Flashing of Binary Mixtures During Rapid Depressurisation

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ABSTRACT

The knowledge of the thermo- and fluiddynamic phenomena in flashing flows is indispensible for the design of blowdown systems or safety devices, but up to now there is only limited information of the thermohydraulic behaviour of hydrocarbons and in particular of their binary mixtures during a blowdown.

In experimental studies on the dynamic phenomena in horizontal pipes of L/d-ratios between 70 and 240 propane/butane binary mixtures of varying concentrations were used as test fluids. The investigations of the interaction of the pipe flow which is fed by a vessel participating in the depressurisation and the outflow through orifices of various diameters focus on boiling delay, acceleration, pressure drop, velocity ratio and composition of the gas and the liquid phase.

In binary mixtures which are characterized by different compositions of the gas and the liquid phase, evaporation is controlled by a coupled heat and mass transfer from the liquid to the vapour. In the range of the maximal difference in composition of the gas and the liquid phase a higher degree of thermal non-equilibrium than for pure fluids can be observed because of the local rise in the boiling point due to the preferential evaporation of the more volatile component during bubble growth. The increased non-equilibrium which is observed in the vessel for the binary mixtures is accompanied by a retardation of flashing inception at the pipe entrance. Due to the subsequent evaporation in the very first section of the pipe the superheat of the liquid is reduced until thermal equilibrium is reached. In the following test section the fluid is saturated along its way through the pipe. The throttling of the flow by different orifices mounted at the downstream end of the pipe shows the mutual interaction of the mass flow rate, the development of void and the temporal course of the pressure in the vessel and along the pipe. The higher level of void fraction which can be observed for higher mass flow rates is caused by the increasing pressure drop and thermal non-equilibrium in the vessel.

INTRODUCTION

The interest in the fluid- and thermodynamic phenomena in two-phase pipe flow has resulted from savety assessment studies related to nuclear power reactors and has predominantly concerned steam-water mixtures. The knowledge of the behaviour of flashing water can not be transfered without difficulties to the flow of multi-component mixtu-res frequently participating in reaction processes of the chemical industry. Studies [Tho84] which focused on boiling of binary mixtures showed a lower heat transfer coefficient of the binary mixture with respect to the simple linear interpolation between the values corresponding to the pure components. While the heat transfer in binary mixtures often was the subject of experimental investigations, only few information on flashing two-phase
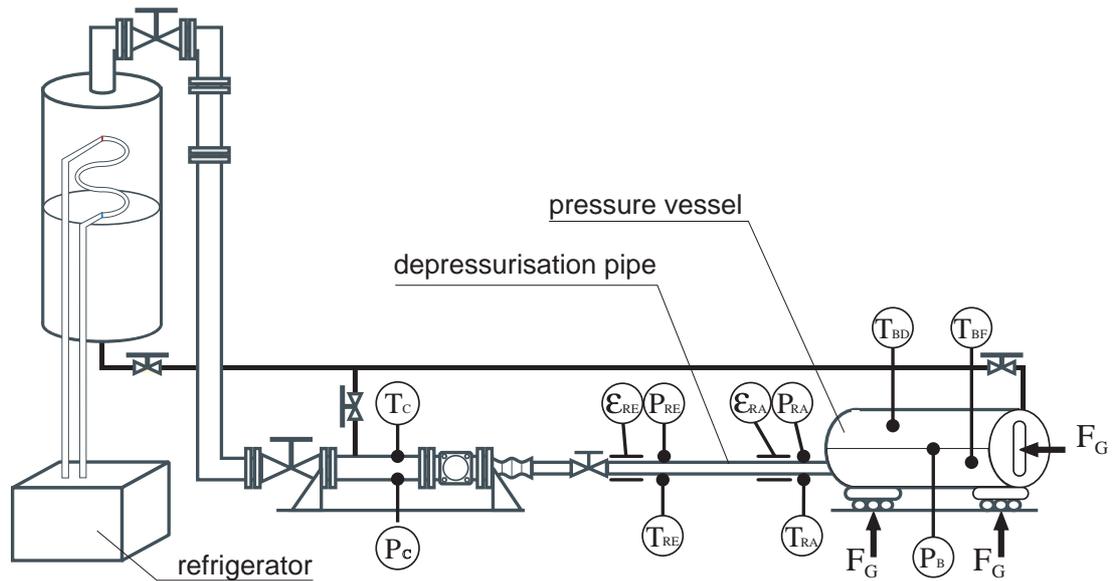
Abbildung 1: *Test facility*

pipe flow of multi-component mixtures is availible. Most of the basic two-phase models for multicomponent mixtures assume equilibrium flow conditions [Che93, Che95] because there is only little knowledge about closure laws which supply information on non-equilibrium effects such as delayed bubble nucleation in superheated liquid. Additionally the thermodynamic equilibrium assumption does simplify the calculation procedure but can lead to an underestimation of the critical flow rate as one of the most important factors in risk assessment.

