

Stabilization of pyrolysis oils by solvent additions

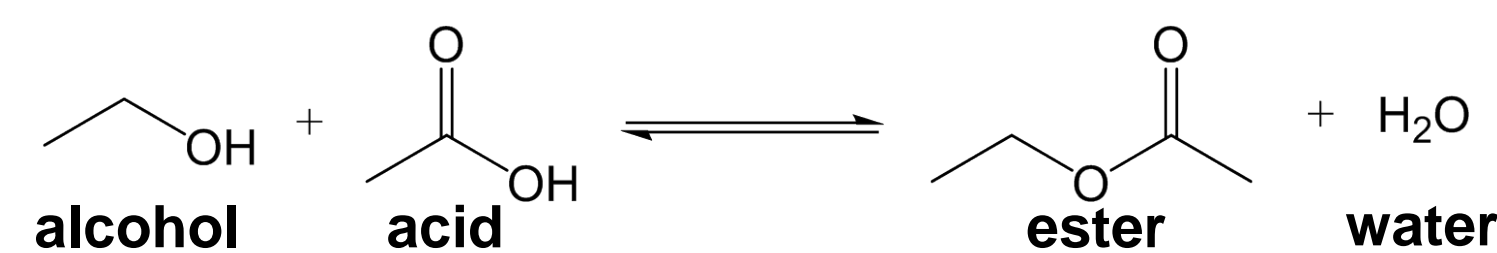
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Motivation

Fast pyrolysis bio oils (FPBO) can consist of more than 300 substances. Because those liquids are not in thermodynamic equilibrium components tend to react with each other and change their properties (aging). The addition of different solvents like alcohols and carbon dioxide can improve their properties. For the detection of their effectiveness, reliable analytical procedures and methods are required.

