Supplementary Materials: Optimisation of the Autothermal NH_3 Production Process for Power-to-Ammonia

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Supporting Information

S.1. Catalyst Bed

For solving the equations 1 and 2, heat of reaction (equation S1), specific heat capacities (equations S2 to S4), rate of reaction (equation S5) and supporting equations of activity (equation S6), fugacity coefficients (equations S7 to S9), mole fraction of components (equations S10 to S13), reaction rate constant (equation S14) and equilibrium constant (equations S15 and S16) are given in table S1. Furthermore, supportive constants and parameters are given in table S2 and S3.

Table S1. Supporting equations [1] for catalyst bed model

Heat of Reaction [2]

$$\Delta H = 4.184\,[-(0.54526 + 846.609\,T^{-1} + 459.734 \times 10^{6}\,T^{-3})P \\ -5.34685\,T - 0.2525 \times 10^{-3}\,T^{2} + 1.69197 \times 10^{-6}\,T^{3} - 9157.09] \tag{S1}$$

Specific Heat Capacity

For real gases $c \in \{N_2, H_2, Ar\}$, C_{p_c} (kJ kmol^{-1} K^{-1}) is calculated by equation S2 (valid for temperature range 500 to 900 K), for constants in table S2 [3]:

$$C_{p_c} = 4.184\,(A_c + B_c\,T + C_c\,T^2 + D_c\,T^3) \tag{S2}$$

Specific heat capacity of NH_3, $C_{p_{NH_3}}$ (kJ kmol^{-1} K^{-1}) is calculated by equation S3 [4] , valid between 500 to 900 K:

$$C_{p_{NH_3}} = 4.184\,\{6.5846 - 0.61251 \times 10^{-2}\,T + 0.23663 \times 10^{-5}\,T^2 - 1.5981 \times 10^{-9}\,T^3 + [96.1678 \\ -0.067571\,P + (-0.2225 + 1.6847 \times 10^{-4}\,P)\,T + (1.289 \times 10^{-4} - 1.0095 \times 10^{-7}\,P)\,T^2]\} \tag{S3}$$

The gas mixture for $c \in \{N_2, H_2, Ar, NH_3\}$ specific heat capacity, $C_{p_{mix}}$ (kJ kg^{-1} K^{-1}) defined as follows:

$$C_{p_{mix}} = (\sum_{c=1}^{n} y_c C_{p_c})\,/\,M_{mix} \tag{S4}$$

Rate of Reaction

The reaction rate is calculated by modified Tempkin equation [5]:

$$R_{NH_3} = k_2\left(K^2 a_{N_2}\left(\frac{{a_{H_2}}^3}{{a_{NH_3}}^2}\right)^{\alpha} - \left(\frac{{a_{NH_3}}^2}{{a_{H_2}}^3}\right)^{1-\alpha}\right) \tag{S5}$$

Activity

Activity of component a_c, where $c \in \{N_2, H_2, NH_3\}$ is expressed as follows:

$$a_c = \frac{f_c}{{f_c}^*} = y_c {f_c}^o = y_c \phi_c P \tag{S6}$$

The fugacity coefficients ϕ_c for $c \in \{N_2$ [6,7], H_2 [6,8], NH_3 [6,7]$\}$ are given as follows:

$$\phi_{N_2} = 0.93431737 + 0.3101804 \times 10^{-3}\, T + 0.295895 \times 10^{-3}\, P - 0.270729 \times 10^{-6}\, T^2 + 0.4775207 \times 10^{-6}\, P^2 \quad (S7)$$

$$\phi_{H_2} = \exp\{e^{(-3.8402\, T^{0.125}+0.541)}\, P - e^{(-0.1263\, T^{0.5}-15.980)}\, P^2 + 300\, [e^{(-0.011901\, T-5.941)}]\, (e^{-P/300} - 1)\} \quad (S8)$$

$$\phi_{NH_3} = 0.1438996 + 0.2028538 \times 10^{-2}\, T - 0.4487672 \times 10^{-3}\, P - 0.1142945 \times 10^{-5} \times T^2 + 0.2761216 \times 10^{-6} P^2 \quad (S9)$$