The object of this research project is to study the non-equilibrium effects – mechanical as well as thermodynamical – in the pipe flow of binary mixtures. Based on the experimental results accompaning theoretical studies are carried out to predict flashing, velocity ratio and friction in highly transient two-phase flow.

EXPERIMENTAL INSTALLATION

The experimental facility in which the blowdown tests were performed consists of three main components:

- a pressure vessel containing the fluid – propane, butane or a mixture of them – under saturated conditions

- a depressurisation pipe through which the flashing fluid flows, equipped with a replaceable orifice of various diameters at its downstream end and

- a low pressure containment system in which the the depressurised two-phase mixture is captured and the vapour is condensed by a refrigerative cooling equipment.

Three different pipe lengths were used having an L/D-ratio of 70, 170 and 240 while the pipe diameter was kept constant with 10 mm. Two different sharp edged orifices were mounted at the downstream end of the pipe having diameters of 3 or 5 mm respectivly. Also experiments with open pipe without orifice were performed.

Before initiating the depressurisation the high pressure part and the low pressure system of the facili-

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ty were separated by a burst disc, mounted behind the orifice at the end of the pipe. The burst disc is designed in such a way, that it can withstand a pressure difference which corresponds to approximately the half of the initial pressure in vessel. Therefore a small room behind the burst disc has to be pressurised to about 5 bar. This is done by closing a large ball valve at the downstream end of this observation chamber and by filling the room with vapour up to the desired pressure. After suddenly opening the large ball valve the pressure in the observation chamber is very rapidly decreasing and finally the disc which cannot withstand the increasing pressure difference bursts and starts the blowdown.

The fluid- and thermodynamic conditions in the pipe during the depressurisation are the main objects of interest for the investigation. During the blowdown

- pressure

- temperature

- void fraction

- inventory of fluid in vessel and

- momentum of the released fluid

are observed.

Vessel and pipe were mounted on a mouveable carriage so that the momentum of the flashing flow leaving the pipe through the orifice could press the vessel against a pressure gauge acting as a dynamometer. Four other dynamometers support the pressure vessel from below and are continuousely indicating the mass inventory of the fluid in vessel. A pressure sensor and up to 6 thermocouples at different levels were installed in the vessel.

The sensor units in the pipe consiting of a pressure gauge, a thermocouple and a void fraction sensor were fitted up to 3x depending on the length of the pipe. Additionally the back pressure in the observation chamber and the temperature in the containment system were recorded.
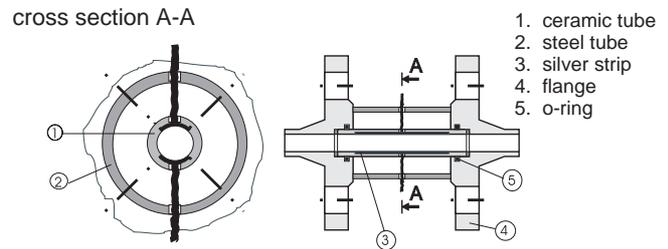

Abbildung 2: *Void Fraction Sensor*

The local and temporal value of void fraction is a key parameter of the experiment. Therefore a special impedance void fraction sensor (fig. 2) acting on a capacative basis and using the difference of the dielectric constant of vapour and liquid was developed. Two silver coatings on the inner side of a ceramic tube form the non-intrusive electrodes of the sensor. The capacitance signal of the impedance sensor was measured by a highly accurate LCR-meter and evaluated into void fraction using the well-known Maxwell equations.

