Aalborg Universitet



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

Cui, Xiaoti; Kær, Søren Knudsen; Nielsen, Mads Pagh

Published in: Fuel

DOI (link to publication from Publisher): 10.1016/j.fuel.2021.121924

Creative Commons License CC BY 4.0

Publication date: 2022

Link to publication from Aalborg University

Citation for published version (APA): Cui, X., Kær, S. K., & Nielsen, M. P. (2022). Energy analysis and surrogate modeling for the green methanol production under dynamic operating conditions. *Fuel*, *307*, Article 121924. https://doi.org/10.1016/j.fuel.2021.121924

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
 You may not further distribute the material or use it for any profit-making activity or commercial gain
 You may freely distribute the URL identifying the publication in the public portal -

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from vbn.aau.dk on: July 04, 2025

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

Xiaoti Cui^a*, Søren Knudsen Kær^{a,b}, Mads Pagh Nielsen^a

^a Department of Energy, Aalborg University, Pontoppidanstr. 111, 9220 Aalborg, Denmark

^b REintegrate ApS, Langerak 15, 9220 Aalborg, Denmark

E-mail: xcu@et.aau.dk

Phone: +45 2667 8192

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.

Reaction kinetics	No.	Ref.
$r_{MeOH} = k_d \frac{P_{CO2} P_{H2} - K_1^{-1} P_{H2O} P_{MeOH} / P_{H2}^2}{(1 + k_c P_{H2O} / P_{H2} + k_a P_{H2}^{0.5} + k_b P_{H2O})^3}$	(1)	[1]
$r_{RWGS} = k_e \frac{P_{CO2} - K_2 P_{H2O} P_{CO} / P_{H2}}{1 + k_c P_{H2O} / P_{H2} + k_a P_{H2}^{0.5} + k_b P_{H2O}}$	(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)	

Table	S1 .	Reaction	kinetics.
-------	-------------	----------	-----------

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.

$k = A \cdot e^{B/RT}$	А	В
k_a [bar ^{-0.5}]	0.499	17197
$k_b [\mathrm{bar}^{-1}]$	6.62×10^{-11}	124119
k_c [—]	3453.38	-
k_d [mole/(kg·s·bar ²]	1.07	36696
k_e [mole/(kg·s·bar]	1.22×10^{10}	-94765

Table S2. Parameters for the kinetic equations.

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].

$k_i = k \cdot exp(-E/RT)$	k	Ε
k _d	0.00107, $\text{kmol}/(\text{kg}_{\text{cat}}\cdot s \cdot \text{bar}^2)$	-36696, kJ/kmol
ke	1.22×10^7 , kmol/(kg _{cat} ·s·bar)	94765, kJ/kmol
$lnK_i = A_i + B_i/T$	A_i	B_i
$ln(1/K_1)$	24.389	-7059.726
lnK_2	-4.762	4773.16
lnK_a	-0.695149	2068.44
lnK_b	-23.438	14928.92
lnK_c	8.14711	-

Table S3. The input values in Aspen plus for the kinetic equations.

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. (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]:

$$\frac{dP}{dz} = -(1.75 + 150\frac{1-\varepsilon}{Re_p^s})\frac{1-\varepsilon}{\varepsilon^3}\frac{\rho_f u^2}{d_p^s}$$
(5)

3. CO₂ solubility predicted by the Predictive Soave–Redlich–Kwong model

The CO_2 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 CO_2 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/ CO_2 /water system, and good agreement was found.