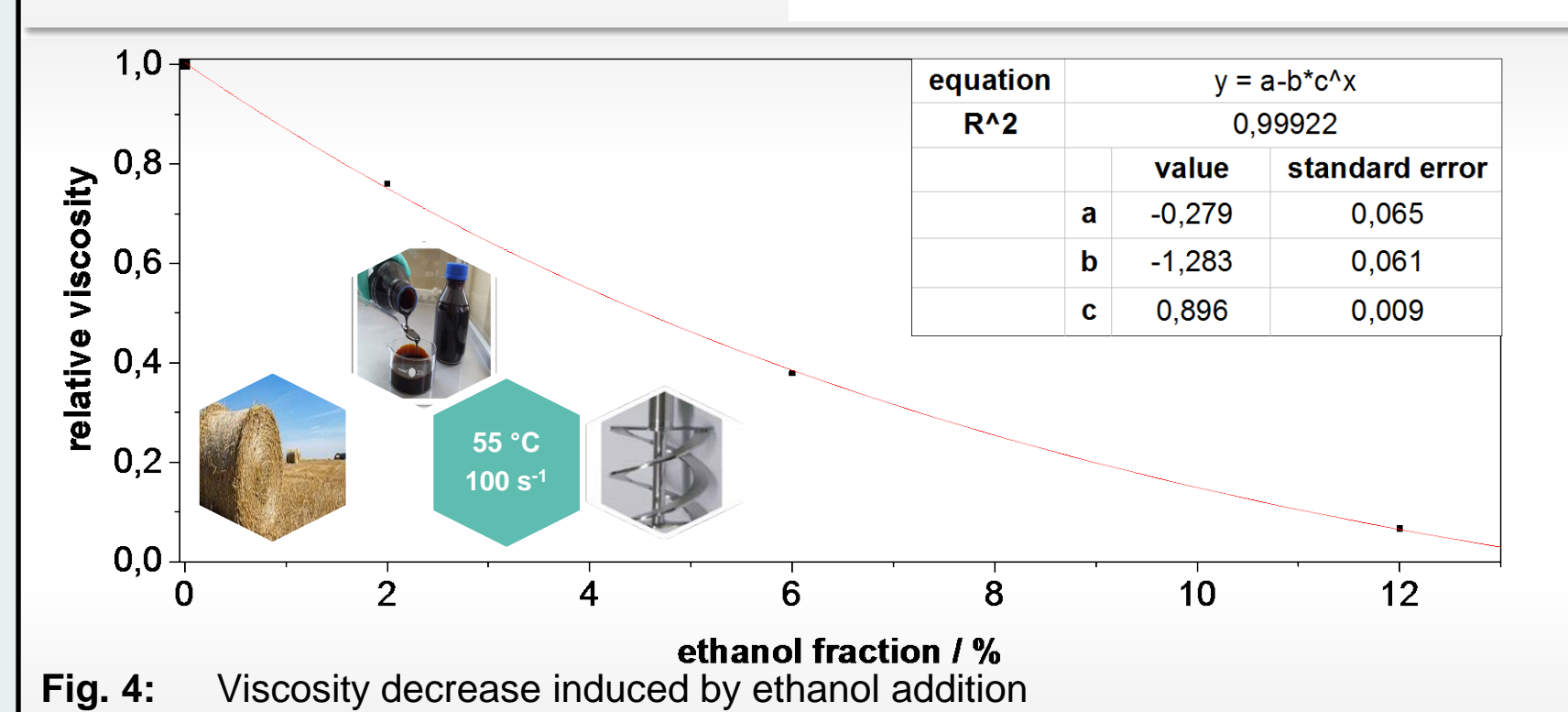
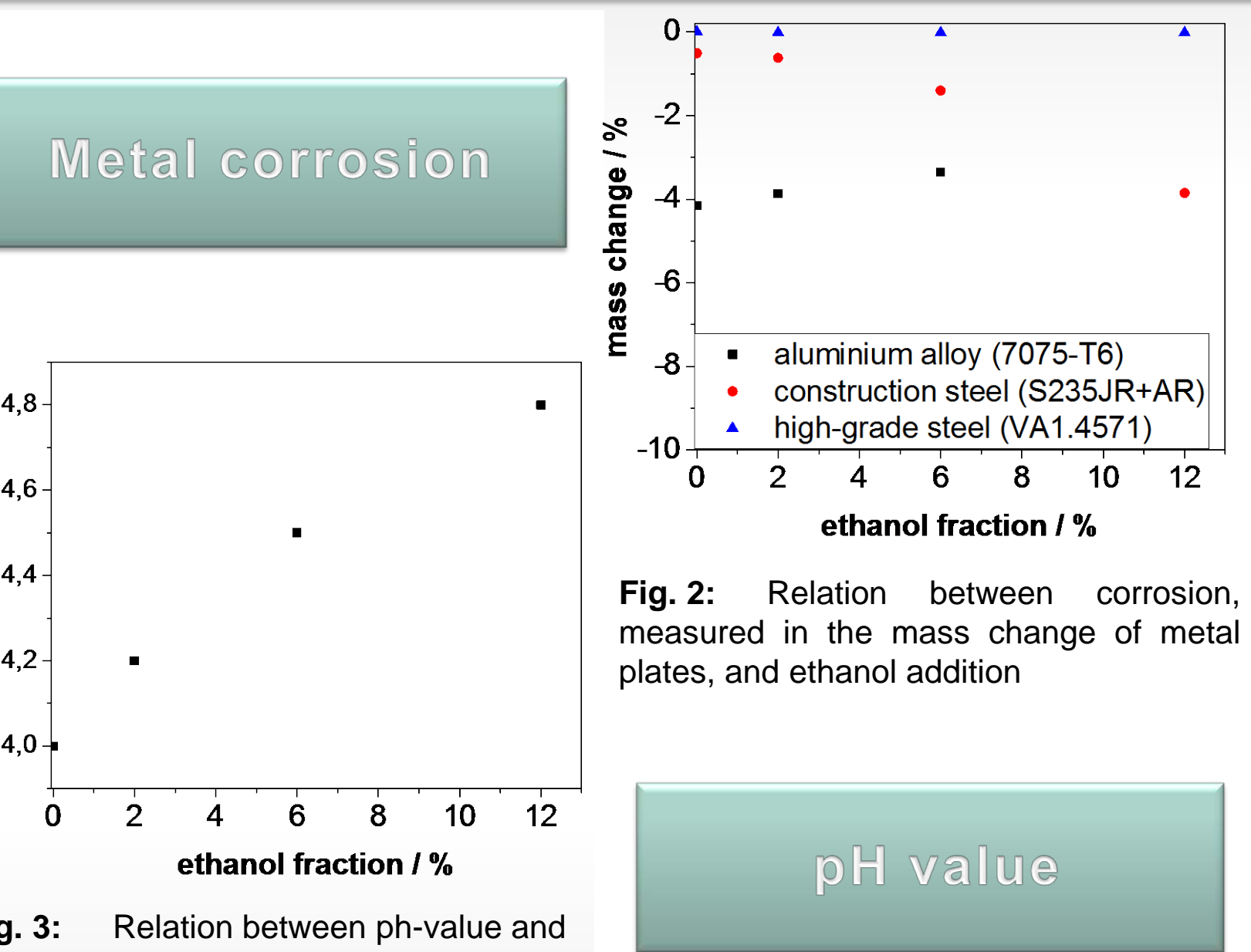
