

Experimental Evaluation of Different Procedures for Liquefaction of Gas Mixtures and the Resulting Changes in Composition

Nils von Preetzmann^{1*}, Reiner Kleinrahm¹, Roland Span¹

¹ Thermodynamics, Faculty of Mechanical Engineering, Ruhr University Bochum, 44801 Bochum, Germany

ABSTRACT

Density measurements on a binary (0.88 methane + 0.12 propane) mixture were carried out to evaluate the impact of different liquefaction procedures on the composition of condensed gas mixture samples. For these experimental investigations, a low-temperature single-sinker magnetic-suspension densimeter was used. The gaseous mixture was liquefied by condensation and via a special supercritical liquefaction procedure. The densities measured after applying the supercritical procedure serve as reference densities. Based on a comparison of the results of both procedures at otherwise same p, T conditions, the changes in composition can be estimated by differences in density, and these changes are caused by the procedure used for condensation.

It was found that the condensed liquids show distortions in composition of up to 0.94 mole-% that cannot be neglected for the accurate measurement of thermophysical properties. But it was also shown that under appropriate conditions and by applying special condensation procedures, single state points in the homogenous liquid region can be approached with just a minor or no detectable distortion in composition. However, when multiple state points shall be measured over a larger pressure or temperature range, no appropriate and easy method has been found to change the state point of the fluid under survey without significantly changing the composition of the liquefied sample. Only a supercritical liquefaction procedure in combination with a special VLE-cell is suitable for this application.

Keywords: cryogenic liquid mixtures, liquefaction techniques, density measurement, magnetic-suspension coupling, single-sinker densimeter

Selection and peer-review under responsibility of the scientific committee of the 13th Int. Conf. on Applied Energy (ICAE2021).

Copyright © 2021 ICAE

1. INTRODUCTION

Liquids that are used in cryogenic applications are often in their gaseous state at ambient temperatures. In the gas industry and the energy sector, natural gas [1], hydrogen-rich mixtures [2], and biogas [3] as energy carriers can be transferred to their liquid state; that results in a significantly higher energy density which is advantageous for transport and storage.

For the development and optimization of technical processes, accurate knowledge of the working media is required to design efficient facilities. For the calculation of thermodynamic properties, equations of state are used, which in turn require a sufficient experimental database for their development. Moreover, when handling mixtures, exact knowledge of the composition is essential. Experimental investigations on cryogenic liquids are often based on reference gas mixtures that are being liquefied. Due to the strong composition dependency of most properties, the liquefaction process must produce a sample of well-known composition. A recently introduced liquefaction procedure at supercritical pressures can liquefy gas mixtures with a composition traceable to the used reference gas mixture [4–6]. However, this technique requires high pressures, which cannot always be supported by the facilities, or by the available filling pressure of the sample cylinder. In the case of natural gas-like mixtures, even a few percent of higher hydrocarbons, e.g. butane, result in a significantly higher cricondenbar pressure of mixtures. Hence, samples of certain mixtures that may be of interest cannot be liquefied at supercritical pressures with the available measuring facilities.

Classical isobaric condensation of gas samples as an alternative does not require high pressures but is prone to distort the composition of the produced liquid sample

due to the zeotropic behavior of fluid mixtures. It is known, that coexisting phases result in partial separation of the components of a mixture [7]. When a gaseous mixture is condensed into an apparatus, liquid and vapor are inevitable present simultaneously. Even if the sample in the measuring cell is completely transferred to the homogenous liquid state, a remaining distortion in composition can result; e.g. due to the apparatus vapor headspace or a stratified liquid.

Here, the challenge is to estimate the actual impact on the composition of the liquefied sample. Measuring the composition at cryogenic conditions directly in the liquefied sample, e.g. via Raman spectroscopy [8], is currently not possible in the uncertainty range required for the accurate measurement of thermophysical properties. Alternatively, to simulate such liquefaction procedures is a virtually infeasible task since condensation into a genuine system is a highly dynamic process with multiple interconnected volumes of different temperatures and correspondingly different fluid characteristics. Current computational fluid dynamics simulations (CFD) do not use accurate mixture models for thermodynamic property calculations that would be required to describe the liquefaction process including the vapor-liquid equilibrium (VLE) with adequate accuracy.

