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Energy analysis and surrogate modeling for the green methanol production under dynamic operating conditions

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Appendix A

1. The reaction kinetics for methanol synthesis

In this study, the reaction kinetics by Van den Bussche and Froment [1] was selected to calculate the reaction rates in the methanol reactor R1 under the investigated conditions with the following equations (shown in Table S1) for reaction (2) and reaction (3) considered in this study.

| Table S1. Reaction kinetics. |
| --- | --- | --- |
| Reaction kinetics | No. | Ref. |
| $r_{\text{MeOH}} = k_d \frac{P_{\text{CO}_2}P_{\text{H}_2} - K_1^{-1}P_{\text{H}_2O}^pP_{\text{MeOH}}/P_{\text{H}_2}^2}{(1 + k_cP_{\text{H}_2O}/P_{\text{H}_2} + k_aP_{\text{H}_2}^{0.5} + k_bP_{\text{H}_2O})^3}$ | (1) | [1] |
| $r_{\text{RWGS}} = k_e \frac{P_{\text{CO}_2}^p - K_2P_{\text{H}_2O}P_{\text{CO}}/P_{\text{H}_2}}{1 + k_cP_{\text{H}_2O}/P_{\text{H}_2} + k_aP_{\text{H}_2}^{0.5} + k_bP_{\text{H}_2O}}$ | (2) | |
| $K_1 = 10^{-10.592+\frac{3066}{T}} \approx \exp(-24.389 + \frac{7059.726}{T})$ | (3) | [2] |
| $K_2 = 10^{2.029+\frac{-2073}{T}} \approx \exp(-4.672 + \frac{4773.26}{T})$ | (4) | |

where the kinetic factors $k_d$ and $k_e$, and the adsorption constants $k_a$, $k_b$ and $k_c$ were calculated with parameters shown in Table S2.

| Table S2. Parameters for the kinetic equations. |
| --- | --- | --- |
| $k = A \cdot e^{B/R\cdot T}$ | A | B |
| $k_d$ [bar$^{-0.5}$] | 0.499 | 17197 |
| $k_b$ [bar$^{-1}$] | $6.62 \times 10^{-11}$ | 124119 |
| $k_c$ [ ] | 3453.38 | - |
| $k_d$ [mole/(kg s bar$^2$)] | 1.07 | 36696 |
| $k_e$ [mole/(kg s bar)] | $1.22 \times 10^{10}$ | $-94765$ |

The parameter values above were adjusted for the input values in Aspen plus due to the unit difference and shown in Table S3. The units of bar, kmol and kmol/(kg cat·s) were used for the pressure, mole flow and reaction rate, respectively. Parameter settings with different units may also be used in Aspen plus e.g. Pascal was used for pressure in the literature [3].
Table S3. The input values in Aspen plus for the kinetic equations.

<table>
<thead>
<tr>
<th>$k_i$ = $k \cdot \exp(-E/RT)$</th>
<th>$k$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_d$</td>
<td>0.00107, kmol/(kg$_{\text{cat}}$·s·bar$^2$)</td>
<td>-36696, kJ/kmol</td>
</tr>
<tr>
<td>$k_e$</td>
<td>1.22×10$^7$, kmol/(kg$_{\text{cat}}$·s·bar)</td>
<td>94765, kJ/kmol</td>
</tr>
</tbody>
</table>

$\ln K_i = A_i + B_i/T$

<table>
<thead>
<tr>
<th>$\ln(1/K_i)$</th>
<th>$A_i$</th>
<th>$B_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\ln K_2$</td>
<td>-4.762</td>
<td>4773.16</td>
</tr>
<tr>
<td>$\ln K_a$</td>
<td>-0.695149</td>
<td>2068.44</td>
</tr>
<tr>
<td>$\ln K_b$</td>
<td>-23.438</td>
<td>14928.92</td>
</tr>
<tr>
<td>$\ln K_c$</td>
<td>8.14711</td>
<td>-</td>
</tr>
</tbody>
</table>

The methanol reactor model developed by using Aspen Plus was validated by comparing with the simulation results in Ref. [1]. Good agreement was shown in Fig. S1. The operating conditions for the simulation of the methanol reactor were also given in Ref. [1].

![Figure S1](image.png)

Figure S1. (a) Gas composition and (b) temperature profiles along the methanol reactor under the operation conditions in Ref [1].