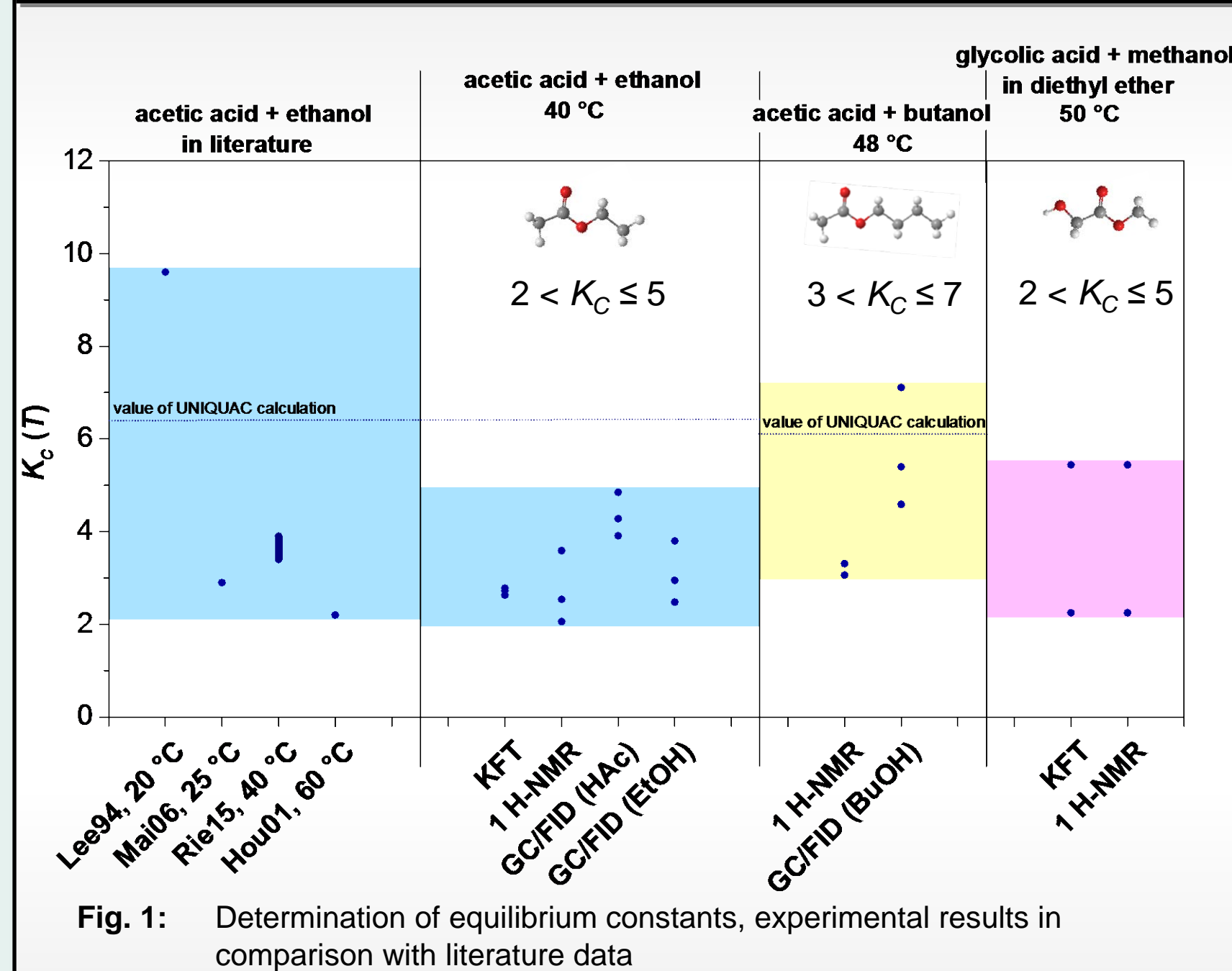
Esterifications

