

## **EVAPORATION OF TERNARY MIXTURE DROPLETS**

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### **ABSTRACT**

The evaporation of ternary mixture droplets consisting of n-alkanes is examined both experimentally and numerically. This study is based on the work of Wilms et al. [1], where the influence of composition and ambient temperature on the evaporation rate of binary mixture droplets is investigated. In order to approach multicomponent droplets, such as gasoline droplets, the number of components is increased from two to three.

In addition, the range of components is extended towards n-alkanes with a high volatility. Measurements of droplets consisting of these substances are not possible with the experimental setup for the optical levitation of single droplets. Therefore, a new experimental setup for single, freely falling droplets has been built up and is used in addition to the experimental setup for optical levitation in order to capture the entire evaporation process. Experimental results are presented for two different mixtures, the first one consisting of n-octane, n-dodecane and n-hexadecane and the second one consisting of n-octane, n-nonane and n-decane.

The experimental results agree well with results from a numerical model, where the evaporation process is controlled by the diffusion of the evaporated liquid in the surrounding gas phase. The basic equations for this model are derived in this work.

### **INTRODUCTION**

Research on fuel evaporation is very important with respect to fuel economy and emission reduction in modern gasoline and diesel engines. Since gasoline and diesel fuel consist of many different hydrocarbon species, evaporation is strongly affected by the broad variety of different fuel volatilities. Therefore, there is a vital interest in an accurate modelling of multicomponent droplet evaporation for the purpose of developing and validating numerical codes.

At the Institute of Aerospace Thermodynamics (ITLR), the evaporation of single fuel droplets is investigated by different experimental setups and measuring techniques. With an optical levitation technique, the temporal evolution of the droplet diameter of binary mixture droplets consisting of n-alkanes has been studied at different ambient temperatures [1]. Low volatile n-alkanes ranging from n-decane until n-hexadecane have been chosen as substances. The ambient temperature has been varied between 302 K and 324 K.

For this study, the number of components within the mixture has been increased from two to three in order to approach multicomponent droplets with many different species. On the other hand, more volatile components such as n-octane and n-nonane are used. For this purpose, a new experimental setup has been built for the investigation of single, freely falling droplets. Also a different measuring technique is used, which allows to capture the fast change in droplet size.

The combination of the two experimental setups, i.e. the setups for single, optically levitated droplets and for single, freely falling droplets, allow the measurement of the entire evaporation process of mixture droplets with both high and low volatile components as will be shown in the present paper.

### **EXPERIMENTAL SETUPS**

Two experimental setups are used for the measurements, one for the investigation of single, freely falling droplets for the initial evaporation phase where the evaporation process is dominated by the high volatile components and one investigating single, optically levitated droplets for the following main evaporation phase where the evaporation process is dominated by the remaining low volatile components, respectively.

#### **Experimental setup for single, freely falling droplets**

The experimental setup for the initial phase investigates single, freely falling droplets. A schematic view of the experimental setup is shown in Fig. 1. The droplets are produced by a droplet on demand generator. In changing the orifice of the generator, the droplet size can be varied from approximately 20  $\mu\text{m}$  to 100  $\mu\text{m}$ . After generation, the droplets are injected horizontally into a vertically orientated squared glass channel. Due to gravity and a slow airflow,

the droplets then start to fall downwards along a laser beam, which is directed upwards within the channel in order to illuminate the falling droplets permanently. When the droplet reaches the laser beam, the measurement starts.

The droplet size at the beginning of the measurement is determined from the fringe spacing of the scattered laser light in the forward hemisphere, which is detected by a CCD camera. For the measurement of the decrease in droplet size during the evaporation, part of the scattered laser light in the forward hemisphere is collected by a lens and detected by a photomultiplier. During the decrease of the droplet diameter, morphology dependent resonances become visible in the intensity of the scattered light [2]. The decrease in droplet diameter between two corresponding resonance peaks depends on the refractive index of the droplet and is nearly independent of the droplet size [3]. This measurement technique allows a very detailed measurement of the temporal evolution of the droplet size since the decrease in droplet diameter between two corresponding resonance peaks is in the order of  $0.1 \mu\text{m}$  compared to a typical initial droplet size of  $50 \mu\text{m}$ .