BOILING OF MULTICOMPONENT MIXTURES

The growth of a vapour bubble in a binary mixture is more complicated in comparison to pure fluids by the difference in the composition of the vapour and the liquid phase. Assuming phase equilibrium as shown in fig. 3 the composition of the more volatile component in the vapour bubble y is greater than that in the liquid phase x near the bubble interface. For a pure fluid the growth of a single bubble in a uniformly superheated liquid is controlled by the pressure difference between bubble and surrounding liquid and the heat conduction towards the bubble interface. Because of the different composition of the vapour and the liquid phase and the preferential evaporation of the more volatile component the bubble growth in a binary mixture is additionally influenced by the mass transport of the more volatile component through
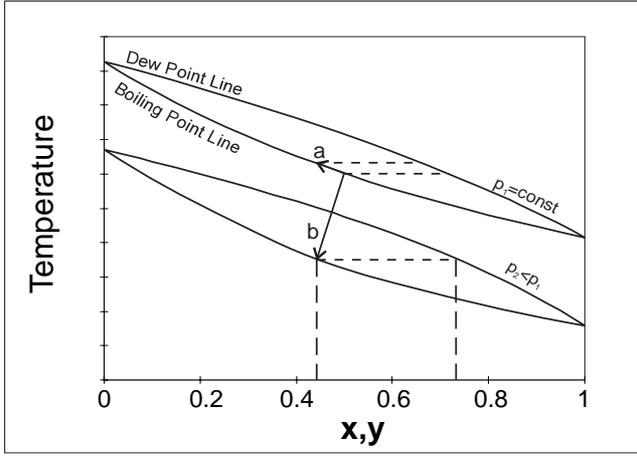
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Abbildung 3: *Phase equilibrium diagram: Decrease of the local concentration of the more volatile compontent*

Abbildung 4: *Thermal boundary layer and diffusion shell around a growing bubble*

the liquid. In consequence, in the liquid near the surface of the bubble the concentration of the less volatile component is increasing and causes a rise of the local boiling temperature higher than the saturation temperature of the initial liquid. While the isobaric case (a) is characterised by a supply of heat, in the case of depressurisation (b) phase equilibrium is reached by a reduction of the sensible heat. But for both cases a enrichment of the less volatile component in the liqid can be observed, which means that the more volatile component has to be transported to the boundary surface. (fig. 4)

Scriven [Scr59] was the first to develop a analytical model for bubble growth in a binary liquid mixture. His model comprises a spherical bubble in an initially superheated liquid. Looking at the aymptotic stage of bubble growth he considered heat and mass transfer by one-dimensional radial conduction and convection to the bubble interface. The expression derived for large superheats reverts the Plesset&Zwick solution [Ple54] for pure fluids

$$R(t) = \left(\frac{12}{\pi}\right)^{1/2} \cdot Ja \cdot (at)^{1/2} \cdot$$
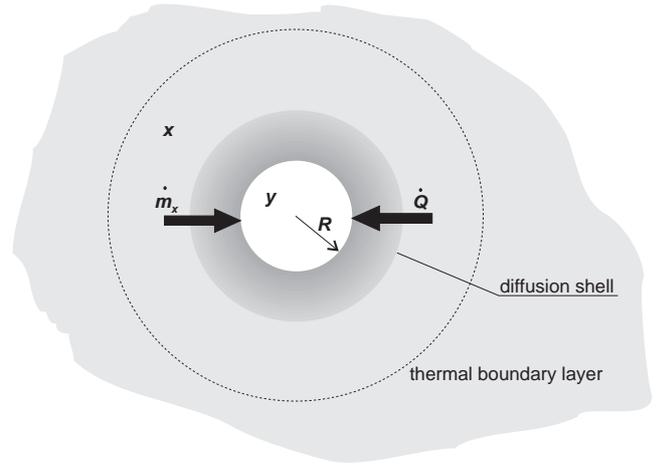$$\cdot \left[1 - (y-x)\, Le^{1/2} \frac{c_{pf}}{h_v - h_l} \frac{dT}{dx}\right]^{1/2} \quad (1)$$

and the additional bracketed term shows the reduced bubble growth of a binary in comparison to a pure fluid and contains the diffence of the concentrations in the vapour and the liquid phase, some physical properties, the slope of the bubble point line and the Lewis-Number. The Lewis-Number $Le = \frac{a}{D}$ – the ratio of thermal diffusivity and the mass diffusion coefficient – compares heat conduction and mass diffusion. Since the thermal
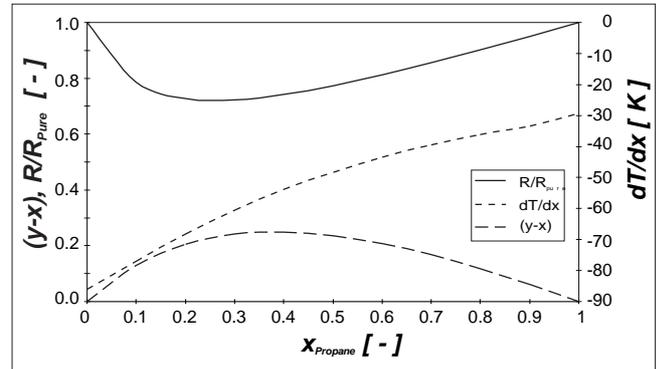