Where, mole fractions of component y_c, where $c \in \{N_2, H_2, NH_3, Ar\}$ is expressed in terms of reactants conversion X_r, for $r \in \{N_2, H_2\}$ as follows:

$$y_{N_2} = \frac{y_{N_2,\,in} - \frac{\nu_{N_2}}{\nu_r} X_r y_{r_{in}}}{1 - \frac{\nu_{NH_3}}{\nu_r} X_r y_{r_{in}}} \quad (S10)$$

$$y_{H_2} = \frac{y_{H_2,\,in} - \frac{\nu_{H_2}}{\nu_r} X_r y_{r_{in}}}{1 - \frac{\nu_{NH_3}}{\nu_r} X_r y_{r_{in}}} \quad (S11)$$

$$y_{NH_3} = \frac{y_{NH_3,\,in} + \frac{\nu_{NH_3}}{\nu_r} X_r y_{r_{in}}}{1 - \frac{\nu_{NH_3}}{\nu_r} X_r y_{r_{in}}} \quad (S12)$$

$$y_{Ar} = \frac{y_{Ar_{in}}}{1 - \frac{\nu_{NH_3}}{\nu_r} X_r y_{r_{in}}} \quad (S13)$$

Reaction Rate Constant
Reaction rate constants are expressed by Arrhenius equation with the values given in table S3:

$$k = k_0\, e^{-E_a/RT} \quad (S14)$$

Equilibrium Constant
The equilibrium constant is given by the Gillespie and Beattie [9] equation:

$$\log K = -2.691122\, \log T - 5.519265 \times 10^{-5} T + 1.848863 \times 10^{-7} T^2 + \frac{2001.6}{T} + 2.67899 \quad (S15)$$

At equilibrium, rate of reaction in forward and reverse direction will be equal, i.e. $R_{NH_3} = 0$, and at equilibrium for $\alpha = 0.5$, equation S5 reduces to:

$$K^2 = \frac{a^2{}_{NH_3}}{a_{N_2} a^3{}_{H_2}} \quad (S16)$$

where, for equilibrium (EQ) line, equation S15 and S16 are solved simultaneously for equilibrium temperature T_{EQ} and conversion X_{EQ}.

The Coefficients of specific heat capacity (equation S2) for $c \in \{N_2, H_2, Ar\}$ are given as follows:

Table S2. Coefficients of Cp_c polynomial for equation S2 [3]

Component	A	$B \times 10^{-2}$	$C \times 10^{-5}$	$D \times 10^{-9}$
N_2	6.903	−0.03753	0.1930	−0.6861
H_2	6.952	−0.04576	0.09563	−0.2079
Ar	4.9675			

The catalyst (Fe_3O_4) properties are given as follows:

Table S3. Catalyst properties [5]

α	k_0 / kmol m^{-3}	E_a / kJ kmol^{-1}
0.5	8.8490×10^{14}	1.7056×10^{5}

S.2. Heat Exchanger

The supporting equations [1,10] in table S4 evaluate heat capacity ratios C^*, number of transfer units NTU and heat exchanger surface area A_{HE}. With respect to 50 W m^{-2} K^{-1} overall heat transfer coefficient U [11] and designed effectiveness ε, C^*, NTU and A_{HE} of shell and tube heat exchangers for reactor systems (2Q, HQ, QH, 2H (2H-2 and 2H-3)) are given in table S5. The effectiveness of heat exchangers is calculated for the optimum design performance of all reactor systems by either equation 5a or 5b. Therein, equation 5a is applied to all three heat exchangers of reactor system 2H and heat exchanger 2 of reactor system HQ, and equation 5b is applied to both heat exchangers of reactor system QH and heat exchanger 1 of reactor systems 2Q and HQ.