With this experimental setup, the evaporation of droplets, consisting of pure n-alkanes, has been measured successfully [4].

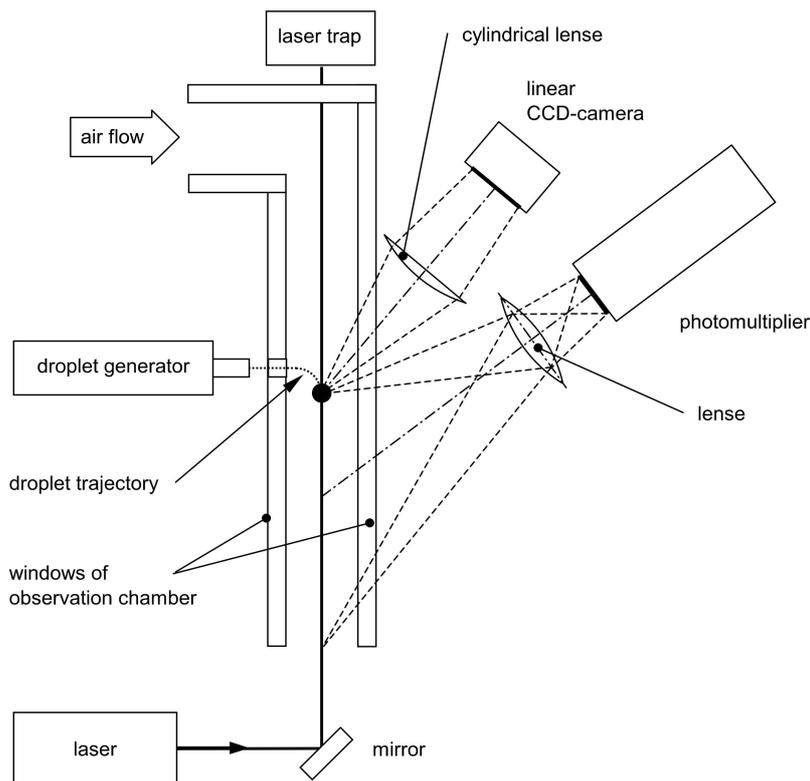


Fig. 1: Schematic view of the experimental setup for single, freely falling droplets.

### Experimental setup for single, optically levitated droplets

In order to capture the following main evaporation phase, another droplet is measured under the same conditions with an experimental setup where the droplet is levitated optically. A schematic view of this experimental setup is depicted in Fig. 2.

The droplet size is measured in the same way as for the initial diameter in the experimental setup of the falling droplets, i.e. from the fringe spacing of the scattered laser light in the forward hemisphere. The difference is that the droplet size is determined by this measurement technique at a certain sampling frequency in order to investigate the temporal evolution of the droplet size. The maximum sampling frequency is 8 Hz.

A second CCD camera has been placed in the backward hemisphere in order to capture the scattered laser light in the region of the rainbow. From this scattered light intensity distribution, the refractive index of the droplet can be measured. Since the refractive index depends on both the temperature and the composition of the droplet mixture, these properties can be determined as has been successfully demonstrated for the case of binary mixture droplets [5].

Further details of this experimental setup can be found in [1].

### Comparison of the experimental setups

Concerning the begin of the measurements, a time period in the order of 1 s passes before the droplet is levitated and stabilized and the measurement can start when the experimental setup for single, optically levitated droplets is used. In contrast, only a time period in the order of 50 ms elapses in the case of the experimental setup of single, freely falling droplets. Therefore, this experimental setup is better suited to measure the initial evaporation phase.

On the other hand, the droplets can be investigated for only up to about 3 s for the experimental setup of single, freely falling droplets due to constraints of the length of the measurement chamber, whereas the other setup allows to measure the droplet until it is nearly completely evaporated. Hence, low volatile substances can only be investigated with the setup for single, optically levitated droplets.

