

Stabilization of pyrolysis oils by solvent additions

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► Motivation

- FPBO (fast pyrolysis bio oil) changes its composition and thereby its properties over time. This aging process can be measured by aldehyde decrease.
- Usual stabilization methods of FPBO deploy modifications by the addition of alcohols or other organics.
- Carbon dioxide can be an alternative additive for conditioning.

► Aging & Analytics

1. Aging of FPBO is related to the reactivity of its components.
 2. Aldehydes belong to the most reactive components.
- Therefore, aging can be observed by the decrease of the aldehyde concentration.

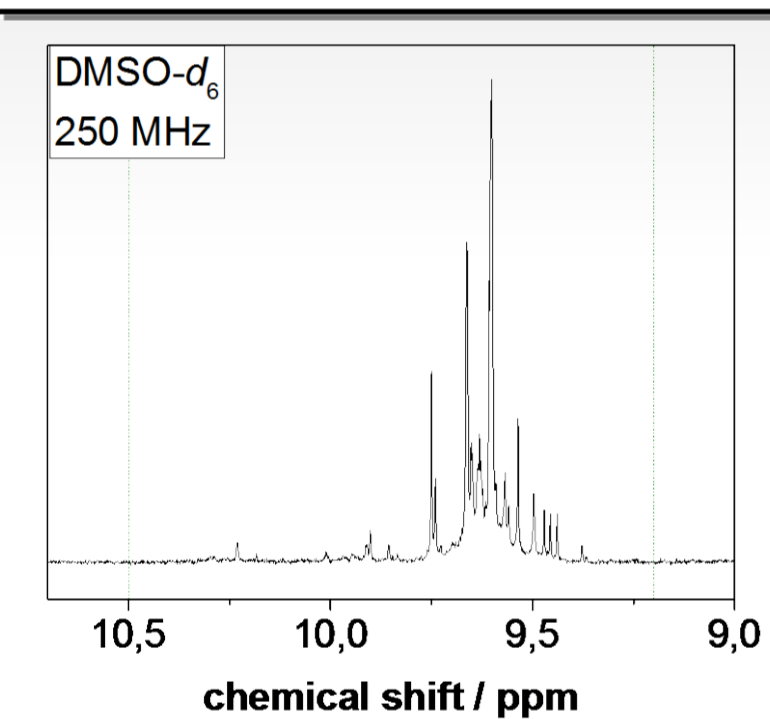
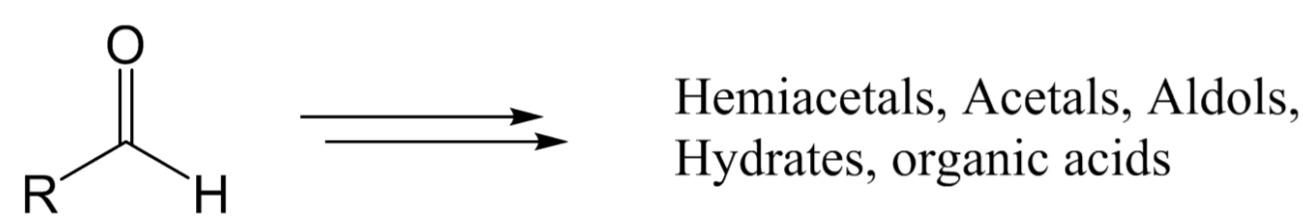


Fig. 1: ¹H-NMR spectrum for the aldehyde region for beech wood FPBO measured in DMSO-d₆