Table S4. Supporting equations [1,10] for shell and tube heat exchanger

$$C^* = \frac{(\dot{m}C_p)_{\mathrm{MIN}}}{(\dot{m}C_p)_{\mathrm{MAX}}} \tag{S17}$$

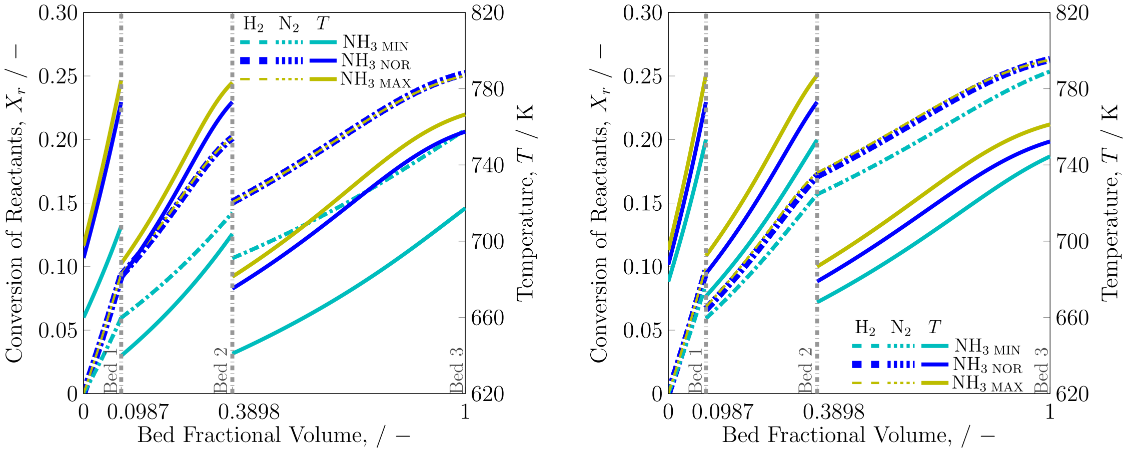
$$\varepsilon = \frac{2}{1 + C^* + \sqrt{1 + C^{*2}}\,\dfrac{1 + \exp[-\mathrm{NTU}\sqrt{1 + C^{*2}}]}{1 - \exp[-\mathrm{NTU}\sqrt{1 + C^{*2}}]}} \tag{S18}$$

$$\mathrm{NTU} = \frac{UA_{HE}}{(\dot{m}C_p)_{\mathrm{MIN}}} \tag{S19}$$

Table S5. Data of heat exchangers used in reactor systems

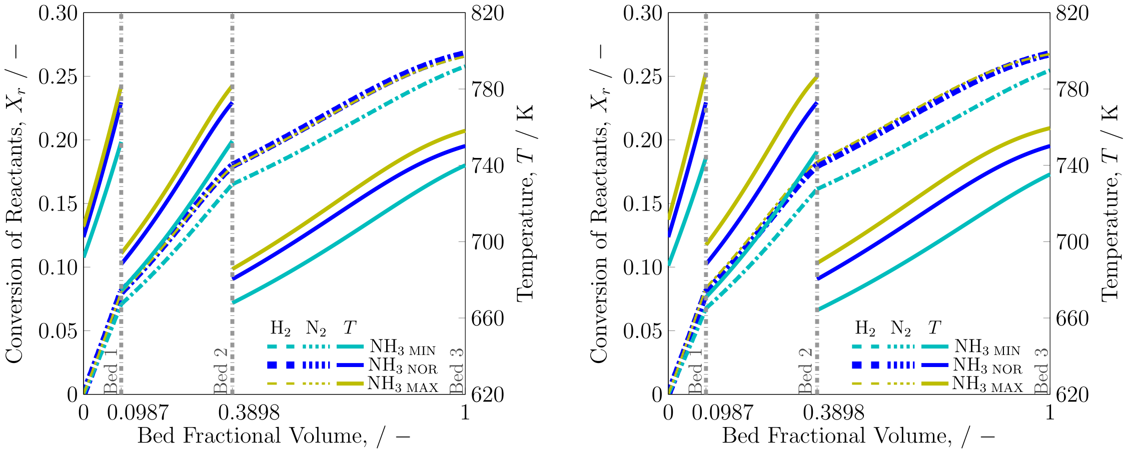
RS	HE	ε / –	C^* / –	NTU / –	A_{HE} / m^2
2Q [1]	HE 1	0.6329	0.5734	1.5984	7.0627
HQ	HE 1	0.5675	0.8758	1.6800	11.2663
	HE 2	0.3680	0.9154	0.5991	4.1103
QH	HE 1	0.4054	0.8182	0.6832	4.1813
	HE 3	0.4821	0.7810	0.9432	5.9077
2H-2	HE 1	0.3398	0.8366	0.5121	4.5437
	HE 2	0.3393	0.9198	0.5244	4.8124
	HE 3	0.5391	0.8888	1.4032	12.5880
2H-3	HE 1	0.3398	0.8366	0.5121	4.5437
	HE 2	0.5007	0.9413	1.1780	10.5640
	HE 3	0.3708	0.8692	0.5967	5.4741