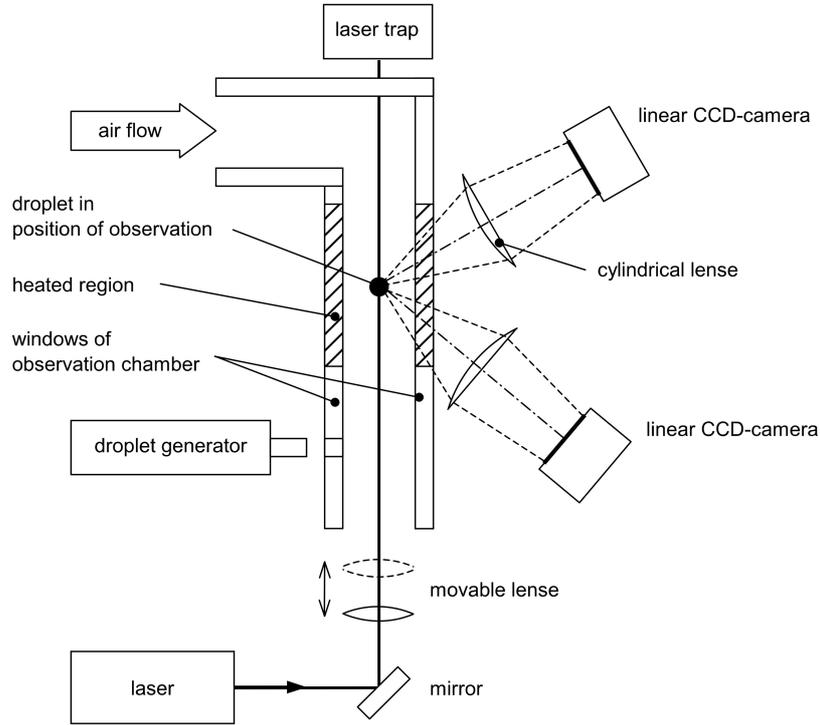


Fig. 2: Schematic view of the experimental setup for single, optically levitated droplets.

### Measurement uncertainties

For the measurement of the droplet size from the fringe spacing of the scattered laser light in the forward hemisphere, Hesselbacher et al. [6] report an accuracy of 2% for the determination of the droplet diameter.

The decrease of the droplet diameter between to corresponding peaks of the morphology dependent resonances depends weakly on the refractive index [3]. During the evaporation of multicomponent droplets, the value of the refractive index changes, but for the evaluation of the measurements a constant mean refractive index has been used. For the presented experimental results, this leads to a maximum error of 0.5 % for the decrease in the droplet diameter, resulting in a maximum error of  $10^{-3}$  % for the first and 1 % for the last diameter during the measurement period.

The air temperature around the droplet has been measured with thermocouples with an accuracy of  $\pm 0.5$  K.

### MODEL FOR NUMERICAL SIMULATIONS

For a fast computation and a rough estimate of the evaporation process a simple model is developed for numerical simulations. The results of this model are used for a comparison with the experimental results.

For the numerical model, the assumption is made that the evaporation process is controlled by the diffusion of the evaporated liquid into the surrounding air. It is further assumed that the evaporation rate is small enough so that the temperature remains constant and uniform within the droplet and the surrounding air. Concentration gradients inside the droplet are neglected.

A model including these assumptions has been developed by Ravindran and Davis [7] for binary mixtures droplets. It has already been successfully applied for measurements of single, optically levitated droplets for two components [1]. Now it is extended to three components.

In this model, the molar flux of the evaporated liquid is obtained by applying Fick's law of diffusion (which is strictly speaking only valid for binary mixtures) as well as the continuity equation to the gas phase surrounding the droplet. In addition, Raoult's law is applied in order to obtain the molar flux  $J_i$  of the species  $i$ :

$$J_i = \frac{\phi_i x_i}{r} \quad \text{with} \quad \phi_i = \frac{D_{ij} p_i}{RT} \quad (1)$$

In Eq.(1),  $r$  represents the droplet radius and  $x_i$  the molar fraction of species  $i$ . The parameter  $\phi_i$  consists of the diffusion coefficient of the liquid  $i$  in the mixture  $j$  consisting of air and the evaporated liquid, the vapour pressure  $p_i$  of the liquid at the droplet surface, the molar gas constant  $R$  and the temperature  $T$ .