2. EXPERIMENTAL METHODS

In this work, we present an experimental approach to estimate the impact of condensation on the liquid sample's composition. For this purpose, we performed comparative density measurements on samples that have been liquefied at supercritical pressures or by different condensation procedures. The differences in density are used as an indicator for the change in composition.

2.1 Apparatus description

The utilized densimeter, which is schematically illustrated in Fig.1, was deliberately designed for accurate density measurements of cryogenic liquefied mixtures, such as LNG [4,5]. It covers a temperature range from (100 to 300) K at pressures up to 12 MPa. The design of the cryogenic densimeter, the temperature and pressure measurement, and the implementation of a special "VLE-cell" as a novel feature were described in detail by Richter *et al.* [4] in 2016 and are only briefly described here.

The single-sinker densimeter, based on the Archimedes principle, utilizes a magnetic suspension

coupling (MSC) and allows for an absolute determination of the fluid density ρ_{fluid} as

$$\rho_{fluid} = \frac{m_{S,vac}^* - m_{S,fluid}^*}{V_S(T,p)} \cdot (1 + \varepsilon)^{-1}, \quad (1)$$

where $V_S(T,p)$ denotes the known volume of the sinker and $m_{S,vac}^*$ and $m_{S,fluid}^*$ are the weighing values in the evacuated measuring cell and in the fluid-filled measuring cell, respectively. The term $(1 + \varepsilon)^{-1}$ corrects a small force-transmission error that is caused by the MSC [9,10].

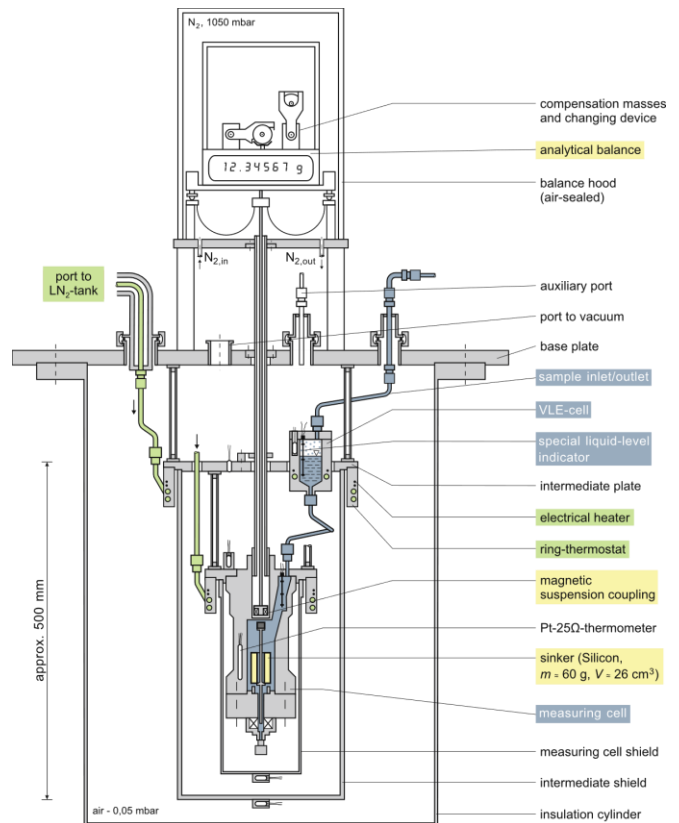


Fig. 1. Schematic diagram of the core apparatus of the single-sinker densimeter as given in Richter *et al.* [4].

The novel VLE-cell of the densimeter ($V_{VLE} \approx 30 \text{ cm}^3$) is located between the measuring cell ($V_{MC} \approx 110 \text{ cm}^3$) and the pressure measurement circuit, inside the cryostat (see Fig. 1). It serves as a measure to separate the measuring cell from the liquid to vapor phase transition and from the accompanying effects of the VLE on the composition of the liquid. Since the pressure measurement is conducted slightly above ambient temperature, a VLE will unavoidably establish somewhere in the system. The location of the phase boundary can be affected by the temperature of the VLE-cell, which can be controlled independently.

