Technische Universität Braunschweig

Model-Based Design and Optimization of Electrochemical Processes for Sustainable Aviation Fuels

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The 1st International Electronic Conference on Processes: Processes System Innovation

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Introduction : electrofuels for aviation

- 12% of the transport-related CO_2 emissions are from aviation
- 2-3% of all anthropogenic emission
- "Flight Path 2050"
  - a 75% reduction in CO_2 per passenger kilometer,
  - a 90% reduction in NOx
- For short range aviation : Electric aviation/battery/fuel cell system
- For long range : Electrofuels (Furfuryl alcohol, n-octane, ammonia, methane, hydrogen)

Electroreduction of furfural

- The raw material, furfural is derived from hydrolysis of biomass
- No toxic catalyst/products, mild operating conditions
- Electrode materials studied: Graphite foil, Polycrystalline graphite sheet, Graphite felt, Lead sheet, Copper sheet, Copper gauge, Nickel sheet, Nickel gauge, Iron sheet, Aluminium sheet, and Platinum sheet
- Reactor types
- Reaction conditions

Mathematical model and systematic framework for process design and optimization missing in literature.

Overview

- Part I : Simplified model for conversion of furfural to furfuryl alcohol
  - Model for furfural to furfuryl alcohol
  - Effect of overpotential on adsorbed hydrogen
  - Effect of overpotential on yield
- Part II : Extended model with conversion of furfural to furfuryl alcohol and methylfuran along with hydrogen evolution
  - Reaction scheme for model with adsorption, without adsorption and hybrid mechanism
  - Model for extended reaction scheme
  - Comparison of model prediction and experimental data

Part I

Simplified model for conversion of furfural to furfuryl alcohol

Reaction scheme: furfuryl alcohol synthesis

$$\begin{array}{ccccc} FF & \xrightarrow{k_{ads}} & FF_{ads} & \xrightarrow[2H_{ads}]{k_{FF}} & FA \\ & & \text{Volmer reaction} & \uparrow e^{-} & \\ & & & H^{+} & \end{array}$$

- FF - Furfural
- FF_{ads} - Adsorbed furfural
- H_{ads} - Adsorbed hydrogen
- FA - Furfuryl alcohol

Red arrow: Electrochemical reaction,
Black arrow: Chemical reaction.

Model assumptions

- The hydrogen fraction of adsorbed hydrogen remains the same during the reaction.
- There is no formation of additional byproducts such as methyl furan, methyltetrahydrofuran, and tetrahydrofurfuryl alcohol.
- The fraction of the surface area available for the reactions does not change over process time.
- Basic conditions.

Model equations

Adsorption (furfural and hydrogen):

$$\mathrm{r_{ads}} = \mathrm{k_{ads}} \cdot \mathrm{FF} \cdot \theta_{\mathrm{v}},$$

$$\theta_{\mathrm{H_0}} = \frac{1}{1 + \exp(-(\mathrm{p_1} + \mathrm{p_2} \cdot \mathrm{E}))}.$$

Conversion of furfural to furfuryl alcohol

$$\mathrm{r_{FF}} = \mathrm{k_{FF}} \cdot \theta_{\mathrm{H}}^2 \cdot \mathrm{FF_{ads}}.$$

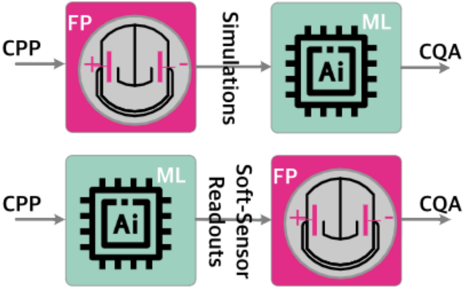
Material balance equations:

$$\frac{\mathrm{dFF_{ads}}}{\mathrm{dt}} = \mathrm{C}(\mathrm{r_{ads}} - \mathrm{r_{FF}}),$$

$$\frac{\mathrm{dFF}}{\mathrm{dt}} = \frac{\mathrm{Q_{in}}}{\mathrm{V}}\mathrm{FF_{in}} - \mathrm{r_{ads}}\mathrm{a} - \frac{\mathrm{Q_{out}}}{\mathrm{V}}\mathrm{FF},$$

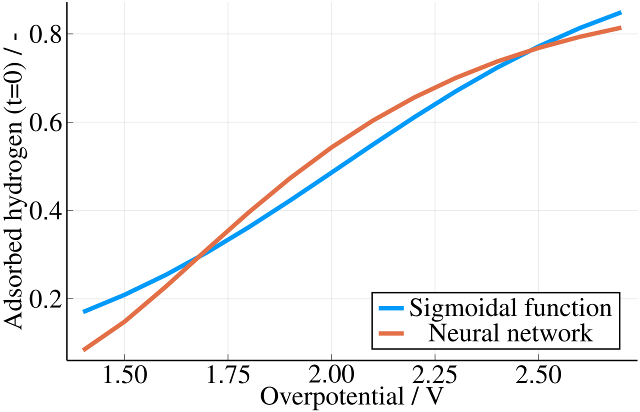
$$\frac{\mathrm{dFA}}{\mathrm{dt}} = \frac{\mathrm{Q_{in}}}{\mathrm{V}}\mathrm{FA_{in}} + \mathrm{r_{FF}}\mathrm{a} - \frac{\mathrm{Q_{out}}}{\mathrm{V}}\mathrm{FA}.$$