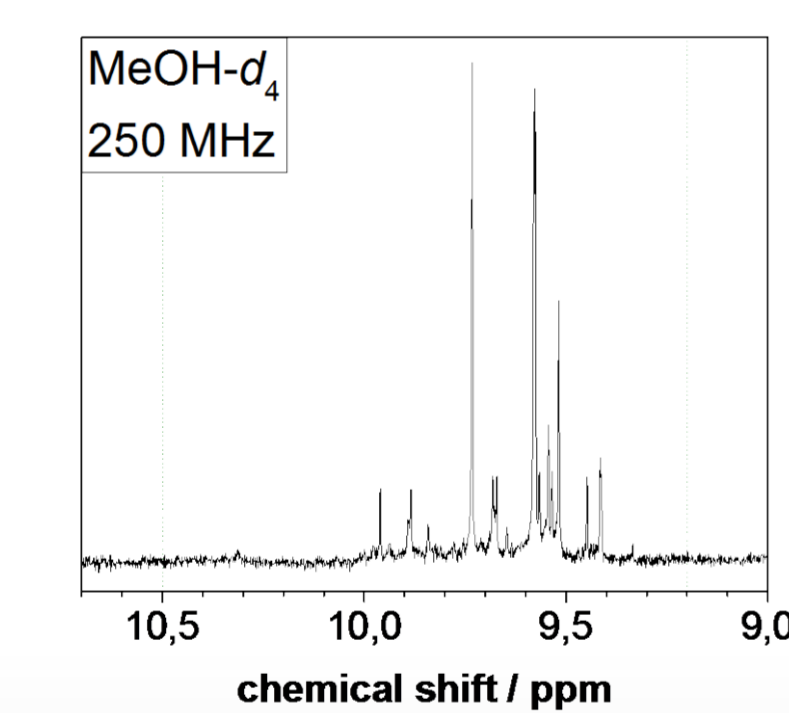


Fig. 2: ¹H-NMR spectrum for the aldehyde region for beech wood FPBO measured in MeOH-d₄

- Aldehydes can be quantified by a ¹H-NMR method.
- Due to the inactivity of aldehydes with DMSO, spectra recorded in DMSO-d₆ exhibit a higher S/N ratio compared to spectra in MeOD-d₄.
- An exponential decline of the aldehyde concentration in FPBO during the aging could be observed.

