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Vapor-Liquid-Equilibria of Pyrolysis Oils

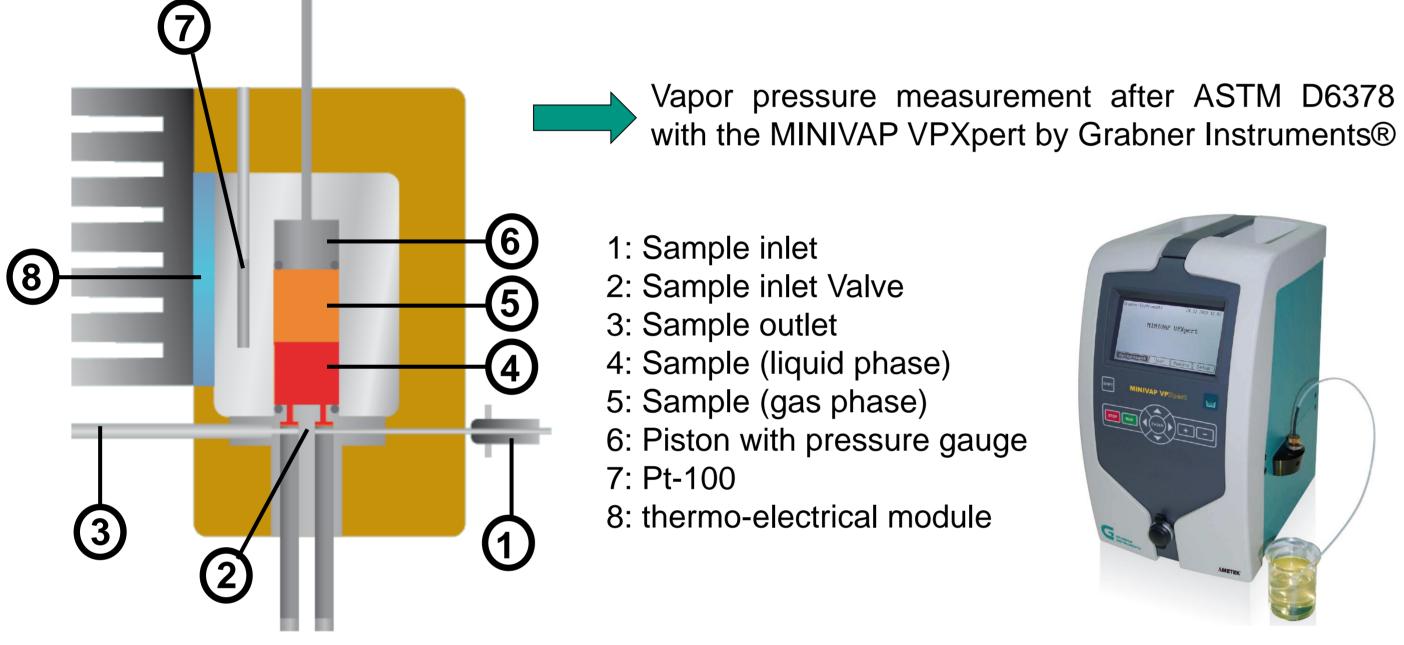
For a better Understanding of the Condensation Process in Fast Pyrolysis Y. Ille^{1,2}, N. Dahmen¹, K. Schaber²

Motivation and Aims

- possible. In a fractional condensation, the adjustment of the composition of each stage is essential. experimental phase equilibrium data and therefore the unknown accuracy of any used model.
- 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.
- For a maximum liquid yield, the pyrolysis vapors must be condensed and cooled down as fast as 🕒 Main problem in the modelling of the condensation of pyrolysis vapors is the lack of
 - 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