Model overview

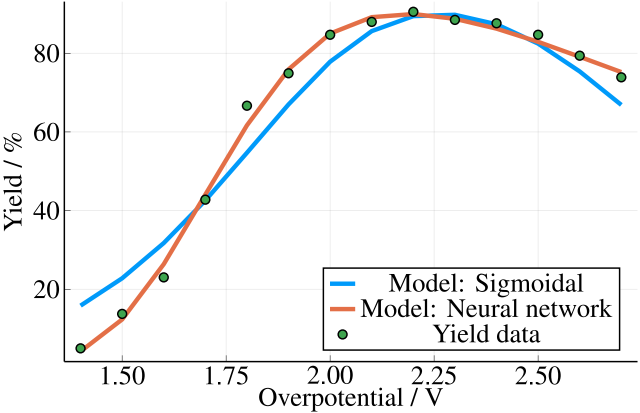


- Initial conditions : Furfural, furfuryl alcohol and adsorbed hydrogen (sigmoid function/Neural Network)
- Reaction dynamics: ODEs

Effect of overpotential on adsorbed hydrogen



Effect of overpotential on yield (ML + process model)



Furfuryl yield data from literature[1]

[1] (Cao2019)

Part II

Extended model with conversion of furfural to furfuryl alcohol and methylfuran along with hydrogen evolution

Acknowlegement: Dr.-Ing. Fabian Kubannek (InES) and Thorben Lenk (IÖNC)

Reaction scheme: Furfuryl Alcohol (FA), Methyl Furan (MF) and H_2

Case 1: With adsorption

$$
\begin{tikzcd}
 & \mathrm{FA} & \mathrm{H_2} \\
\mathrm{FF} \arrow[r] & \mathrm{FF_{ads}} \arrow[u, "2\mathrm{H_{ads}}"'] \arrow[d, "4\mathrm{H_{ads}}"'] & \mathrm{H_{ads}} \arrow[u, "\text{Tafel}"', "\text{Heyvrosky}"] \\
 & \mathrm{MF} & \mathrm{H^+} \arrow[u, "\text{Volmer}"]
\end{tikzcd}
$$

Case 2: Without adsorption

$$
\begin{tikzcd}
\mathrm{FA} & \mathrm{H_2} \\
\mathrm{FF} \arrow[u, "2\mathrm{H_{ads}}"'] \arrow[d, "4\mathrm{H_{ads}}"'] & \mathrm{H_{ads}} \arrow[u, "\text{Tafel}"', "\text{Heyvrosky}"] \\
\mathrm{MF} & \mathrm{H^+} \arrow[u, "\text{Volmer}"]
\end{tikzcd}
$$

Case 3: Hybrid mechanism

$$\mathrm{H^+} \xrightarrow{\text{Volmer}} \mathrm{H_{ads}} \xrightarrow[\text{Heyvrosky}]{\text{Tafel}} \mathrm{H_2}$$

$$\mathrm{FA} \xleftarrow{2\mathrm{H_{ads}}} \mathrm{FF} \longrightarrow \mathrm{FF_{ads}} \xrightarrow{4\mathrm{H_{ads}}} \mathrm{MF}$$

Model assumptions

- The formation of adsorbed hydrogen by Volmer reaction and adsorption of furfural on the electrode surface are reversible reactions and follows Frumkin type isotherm
- The conversion of furfural to furfuryl alcohol and methylfuran are irreversible reactions
- Evaporative loss of furfuryl alcohol and methyl furan

Model equations

- Case 1:

  $r_{FA} = k_{FA} \cdot FF_{ads} \cdot H_{ads}^2$

  $r_{MF} = k_{MF} \cdot FF_{ads} \cdot H_{ads}^2$

- Case 2:

  $FF_{ads} = 0 \; \& \; \theta_{FF} = 0$

  $r_{FA} = k_{FA} \cdot FF \cdot H_{ads}^2$

  $r_{MF} = k_{MF} \cdot FF \cdot H_{ads}^2$

- Case 3:

