

# Messung von Hydrierkinetiken flüssiger Wasserstoffträger (LOHC)

## Measurement of hydrogenation kinetics of liquid organic hydrogen carriers

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### Abstract

Liquid Organic Hydrogen Carrier (LOHC) have attracted attention in recent years as an attractive technology for chemical energy storage and hydrogen transportation. LOHC stores hydrogen at ambient conditions with a high volumetric density. The LOHC-concept is based on a reversible hydrogenation and dehydrogenation reaction of an aromatic compound. Thus, for design and scaling of LOHC-systems, knowledge about the reaction kinetics of the hydrogenation and dehydrogenation of LOHC is crucial. LOHC material, which is currently under research are toluene, N-ethylcarbazole and dibenzyltoluene.

This work focusses on the hydrogenation of LOHC. Primarily, an experimental setup is developed to study reaction kinetics of hydrogenation in the liquid phase. The main part of it is an autoclave, which allows operation at temperatures up to 573 K and pressures up to 25 MPa. As a specialty, the analysis of the liquid phase is carried out with in-situ Raman-spectroscopy. Therefore, the laser beam is focused with a fiber optical probe into the autoclave. The Raman-spectroscopy allows continuous samplings times lower than 30 s and is noninvasive. A method to obtain concentrations of the reaction mixture from Raman-spectra is presented. To put the autoclave into operation, the hydrogenation of 1-octene is analyzed. The results show a good agreement with data reported in literature.

Furthermore, the hydrogenation of toluene and N-ethylcarbazole were studied. Both reactions were carried out with pure substances and in the liquid state. During hydrogenation of toluene almost no intermediates were found. This system was used to compare two modelling approaches for the reaction kinetics, the classic kinetic model, and the thermodynamic kinetic model. The analysis of the much more complex hydrogenation of N-ethylcarbazole showed a stepwise reaction forming the intermediates tetrahydro-N-ethylcarbazole and octahydro-N-ethylcarbazole. The fully hydrogenated form of N-ethylcarbazole, perhydro-N-ethylcarbazole, forms three stereoisomers during the hydrogenation. The reaction process of all components, including the isomers, were monitored and the reaction parameters determined. Using the kinetic models, the measured reaction process could be well described. The analysis of the reaction kinetic showed, that temperatures above 448 K do not lead to an enhancement of the reaction rate. In experiments at temperatures above 448 K bicyclohexyl as a decomposition product was found. Most likely, amines were formed due to the decomposition, which deactivated the catalyst.