20 *S.3. Design & Off-Design Performance*



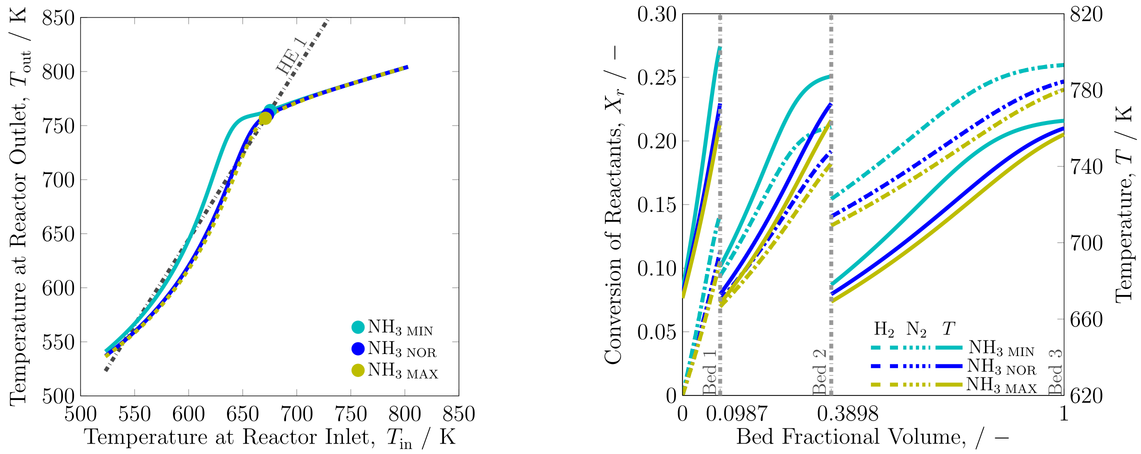
(a) **(b)**

Figure S1. Reactants conversion and temperature profiles for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying argon gas composition in (a) reactor system HQ and (b) reactor system QH.