2. Ergun equation

The pressure drop over the catalyst bed was evaluated by the Ergun equation [4]:
3. CO₂ solubility predicted by the Predictive Soave–Redlich–Kwong model

The CO₂ dissolved in the liquid phase of the gas–liquid separator after the methanol reactor may influence the composition of the recycle stream as well as the performance of the downstream distillation process. In this study, the Predictive Soave–Redlich–Kwong (PSRK) model was employed as the equation of state for the methanol synthesis system. The predicted CO₂ mole fraction in the liquid phase at different pressure and 298.15 K was shown in Fig. S2, and compared with the experimental data by Chang and Rousseau [5] for methanol/CO₂/water system, and good agreement was found.

![Equilibrium mole fraction CO₂ in the liquid phase of methanol/CO₂/water system at different pressure and 298.15 K.](image)

Figure S2. Equilibrium mole fraction CO₂ in the liquid phase of methanol/CO₂/water system at different pressure and 298.15 K.

**Appendix B**

The simulation results for full-load methanol production at steady state was shown in Table S4.

**Table S4. Steady state simulation results of the main streams operating at full-load**

---

\[
\frac{dP}{dz} = -(1.75 + 150 \frac{1 - \varepsilon}{Re_p^S} \frac{1 - \varepsilon \rho_f u^2}{\varepsilon^3} \frac{d \rho_f}{dP})
\] (5)
The gas composition slowly changed after the LC operations between full-load and half-load. It takes more than 20 hours for the methanol synthesis system to achieve steady state. For example, the hydrogen content at the reactor inlet (stream S21) was presented in Fig. S3 under the LC operation conditions (load decreased at t = 1–2 h and increased at t = 21–22 h).

![Figure S3](image)

Figure S3. Hydrogen mole fraction at the reactor inlet under the load change operations between full-load and half-load operation.

### Appendix C

1. The heat transfer in the methanol reactor
In the adiabatic methanol reactor, the heat transfer process occurs among the bulk gas phase, solid catalyst, reactor wall and also small amount of loss to the environment. Therefore the following heat transfer coefficients were considered to evaluate the heat transfer process in the direction of the reactor.

### Table S5. Radial heat transfer coefficients in the methanol reactor

<table>
<thead>
<tr>
<th>Domains</th>
<th>Equation</th>
<th>No.</th>
<th>Ref.</th>
</tr>
</thead>
</table>
| Overall heat transfer       | \[
\begin{align*}
\frac{1}{U_t} &= \frac{R}{3k_{er} B t + 4} + \frac{1}{h_w} + \frac{\delta}{k_w} + \frac{1}{h_{loss}}
\end{align*}
\] | (6) | [6]  |
| Solid catalyst bed          | \[
\begin{align*}
\frac{k_{er}}{k_f} &= \frac{k_r^0}{k_f} + \frac{Pe_h^0}{Pe_{h,r}^\infty}
\end{align*}
\] | (7) | [7, 8] |
|                            | \[
\begin{align*}
\frac{k_r^0}{k_f} &= \left(1 - \sqrt{1 - \varepsilon}\right) + \frac{2\sqrt{1 - \varepsilon}}{1 - B \kappa^{-1}} \left[\frac{B(1 - \kappa^{-1})}{(1 - B \kappa^{-1})^2} \ln\left(\frac{\kappa}{B}\right) - \frac{B - 1}{1 - B \kappa^{-1}} + \frac{B + 1}{2}\right]
\end{align*}
\] | (8) |      |
|                            | \[
B = C_f \left(\frac{1 - \varepsilon}{\varepsilon}\right)^{1.11}; C_f = 1.25 (sphere), 2.5 (cylinder) or 2.5 \left(1 + \frac{d_s}{d_p}\right) (rings)
\] | (9) |      |
|                            | \[
\begin{align*}
k_p &= 0.21 + 0.00015T
\end{align*}
\] | (10) |      |
|                            | \[
\begin{align*}
Pe_h^0 &= \frac{u \rho_f c_p d_p^\nu}{k_f} = RePr
\end{align*}
\] | (11) |      |
|                            | \[
\begin{align*}
Pe_{h,r}^\infty &= 8 \left[2 - \left(1 - \frac{2}{N}\right)^2\right]
\end{align*}
\] | (12) |      |
| Near-wall region            | \[
Nu_w = Nu_{w0} + \left(1/Nu_{w0} + 1/Nu_m\right)^{-1}
\] | (13) | [8]  |
|                            | \[
Nu_{w0} = (1.3 + \frac{5}{N^4}) \left(\frac{k_r^0}{k_f}\right)
\] | (14) |      |
|                            | \[
Nu_w^* = 0.3Pr^{1/3}Re^{0.75}
\] | (15) |      |
|                            | \[
Nu_m = 0.054PrRe
\] | (16) |      |
| Gas phase and solid catalyst| \[
\begin{align*}
\frac{h_s d_p^\nu k_f}{2} + 1.1Pr^{1/3}Re^{0.6}
\end{align*}
\] | (17) | [9]  |