A mass balance of the droplet requires that

$$J_i = -\frac{1}{4\pi r^2} \frac{d}{dt} \left( \frac{4}{3} \pi r^3 \rho_m x_i \right) \quad (2)$$

In Eq.(2),  $\rho_m$  represents the molar density of the mixture. By assuming a homogeneous mixture, the molar density of the mixture can be expressed by means of the molar volumes  $V_i$  of the substances:

$$\rho_m = \frac{1}{\sum_i x_i V_i} \quad (3)$$

Combining Eqs.(1) and (2) and differentiating the term in brackets in Eq.(2) yields to

$$\rho_m x_i \frac{dr}{dt} + \frac{r}{3} \frac{d}{dt} (\rho_m x_i) = -\phi_n \frac{x_i}{r} \quad (4)$$

In the case of three components  $i = 1, 2$  and  $3$ , Eq.(4) results in three equations. Together with Eq.(3) and the summation rule for the molar fraction,

$$\sum_i x_i = 1, \quad (5)$$

there are 5 equations for the 5 unknowns  $r, x_1, x_2, x_3$  and  $\rho_m$ . Eliminating  $x_3$  and  $\rho_m$  and rearranging leads to

$$\begin{aligned} \frac{d\xi}{dt} = & -\frac{2}{r_0^2} (x_1[(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + (\phi_3 - \phi_1)](V_3 - V_1) \\ & + x_1[(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + (\phi_3 - \phi_1)](V_3 - V_1) \\ & + [(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + \phi_3][(V_1 - V_3)x_1 + (V_2 - V_3)x_2 + V_3]) \end{aligned} \quad (6)$$

$$\frac{dx_1}{dt} = \frac{3}{r_0^2 \xi} x_1 [(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + (\phi_3 - \phi_1)][(V_1 - V_3)x_1 + (V_2 - V_3)x_2 + V_3] \quad (7)$$

$$\frac{dx_2}{dt} = \frac{3}{r_0^2 \xi} x_2 [(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + (\phi_3 - \phi_2)][(V_1 - V_3)x_1 + (V_2 - V_3)x_2 + V_3] \quad (8)$$

For Eq.(6), the droplet radius has been replaced by the dimensionless droplet surface  $\xi$  with

$$\xi = \left( \frac{r}{r_0} \right)^2 \Rightarrow \frac{d\xi}{dt} = \frac{2r}{r_0^2} \frac{dr}{dt}, \quad (9)$$

where  $r_0$  is the initial droplet radius. Eqs.(6) - (8) allow to calculate both the temporal evolution of the droplet size and the droplet composition. Eq.(6) can be used to determine the droplet surface regression rate  $\beta$  [8], also called evaporation rate:

$$\beta := -\frac{d(r^2)}{dt} \Rightarrow \beta = -\frac{1}{r_0^2} \frac{d\xi}{dt}, \quad (10)$$

For a monocomponent droplet, the evaporation rate is a constant according to this model, but for the case of three components, the evaporation rates varies with time and can be expressed as a function of the molar fractions by introducing Eq. (6) into Eq. (10):

$$\begin{aligned} \beta = & 2(x_1[(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + (\phi_3 - \phi_1)](V_3 - V_1), \\ & + x_1[(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + (\phi_3 - \phi_1)](V_3 - V_1) \\ & + [(\phi_1 - \phi_3)x_1 + (\phi_2 - \phi_3)x_2 + \phi_3][(V_1 - V_3)x_1 + (V_2 - V_3)x_2 + V_3]) \end{aligned} \quad (11)$$

## RESULTS

In the following, results for two different ternary mixture droplets evaporating in air are presented. For both cases, the initial volume fraction for each of the three components is one third. In the first case, a mixture of n-octane, n-nonane and n-dodecane is investigated at an ambient temperature of 300 K. In this case, the evaporation time is short enough so that the entire evaporation process can be investigated with the experimental setup of single, freely falling droplets. The experimental results can be seen in Fig. 3. The values of the axis of the plot are normalized with the square of the initial droplet diameter  $d_0$  so that droplets of different initial size can be compared with each other. Measurements from three different droplets are depicted for this mixture. These measurements coincide very well. Only one out of 10 data points are shown for a better illustration. The results of the numerical simulation show good agreement with the experimental results.

