

Vapor-Liquid-Equilibria of Pyrolysis Oils

For a better Understanding of the Condensation Process in Fast Pyrolysis

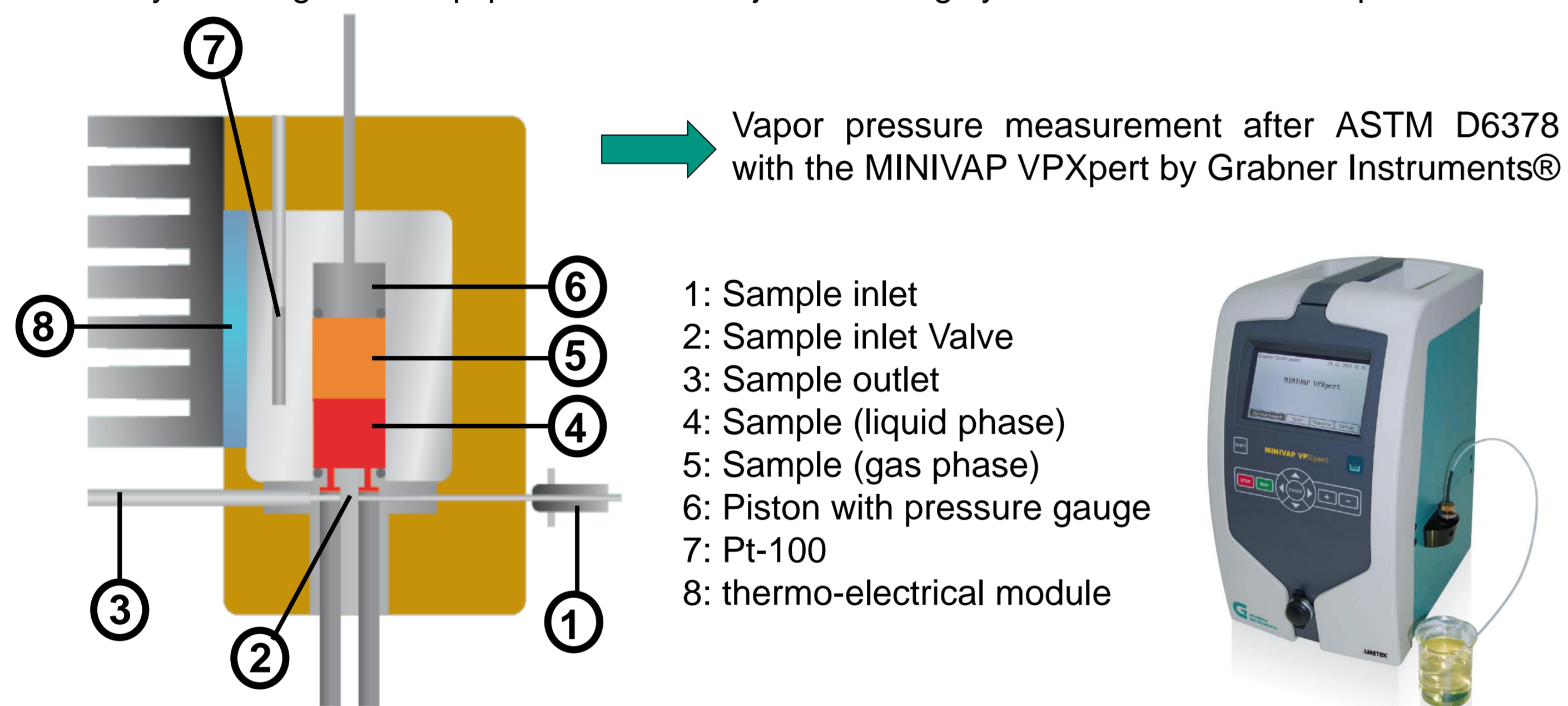
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Motivation and Aims

- For a maximum liquid yield, the pyrolysis vapors must be condensed and cooled down as fast as possible. In a fractional condensation, the adjustment of the composition of each stage is essential.
- Pyrolysis oils and vapors are complex mixture with several hundreds of different compounds. The definition of a model mixture and the calculation of physical properties is due to the partly unknown molecules and aging processes very difficult.
- Main problem in the modelling of the condensation of pyrolysis vapors is the lack of experimental phase equilibrium data and therefore the unknown accuracy of any used model.
- Aim of this work is to generate experimental data. Therefore methods must be found/developed that suit the special challenge of pyrolysis oils.