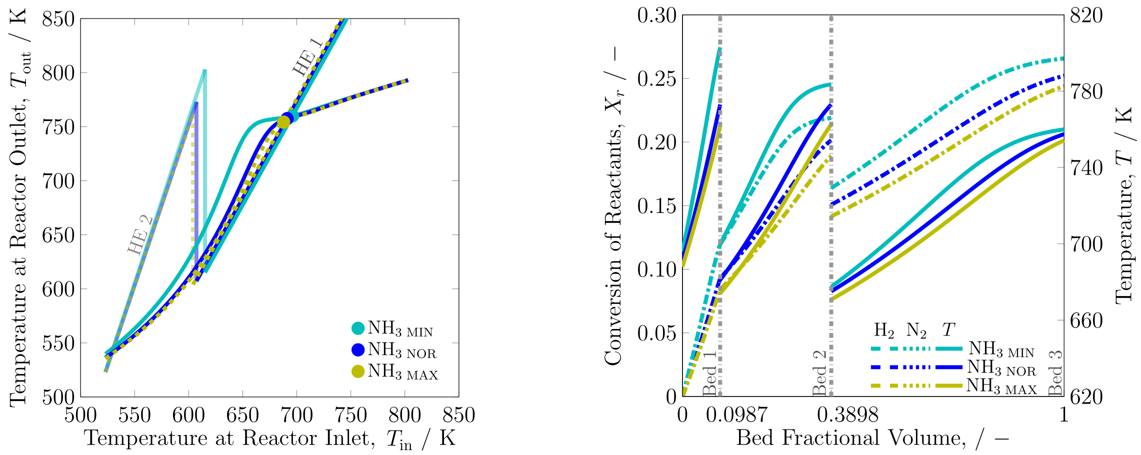
(a) **(b)**

Figure S2. Reactants conversion and temperature profiles for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying argon gas composition in (a) reactor system 2H-2 and (b) reactor system 2H-3.



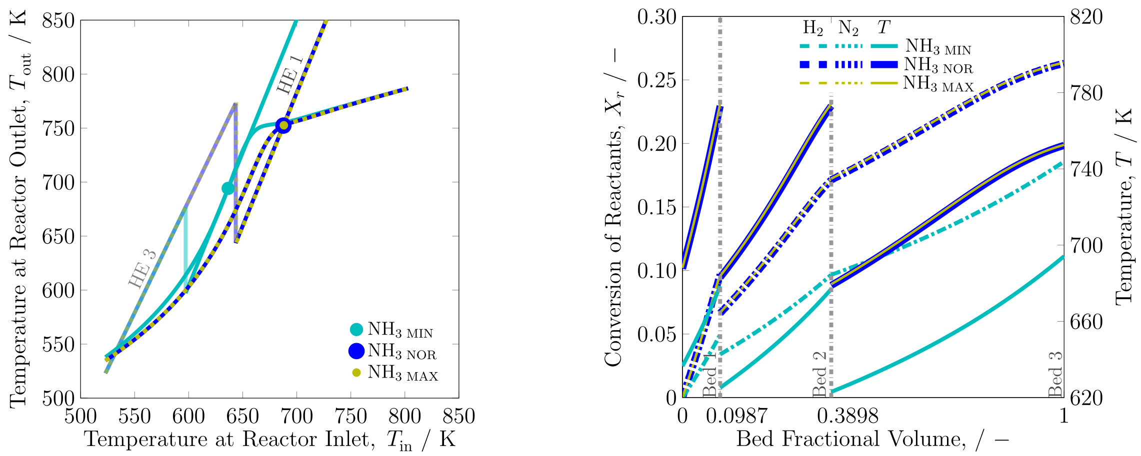
(a) (b)

Figure S3. Direct cooling by quenching reactor system (2Q) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying process feed flow rate: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



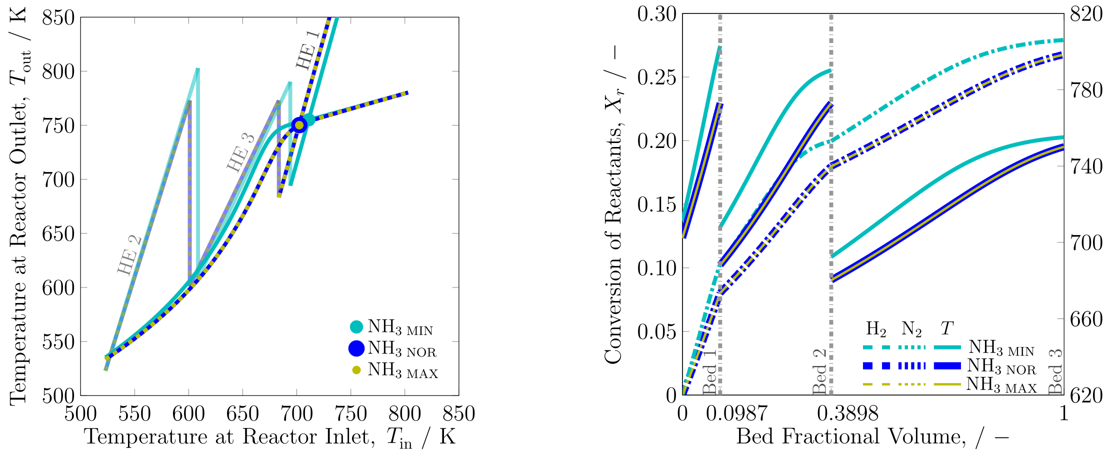
(a) (b)