2.2 Experimental Procedures

As mentioned above, the cryogenic densimeter was designed to liquefy gas mixtures at supercritical pressures [4], and it is used for measurements along isotherms in the homogenous liquid and supercritical region of cryogenic liquids. This procedure is described in detail by *Richter et al.* [4] and illustrated in Fig. 2 (red graph). The special supercritical liquefaction produces a liquid sample in the measuring cell that exactly preserves the original composition of the reference gas mixture. Diffusion effects between the liquid phase inside the VLE-cell (which has a different composition since the phase boundary is located in the VLE-cell) and the liquid in the measuring cell are minimal and they have no detectable effect on the composition of the sample in the measuring cell [6]. Hence, this procedure includes traceability to the composition of the gas mixture. Accordingly, density data based on this liquefaction procedure can serve as reference data for density measurements on condensed liquid produced by different liquefaction procedures. However, the VLE-cell is a sophisticated part of the densimeter, and it was the aim of the current work to evaluate liquefaction procedures that do not require a VLE-cell and supercritical pressures of the gas mixture sample as well.

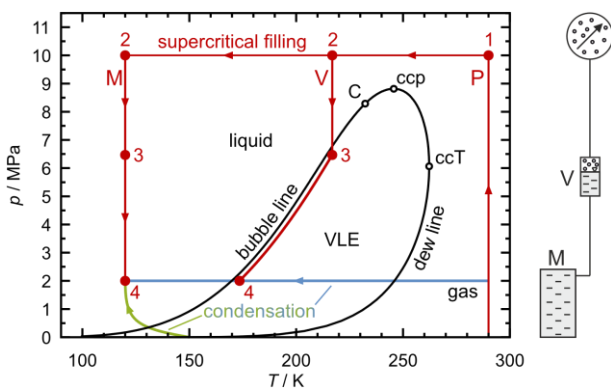


Fig. 2. Schematic procedures to reach a state point 4 in the homogenous liquid region. Illustrated are the liquefaction at a supercritical pressure in conjunction with a special VLE-cell (red) and two condensation variants (blue and green).

For the condensation, two basic variants are feasible to produce a homogenous liquid sample in the measuring cell (blue and green in Fig. 2). At the first variant, the system can be filled to a subcritical pressure at ambient temperature; then it can subsequently be cooled down to the target temperature while keeping the pressure approximately constant (blue in Fig. 2). Depending on the pressure, the shape of the phase boundary, and the achievable cooling rate of the cryostat, a VLE is present in the measuring cell for a

relatively long time. The second variant for condensation is to cool the apparatus to the target temperatures with a vacuum in the measuring cell. Then, the gas mixture is filled from the sample cylinder into the precooled apparatus until the desired pressure is reached (green in Fig. 2). Here, the time during which the fluid is present in the measuring cell in two phases is relatively short, and the amount of sample in the gas phase is smaller due to the low vapor density. As soon as the saturated-liquid pressure at the pre-set temperature is reached, theoretically, the entire measuring cell would be filled with liquid. This only takes a few minutes. In a previous study, we observed that this variant is advantageous concerning changes in composition, compared to the variant described first [11]. It was shown that for the condensation into the precooled apparatus (green in Fig. 2), the deviations of the recorded densities from reference densities based on a supercritical liquefaction procedure were all within the experimental uncertainty of $U(\rho)/\rho = 0.015\%$ over a small pressure range. The deviations of densities based on an isobaric condensed liquid (blue in Fig. 2), in turn, were up to 0.093% in density. Hence, all investigations presented in this work are based on the second variant, where the mixture is filled into a precooled and evacuated system. Here, the aim was to examine if this procedure can be also applied to investigate larger pressure or temperature ranges.

For the density measurements on condensed liquids, several parameters of the liquefaction procedure were varied between different fillings of the apparatus. First, measurements were performed with a subcritical filling pressure of $p \approx 7.0$ MPa at $T = 120$ K. The measurements were carried out along isotherms. Here, sophisticated tests were carried out, in particular, to determine how fluid properties can best be measured when the maximum pressure is less than the critical pressure of the mixture. At the beginning of each test run, the evacuated and precooled apparatus was filled to the respective maximum pressure of interest. Then, the pressure was sequentially reduced by venting sample from the system.

During the condensation in the measuring cell, the VLE-cell was kept in the gas region, since condensation inside the VLE-cell would result in a liquid phase enriched with the heavier components and this distorted liquid is being flushed into the measuring cell during the filling process. This would have a strong influence on the composition of the produced liquid sample in the measuring cell and must therefore be prevented (see section 3 and Ref. [11]). Although no vapor headspace is present in the measuring cell itself, the transition from

liquid to vapor (and the liquid level) is located in the connecting tube between the measuring cell and the VLE-cell (see Fig. 1). Moreover, it was also tested whether the VLE-cell can be filled with liquid after the condensation in the measuring cell is completed. This would allow measurements along isotherms without the need for venting the system. By adjusting the temperature of the VLE-cell, it can be used to control the system pressure when the VLE-cell is filled with liquid, either only partially [4] or completely [12].