Vapor pressure measurement

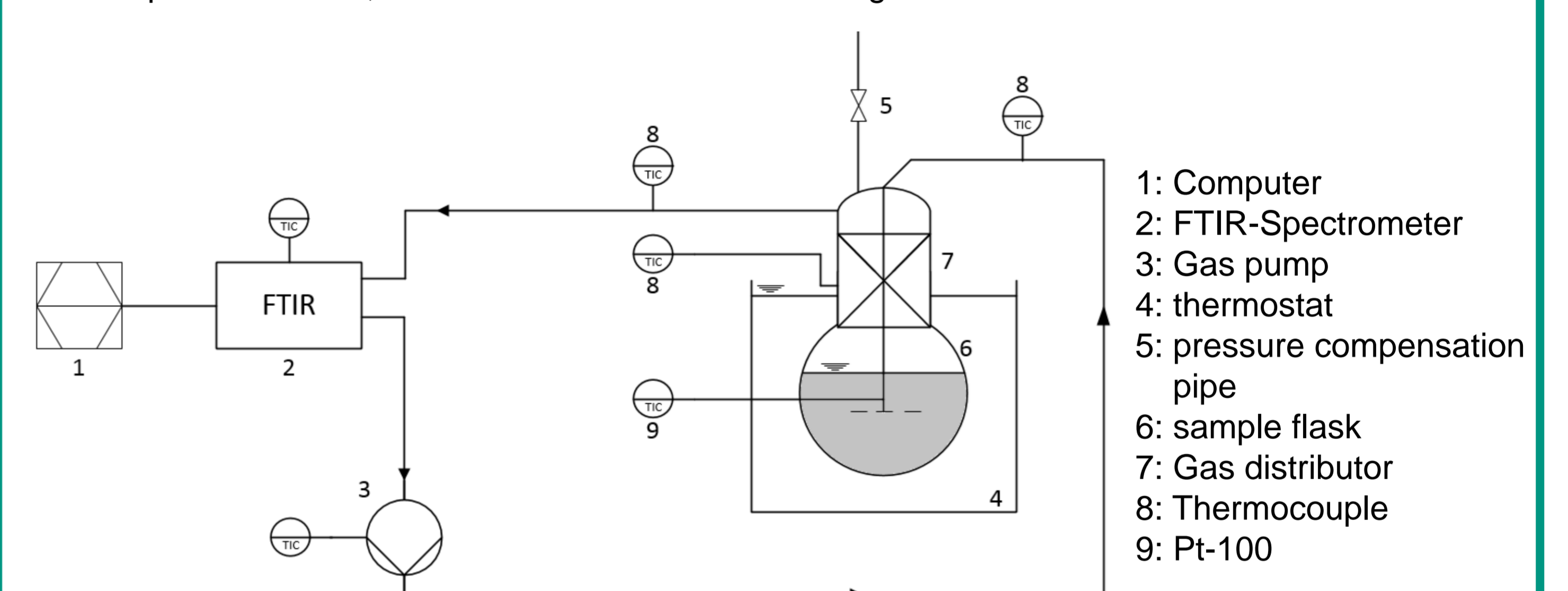
- Pyrolysis oils are wide boiling mixture. Applying vacuum to such a system would lead to a significant change in the composition and is therefore no option.
- A sample preparation concerning solute gases is problematic for the same reasons.
- Easy cleaning of the equipment and the injection of highly viscose oils has to be possible



- Static phase equilibrium cell with a sample volume of 1ml
- Temperature range from 0 to 120 °C
- Pressure range up to 10 bar
- Simple rinsing and multiple measurement
- Crude oil package for highly viscose liquids
- No sample preparation due to the triple expansion method

