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# Green Hydrogen Storage in LOHCs via Catalytic Hydrogenation: In-depth Compound Analysis and Kinetic Study of Commercial Dibenzyltoluene Mixture

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# Green Hydrogen Storage in LOHCs via Catalytic Hydrogenation: In-depth Compound Analysis and Kinetic Study of Commercial Dibenzyltoluene Mixture

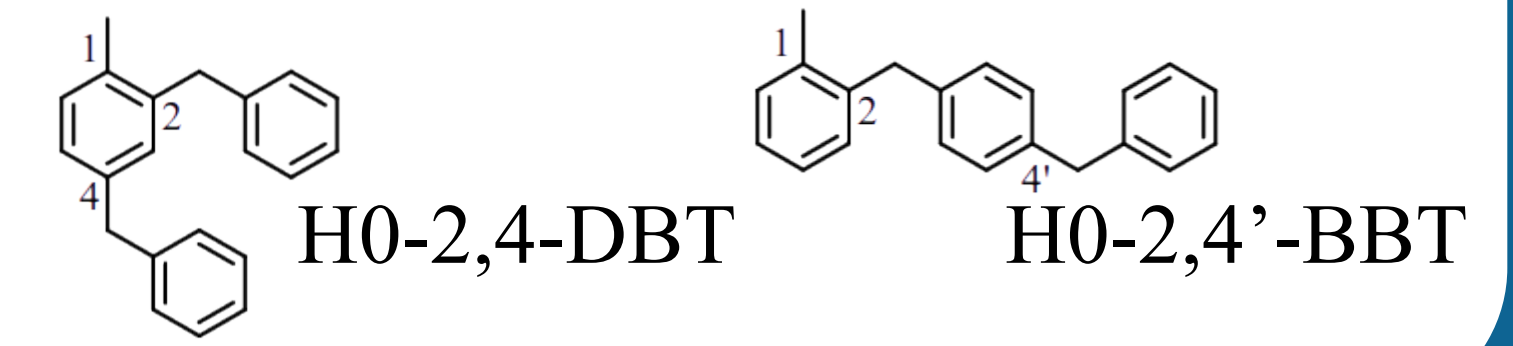
Xiaolong Ji<sup>1,2</sup>, Casimir Maudet<sup>2</sup>, Fabienne Fache<sup>3</sup>, Essyllt Louarn<sup>1</sup>, Valérie Meille<sup>1</sup>, Isabelle Pitault<sup>2</sup>

<sup>1</sup>IRCELYON, <sup>2</sup>LAGEPP, <sup>3</sup>ICBMS, Université Claude Bernard Lyon 1, 69100 Villeurbanne, France  
 isabelle.pitault@univ-lyon1.fr; valerie.meille@ircelyon.univ-lyon1.fr Grant N° ANR-21-CE50-0045