Moreover, to assess the influence of the pre-set temperature of the measuring cell during the liquefaction, condensation into the precooled and evacuated system (green in Fig. 2) was performed at four temperatures $T = (100, 120, 140, \text{ and } 160)$ K. The gas mixture was condensed in each case into the precooled and evacuated system and the pressure was increased continuously until about 9.5 MPa were reached, which is supercritical. However, the condensation through the VLE-region was still carried out at subcritical pressures. For each of the four temperatures, reference densities were recorded that are based on the special supercritical liquefaction procedure (red in Fig. 2).

2.3 Evaluation

For the investigations presented in this work, a gravimetrically prepared binary (0.88 methane + 0.12 propane) mixture was used. Exactly this mixture was already studied in a previous project over the temperature range of $T = (100 \text{ to } 160)$ K and at pressures up to 9.5 MPa [6]. There, it was shown that the GERG-2008 equation of state [13] is capable to describe the experimental densities within their experimental uncertainty of about 0.015% ($k = 2$). Therefore, it can also be assumed that the equation is capable of accurately predicting the correlation between density and composition for this mixture. For this reason, we chose this mixture for the presented investigations.

To evaluate different procedures for the liquefaction of gas mixtures, density measurements based on a special liquefaction procedure at supercritical pressures were used as reference. A change in density compared to this reference data at otherwise same p, T conditions can then be directly translated to a shift in composition since a binary mixture has only one degree of freedom in composition. The sensitivity of density to composition, $(\partial\rho/\partial x_i)_{p,T}$, can be calculated with sufficient accuracy with the GERG-2008 equation of state [13]. Hence, the change in composition $\Delta x_{i,\text{liq}}$ can be estimated with

$$\Delta x_{i,\text{liq}} = \left(\frac{\partial\rho}{\partial x_i} \right)_{p,T}^{-1} \cdot \Delta\rho_{\text{exp}}, \quad (2)$$

where $\Delta\rho_{\text{exp}}$ is the observed difference of the density measurements on a condensed liquid compared to the reference data. When the deviation in density is within the measurement uncertainty, a change in composition cannot be confirmed. Here, the uncertainty in composition of the gravimetric preparation of the reference gas mixture can be neglected, as the identical mixture was used for all comparative measurements.

3. RESULTS AND DISCUSSION

The first two tests were carried out at $T = 120$ K. Here, the gas mixture was filled into the precooled and evacuated system to a final pressure of $p \approx 7.0$ MPa which is below the mixture's critical pressure ($p_c = 8.29$ MPa). For the first test, the VLE-cell was continuously kept in the gas phase at $T_{\text{VLE}} \approx 270$ K in order to prevent any major condensation outside of the measuring cell. Further state points along the isotherm were approached by venting sample from the system to reduce the pressure. For the second filling, the VLE-cell and the fluid in it were cooled isobarically to $T_{\text{VLE}} \approx 205$ K, which is below the saturated-liquid temperature $T_s(p = 7.0 \text{ MPa}) = 218.89$ K, after the condensation in the measuring cell was completed. This cooling at subcritical pressures implies that a VLE had established in the VLE-cell and, henceforth, the heavy liquid phase descended into the connecting tube. After the VLE-cell reached $T_{\text{VLE}} \approx 205$ K, it was completely filled with liquid sample. To approach further state points along the isotherm, pressure reductions could be now achieved by adjusting the VLE-cell temperature [4] instead of venting sample.

Fig. 3 shows the relative deviations of the measured densities from the GERG-2008 equation of state [13]. The first densities measured on the condensed liquid where the VLE-cell was kept in the gas region (\times in Fig. 3) agree with the reference data within their experimental uncertainty. Hence, the condensation provided a liquid sample that shows no detectable change in composition. However, the venting of sample, required to reduce the system pressure, resulted in a successive increase in the relative deviation of up to 0.20% (at $p \approx 2.0$ MPa) which corresponds to a change in composition of approximately 0.42 mole-% according to equation (2).