Esterifications are an often applied treatment for the stabilization of FPBO. Here the FPBO is mixed with an alcohol of a low molecular weight, so that the acidic components can react with the alcohol.

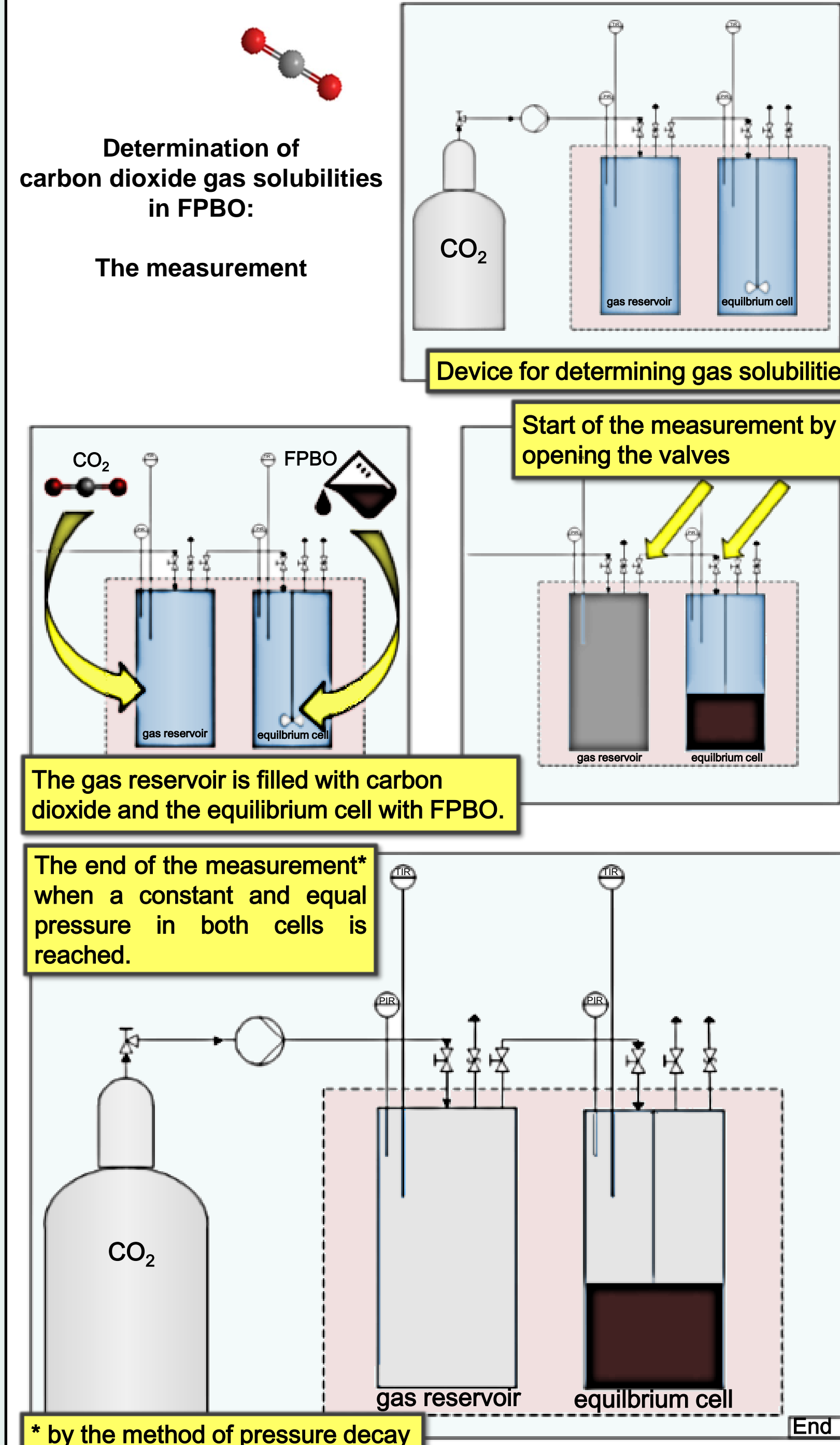


For elucidating the frame of this treatment the equilibrium constants of different esterifications were investigated (Fig. 1). They are in the magnitude of 1-10.

The dilution of FPBO with ethanol leads to a reduced viscosity and pH value of the blend, but an enhanced corrosion (Fig. 2 - Fig. 4).