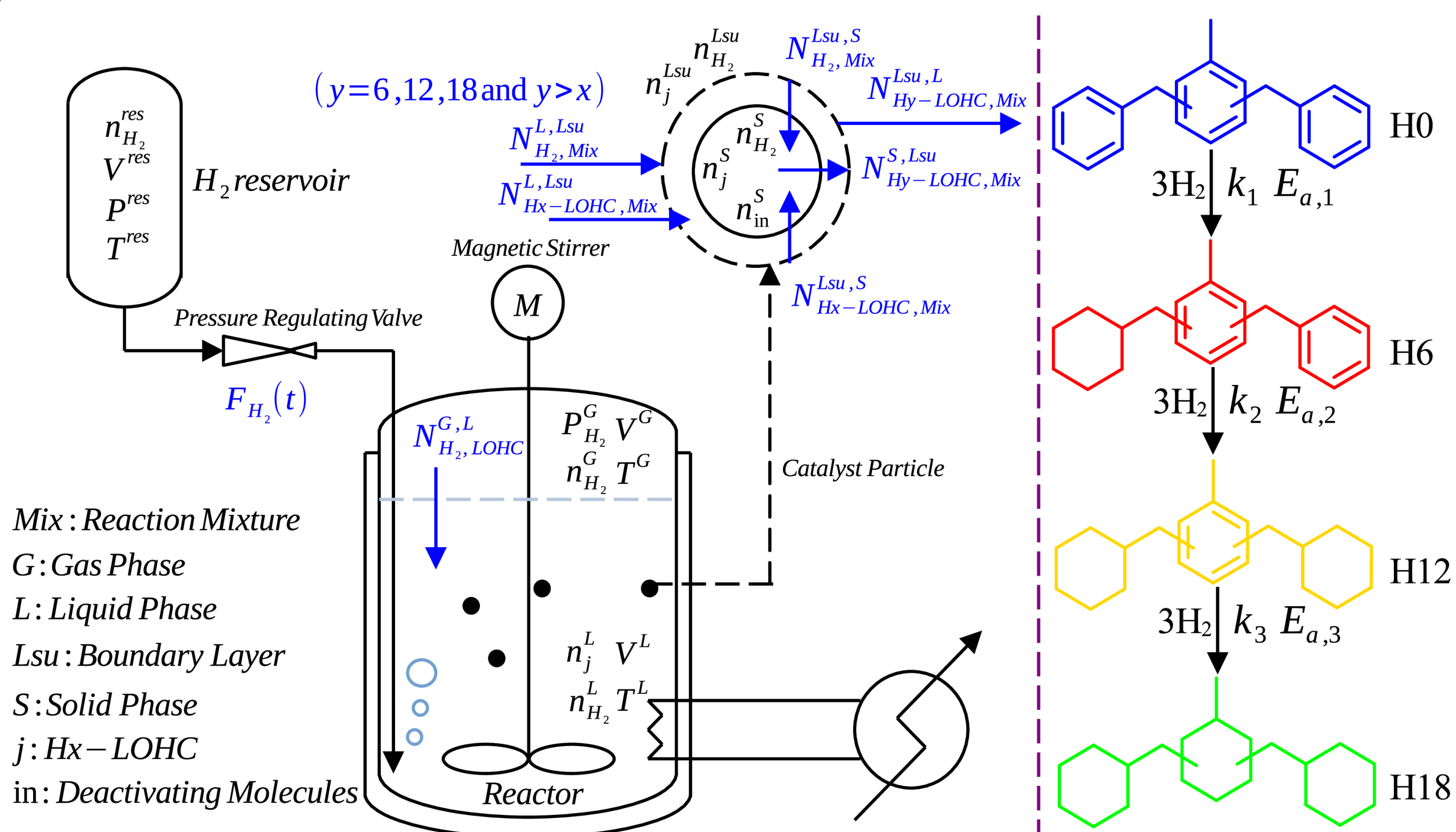
## Introduction

- The storage and transport of hydrogen is one of the major challenges in hydrogen processes.  
 Liquid Organic Hydrogen Carriers (LOHCs) → cheap, safe and efficient storage method using (de)hydrogenation.  
 Dibenzyltoluene and benzylbenzyltoluene (H0-DBT/BBT) mixture → wide liquid range (-34 to 386 °C), high storage capacity (6.2 wt-%).  
 In this study:
- Identification of Hx-DBT/BBT isomers with the help of GC/MS and mass balance.
  - Hydrogenation experiments in a batch reactor under different conditions.
  - Kinetic studies using commercial 5 wt-% Pt/C catalyst under different conditions.