Activity coefficient measurement

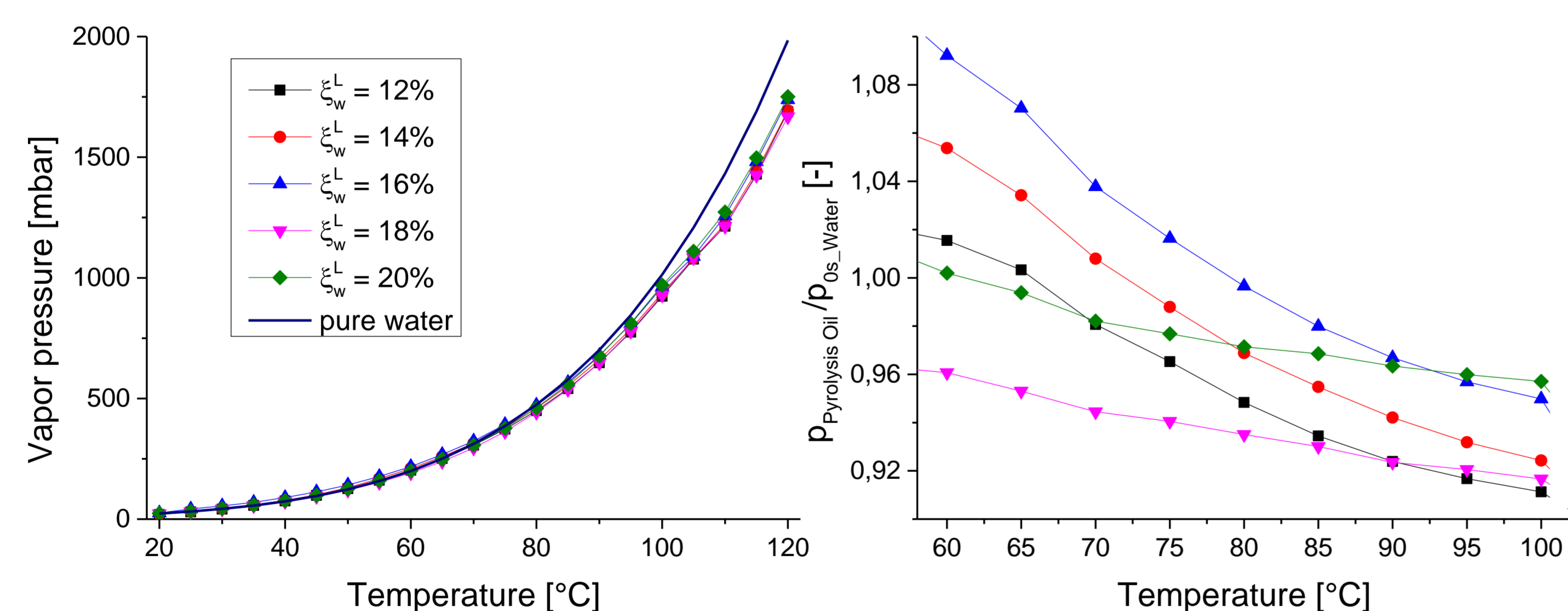
- In multicomponent mixtures, spectroscopic methods can be difficult due to the interference of the different signals
- In-situ measurement is preferable to a sampling
- In optical methods, a contamination of the measuring cell must be avoided



- Dynamic phase equilibrium cell with a sample volume of 250 ml
- Operation at atmospheric pressure through a pressure compensation pipe
- Temperature range from 5 to 80 °C
- Recording of the spectrum at 110 °C
- Thanks to the strong IR activity of water, the evaluation of the spectrum for water is always possible

