



## Experimental study and model of reaction kinetics of heterogeneously catalyzed methylal synthesis

Jan-Oliver Drunsel<sup>a</sup>, Mario Renner<sup>b</sup>, Hans Hasse<sup>a,\*</sup>

<sup>a</sup> Laboratory of Engineering Thermodynamics, University of Kaiserslautern, Erwin-Schrödinger-Straße 44, 67663 Kaiserslautern, Germany

<sup>b</sup> Ineos Paraform GmbH, Hauptstrasse 30, 55120 Mainz, Germany

### A B S T R A C T

Reaction kinetics of the heterogeneously catalyzed formation of methylal from aqueous methanolic formaldehyde solutions are studied in a plug flow reactor at 323, 333 and 343 K using the acidic ion exchange resin Amberlyst 15 (Rohm and Haas) as catalyst. Parameters of an activity-based pseudo-homogeneous reaction kinetic model are fitted to the experimental results. The model is based on the true speciation in the reacting solution and explicitly includes the oligomerization reactions of formaldehyde in aqueous methanolic solutions. The reaction kinetic model describes the experimental data well and is suited for process simulations in which both chemical reactions and phase equilibria have to be described simultaneously.

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### 1. Introduction

Methylal is an important chemical which can be used as a solvent or for producing concentrated formaldehyde-solutions (Lojewska et al., 2008). Recent studies have shown that it might also become an important resource in the production of fuel additives (Burger et al., 2010). Methylal is produced from methanolic formaldehyde solutions which typically also contain water from the formaldehyde-production process. The common process of methylal synthesis consists of a serial arrangement of a reactor in which the feed is converted using a heterogeneous acidic catalyst and a downstream separation sequence which is needed to separate the product from the unreacted educts and eventually from byproducts (see e.g. Göring et al., 2004; Kaufhold and Müller, 1982). One major disadvantage of that configuration results from the chemical equilibrium which limits the formaldehyde-conversion in the reactor. Realizing chemical reaction and separation within one apparatus using reactive distillation can overcome this limitation. Therefore, producing methylal by reactive distillation has been focus of research of different groups over the

last years (Kolah et al., 1996; Masamoto and Matsuzaki, 1994; Zhang et al., 2011).

The key to a successful design of such methylal processes is the detailed knowledge of the reaction kinetics. In order to keep thermodynamic consistency to phase equilibrium model, also reaction kinetics must be described by an activity-based model (Hasse, 2003). Moreover, it must be considered that the educt of methylal synthesis, the methanolic, aqueous formaldehyde solution, is itself a complex reacting solution in which oligomerization reactions occur (Hahnenstein et al., 1994). They have to be taken into account explicitly in developing predictive reaction kinetic models of reactions in which formaldehyde solutions are used as educts (Maiwald et al., 2006).

Masamoto and Matsuzaki (1994) carried out reaction kinetics experiments of methylal synthesis in a batch and tubular-fixed-bed-reactor at very low initial formaldehyde-concentrations (up to 0.051 g/g, initial methanol-concentrations between 0.2 and 0.6 g/g). The model these authors use to describe their experimental data is based on overall concentrations rather than on true speciation, i.e.

\* Corresponding author. Tel.: +49 631 205 3464; fax: +49 631 205 3835.

E-mail address: [hans.hasse@mv.uni-kl.de](mailto:hans.hasse@mv.uni-kl.de) (H. Hasse).

URL: <http://thermo.mv.uni-kl.de> (H. Hasse).

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