Figure S4. Combination of indirect and direct cooling reactor system (HQ) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying process feed flow rate: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



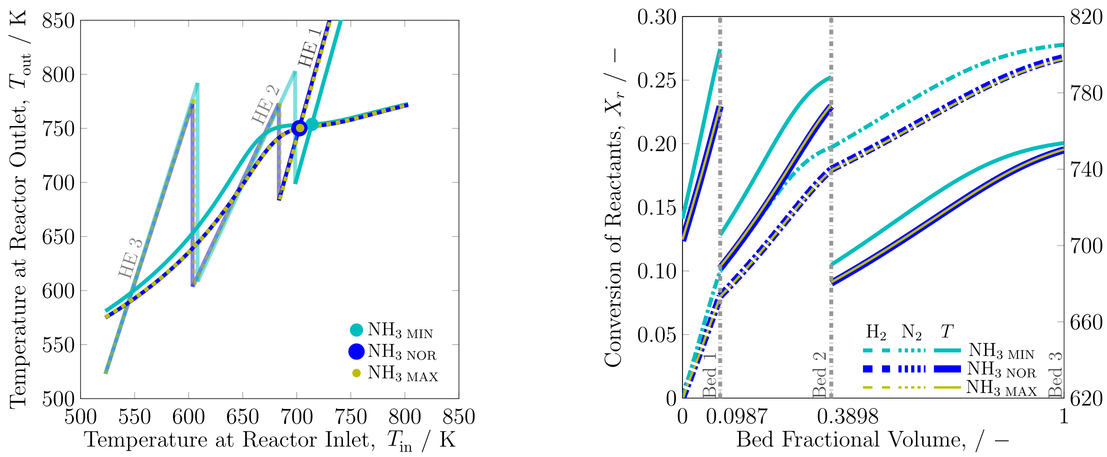
(a) (b)

Figure S5. Combination of direct and indirect cooling reactor system (QH) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying process feed flow rate: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



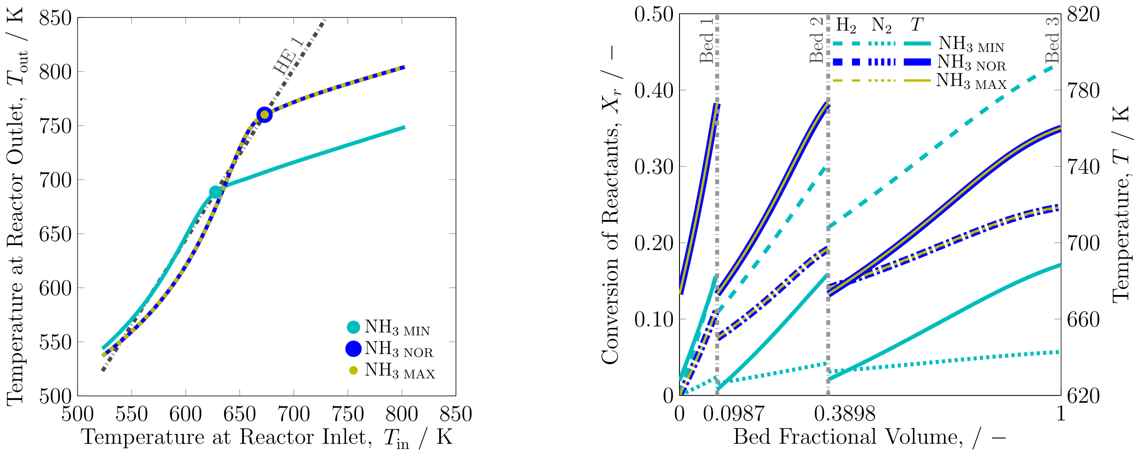
(a) **(b)**

Figure S6. Indirect cooling by inter-stage heat exchangers (with process feed exchanging heat first in HE 2) reactor system (2H-2) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying process feed flow rate: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