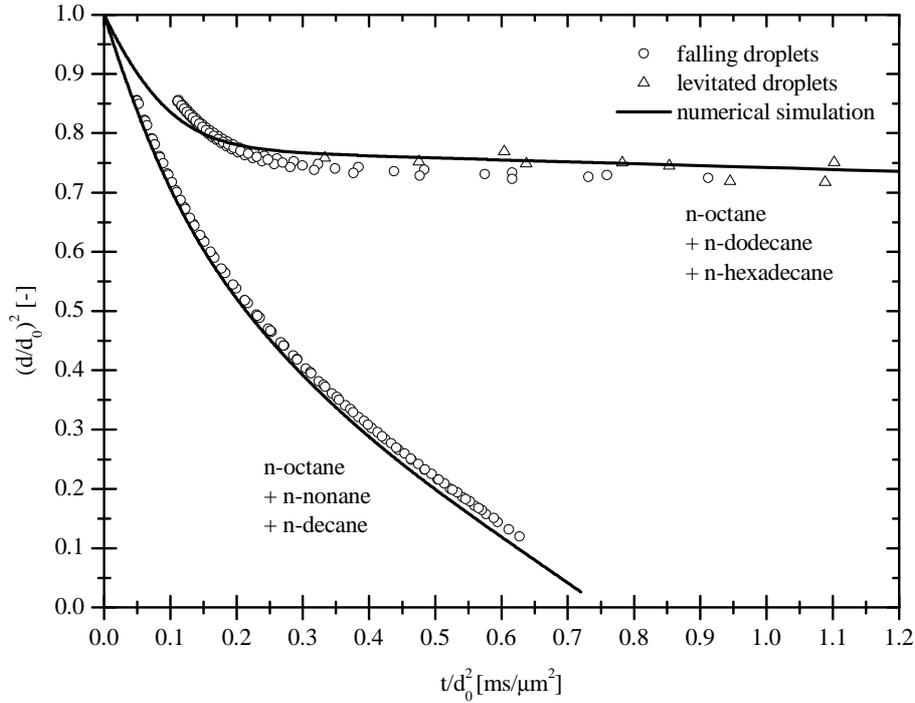


Fig. 3: Experimental and numerical results of the evaporation of ternary mixture droplets.