Abbildung 5: *Reduced bubble growth of a Propane/Butane binary mixture in comparison to a pure fluid*

diffusivity is an magnitude greater then the mass diffusion coefficient the thermal boundary layer is

much thicker than the diffusion shell. (fig. 4)

The reduced bubble growth of a Propane/Butane binary mixture in comparison to the pure fluid is characterised by the bracketed term in the Scriven solution which is plotted versus the fraction of the more volatile component in fig. 5. The minimum of the growth constant is shifted to the maximal difference in composition of the vapour and the liquid phase due to the slope of the boiling line.

EXPERIMENTAL RESULTS

Comparison of Fluids

The comparison of the temporal course of the blowdown of a pure fluid (Butane) and a binary mixture (Propane/Butane 50mole%) shows the most important quantities – pressure and void fraction – (fig. 6).

Before initiation the blowdown the pressure was set to 21% of the critical value, the fluid in the vessel and along the test section was in a saturated state. The time histories of the pressures in the vessel and along the pipe a one major quantity for the understanding of the blowdown and the evaporation processes. The depressurisation caused by the discharge of mass and energy is superposed with the evaporation and increase in volume in the vessel. With the beginning of the blowdown (upward showing arrow) the pressure in the vessel drops and with increasing superheat of the liquid evaporation starts and works against the presssure drop. The larger pressure drop of the mixture in comparison to the pure fluid leads to a higher degree of thermal non-equilibrium in the vessel. Because of the low velocities the pressure drop along the pipe is small and the throttling at the orifice dominates the blowdown. The upward showing arrow indicates the moment when the vessel nearly gets empty and from which on mainly vapour is entering the pipe and in consequence the pressure in the vessel is falling quicker.

While the pressure time histories show only small differences in the behaviour of the pure fluid and the mixture, the deviation of the development of the void fraction along the pipe for the binary mixture from the pure fluid can be clearly seen: Because of the high degree of evaporation at the pipe entrance the development of void shows only small changes along the pipe for the pure substance (butane). For the binary mixture a lower level of void fraction is observed and the changes along the depressurisation pipe are more obvious, because at the end of the pipe the void fraction is higher. This higher level of void can be explained by the increasing superheat of the fluid in the vessel.

This retarded evaporation can be seen from the last graphs in fig. 6, in which the temperature is plotted versus the pressure. For the pure fluid the temperature follows the line of boiling points quite well, but for the binary mixture the degree of thermal nonequilibrium can be depicted as the distance from the saturation line. The superheat of fluid which enters the pipe represents the driving force of the evaporation. The non-equilibrium monitored at the first sensor unit near the pipe entrance shows that for the binary mixture the evaporation is retarded compared to the pure fluid. The level of void fraction is fixed by the the superheat of the entering fluid and the saturation state in pipe because at the pipe end thermal equilibrium is observed for all experiments.