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

Appendix B

	CO2	H2	S1	S21	S 3	S5	REC	PUR1	CRD	REF	WST	MOH
T, ℃	25.00	25.00	50.80	220.00	258.73	75.00	54.50	30.47	30.50	55.07	100.13	54.92
P, bar	35.00	35.00	32.00	31.00	29.39	1.10	32.00	10.00	1.50	1.10	1.02	1.02
Mole flow rate,												
kmol/h	89.00	267.00	4359.81	4359.81	4184.64	175.86	4003.81	4.01	175.86	106.21	87.74	86.90
CO mol%,	0.000	0.000	0.037	0.037	0.038	0.000	0.040	0.040	0.000	0.000	0.000	0.000
CO ₂ mol%	1.000	0.000	0.091	0.091	0.074	0.003	0.077	0.077	0.002	0.000	0.002	0.002
H ₂ mol%	0.000	1.000	0.866	0.866	0.840	0.000	0.877	0.877	0.000	0.000	0.000	0.000
H ₂ O mol%	0.000	0.000	0.001	0.001	0.022	0.499	0.001	0.001	0.000	1.000	0.000	0.000
CH ₃ OH mol%	0.000	0.000	0.005	0.005	0.026	0.498	0.005	0.005	0.998	0.000	0.998	0.998
Mass flow rate,	3916.87	538.24	30364.60	30364.60	30364.60	4409.18	25909.49	25.94	3404.94	1580.88	2785.86	3404.94
kg/h						.,						

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

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. 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.

· · · · · · · · · · · · · · · · · · ·			
Domains	Equation	No.	Ref.
Overall heat transfer	$\frac{1}{U_t} = \frac{R_t}{3k_{e,r}} \frac{Bi+3}{Bi+4} + \frac{1}{h_w} + \frac{\delta}{k_w} + \frac{1}{h_{loss}}$	(6)	[6]
Solid catalyst bed	$\frac{k_{e,r}}{k_f} = \frac{k_r^0}{k_f} + \frac{Pe_h^0}{Pe_{h,r}^\infty}$	(7)	[7, 8]
	$\frac{k_r^0}{k_f} = \left(1 - \sqrt{1 - \varepsilon}\right) + \frac{2\sqrt{1 - \varepsilon}}{1 - B\kappa^{-1}} \left[\frac{B(1 - \kappa^{-1})}{(1 - B\kappa^{-1})^2} \ln\left(\frac{\kappa}{B}\right) - \frac{B - 1}{1 - B\kappa^{-1}} + \frac{B + 1}{2}\right]$	(8)	
	$B = C_f \left(\frac{1-\varepsilon}{\varepsilon}\right)^{1.11}; C_f = 1.25 \text{ (sphere)}, 2.5 \text{ (cylinder)} \text{ or } 2.5 \left(1 + \frac{d_i}{d_p}\right) \text{ (rings)}$	(9)	
	$k_p = 0.21 + 0.00015T$	(10)	
	$\mathbf{P}e_h^0 = \frac{u\rho_f c_{p,f} d_p^v}{k_f} = RePr$	(11)	
	$Pe_{h,r}^{\infty} = 8\left[2 - \left(1 - \frac{2}{N}\right)^2\right]$	(12)	
Near-wall region	$Nu_w = Nu_{w0} + (1/Nu_W^* + 1/Nu_m)^{-1}$	(13)	[8]
	$Nu_{w0} = (1.3 + \frac{5}{N})(\frac{k_r^0}{k_f})$	(14)	
	$Nu_w^* = 0.3Pr^{1/3}Re^{0.75}$	(15)	
	$Nu_m = 0.054 PrRe$	(16)	
Gas phase and solid	$h_s d_p^v k_f = 2 + 1.1 P r^{1/3} R e^{0.6}$	(17)	[9]
catalyst			

Table S5. Radial heat transfer coefficients in the methanol reactor

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:

