	n-Pentane [% vol.]	n-Hexane [% vol.]	n-Heptane [% vol.]	n-Octane [% vol.]	M [kg/kmol]	ρ_{liq} [kg/m^3]	p_{vap} [bar]
1	66	-	34	-	81,5	649	0,270
2	34	-	66	-	90,9	667	0,177
3	47	35	12	6	82,7	652	0,236
4	17	33	33	17	92,7	671	0,143

Table 1: Summary of n-alkane mixtures. Composition is given in terms of volume fraction.

All investigations are carried out under ambient conditions (1 bar, 23 °C). Starting from the injector orifice the evaporating droplet stream is collected at six different vertical positions. This is done by applying contaminant free glass sample containers (5 ml) with Teflon-lined septa in the caps. All containers are partly filled with very low volatile solvent (n-Hexadecane Tb= 287 °C). This is necessary to freeze the evaporation immediately after the sampled liquid reaches the container. Gas chromatography detection is achieved by a flame ionization detector (FID) with photoionization detector in series (PID).
In vertical direction the observation area covers a distance of approximately 15 cm corresponding to a droplet life time of only a few milliseconds. Throughout such a short distance interlace images reveal that the droplet velocity remains nearly constant due to the strong wake effect of the droplet stream. As a consequence a very simple conversion of droplet penetration to droplet life time is possible. For a more elaborate treatment of this issue refer to [5].

Experimental and numerical results
Since the thermodynamic behaviour of complex fuel blends is very difficult to grasp, the basic idea of this work is to chose low-level multicomponent mixtures for the first step (table 1). This allows detailed understanding and hence is reasonable for the purpose of model evaluation.

Starting with the discrete multicomponent model, Figure 3 indicates the evaporation of a binary mixture. The mixture comprises two thirds of n-pentane (T_b=36,5°C) and one third of n-heptane (T_b=98°C). While the diagram on the left reveals the temporal evolution of the droplet mass with reference to its initial mass, the diagram on the right outlines the droplets molecular composition. The transient nature of binary mixture evaporation is evident from both diagrams. In detail two different effects are involved. On the one hand the different volatilities of both compounds shift the overall budget of the species towards the heavier compound n-heptane and therefore the rate of evaporation declines. On the other hand demand for latent heat causes a significant reduction of the droplet temperature. This accounts for the concave shape of the mass curve in Figure 3. Since both phenomena are strongly affected by mixture composition there is a great demand for proper multicomponent modeling.

Applying the discrete multicomponent model to blend no. 1 shows that there is good agreement between the experimental data and the computational results (Fig. 3). This suggests that the numerical model is suitable. Particularly convincing is that there is simultaneous correspondence for two different droplet properties.

Figure 4 shows another example. Except for the blend levels of n-pentane and n-heptane all experimental and numerical parameters are maintained. Again experiment and numerical simulation agree well. The rate of evaporation however is lower. The apparent reason for this behaviour is that the composition contains a smaller fraction of the light weight compound n-pentane (33% vol.).

In case of quaternary mixture the results of our study are given in Figure 5 and Figure 6. Both mixtures are composed of n-pentane, n-hexane, n-heptane and n-octane (table 1). A specific feature of Figure 5 is, that the mixture contains a rather large fraction of n-pentane. Correspondingly the mass transfer is strongly dominated by the vaporization of n-pentane. Therefore the mass fractions of the other three species are increasing with time. Although the experimental mass curves in Figure 5 and Figure 6 suggest more uncertainty than the curves in Figure 3 and Figure 4, experimental and computational data are still basically sound. As a result it can be concluded that the discrete multicomponent model is a suitable approach. Furthermore it is a proper basis for even more refined models like e.g. the continuous thermodynamics model.

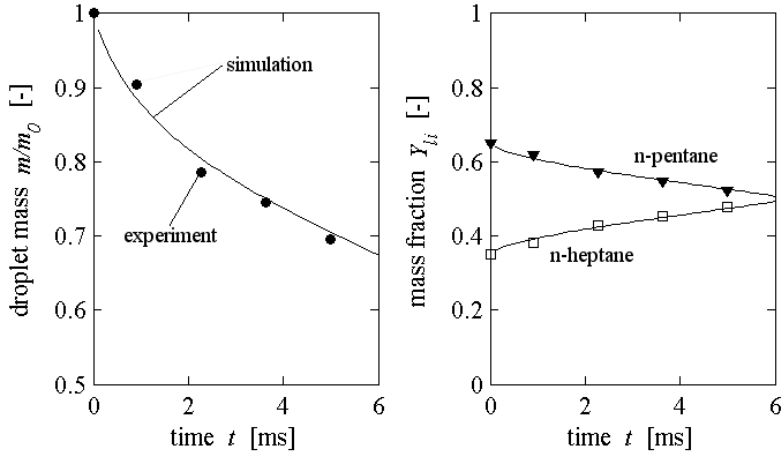

Figure 3 Evaporation of 57 µm binary droplet; blend 1: n-pentane 66 % vol., n-heptane 34 % vol.; droplet velocity 22 m/s; ● □ ▼ experiment; ▬ discrete multicomponent model

