6 Conclusion

The main focus of the presented work was to carry out highly accurate \((p, \rho, T)\) measurements of liquefied natural gases (LNG) in the supercritical region, on the saturated liquid line and, especially, in the homogenous liquid region, where so far no experimental data existed at all. The new data allow an evaluation of the existing thermodynamic models (e.g., the revised Klosek and McKinley method, the GERG-2008 equation of state and different equations implemented in commercial software) used for LNG custody transfer and for density calculations in LNG process simulation tools. Older experimental techniques were limited in accuracy because the composition of the fluid mixture was changed during the measurements. Richter (2011) and Richter et al. (2010, 2011, 2016) suggested to use a combination of the well-established single-sinker density measurement technique and a special VLE-cell with a supercritical filling procedure to enable measurements in the homogenous liquid region of mixtures at cryogenic temperatures.

As described in the third chapter of this work, first test measurements on methane with the densimeter revealed a significant temperature dependence of the force transmission error arising from the coupling housing of the measuring cell. Therefore, the coupling housing made of copper-chrome-zircon (CuCr1Zr) was replaced by a coupling housing made of copper-beryllium (CuBe2). Repeated test measurements with the coupling housing showed only a relatively small error at ambient temperature but still a large error at cryogenic temperatures. Further investigations showed a magnetic influence of the Inconel 600 components installed in the core apparatus. Consequently, some of the Inconel 600 parts used in the core apparatus were replaced by identical components made of Inconel 625. Thereby, the force transmission error at cryogenic temperatures could be reduced. To verify the performance of the densimeter, again density measurements of methane were carried out. Relative deviations from the reference equation of state for methane were between \(-0.001\%\) at \(T = 135\) K and \(0.017\%\) at \(T = 105\) K. However, these deviations were still considered too high. Therefore, a small correction term was introduced, by which the experimental densities are corrected in reference to the equation of state for methane of Setzmann and Wagner (1991). Afterwards, first density measurements on LNG-Norway were carried out, where a temporal drift of the experimental values was observed. Based on this knowledge, a special correction method was developed. With this method, the experimental values of the six different synthetic LNG mixtures were corrected so that an almost linear trend emerged for each measured isotherm. Saturated liquid densities were measured...
as well. First test measurements revealed a reproducibility not much better than 0.1%, which was considered unsatisfactory. The reason was probably a change in composition. Hence, to achieve a smaller uncertainty, the saturated liquid densities were determined by extrapolation of the experimental single-phase liquid densities to the vapor pressure calculated with the GERG-2008 equation of state.

The density of six different synthetic LNG mixtures was measured over the temperature range from $T = (105$ to $135)$ K at pressures from $p = (0.2$ to $9)$ MPa. The relative combined expanded uncertainty ($k = 2$) in density considering all effects, including the uncertainty in composition, was estimated to approximately 0.044% for all measurements. A comparison of the new values of saturated liquid densities with values calculated with the revised Klosek and McKinley method of McCarty (1980) has shown that this method can describe the experimental data very well. In some cases, the saturated liquid densities were described better than by the GERG-2008 equation of state. When the simplicity of density calculations is of importance, then, enhancing the revised Klosek and McKinley model was an option to enable accurate pressure dependent calculations. Towards this end, Tietz et al. (2017) developed an enhanced revised Klosek and McKinley method based on the data set presented in this work. The experimental results in the supercritical and homogenous liquid region were compared with the GERG-2008 equation of state, the enhanced revised Klosek and McKinley method (ERKM) and the COSTALD correlation. Moreover, to verify the statements in the publications of Dauber and Span (2011, 2012), comparisons of equations of state often used in industry with the new experimental values were carried out as well. In most cases, the ERKM method and the GERG-2008 equation showed the best agreement with the experimental values, whereas the COSTALD correlation and for instance cubic equations showed no good agreement with the new experimental values.

After density measurements on these six LNGs were completed, further modifications of the cryogenic densimeter were carried out. The first part of the modifications concentrated on exchanging the remaining components made of Inconel 600 with equivalent components made of Inconel 625. Thereby, the force transmission error of the magnetic suspension coupling was reduced to $+12$ ppm at cryogenic temperatures. The second part of the modifications focused on the reduction of the large leakages in the area between the measuring cell and the VLE-cell. Therefore, a revised new VLE-cell was fabricated. Thus, density measurements of up to 12 MPa are now possible. Finally, the third part of the modifications aimed to reduce the diffusion of the mixture components between the measuring cell and the VLE-cell. For this purpose, the connecting tube was replaced by a longer tube with a smaller inner diameter. To validate the modifications, density measurements of
three different pure substances (methane, nitrogen, and argon) were performed in the temperature range between $T = (100$ and $298.15) \text{ K}$ with pressures of up to $8 \text{ MPa}$. Comparisons to the respective equations of state and experimental reference data were carried out. In general, the relative deviations of the experimental values from values calculated with the reference equations of state are within the uncertainties reported by the authors.

Since the range of application of the ERKM method is still limited, developing a fundamental equation of state, which can be used for the prediction of several thermodynamic properties across all fluid states. Therefore, the density of four (methane + hydrocarbon) mixtures and three different (methane + nitrogen) mixtures was measured over the temperature range of $T = (100$ to $180) \text{ K}$ with pressures from $p = (0.2$ to $10) \text{ MPa}$. Due to the modifications of the cryogenic densimeter, the relative combined expanded uncertainty ($k = 2$) for all measurements was reduced to $0.020\%$. The experimental results were compared with the GERG-2008 equation of state, the enhanced revised Klosek and McKinley method and the COSTALD correlation and equations of state frequently used in industry. Generally, the experimental values agree most exactly with the GERG-2008 equation of state for all investigated binary mixtures, whereas for all other investigated equations no good agreement could be identified. Based on the measurements of binary mixtures carried out in this work, Thol (2017) improved binary specific functions of the default GERG-2008 equation of state of Kunz and Wagner (2012). In contrast to Thol (2017), Rowland et al. (2016) only improved the (methane + butane) binary-specific function of the default GERG-2008 equation. Compared to the default GERG-2008 equation of state, the two modified GERG-2008 equations represent the results for the different LNGs much better. The modified GERG-2008 equation (EOS-LNG) described by Thol (2017) showed an even better agreement with the experimental values, as the equation of Rowland et al. (2016) does.

For future work, the cryogenic densimeter will be used within the scope of an EU project. The overall aim of this project is to enable the large scale roll-out of LNG and LBG as a transport fuel. Therefore, physical and chemical measurements (e.g., density) to accurately define each LNG/LBG mixture are needed. Nevertheless, more accurate experimental data are required to improve the GERG-2008 equation of state. According to Thol (2017) the (methane + isopentane) system as well as higher hydrocarbon system (e.g., ethane + butane), except for the (propane + n-butane) system where sufficient data are available, would be extremely useful.