The second filling, where the VLE-cell was completely filled with liquid at $T_{\text{VLE}} \approx 205$ K, however, shows relative deviations to the reference densities of about 0.46% in density over the entire pressure range (\diamond in Fig. 3). This corresponds to an increase of the propane concentration

of approximately 0.94 mole-%. This density increase is caused by the VLE that formed in the VLE-cell when it was cooled down isobarically to $T_{\text{VLE}} \approx 205$ K. The respective propane-rich liquid phase of the VLE descended into the connecting tube and mixed with the liquid under survey in the measuring cell.

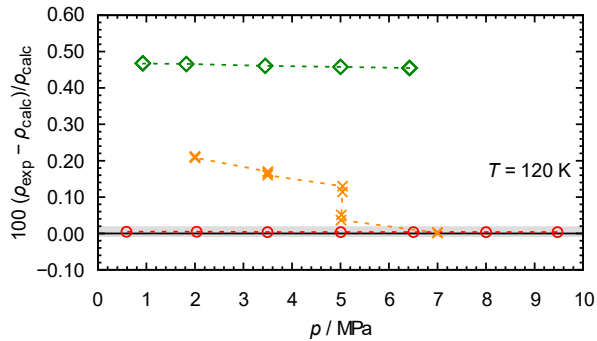


Fig. 3. Relative deviations of experimental densities at $T = 120$ K from densities calculated with the GERG-2008 equation. \circ , reference densities (uncertainty 0.015%, $k = 2$); \times , condensation into the pre-cooled measuring cell and filling to $p \approx 7.0$ Mpa, $T_{\text{VLE}} \approx 270$ K; \diamond , condensation as before, but after the measuring cell was completely filled, the VLE-cell and the fluid in it were cooled to $T_{\text{VLE}} \approx 205$ K.

For the four following tests at varying target sub-cooling of the measuring cell, the VLE-cell was kept in the gas region at $T_{\text{VLE}} \approx 270$ K. The evacuated system was filled to $p_{\text{fill}} \approx 9.5$ MPa, which is supercritical. The condensation through the VLE inside the pre-cooled measuring cell nevertheless took place at subcritical pressures. Here, the observed relative deviations in density at $p \approx 9.5$ MPa from the reference data were $(-0.023, -0.004, -0.149, \text{ and } -0.930)\%$ in density at $T = (100, 120, 140, \text{ and } 160)$ K, respectively. This corresponds to changes of the propane fraction of $(-0.06, -0.02, -0.27, \text{ and } -0.93)$ mole-% at the respective temperatures. We ascertained that the lower temperatures show smaller deviations. This is probably caused by the fact that the homogenous liquid region is reached relatively quickly, as the saturated-liquid pressure decreases with decreasing temperature. Moreover, as the vapor density decreases with decreasing saturated-liquid pressure, a smaller amount of gas phase with a shift in composition is present in the measuring cell while a VLE is occurring inside the measuring cell.

For all four temperatures, further state points along the isotherms were approached by venting sample from the system. Here, we again observed that venting of sample to reduce the pressure caused a sequential increase of the relative deviations in density, as soon as the pressure is below the critical pressure of the mixture.

This behavior occurred at all four temperatures and is caused by an accumulation of propane in the liquid sample during the venting. Since the vapor phase of the VLE consists primarily of methane, the liquid phase of the VLE further enriches with propane, the more gas is withdrawn from the system by venting. Fig. 4 shows the results for the test run at $T = 120$ K with $p_{\text{fill}} \approx 9.5$ MPa. Here, the relative deviations from the GERG-2008 equation [13] are plotted for the respective test run and the reference data at $T = 120$ K, as well as for two further tests at the same temperature. The first test run, in Fig. 4 (\diamond) shows deviations of up to 0.13% in density. This corresponds to a change in composition along the entire isotherm of less than 0.3 mole-%, which may be negligible for some applications.