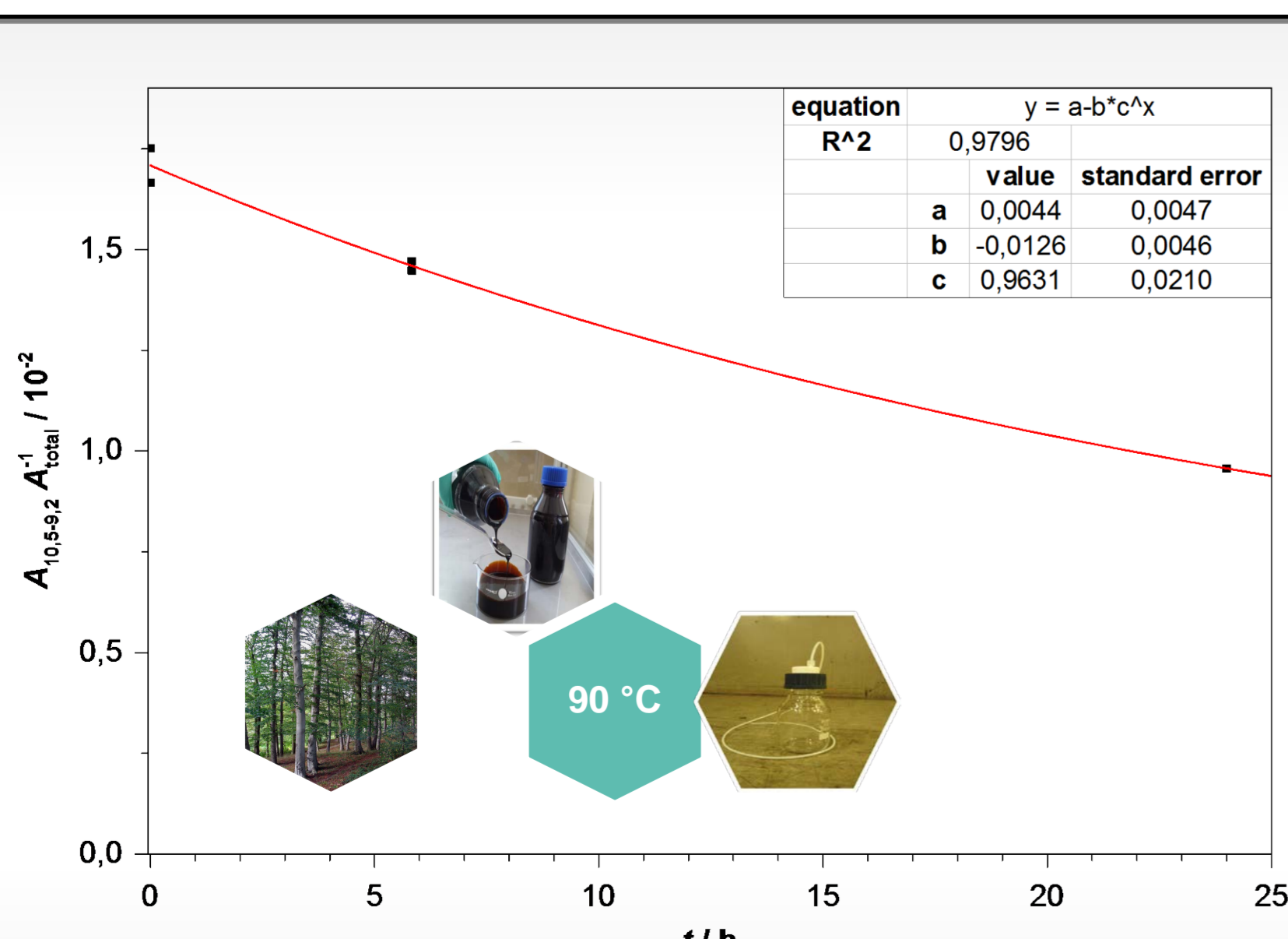