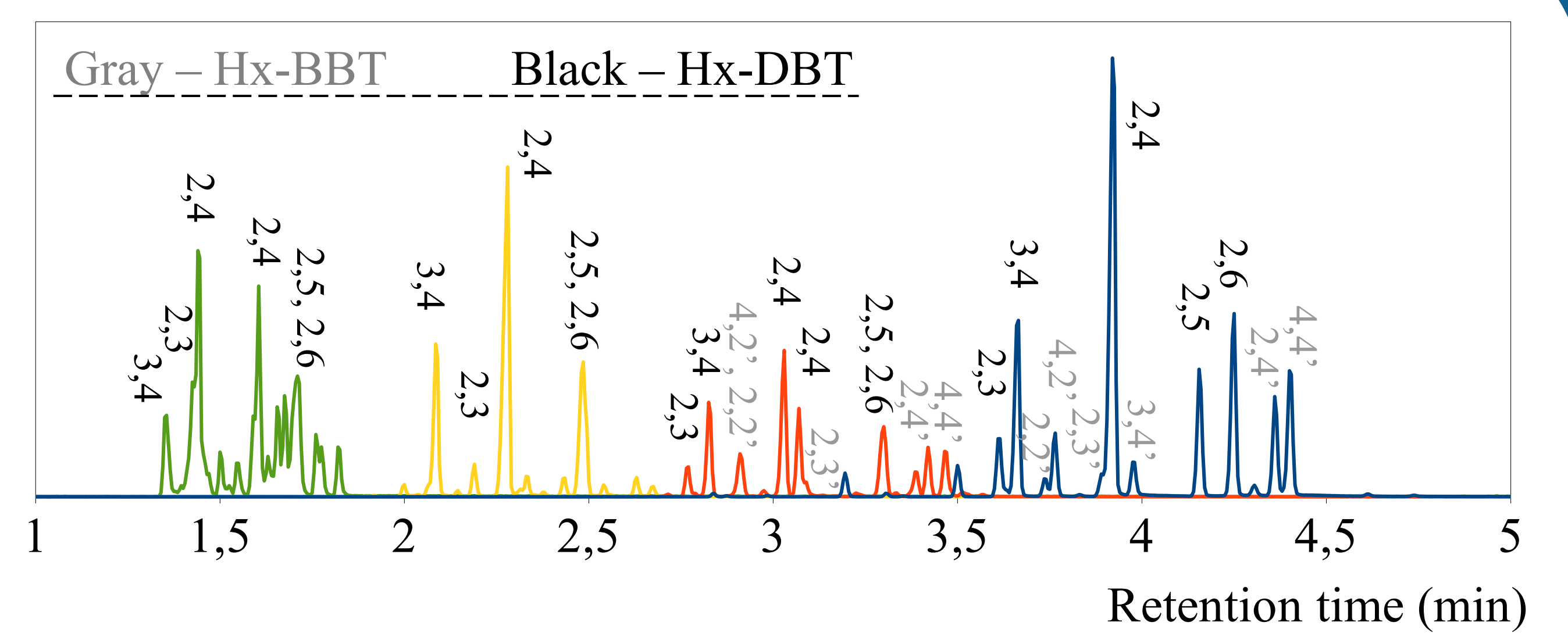
Nomenclature



## Reaction schematic



## Isomer Identification

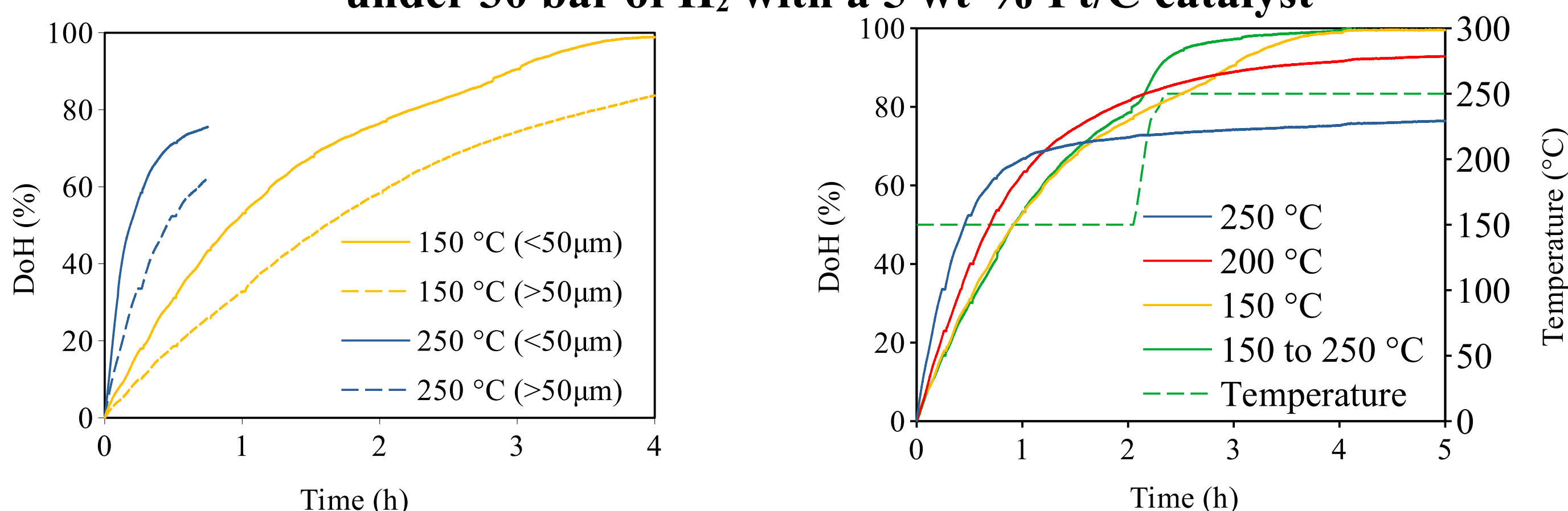


**Fast GC analysis:** Separation and study of most isomers present during reactions.

**Fragmentation and rearrangement mechanisms combined with reaction mass balance:** Identification of isomers.

## Experimental Results

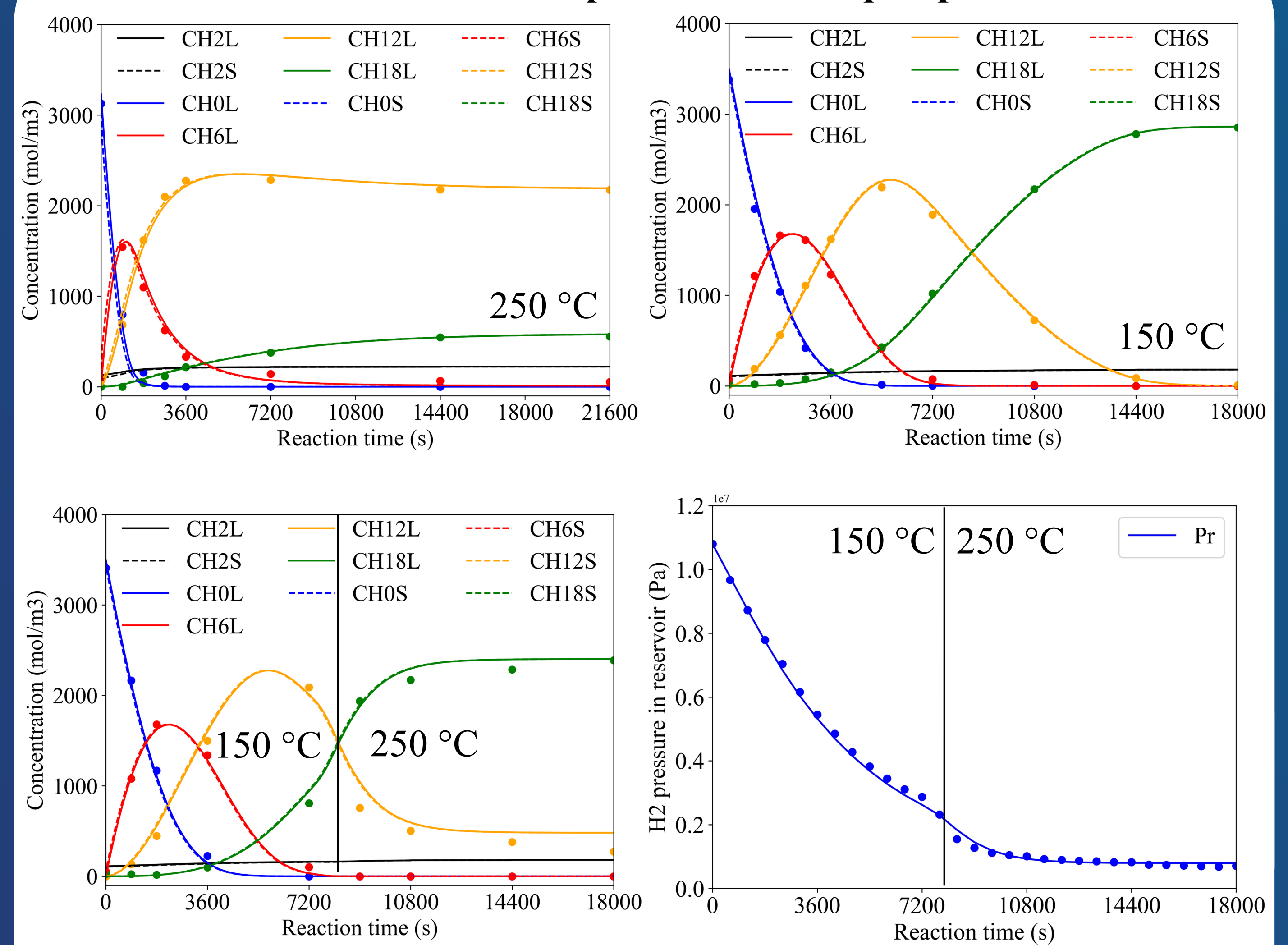
### Hydrogenation of commercial mixture of H0-DBT/BBT under 30 bar of H<sub>2</sub> with a 5 wt-% Pt/C catalyst



- Mass transfer limitation
- Deactivation increases with temperature

## Model Fitting

### Concentration of lumps in solid and liquid phases



### Parameter estimation (SI) and confidence intervals

Parameter	$k_1^0$	$k_2^0$	$k_3^0$	$E_{a,1}$	$E_{a,2}$	$E_{a,3}$	$K_{in,s}$	$K_{in,m}$
Opt value	$5.1 \cdot 10^5$	2700	2.9	48000	33000	17000	0.026	$7.8 \cdot 10^{-3}$
CI	3100	94	$2.2 \cdot 10^{-3}$	19	14	100	$8.2 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$