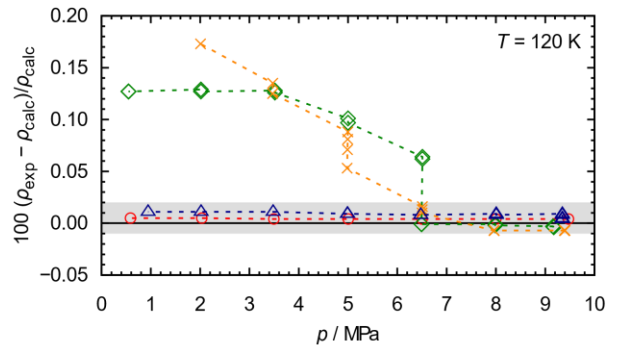


Fig. 4. Relative deviations of experimental densities at $T = 120$ K and $p_{\text{fill}} \approx 9.5$ MPa from densities calculated with GERG-2008 equation. \circ , reference densities (uncertainty 0.015%, $k = 2$); \diamond , condensation; \times , condensation with thermal bridge; \triangle , condensation with liquid in the VLE-cell.

Due to the high temperature difference between the measuring cell and the VLE-cell, the liquid to vapor transition of the fluid is located in the connecting tube very close to the measuring cell. Hence, we first presumed that the propane-rich liquid reaches the measuring cell via diffusion. To reduce the presumed diffusion, a thermal bridge has been installed between the intermediate plate (see Fig. 1, $T_{\text{IP}} \approx 110$ K) and the upper end of the connecting tube, close to the VLE-cell. This measure significantly changes the temperature profile of the connecting tube and thereby causes the phase transition to occur close to the VLE-cell and, therefore, further away from the measuring cell. However, the results for a new filling with the installed thermal bridge (\times in Fig. 4) show no reduction of the relative deviations in density to the reference. Therefore, we assume that the propane-rich liquid of the VLE does not affect the composition of the fluid inside the measuring cell via diffusion, but that it descends into the measuring cell due to the density difference.

For $T = 120$ K, the densities measured for liquids prepared by condensation (\diamond and \times in Fig. 4) deviate from the reference data (\circ in Fig. 4) initially at $p \approx (9.4, 8.0, \text{ and } 6.4)$ MPa only within their experimental uncertainty of 0.015% (shaded area in Fig. 4). As with the tests with a subcritical filling pressure of $p \approx 7.0$ MPa, this indicates that the condensation itself did not noticeably change the composition of the liquid in the measuring cell. However, as described above, pressure changes below the critical pressure resulted in a significant change in composition and density.

For a further test at $T = 120$ K, the VLE-cell was cooled to $T_{\text{VLE}} \approx 233$ K at constant supercritical pressure of $p \approx 9.4$ MPa, after the condensation in the measuring cell was completed. This temperature is below the cricondenbar temperature of the mixture, which implies that the VLE-cell could again be used to regulate the system pressure by stepwise decreasing the VLE-cell temperature [4]. Accordingly, the venting of sample which causes the changes in composition was no longer needed. However, supercritical pressures were applied for this procedure; i.e., the main advantage of the low-pressure condensation was not utilized. Nevertheless, we could show for this special case that the density measurements on the liquid condensed in the measuring cell agreed with the reference densities within their experimental uncertainty of 0.015% over the entire pressure range (\triangle in Fig. 4).

Finally, it was also tested whether several state points of a single liquefied sample can be approached by increasing the measuring cell temperature and thus the pressure of the closed system. For this test (not plotted), we filled the system to $p \approx 2.3$ MPa with the measuring cell being precooled to $T = 120$ K while the VLE-cell was kept at $T_{\text{VLE}} \approx 270$ K. At this starting point, the measured densities show a small drift over time and deviate by about (0.026 to 0.043)% in density from the reference data. This slightly exceeds the experimental uncertainty but the corresponding estimated change in composition is about just (0.05 to 0.09) mole-%. Then, the temperature of the measuring cell was increased to 130 K ($p \approx 3.6$ MPa) and afterwards to 140 K ($p \approx 4.9$ MPa). The deviations of the measured densities from the reference data increased significantly to (0.31 and 0.54)%, respectively, which corresponds to an increase of the propane concentration of approximately (0.68 to 1.35) mole-%. We assume that the temperature increase leads to a predominant evaporation of methane at the phase boundary, which results in an accumulation of propane in the liquid phase again.

4. CONCLUSION

Accurate density measurements on a binary (0.88 methane + 0.12 propane) mixture were used to investigate the impact of condensation of this gas mixture on the composition of the liquefied sample. By comparing densities measured on the condensed liquid to reference densities which are based on a special supercritical liquefaction procedure, it was shown that condensation through the two-phase region is prone to produce a liquid with a change in composition; e.g. up to about 0.94 mole-%. However, at low temperatures, e.g. $T = (100 \text{ or } 120)$ K, condensation into a precooled and evacuated system can approach single state points in the homogenous liquid region without a detectable or just a minor distortion of the composition. Moreover, it must be ensured that condensation preferably only occurs inside the measuring cell. Substantial condensation along the gas inlet (in our case in the VLE-cell) can lead to the respective heavier liquid phase of the VLE being flushed into the measuring cell; i.e. affecting the composition of the liquid sample under survey.