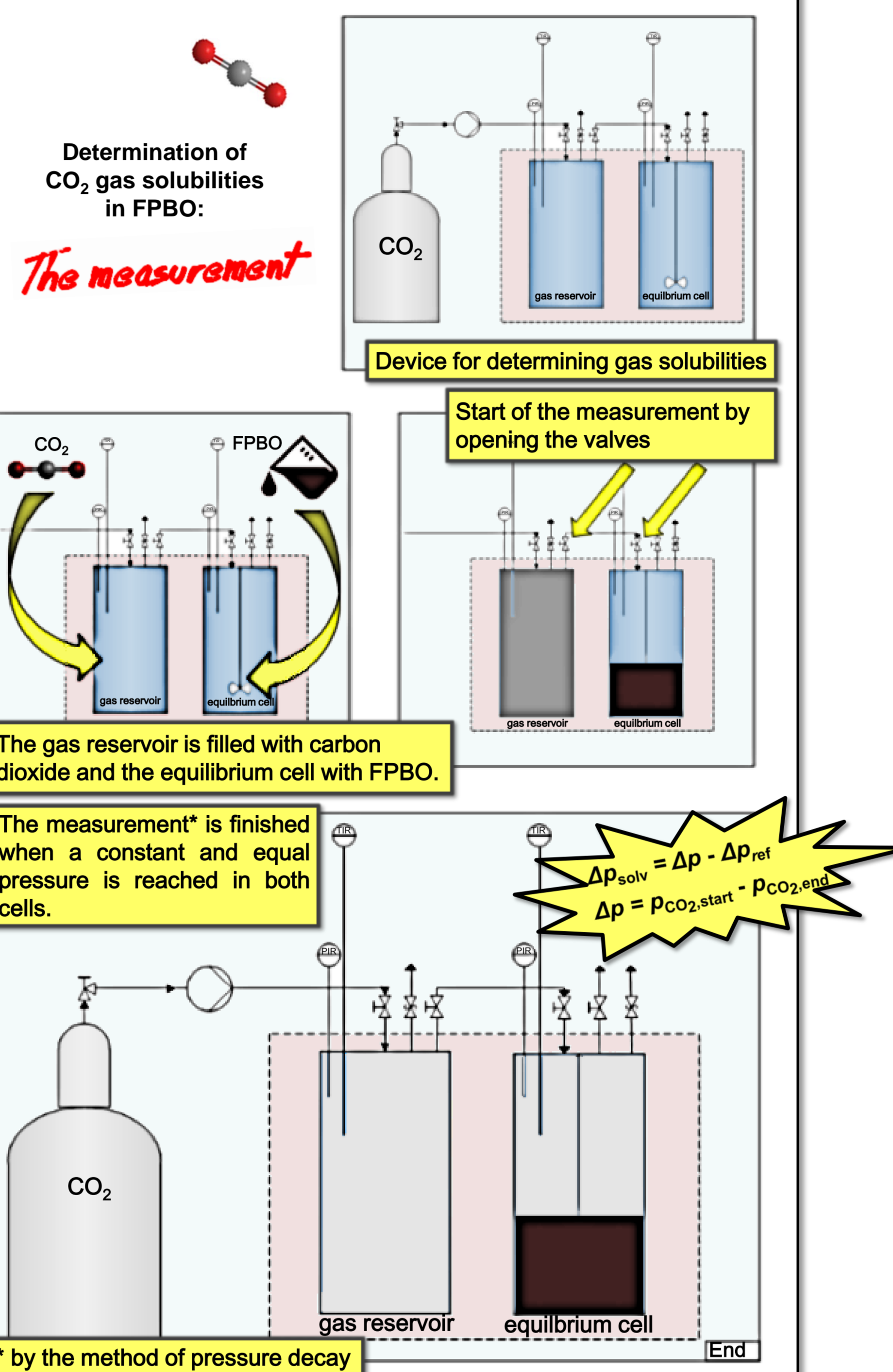