Parameter	$k_{in,H6}^0$	$k_{in,H18}^0$	$E_{a,in1}$	$E_{a,in2}$	$k_{La}$	$k_{D,H2}$	$k_{D,Hx}$
Opt value	0.69	0.42	38000	39000	0.32	$1.8 \cdot 10^{-3}$	$4.7 \cdot 10^{-5}$
CI	0.015	$2.6 \cdot 10^{-4}$	0.26	0.38	$2.3 \cdot 10^{-3}$	$2.5 \cdot 10^{-4}$	$3.0 \cdot 10^{-8}$

- Successful fitting of model and experimental results with small CI.
- G-L mass transfer limitation at the beginning at higher T (°C).
- Small but visible gap between C<sup>L</sup> and C<sup>Lsu</sup>, characteristic for L-S mass transfer limitation.

## Kinetic and Reactor Model

### Pseudo-LH reaction kinetics with aromatic ring inhibition

$$r_i^s = \frac{f_d k_i^0 e^{-\frac{E_{a,i}}{RT}} C_i^s C_{H_2}^s}{1 + K_{in,m} C_{aromatic,m} + K_{in,s} C_{aromatic,s}}$$

$$r_{in,Hx} = f_d k_{in}^0 e^{-\frac{E_{a,in}}{RT}} C_{Hx} \quad x=6 \text{ or } 18$$

**Catalyst deactivation**  $f_d = 1 - \frac{\theta_{in}}{\theta_{pt}}$   $r_{in,Hx} = f_d k_{in}^0 e^{-\frac{E_{a,in}}{RT}} C_{Hx}$  x=6 or 18  
 ➤ Deactivating molecules formed from H6 and H18 are also influenced by deactivation

### Mass balance – Gas phase

$$H_2: F_{H_2}(t) = V^L k_L a \left( C_{H_2}^* - \frac{n_{H_2}^L}{V^L} \right) + \frac{dn_{H_2}^G}{dt}$$

### Mass balance – Liquid phase

$$Hx: 0 = V^P k_{D,j} a_s \left( \frac{n_j^L}{V^L} - \frac{n_j^S}{V^{Lw}} \right) + \frac{dn_j^L}{dt}$$

$$H_2: V^L k_L a \left( C_{H_2}^* - \frac{n_{H_2}^L}{V^L} \right) = V^P k_{D,H_2} a_s \left( \frac{n_{H_2}^L}{V^L} - \frac{n_{H_2}^S}{V^{Lw}} \right) + \frac{dn_{H_2}^L}{dt}$$

$$\text{Volume (} v \text{ molar volume): } \frac{dV^L}{dt} = \sum \frac{dn_j^L}{dt} v_j^L$$

$$H_2 \text{ Solubility (} S_{H_2} \text{): } \frac{ds_{H_2}^L}{dt} = \sum \frac{dn_j^L}{dt} s_{H_2}^j$$

### Mass balance – Solid phase

$$Hx: V^P k_{D,H_2} a_s \left( \frac{n_{H_2}^L}{V^L} - \frac{n_{H_2}^S}{V^{Lw}} \right) + V^P \sum_i v_{H_2,i} \eta_i r_i^s = \frac{dn_{H_2}^S}{dt}$$

$$H_2: V^P k_{D,j} a_s \left( \frac{n_j^L}{V^L} - \frac{n_j^S}{V^{Lw}} \right) + V^P \sum_i v_{j,i} \eta_i r_i^s = \frac{dn_j^S}{dt}$$

$$\text{Active sites: } \frac{d\theta_{in}}{dt} = V^P (r_{in,H6} + r_{in,H18})$$

### Mass balance – H<sub>2</sub> Reservoir

$$H_2: \frac{dn_{H_2}^{res}}{dt} = -F_{H_2}(t)$$

Scipy.integrate.solve\_ivp  
 Scipy.optimize.least-squares

Modeling using Python Fast optimization routine

## Conclusions

- ✓ Identification of all Hx-DBT isomers and H0, H6-BBT isomers.
- ✓ Experiments under different conditions demonstrated transfer limitations and catalyst deactivation during hydrogenation.
- ✓ Kinetic model taking into account reaction mixture property change (density, H<sub>2</sub> solubility), mass transfer (G-L-S), compound adsorption and catalyst deactivation.
- ✓ The sources of deactivating species were found to be H6 and H18-DBT/BBT, which largely depend on the reaction temperature.
- ✓ Modeling of single isomers in progress.