Influence of Orifice Diameter for the Binary Mixture

The influence of orifice diameter is demonstrated for the longest test section with an L/d-ratio of 240 and a binary mixture of propane and butane with a molar concentration of 50%. Because of the reduced mass velocities caused by the throttling at the orifice the pressure drop in the vessel is smaller than for the open pipe end. The pressure drop along the pipe consists of the acceleration part predoninant at the pipe entrance and the friction which dominates along the consecutive pipe section. With decreasing cross section of the orifice the pressure drop along the pipe gets smaller be-
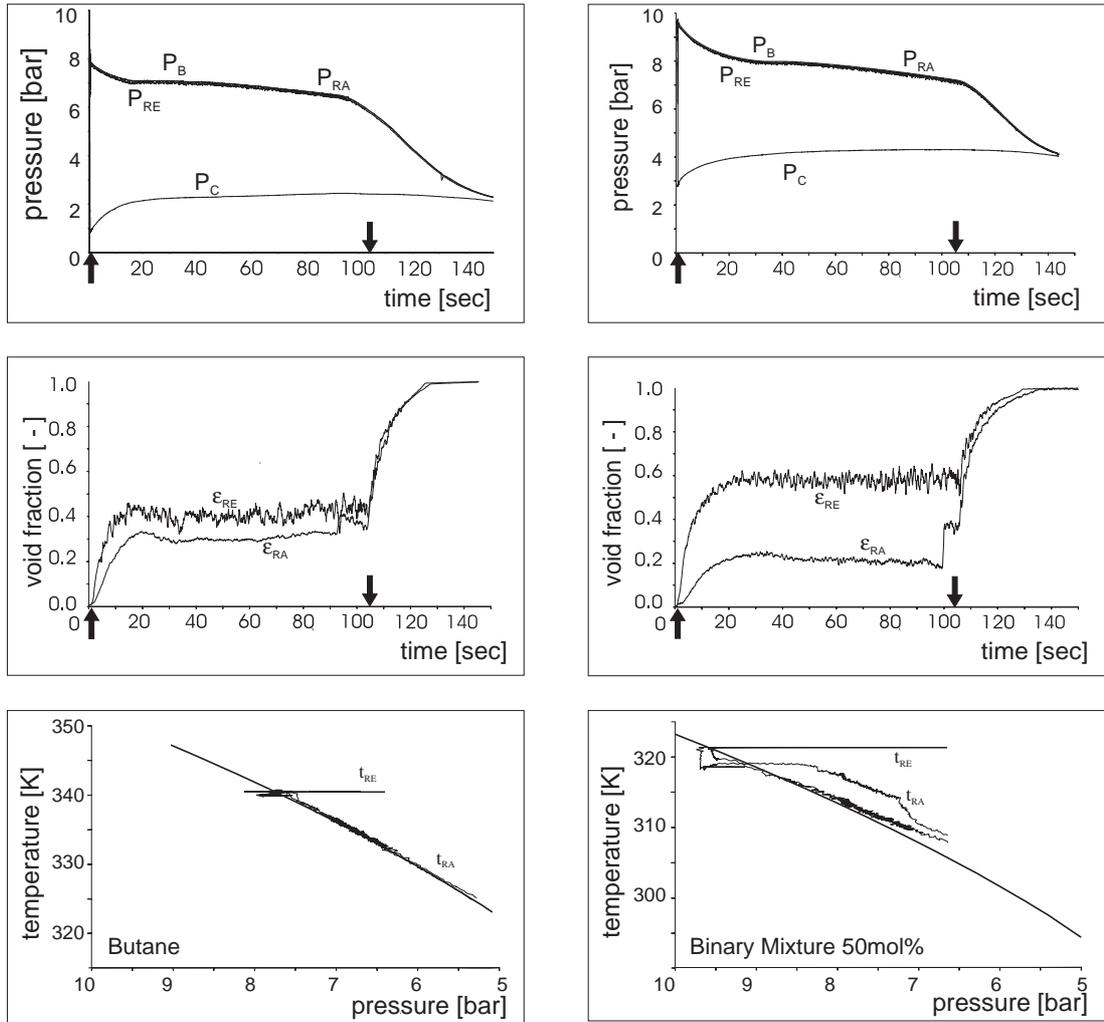
Abbildung 6: *Comparison of Fluids: Butane and a Propane/Butane binary mixture (50mol%), L/D = 170, $d_B = 3\,mm$*

cause of the lower velocities and the predominant influence of the throttling.

The temporal course of the void fraction for the open pipe or the use of an orifice with 5mm ID shows that thermal equilibrium is reached by the evaporation. Because of the flashing in the very first section of the pipe the sensible heat of the superheated liquid pouring out the vessel is reduced and thermal equilibrium is oberved along the whole test section. The higher superheat of the liquid in the vessel and the larger pressure drop along the pi-