Fig. 3: Decline of the aldehyde concentration during the aging of beech wood FPBO measured by ¹H-NMR in DMSO-d₆

► Carbon Dioxide Gas Addition



- FPBO consists of many substances that can solve CO₂.
- Experimentally the CO₂ gas solubility in the multi component mixture FPBO can be determined by the method of pressure decay.
- FPBO with solved CO₂ shows a significant reduction of the viscosity.

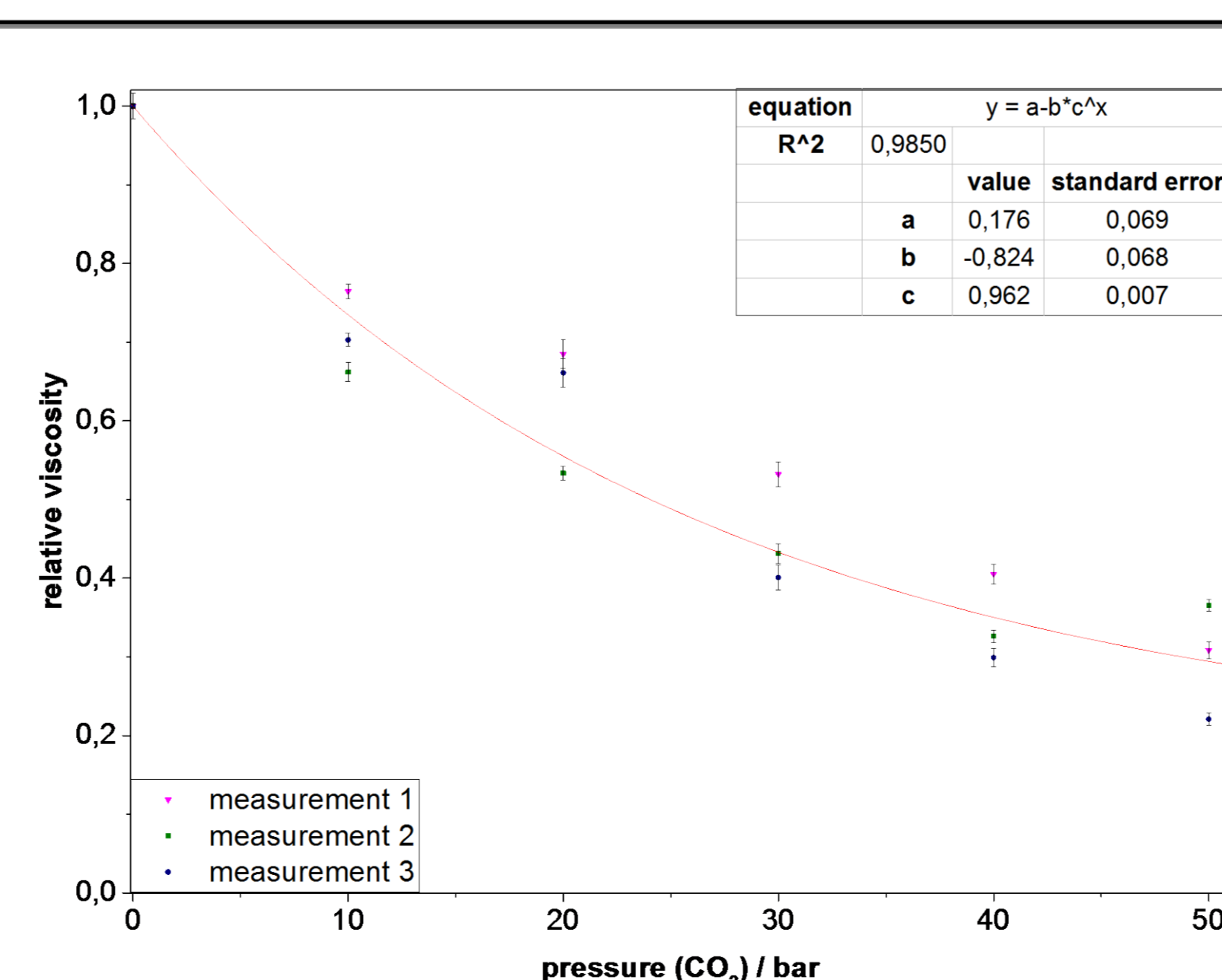
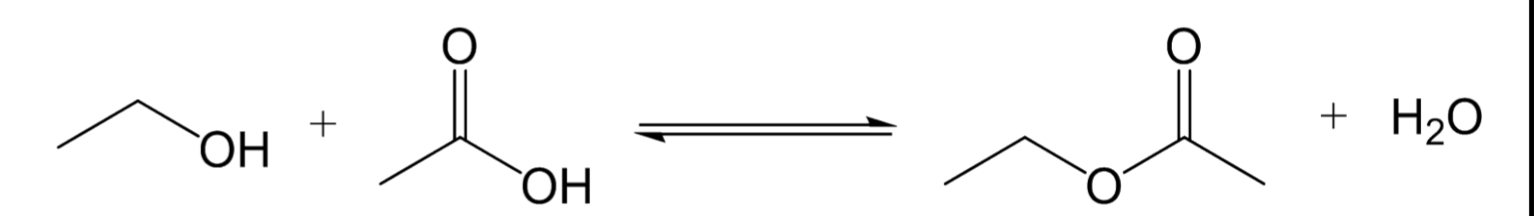