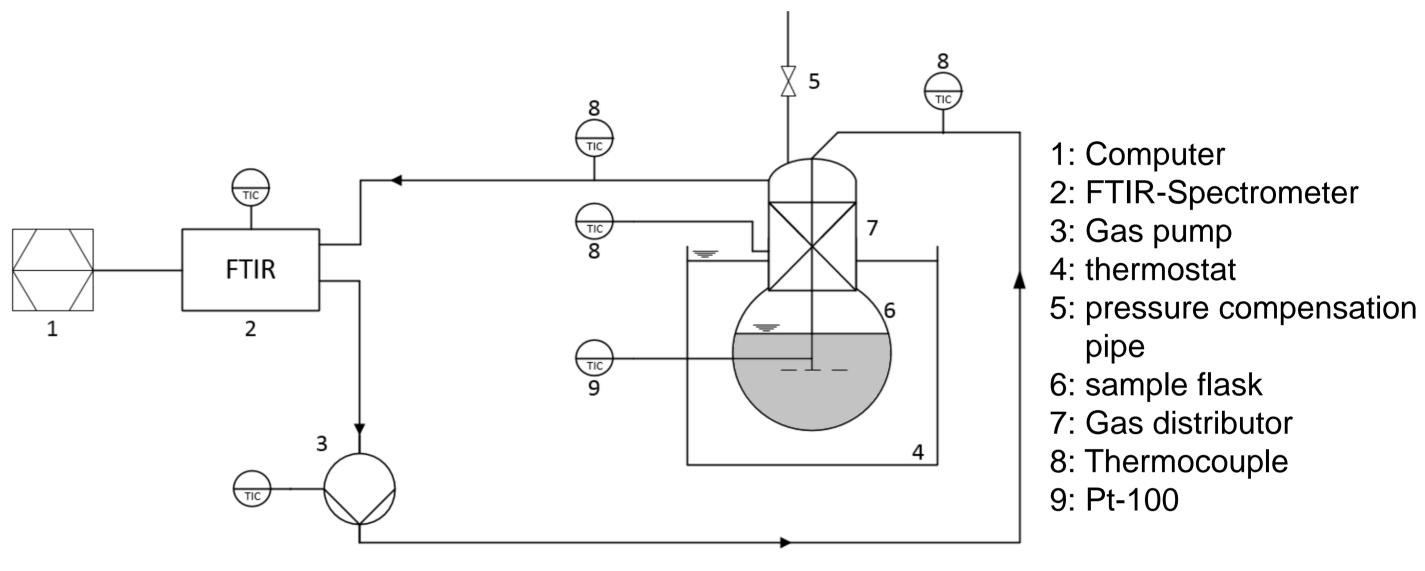




- Static phase equilibrium cell with a sample volume of 1ml
- Temperature range from 0 to 120 °C
- Pressure range up to 10 bar
- Simple rinsing and multiple measurement
- Crude oil package for highly viscose liquids
- No sample preparation due to the triple expansion method

Activity coefficient measurement

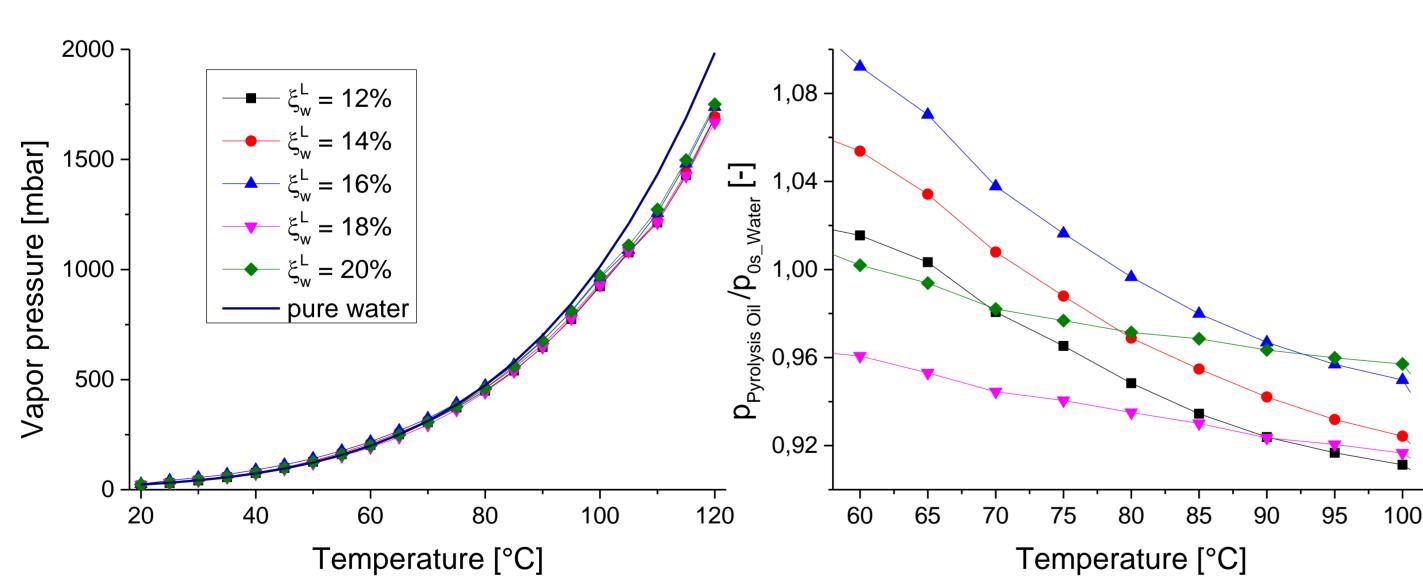
- In multicomponent mixtures, spectroscopic methods can be difficult due to the interference of the different signals
- In-situ measurement is preferable to a sampling
- In optical methods, a contamination of the measuring cell must be avoided