Carbon Dioxide Gas Solubility



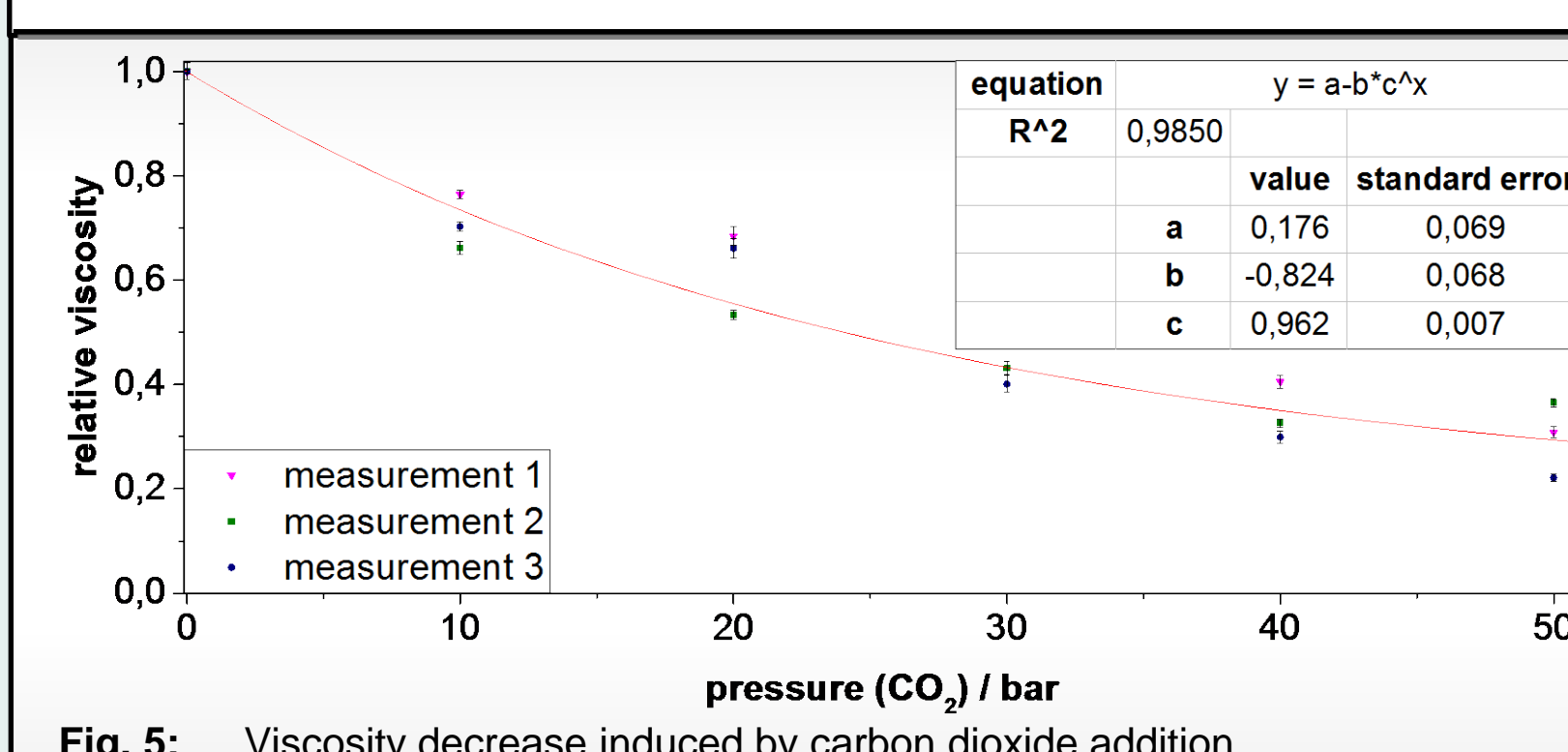
Carbon dioxide is known as a non-toxic and cheap solvent. Blends of FPBO with carbon dioxide can probably be filtrated, gasified and hydrodeoxygenated simpler. It is also discussed as a solvent for extracting valuable substances of FPBO.

For a targeted deployment the knowledge of the carbon dioxide solubility is useful. It can be measured by the method of pressure decay (see above).

$$\Delta p = p_{\text{CO}_2, \text{start}} - p_{\text{CO}_2, \text{end}} \quad (1)$$

$$\Delta p_{\text{solvl}} = \Delta p - \Delta p_{\text{ref}} \quad (2)$$

Moreover the viscosity of FPBO can be reduced significantly (Fig. 5).