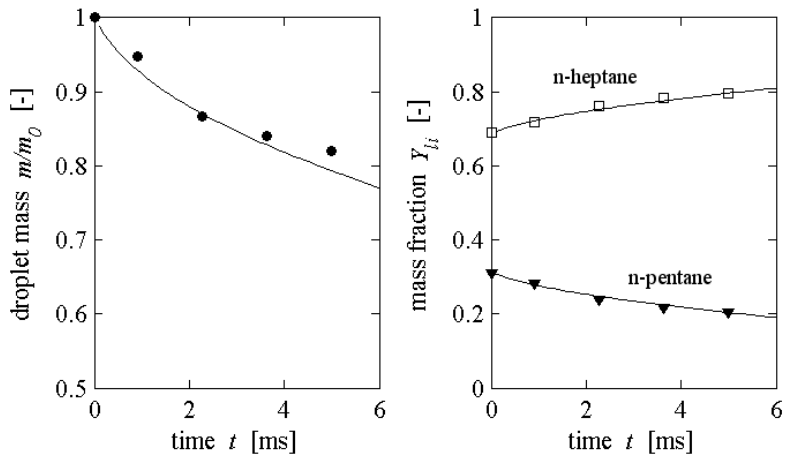

Figure 4 Evaporation of 57 µm binary droplet; blend 2: n-pentane 34 % vol., n-heptane 66 % vol.; droplet velocity 22 m/s; ● □ ▼ experiment; ▬ discrete multicomponent model

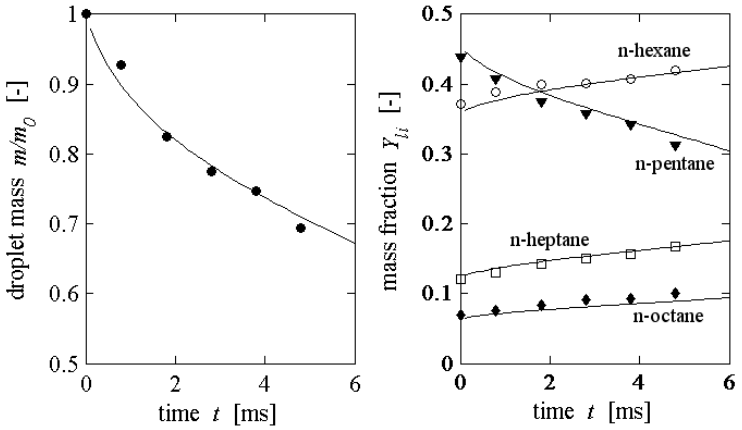

Figure 5 Evaporation of 57 µm quaternary droplet; blend 3: n-pentane 47 % vol., n-hexane 35 % vol, n-heptane 12 % vol, n-octane 6 % vol; ●□▼♦○ experiment ▬ discrete multicomponent model

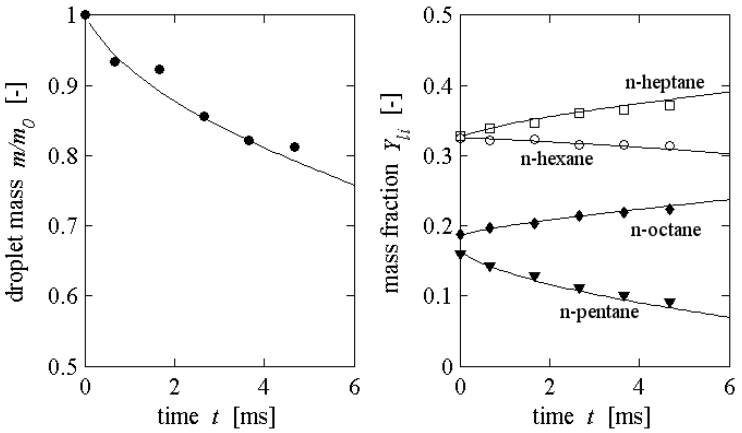

Figure 6 Evaporation of 57 µm quaternary droplet; blend 4: n-pentane 17 % vol, n-hexane 33 % vol, n-heptane 33 % vol, n-octane 17 % vol; ●□▼♦○ experiment ▬ discrete multicomponent model

Concerning the experimental technique the investigations confirm that droplet sampling along with gas chromatography is very straightforward and an appropriate means for time-resolved evaluation of theoretical models. The only drawback of this technique is, that the droplet stream becomes blurred approx. 20 cm downstream the droplet generators orifice. As a consequence the investigation is limited to a time interval of only a few milliseconds. During such a short period of time only 20% to 30% of the initial droplet mass is vaporized.

Regarding the continuous thermodynamics model, two different issues are interesting. The first one is to find out if the numerical results match with experimental data. The second one is to figure out how versatile the statistical approach works. Therefore the continuous multicomponent model is compared to the discrete model. Since both models originate from the same physical principles and are based on thermophysical properties of the same standard (Fig. 1) the result of this comparison can directly be attributed to the different implementations of the mixture composition.

In this paper only two examples are discussed – one binary mixture (blend no. 2) and one quaternary mixture (blend no. 4). The initial values of the continuous distribution are obtained by adapting its first moment θ, second moment ψ and its variance σ^2 to the corresponding moments of the discrete distribution.