2. The heat transfer coefficient for the heat exchanger HX1
The heat transfer coefficient \( (W/(m^2\cdot K)) \) for HX1 was evaluated by using the software of Aspen EDR assuming that a shell-tube heat exchanger with countercurrent flow, and the heat transfer coefficient at different flow conditions is expressed by:

\[
h_{HX1} = 517.9 \times \left( \frac{F}{30368.1} \right)^{0.655}
\]

(18)

where \( F \) is the mass flow rate (kg/h) of stream S1 in Fig. 2.

**Nomenclature**

- \( Bi \) (-) Tube Bilot number, \( h_nR_c/k_{e,r} \)
- \( C_{p,f} \) J kg\(^{-1}\)K\(^{-1}\) Heat capacity of the gas phase
- \( d \) m Diameter of cylinder pellet
- \( d_p^v \) m Volume-equivalent particle diameter of the catalyst pellet, for a cylinder \( d_p^v = d \left( \frac{3N}{2d} \right)^{\frac{1}{3}} \)
- \( d_p^s \) m Diameter of sphere with equal specific surface area, for a cylinder \( d_p^s = 3d_h/(d + 2h) \)
- \( h \) m Height of cylinder pellet
- \( h_{loss} \) W m\(^{-2}\)K\(^{-1}\) Heat transfer coefficient between reactor wall and environment
- \( h_w \) W m\(^{-2}\)K\(^{-1}\) Heat transfer coefficient in the near-wall region
- \( k \) W/m K Thermal conductivity, parameters in reaction rate equations
- \( k_f \) W/m K Thermal conductivity of the bulk fluid
- \( k_r \) W/m K Effective stagnant thermal conductivity
- \( k_{e,r} \) W/m K Effective radial thermal conductivity
- \( K \) (-) Equilibrium constant
- \( N \) (-) The ratio of the tube diameter and volume-equivalent diameter, \( N = 2R_t/d_p^v \)
- \( Nu_w \) (-) Wall Nusselt number \( (h_{loss}d_p^v/k_f) \)
- \( Nu_{w,0} \) (-) Wall Nusselt number at zero flow rate \( (h_{loss}d_p^v/k_f) \)
- \( Nu_{w,f} \) (-) Wall film Nusselt number \( (h_wd_p^v/k_f) \)
- \( Nu_{a} \) (-) Fluid mechanical Nusselt number \( (h_wd_p^v/k_f) \)
- \( P \) Pa Pressure
- \( Pe_{r,h}^f \) (-) Fluid Peclet number for heat transfer \( (u_f c_{p,f} d_p^v/k_f) \)
- \( Pe_{h,r}^f \) (-) Peclet radial heat transfer for fully developed turbulent flow
- \( Pr \) (-) Prandtl number \( (u_f c_{p,f}/k_f) \)
- \( r \) mol/(kg cat\(_s\)) Reaction rate
- \( R_t \) m Radius of reactor tube
- \( Re \) (-) Reynold's number \( (u_d d_p^v/\mu_f) \)
- \( Re_p^f \) (-) Reynold's number \( (u_d d_p^v/\mu_f) \)
- \( T \) K Temperature
- \( u \) m/s Superficial gas velocity
- \( U_t \) W m\(^{-2}\)K\(^{-1}\) Overall heat transfer coefficient
Supporting Information

Greek letters
\( \delta \) m Thickness of reactor wall
\( \varepsilon \) (-) Porosity of catalyst bed
\( \kappa \) (-) The ratio of the thermal conductivity of the solid catalyst pellet and the gas fluid \( k_p/k_f \)
\( \mu_f \) kg/m s Gas viscosity
\( \rho_f \) kg/m\(^3\) Gas density

Subscripts
\( 0 \) Stagnant
\( e \) Effective
\( f \) Gas phase
\( p \) Pellet
\( r \) Radial
\( t \) Tube
\( w \) Reactor wall

Reference