Aging & Analytics

Aging of FPBO leads to undesired changes regarding its properties and composition. Very reactive compounds in FPBO are aldehydes that are degraded by aging. Their concentration is small and so are the concentration changes. Hence, the analytical detection of this process is difficult.

By ¹H-NMR the aldehydes can be detected at 9.2-10.5 ppm. If the signal/noise ratio is high they can be quantified additionally. Measurements in MeOH-*d*₄ and DMSO-*d*₆ allow the detection of different aldehydes. In the case of MeOH-*d*₄ probably the aldehydes are reacting by acetylation and lower the signal/noise ratio. By measurements in DMSO-*d*₆ an exponential degradation process could be proven.

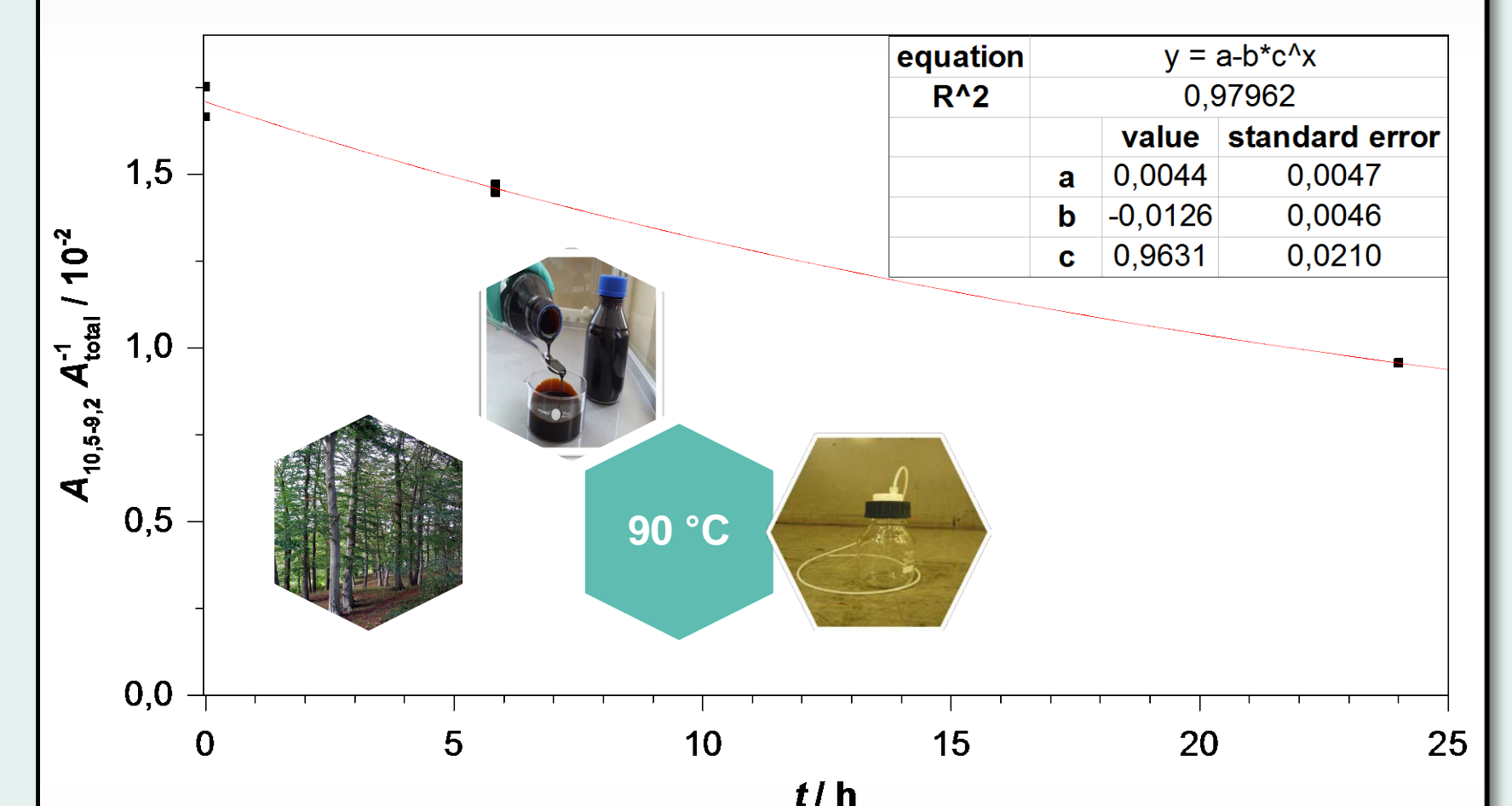
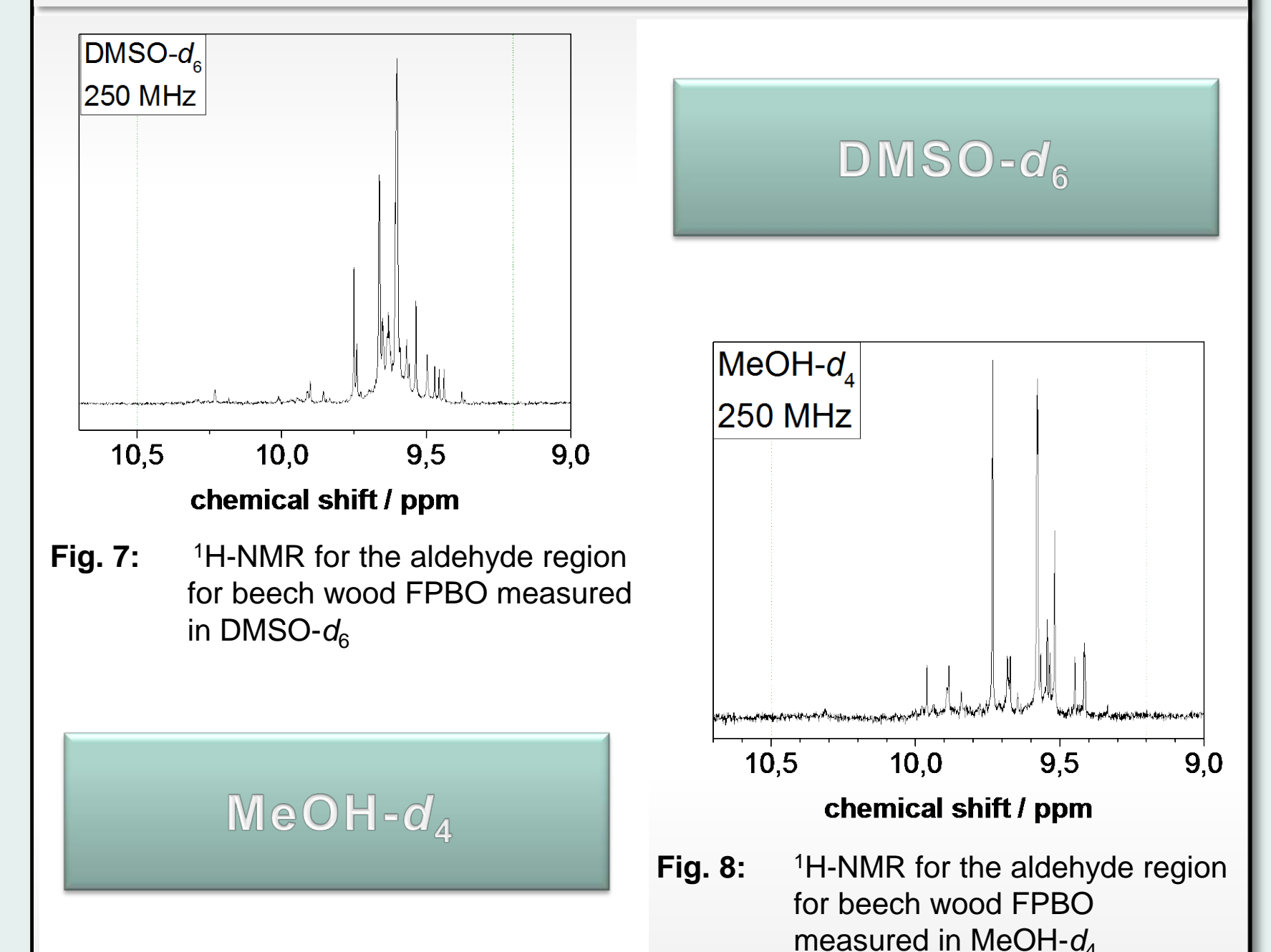


Fig. 6: Declination of aldehydes by aging of beech wood FPBO measured by ¹H-NMR in DMSO-*d*₆



References

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