pe for the open pipe causes a higher level of void fraction compared to that of a blowdown with a reduced area of the outlet orifice. For the lowest mass flow rate caused by the throttling of the orifice with the smallest cross section (ID 3mm) a retarded evaporation of the liquid can be observed at the first sensor unit ($z/d \approx 30$). The non-equilibrium of the fluid is reduced until saturated conditions can be observed at the 2nd void fraction sensor and the consecutive test section.
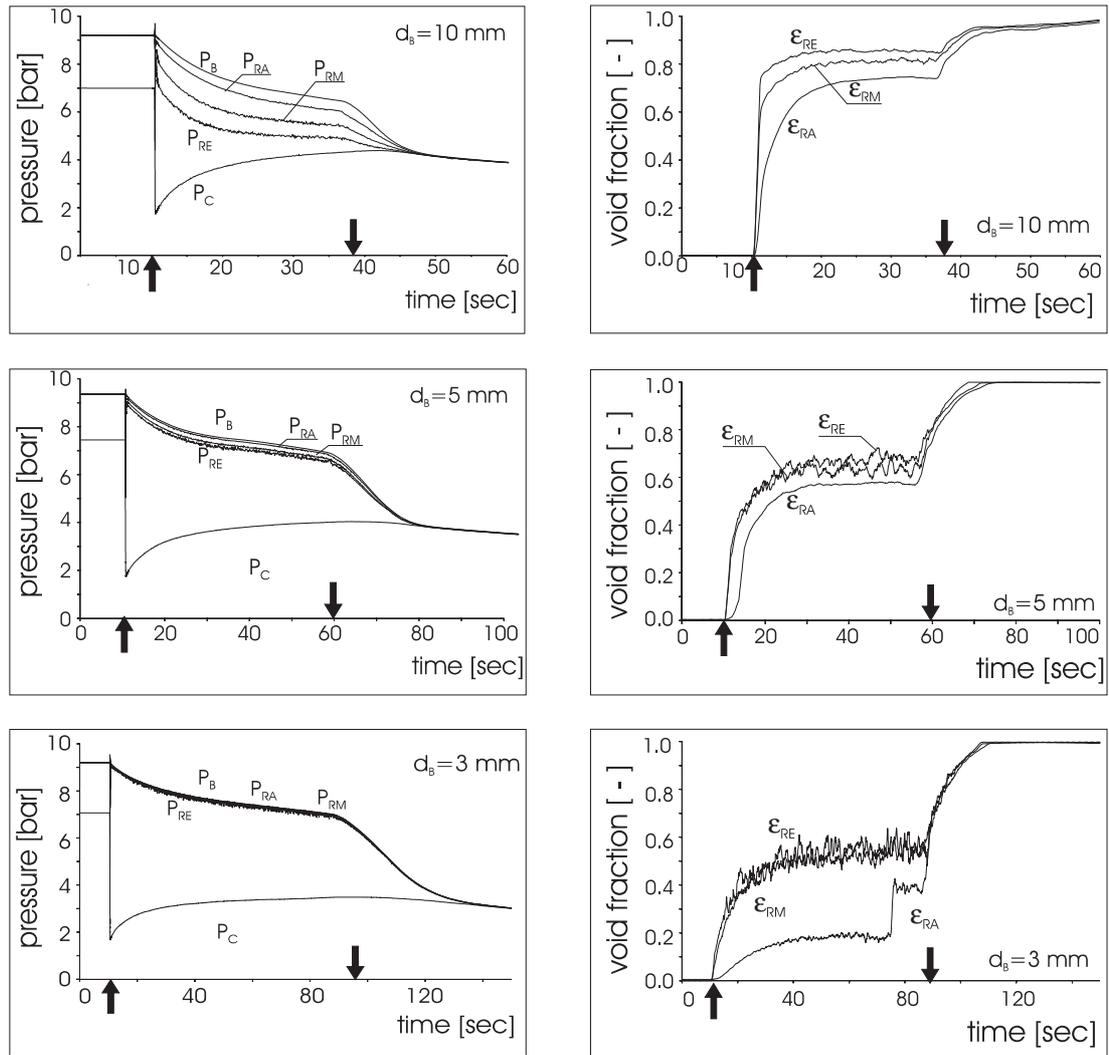
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Abbildung 7: *Influence of Diameter of Orifice, Propane/Butane Binary Mixture (50mol%), L/d =240*

Liquid Superheat in the Vessel and Void Development along the Pipe

A comparison of the experimental data shows that for binary mixtures the superheat in the vessel (fig. 8) is larger than for the pure fluids. This effect becomes more important with higher mass flow rate. With increasing discharge the initial depressurisation rate in the vessel gets higher and the result is a higher degree of thermal non-equilibrium when the evaporation rate in the vessel balances almost the outflow. The highest degree of thermal non-

equilibrium is always observed for the binary mixture with a concentration of 25% of the more volatile component and this shows a good agreement with the reduced bubble growth for binary mixtures.