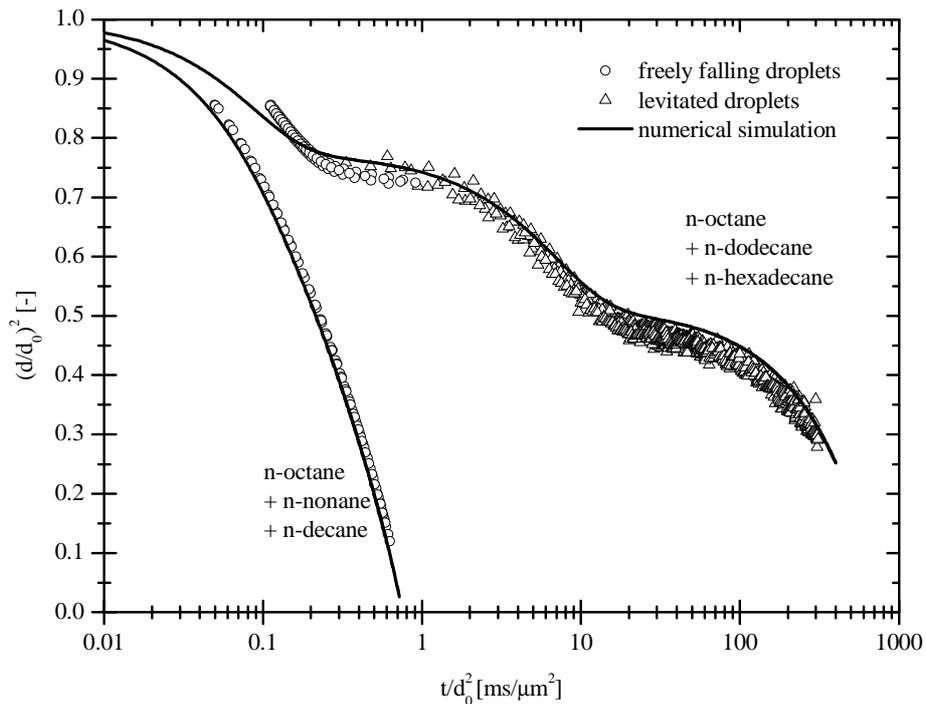


Fig. 4: Experimental and numerical results of the evaporation of ternary mixture droplets.

The second mixture consists of n-octane, n-dodecane and n-hexadecane. This means that the difference in volatility between the components is larger than for the other mixture. The ambient temperature was slightly lower at 296 K. For this mixture, both experimental setups had to be used in combination in order to capture the entire evaporation process. In Fig. 3, the initial evaporation phase is shown and also the region where results from both experimental setups overlap. It can be seen that the results from the different setups agree very well with each other. One difficulty in combining the two experimental setups is to ensure exactly the same ambient temperature. In order to illustrate clearly the entire evaporation process, a logarithmic scale for the time axis has been chosen in Fig. 4. Also for this mixture, results from 3 different droplets are depicted. The results of the numerical simulation show also for this mixture a good agreement with the experimental results. There is some deviation at the beginning of the droplet evaporation which is due to difficulties in the determination of the initial droplet diameter  $d_0$ . This is because the diameter  $d_0$  is obtained by extrapolation of the experimental data for  $t$  towards 0 s.

For the second mixture, due to the large differences in volatilities, the points in time can be clearly identified, where the different components cease to exist in the liquid state. It can be assumed that after  $0.4 \text{ ms}/\mu\text{m}^2$  only a mixture of n-dodecane and n-hexadecane is left. After about  $30 \text{ ms}/\mu\text{m}^2$  also n-dodecane is evaporated and only n-hexadecane remains. This is confirmed by the experimental results, since after this point in time the droplet evaporates at a constant evaporation rate which corresponds to the one of pure n-hexadecane. However for the first mixture, these different regimes cannot be distinguished. But still after a certain point in time, the evaporation rate remains constant and corresponds to the one of pure n-decane.

## CONCLUSION

The experimental results demonstrate the possibility of measuring the entire evaporation process of multicomponent droplets with both high and low volatile components by combining two types of experimental setups, one for the investigation of single, freely falling droplets and another one for single, optically levitated droplets. When there are large differences in volatilities of the components, different regimes can be distinguished where only two components and then one component evaporate. In the opposite case, when the differences in volatilities of the components are small, these different regimes cannot be identified.

The results of the simple numerical model show good agreement with the experimental data.

## NOMENCLATURE

Latin symbols		Greek Symbols	
$d$	droplet diameter [m]	$\beta$	evaporation rate [m <sup>2</sup> /s]
$p$	vapour pressure [N/m <sup>2</sup> ]	$\xi$	dimensionless droplet surface [-]
$r$	droplet radius [m]	$\rho$	molar density [mol/m <sup>3</sup> ]
$R$	molar gas constant [J/K mol]	$\phi_i$	species parameter [mol/m s]
$t$	time [s]	Subscripts	
$T$	temperature [K]	$0$	initial
$V$	molar volume [m <sup>3</sup> /mol]	$i$	index for liquid components
$x$	molar fraction [-]	$j$	mixture of air and evaporated liquids
		$m$	mixture of liquid components

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