

# Hydrogen Storage Using a Hot Pressure Swing Reactor

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## Supporting Information

### Determination of the degree of hydrogenation

The degree of hydrogenation is calculated from stoichiometry, mass-flow measurements and the amount of LOHC present in the system during step  $i$ ,  $n_{Hx-DBT,i}$ . Calculations are based on the DoH of the previous step as can be seen in Equation (1). The index  $i$  corresponds to the respective charging and discharging sequence. Thus,  $t_{0,i}$  represents the starting time of the current sequence.

$$DoH_i(t) = DoH_i(t_{0,i}) + \frac{\int_{t_{0,i}}^t \dot{n}_{H_2, reaction}(t) dt}{n_{i, H_2, max}} = DoH_i(0) + \frac{\int_{t_{0,i}}^t \dot{n}_{H_2, reaction}(t) dt}{9 \cdot n_{Hx-DBT,i}} \quad (1)$$

The amount of LOHC present in the system can be derived from the amount of LOHC given at the starting point of the multi-cycle experiment,  $n_{H_0-DBT, start}$ , and the amount of LOHC which has been removed by liquid sampling during the previous  $(i-1)$  sequences:

$$n_{Hx-DBT,i} = n_{H_0-DBT, start} - \sum_{j=1}^{i-1} n_{sample,j} \quad (2)$$

As the samples taken in these sequences may differ in the degree of hydrogenation, the same sample mass not necessarily accounts for the same amount of carrier molecules. Each amount  $n_{sample,j}$  of Hx-DBT molecules can be calculated from each sample mass  $m_{sample,j}$  via the corresponding corrected average molecular mass that is a function of DoH<sub>j</sub>.

$$n_{sample,j} = \frac{m_{sample,j}}{M_{Hx-DBT,j}} = \frac{m_{j,sample}}{M_{H0-DBT} + DoH_j \cdot 9 \cdot M_{H_2}} \quad (3)$$

Combining the given equations results in equation (4)

$$DoH_i(t) = DoH_i(0) + \frac{\int_{t_{0,i}}^t \dot{m}_{H_2, reaction}(t) dt}{9 \cdot M_{H_2} \cdot \left( \frac{m_{H0-DBT, start}}{M_{H0-DBT}} - \sum_{j=1}^{i-1} \frac{m_{j,sample}}{M_{H0-DBT} + DoH_j \cdot 9 \cdot M_{H_2}} \right)} \quad (4)$$

### Calculating reaction equilibria with superimposed phase equilibria

(De)hydrogenation of H18/H0-DBT is happening in a two phase system consisting of a vapor and a liquid phase. All compounds are distributed between the two phases. Each substance occurs in each phase, but hydrogen for example accumulates mainly in the gas phase, while the H18/H0-DBT species mainly occur in the liquid phase. When calculating the reaction equilibrium, the superimposed phase equilibrium has to be considered. The equation for the vapor-liquid-equilibrium conditions can be written as

$$1 = \sum_{i=1}^m \frac{\left( n_i^{initial} + \sum_{l=1}^n v_{i,l} \lambda_l \right) \cdot \gamma_i \cdot P_{0i}^{LV} \cdot \varphi_{oi}^{LV} \cdot \Pi_{0i}}{\left( \varepsilon + \frac{\gamma_i P_{0i}^{LV} \varphi_{oi}^{LV} \Pi_{0i}}{P \varphi_i} \cdot (1 - \varepsilon) \right) \cdot \left( n_{overall}^{initial} + \sum_{l=1}^n \sum_{k=1}^m v_{k,l} \lambda_l \right) \cdot \varphi_i \cdot P} \quad (5)$$

This equation has to be solved simultaneously with the equation for the condition of the reaction equilibrium (if more than one reaction occur it has to be solved simultaneously for each reaction j):

$$K_{f,j} = \prod_i \left( \frac{\left( n_i^{initial} + \sum_{l=1}^n \nu_{i,l} \lambda_l \right) \cdot \left( \gamma_i P_{0i}^{LV} \varphi_{oi}^{LV} \Pi_{0i} \right) \cdot P \cdot \varphi_i}{\left( \varepsilon + \frac{\gamma_i P_{0i}^{LV} \varphi_{oi}^{LV} \Pi_{0i}}{P \varphi_i} \cdot (1 - \varepsilon) \right) \cdot \left( n_{overall}^{initial} + \sum_{l=1}^n \sum_{k=1}^m \nu_{k,l} \lambda_l \right) \cdot P \varphi_i P^+} \right)^{\nu_{i,j}} \quad (6)$$

The symbols in these equations mean the following:

- $K_{f,j}$ : Equilibrium constant of reaction j expressed in terms of fugacities
- $\nu_{i,j}$ : Stoichiometric coefficient of compound i in reaction j (negative for reactants)
- $n_i^{initial}$ : Amount of substance before the start of the reaction
- $\lambda$ : Extent of the respective reaction
- $P$ : System pressure
- $P^+$ : Reference pressure (usually 1.01325 bar)
- $\varphi_i, \varphi_{oi}^{LV}$ : Fugacity coefficient of compound i in the vapor phase and on the vapor pressure curve respectively
- $P_{0i}^{LV}$ : Vapor pressure of the pure compound i (Since the temperature in the systems under consideration is above the critical temperature of hydrogen there is no vapor pressure for hydrogen. Hence, it has to be replaced by the Henry coefficient of hydrogen in the respective mixture).
- $\gamma_i$ : Activity coefficient of compound i
- $\Pi_{0i}$ : Poynting factor for compound i
- $\varepsilon$ : Molar phase ratio (1, if fully liquid; 0, if fully evaporated)

The equation system has to be solved with respect to the extent of reaction  $\lambda$  and the pressure  $P$ .

The fugacity and activity coefficients can be calculated using equations of state and  $g^E$ -models, respectively. For a first approximation ideal behavior can be assumed (i.e. both are set to unity).

The equilibrium constant can be calculated from the Gibbs energy of reaction  $\Delta^R g^{IG}$ :

$$K_f = e^{-\frac{\Delta^R g^{IG}}{RT}} \quad (7)$$

Where R is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>) and T is the absolute temperature. The Gibbs energy of reaction  $\Delta^R g^{IG}$  can be calculated from the Gibbs energies of formation  $\Delta^F g_i^{IG}$  of each compound *i* involved in the reaction:

$$\Delta^R g^{IG} = \sum_i \nu_i \cdot \Delta^F g_i^{IG} \quad (8)$$

The Gibbs energies of formation  $\Delta^F g_i^{IG}$  can be calculated from the enthalpies of formation  $\Delta^F h_i^{IG}$  and the entropies of formation  $\Delta^F s_i^{IG}$ :

$$\Delta^F g_i^{IG} = \Delta^F h_i^{IG} + T \cdot \Delta^F s_i^{IG} \quad (9)$$