The graph in fig. 9 shows the measured void fraction at the first sensor unit at the pipe entrance (L/d =30). The retarded evaporation of the binary mixtures for the lowest mass flow rates can be seen from the lower void fraction. With increasing mass flux this effect is not observed and the measured
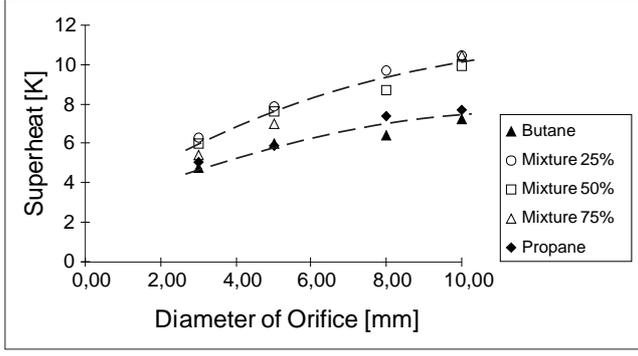
Abbildung 8: *Thermal Non-Equilibrium in Vessel in Dependence of Composition and Diameter of Orifice*
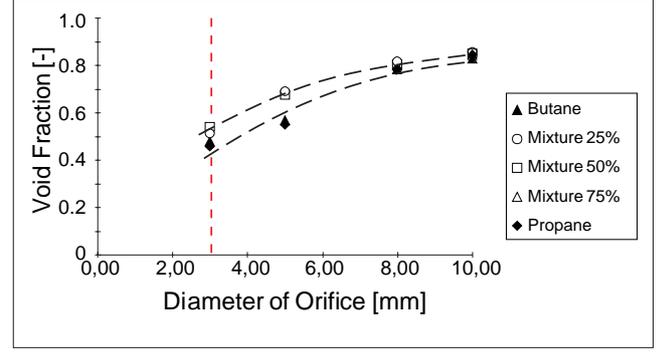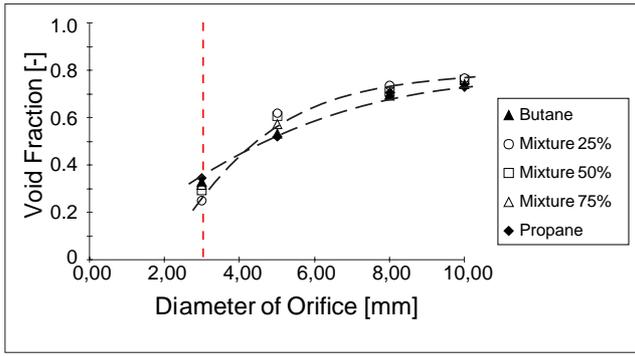

Abbildung 9: *Measured Void Fraction at the Pipe Entrance in Dependence of Composition and Diameter of Orifice*

void fraction of the binary mixture is higher than for the pure fluid. The development of the volumetric composition of the two-phase mixture can be depicted from fig. 10, which shows a higher level of void. Because of the thermal equilibrium, which is observed in the pipe exept for the use of the orifice of 3 mm diameter the level of void is fixed by the superheat in the vessel. The higher degree of thermal non-equilibrium in the vessel for the mixtures causes an increased level of void fraction.

For the case of the orifice with 3mm diameter the non-equilibium in the vessel is almost the same for the pure fluids as well as for the binary mixtures.

Abbildung 10: *Measured Void Fraction at the Pipe Exit in Dependence of Composition and Diameter of Orifice*

The reduced bubble growth because of the diffusive mass transport results in a smaller evaporation rate at the pipe entrance. For all other cases the non-equilibrium in the vessel of the binary mixtures is higher than for the pure fluids. This larger superheat predominates the diffusive mass transport mechanism in bubble growth.