Fig. 4: Viscosity decrease induced by carbon dioxide addition

► Esterification

1. Dilution with alcohols lead to an esterification in pyrolysis oils.
 2. By esterification the acids are decomposed and the viscosity of the FPBO is reduced.
- Alcohol additions lead to a lower pH value, but enhance corrosion.



Metal corrosion

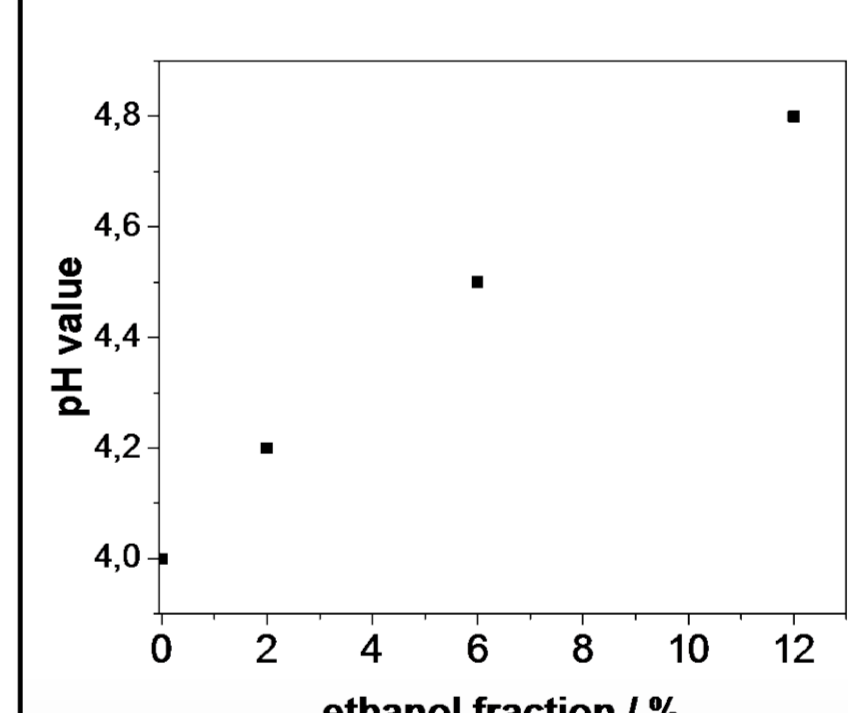


Fig. 6: Relationship between pH value and ethanol addition

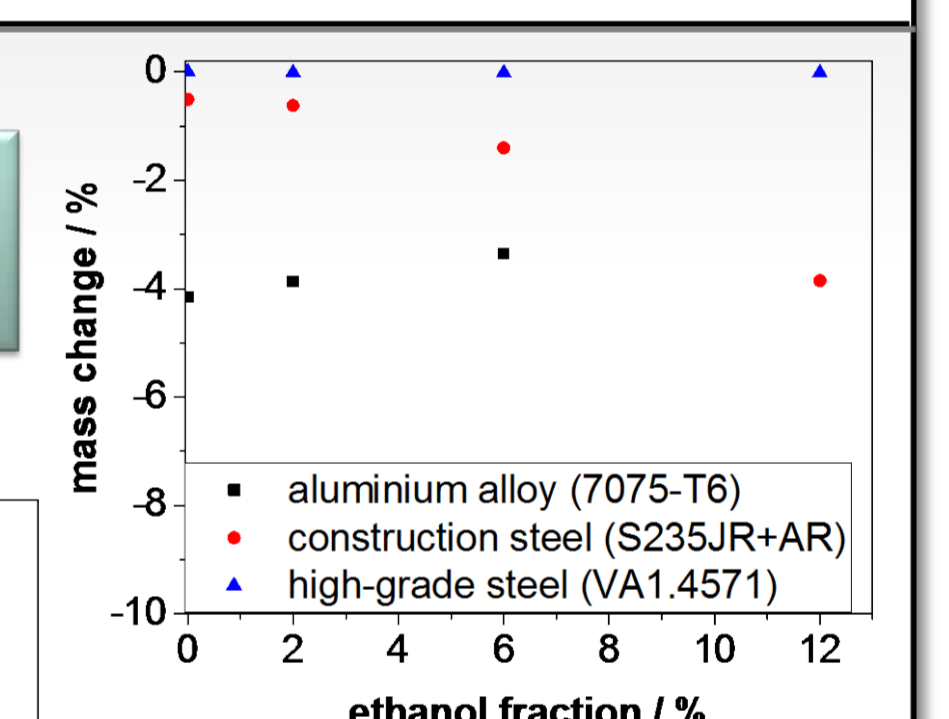


Fig. 5: Relationship between corrosion, measured as the mass change of metal plates, and ethanol addition