Vapor pressure results

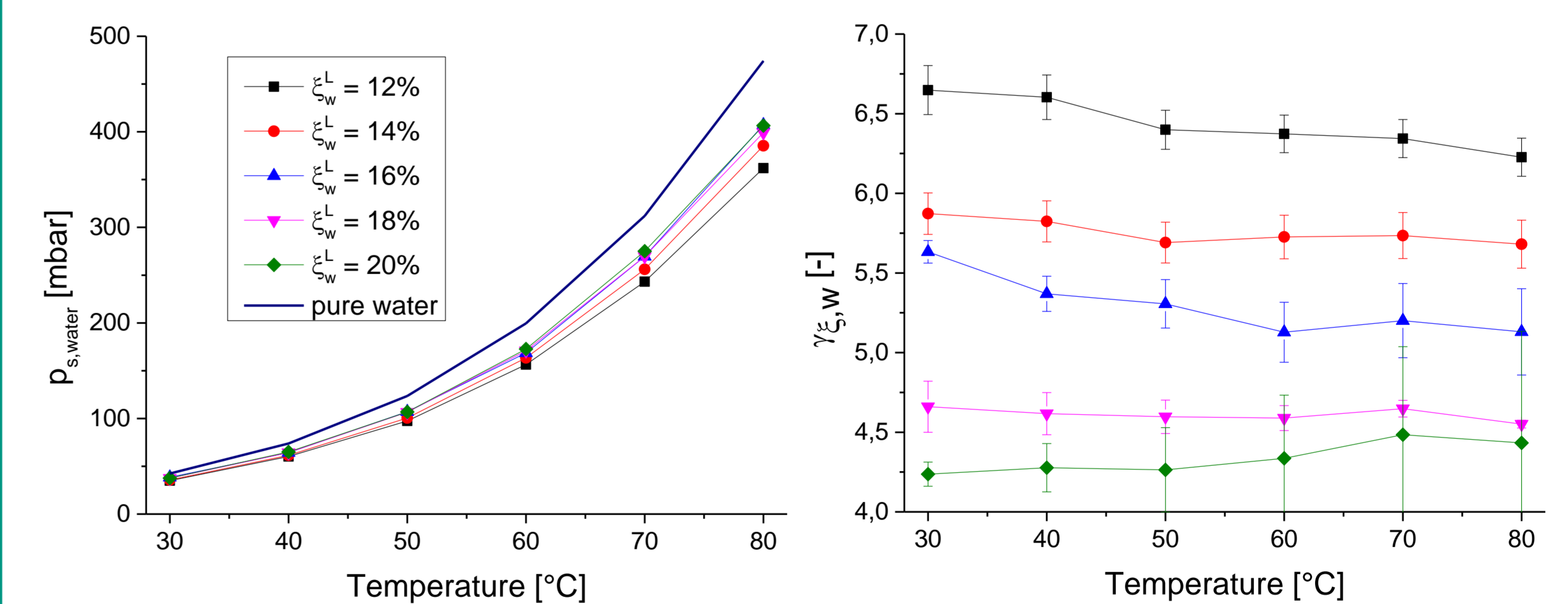
- Samples: Pyrolysis oils from the bioliq® campaign spring 2015 condensed at 80 °C
- Adding of more water for a different water contents



- In first order, the vapor pressure of pyrolysis oil can be approximated with water
- At low temperatures, the lower boiling components lead to a higher vapor pressure than the saturation vapor pressure water
- At high temperatures, the vapor pressure shows no exact exponential behaviour due to reactions

Activity coefficient results

- Same samples as in the vapor pressure measuring
- Water content is measured before and after with Karl-Fischer titration



- Mass related activity coefficients of water are strongly increased ($>>1$)
- The activity coefficients fall with higher water contents
- Phase separation at higher water contents leads to high uncertainties in the measured water content

Conclusion and Outlook

- Experimental methods for the investigation of the phase behaviour of pyrolysis oil have been developed and tested
- First results of the real phase behaviour of pyrolysis oil show an increased activity coefficient of water with the result of a phase separation at about 18 % water
- Comparing data of different pyrolysis oils from different campaigns
- Using the experimental values to validate and adapt the modeling
- Measuring of actual model mixtures for pyrolysis oils has to be done

Cooperation partner:



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