DATA ANALYSIS

A numerical analyses shall prove that the retardet evaporation at the pipe entrance for the lowest mass flow rates can be explained by the effect of diffusive mass transfer machanism on bubble growth. The numercial integration of the conservation laws for

— mass of the mixture

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)\,\varrho_l + \varepsilon\varrho_v\right] + \qquad (2)$$

$$+\frac{\partial}{\partial z}\left[(1-\varepsilon)\,\varrho_l w_l + \varepsilon\varrho_v w_v\right] = 0$$

— the mass of the vapour phase

$$\frac{\partial}{\partial t}\left(\varepsilon\varrho_v\right) + \frac{\partial}{\partial z}\left(\varepsilon\varrho_v w_v\right) = \Gamma \qquad (3)$$

— the momentum of the mixture

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)\,\varrho_l w_l + \varepsilon\varrho_v w_v\right] + \qquad (4)$$

$$+\frac{\partial}{\partial z}\left[(1-\varepsilon)\,\varrho_l w_l^2 + \varepsilon\varrho_v w_v^2\right] + \tau\frac{U_n}{A} = \frac{\partial p}{\partial z}$$

— the energy of the mixture

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)\,\varrho_l h_l + \varepsilon\varrho_v h_v\right] + \tag{5}$$

$$+\frac{\partial}{\partial z}\left[(1-\varepsilon)\,\varrho_l h_l w_l + \varepsilon\varrho_v h_v w_v\right] = \dot{q}\frac{U_b}{A}$$

— and the mass of the component i

$$\frac{\partial}{\partial t}\left[(1-\varepsilon)\,\varrho_l x_i + \varepsilon\varrho_v y_i\right] + \tag{6}$$

$$\frac{\partial}{\partial z}\left[(1-\varepsilon)\,\varrho_l x_i w_l + \varepsilon\varrho_v y_i w_v\right] = 0$$

combined with correlations for the frictional pressure drop [Chi73] gives the development of void fraction and the pressure profile along the pipe. The vapour phase is assumed to be saturated and thermal non-equilibrium is included by a superheated liquid. With the assumption of bubble flow
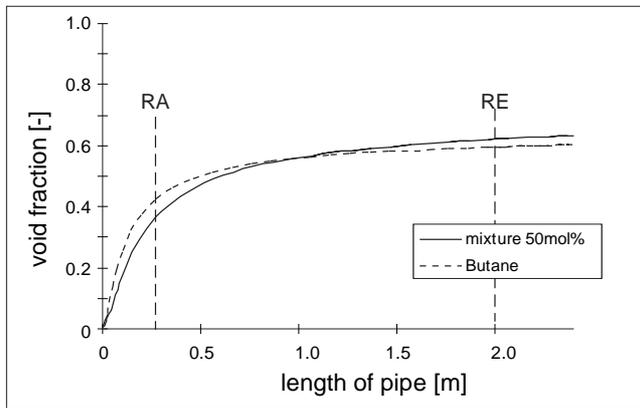

Abbildung 11: *Comparison of the void fraction development for a pure fluid and a binary mixture*

the interfacial mass transfer is derived according to [Kol86] by the correlation of bubble growth and the relation between void fraction and volume of a single bubble. To simplify the calculations the compositions of the vapour and the liquid phase are assumed to be in equilibrium.

The calculated development (fig. 11) describes the trend of the measured data quite well. The pure fluid – butane – shows a steeper increase of void fraction at the pipe entrance. In the subsequent section the fluid reaches thermal equilibrium and the changes in volumetric composition are small.

SUMMARY

Experimental investigations on the depressurisation of binary mixtures indicate the following trends:

- Thermal non-equilibrium in the vessel is influenced by the discharge rate. A higher mass flow rate increases the superheat of the liquid stored in the vessel.

- For binary mixtures a raise of thermal non-equlibrium of the fluid in the vessel in comparison to the pure substances is observed and is in accordance to the diffusive controlled bubble growth.

- In the depressurisation pipe thermal equilibrium is reached by the evaporation and the volumetric composition of the two-phase mixture is fixed by the saturation state.

- An influence of diffusive mass transport mechanism on the flashing of the liquid is observed for low velocities.

ACKNOWLEDGEMENT

NOTATION

a	thermal diffusivity
A	area
c_p	isobaric heat capacity
d	diameter of the pipe
D	diffusivity
$\dot{q}$	heat flux
h	enthalpy
R	bubble radius
t	time
T	temperature
U	circumferance
w	velocity
x	mass fraction in liquid
y	mass fraction in vapour
z	axial coordinate

Le	Lewis-Number	$Le = \frac{a}{D}$
Ja	Jakob-Number	$Ja = \frac{\varrho_l c_{pl} T_{sup}}{\varrho_v (h_v - h_l)}$

ε	volumetric void fraction
ϱ	density
τ	shear stress
Γ	interfacial mass transfer rate

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