It was ascertained that condensation of a gas mixture can produce a representative liquid sample under special conditions. But it was also shown that, for a single filling of the apparatus, it is not easily possible to perform multiple measurements over a larger temperature or pressure range without significant changes in composition. This is only possible when an integrated VLE-cell of a special densimeter is being filled with the gas mixture at supercritical pressures. Here, we found a special procedure where measurements along an isotherm could be performed on a liquid sample that was condensed through the VLE without a detectable change in composition. This special condensation procedure, however, required supercritical pressures while utilizing the VLE-cell and consequently loses its advantages compared to the supercritical liquefaction procedure that was used to record the reference data. However, when changes in composition can be tolerated, e.g. for applications with low accuracy requirements, condensation at subcritical pressures can be a feasible alternative to liquefy gas mixtures without the need for a special VLE-cell.

As a final result, we did not find an appropriate and easy way for the liquefaction of a gas mixture sample that does not require a suitable VLE-cell and supercritical pressures of the gas sample. Only single state points in the homogenous liquid region can be approached at subcritical pressures without significantly changing the liquid sample composition.

REFERENCES

- [1] International Energy Agency. World Energy Outlook 2021. OECD Publishing 2021, Paris.
- [2] Fuel Cells and Hydrogen. Hydrogen Roadmap Europe: A Sustainable Pathway for the European Energy Transition. Publications Office of the European Union 2019, Luxembourg.
- [3] Gustafsson M, Svensson N. Cleaner heavy transports – Environmental and economic analysis of liquefied natural gas and biomethane. *J Clean Prod* 2021;278:123535.
- [4] Richter M, Kleinrahm R, Lentner R, Span, R. Development of a special single-sinker densimeter for cryogenic liquid mixtures and first results for a liquefied natural gas (LNG). *J Chem Thermodyn* 2016;93:205–221.
- [5] Lentner R, Richter M, Kleinrahm R, Span R. Density measurements of liquefied natural gas (LNG) over the temperature range from (105 to 135) K at pressures up to 8.9 MPa. *J Chem Thermodyn* 2017;112:68–76.
- [6] Lentner R, Eckmann P, Kleinrahm R, Span R, Richter M. Density measurements of seven methane-rich binary mixtures over the temperature range from (100 to 180) K at pressures up to 9.7 MPa. *J Chem Thermodyn* 2020;142:106002.
- [7] Haynes WM. Orthobaric liquid densities and dielectric constants of (methane + 2-methylpropane) and (methane + n-butane) at low temperatures, *J Chem Thermodyn* 1983;15:903–911.
- [8] Walker J, Holland PE, Vargha GM, Squire GD. New facility for production of liquefied natural gas reference standards. *J Nat Gas Sci Eng* 2020;73:103069.
- [9] McLinden MO, Kleinrahm R, Wagner W. Force Transmission Errors in Magnetic Suspension Densimeters. *Int J Thermophys* 2007;28:429–448.
- [10] Kleinrahm R, Yang, X, McLinden MO, Richter M. Analysis of the systematic force-transmission error of the magnetic-suspension coupling in single-sinker densimeters and commercial gravimetric sorption analyzers. *Adsorption* 2019;25(4):717–735.
- [11] von Preetzmann N, Eckmann P, van der Veen AMH, Li J. Laboratory-scale liquefiers for natural gas: A design and assessment study. *AIChE J* 2021;67(7): e17128.
- [12] Eckmann P, von Preetzmann N, Cavuoto G, Li J, van der Veen AMH, Kleinrahm R, Richter M. Density Measurements of (0.99 Methane + 0.01 Butane) and (0.98 Methane + 0.02 Isopentane) over the Temperature Range from (100 to 160) K at Pressures up to 10.8 MPa. *Int J Thermophys* 2020;41:156.
- [13] Kunz O, Wagner W. The GERG-2008 wide-range equation of state for natural gases and other mixtures:

An expansion of GERG-2004. *J Chem Eng Data* 2012;57:3032–3091.