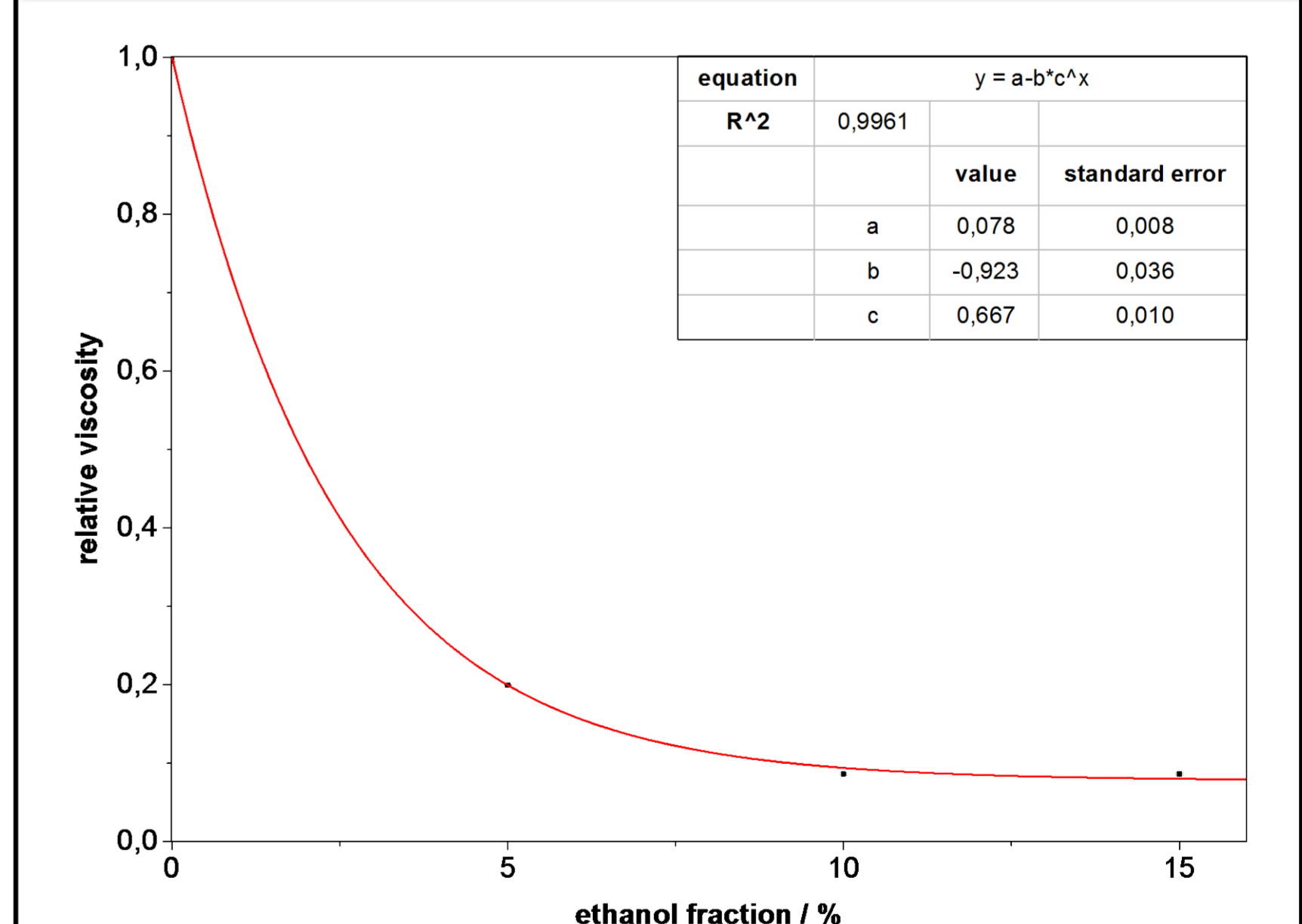
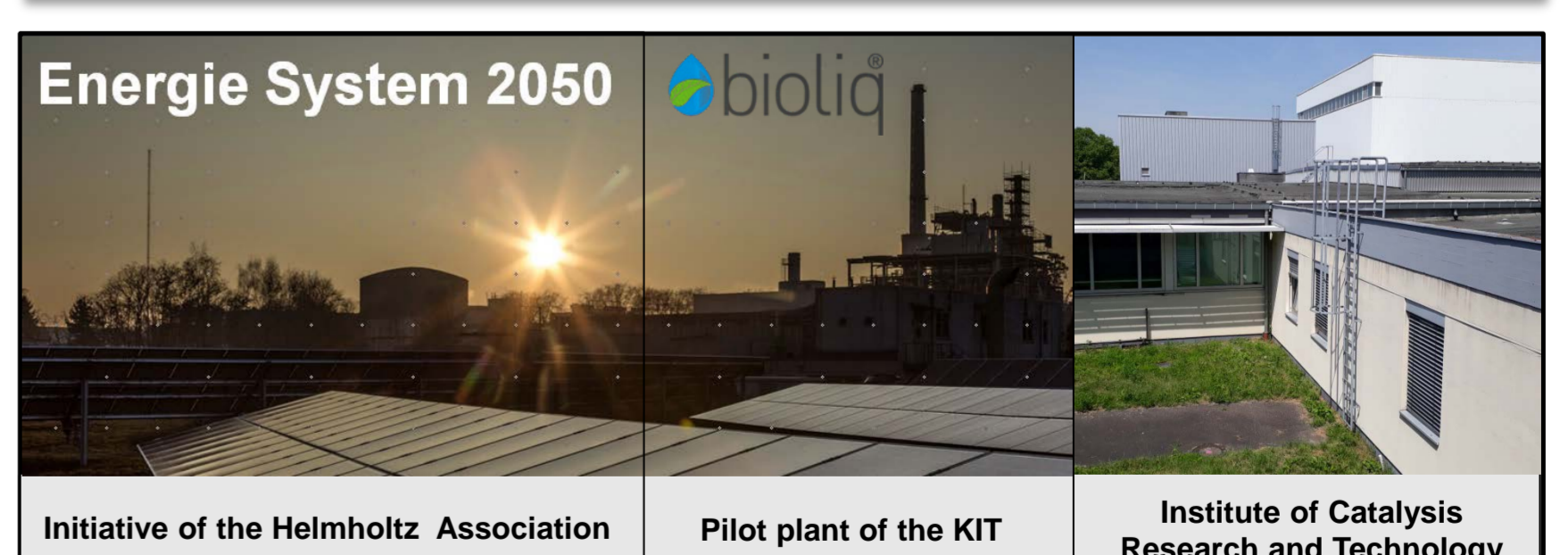


Fig. 7: Viscosity decrease induced by ethanol addition



Thank you
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References

M. Riazi *J. Pet. Sci. Technol.* 1996, 14, 235-250