- 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

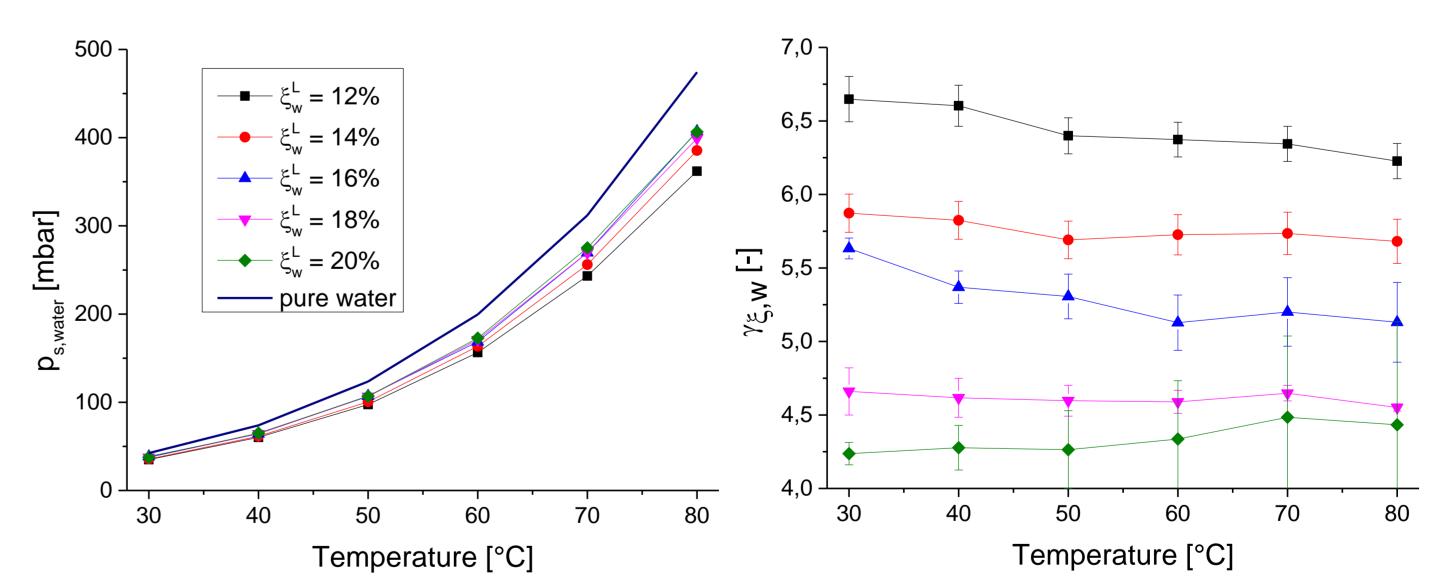
- Samples: Pyrolysis oils from the bioliq® campaign spring 2015 condensed at 80 °C
- Adding of more water for a different water contents



- 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 bean
- 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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