  $r_{FA} = k_{FA} \cdot FF \cdot H_{ads}^2$

  $r_{MF} = k_{MF} \cdot FF_{ads} \cdot H_{ads}^2$

$$\frac{d\theta_H}{dt} = \frac{F}{\sigma}[r_v - r_T - r_H - r_{FA} - r_{MF}]$$

$$\frac{d\theta_{FF}}{dt} = \frac{F}{\sigma}[r_{FFads} - r_{FA} - r_{MF}]$$

$$\frac{dFF}{dt} = -r_{FFads} \cdot a$$

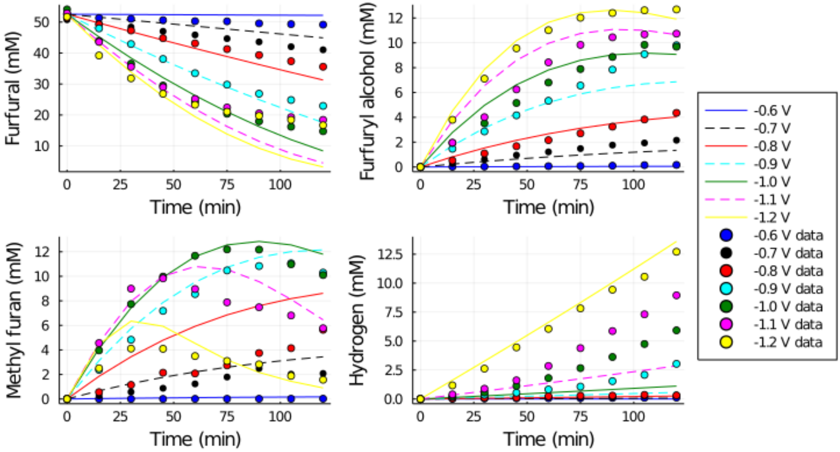
$$\frac{dFF_{ads}}{dt} = r_{FFads} - r_{FA} - r_{MF}$$

$$\frac{dFA}{dt} = r_{FA} \cdot a - r_{evap,FA}$$

$$\frac{dMF}{dt} = r_{MF} \cdot a - r_{evap,MF}$$

$$\frac{dH_2}{dt} = (r_T + r_H)a$$

Results: Hybrid mechanism



Summary and conclusions

- The concept of hybrid modeling implemented for a simplified model for electroreduction of furfural for overpotential between 1.4 to 2.7 V.

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Hybrid Process Models in Electrochemical Syntheses under Deep Uncertainty

by Fenila Francis-Xavier [1,2], Fabian Kubannek [1] and René Schenkendorf [1,2,*]

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- The extended model with hybrid mechanism fits the experimental data better. The model structure developed can be used for further studies on model-based optimization.

Cluster of Excellence “SE²A - Sustainable and Energy-Efficient Aviation”, TU Braunschweig.

Thank You!

Model parameters for simplified model

Table 1: Model parameters and initial value for electrochemical synthesis of furfuryl alcohol.

Parameter	k_{ads}	k_{FF}	C	$FF(t=0)$	$FA(t =$
Value	0.5969	5.6437×10^{-8}	1.6081×10^{9}	0.1×10^{-3}	0
Unit	$cm\,s^{-1}$	s^{-1}	-	$mol\,cm^{-3}$	mol cr

Rate equations - case 1

$$r_v = k_{f,v}\theta_v \exp(-\lambda \cdot u_{f,h} \cdot \theta_H) - k_{b,v}\theta_H \exp((1-\lambda) \cdot u_{b,h} \cdot \theta_H)$$

$$k_{f,v} = k^0_{f,v}\exp(-\beta \cdot f \cdot E_c)$$

$$k_{b,v} = k^0_{b,v}\exp((1-\beta) \cdot f \cdot E_c)$$

$$r_{FFads} = r_{FFadsf} - r_{FFadsb}$$

$$r_{FA} = k_{FA} \cdot F_{ads} \cdot H^2_{ads}$$

$$r_{MF} = k_{MF} \cdot F_{ads} \cdot H^2_{ads}$$

$$r_T = k_T \cdot \theta^2_H$$

$$r_H = k_H \cdot \theta_H$$

$$k_H = k^0_H \cdot \exp(-\beta f E_c)$$

$$r_{HER} = (r_T + r_H) \cdot a$$

Adsorption and evaporation kinetics

$$r_{\mathrm{FFadsf}} = k_{\mathrm{f,ads}} \cdot \mathrm{FF} \cdot \theta_{\mathrm{v}} \cdot \exp(-\lambda \cdot u_{\mathrm{f,f}} \cdot \theta_{\mathrm{FF}})$$

$$r_{\mathrm{FFadsb}} = k_{\mathrm{b,ads}} \cdot \theta_{\mathrm{F}}\mathrm{F} \cdot \exp((1-\lambda) \cdot u_{\mathrm{b,f}} \cdot \theta_{\mathrm{FF}})$$

$$r_{\mathrm{evap,MF}} = (k_{\mathrm{evap,MF,1}} \cdot H_2 + k_{\mathrm{evap,MF,2}}) \cdot \mathrm{MF}$$

$$r_{\mathrm{evap,FA}} = (k_{\mathrm{evap,FA,1}} \cdot H_2 + k_{\mathrm{evap,FA,2}}) \cdot \mathrm{FA}$$

Rate equations - case 2 & 3

Case 2:

$$r_{FA} = k_{FA} \cdot FF \cdot H_{ads}^{2}$$

$$r_{MF} = k_{MF} \cdot FF \cdot H_{ads}^{2}$$

Case 3:

$$r_{FA} = k_{FA} \cdot FF \cdot H_{ads}^{2}$$

$$r_{MF} = k_{MF} \cdot F_{ads} \cdot H_{ads}^{2}$$