The results from the continuous multicomponent calculation are given in Figure 7 and Figure 8. The droplet diameter is presented in terms of $(D/D_0)^2$ and the mixture composition is given in terms of molecular weight M. In case of the discrete model the latter one is calculated from the overall budget of the species. Whereas in case of the continuous model the molecular weight is equal to the first moment θ_1 of the distribution function.

Comparison of both modelling strategies shows that the continuous model provides reasonable results. Particularly in case of the quaternary mixture both models are in good agreement (Fig. 8). Only at the final stage a small deviation occurs. But as the droplet mass is already very small at that stage the discrepancy is not very significant. In case of the binary mixture the situation is different (Fig. 7). Although both models produce results of similar magnitude a clear difference is observed. This difference indicates that there are some limitations to the application of the unimodal Γ-distribution for two-component blends as these are bimodal in nature. Nevertheless the continuous model is very advantageous. Its most important benefit is that only a few independent variables suffice to describe even a complex multicomponent system. Therefore the model is very interesting for spray simulations with high spatial and temporal resolution.

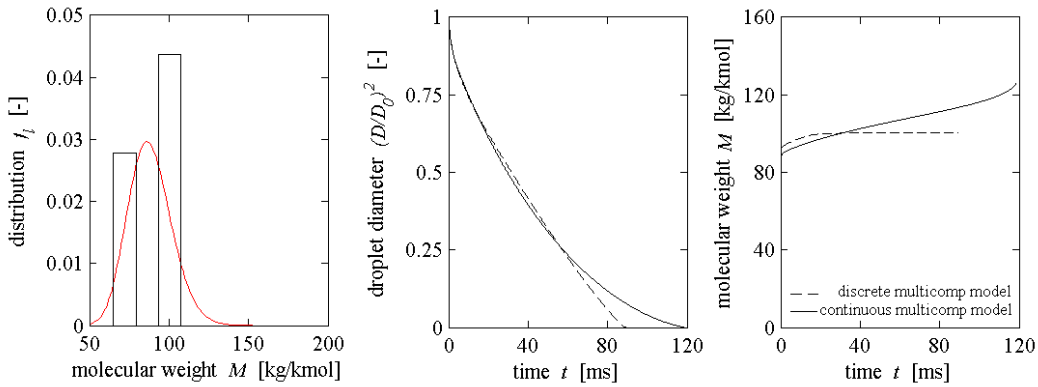

Figure 7 Comparison of theoretical models; evaporation of 57 µm binary droplet; blend 2: n-pentane 34 % vol., n-heptane 66 % vol.; droplet velocity 22 m/s

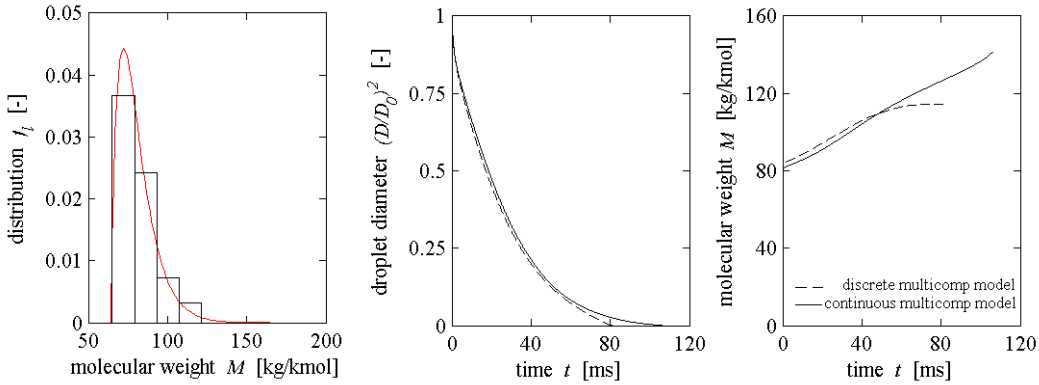

Figure 8 Comparison of theoretical models; evaporation of 57 µm quaternary droplet; blend 4: n-pentane 17 % vol., n-hexane 33 % vol., n-heptane 33 % vol., n-octane 17 % vol.

Conclusion

An important issue for the modeling of automotive mixture preparation is multicomponent droplet evaporation. In the present study this phenomenon is addressed from an experimental and a numerical point of view. Two different models are discussed and compared to experimental data.

The experimental technique is based on droplet sampling and allows to measure the instantaneous droplet mass and the liquid composition simultaneously. Besides providing useful information for the evaluation of numerical models the experimental results indicate quantitatively how strong the species budget shifts due to evaporation.

For the discrete multicomponent model it is demonstrated by two exemplary cases that results from numerical analysis are in good agreement with data retrieved from physical experiments. Whereas in case of the continuous multicomponent model the suitability of the continuous Γ-distribution may be poor if the mixture contains only two components. However, for mixtures of four or more components, conditions which prevail in practice, the continuous multicomponent model has passed basic tests successfully and has proven its suitability for practical application by a series of calculations.

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