$$h_{HX1} = 517.9 \times \left(\frac{F}{30368.1}\right)^{0.655} \tag{18}$$

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

Nomenclature

Bi $C_{p,f}$	(-) J kg ⁻¹ K ⁻¹	Tube Bilot number, $h_w R_t/k_{e,r}$ Heat capacity of the gas phase
d^{v}	m	Volume equivalent particle diameter of the catalyst pellet for a
u_p	111	Volume-equivalent particle drameter of the eataryst penet, for a $3h^{\frac{1}{2}}$
		cylinder $d_p^{\nu} = d(\frac{d}{2d})^3$
d_p^s	m	Diameter of sphere with equal specific surface area, for a cylinder
		$d_p^s = 3dh/(d+2h)$
h	m	Height of cylinder pellet
hloss	$W m^{-2}K^{-1}$	Heat transfer coefficient between reactor wall and environment
h_s	$W m^{-2}K^{-1}$	Heat transfer coefficient between the gas phase and catalyst
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^0	W/m·K	Effective stagnant thermal conductivity
k_w	W/m·K	Thermal conductivity of reactor wall
k _{e,r}	W/m·K	Effective radial thermal conductivity
K	(-)	Equilibrium constant
Ν	(-)	The ratio of the tube diameter and volume-equivalent diameter, $N=2R_t/d_p^v$.
Nu_w	(-)	Wall Nusselt number $(h_w d_p^v / k_f)$
Nu_{w0}	(-)	Wall Nusselt number at zero flow rate $(h_{w0}d_p^v/k_f)$
Nu_W^*	(-)	Wall film Nusselt number $(h_w^* d_p^v / k_f)$
Num	(-)	Fluid mechanical Nusselt number $(h_{wm}d_p^{\nu}/k_f)$
Р	Pa	Pressure
Pe_h^0	(-)	Fluid Peclet number for heat transfer $(u\rho_f c_{n,f} d_n^v/k_f)$
$Pe_{h,r}^{\infty}$	(-)	Peclet radial heat transfer for fully developed turbulent flow
Pr	(-)	Prandtl number $(\mu_f c_{p,f}/k_f)$
r	$mol/(kg_{cat} \cdot s)$	Reaction rate
R_t	m	Radius of reactor tube
Re	(-)	Reynolds number $(u\rho_f d_p^v/\mu_f)$
Re_p^s	(-)	Reynolds number $(u\rho_f d_p^s/\mu_f)$
T	К	Temperature

и	m/s	Superficial gas velocity
U_t	$W m^{-2}K^{-1}$	Overall heat transfer coefficient
Graak lattars		
Sieek lellers		Thistory of accessory 11
0	III	Thickness of reactor wan
З	(-)	Porosity of catalyst bed
κ	(-)	The ratio of the thermal conductivity of the solid catalyst pellet and
		the gas fluid k_p/k_f
μ_f	kg/m s	Gas viscosity
$ ho_f$	kg/m ³	Gas density
Subscripts		
0		Stagnant
е		Effective
f		Gas phase
p		Pellet
r		Radial
t		Tube
w		Reactor wall

Reference

[1] K. Van den Bussche, G. Froment, A steady-state kinetic model for methanol synthesis and the water gas shift reaction on a commercial Cu/ZnO/Al₂O₃ catalyst. J. Cata. 161 (1996) 1–10.

[2] G. H. Graaf, P. J. J. M. Sijtsema, E. J. Stamhuis and G. E. H. Joosten. Chemical equilibria in methanol synthesis. Chem. Eng. Sci. 41(1986) 2883–2890.

[3] Leonie E. Lücking. Methanol Production from Syngas Process modelling and design utilising biomass gasification and integrating hydrogen supply, Master Thesis (2017), Delft University of Technology.

[4] Zhu J, Araya SS, Cui X, Sahlin LS, Kær SK. Modeling and Design of a Multi-Tubular Packed-Bed Reactor for Methanol Steam Reforming over a Cu/ZnO/Al2O3 Catalyst. Energies 2020;13:610. https://doi.org/10.3390/en13030610.

[5] TE Chang, RW Rousseau. Solubilities of carbon dioxide in methanol and methanol-water at high pressures: experimental data and modeling. Fluid Phase Equilibria 23 (1985) 243-258.

[6] A. G. Dixon, An improved equation for the overall heat transfer coefficient in packed beds, Chemical Engineering and Processing 35 (1996) 323–331.

[7] B. Koning. Heat and Mass transport in tubular packed bed reactor at reacting and non-reacting conditions, PhD Thesis (2002), University of Twente.

[8] A. G. Dixon. Fixed Bed Catalytic Reactor Modelling—the Radial Heat Transfer Problem. Can. J. Chem. Eng. 90 (3) (2012) 507–527.

[9] N. Wakao, S. Kaguei, T. Funazkri. Effect of fluid dispersion coefficients on particle-to-fluid heat transfer coefficients in packed beds: Correlation of nusselt numbers. Chem Eng Sci 34(3) (1979) 325-336.