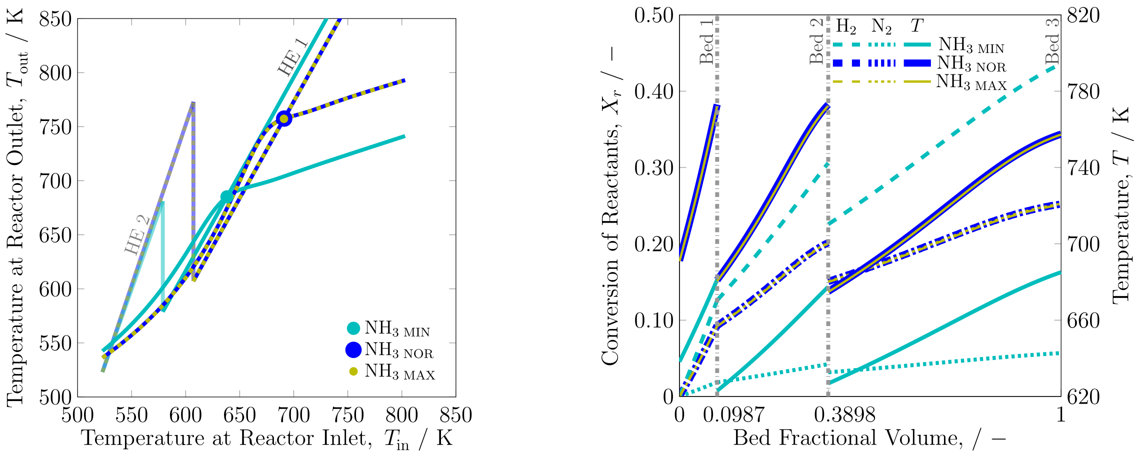
(a) **(b)**

Figure S7. Indirect cooling by inter-stage heat exchangers (with process feed exchanging heat first in HE 3) reactor system (2H-3) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying process feed flow rate: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



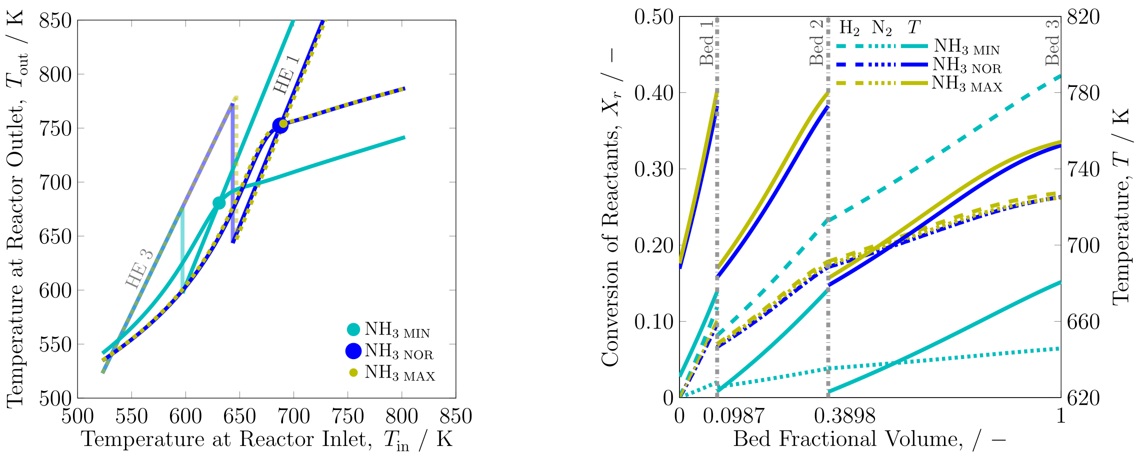
(a) (b)

Figure S8. Direct cooling by quenching reactor system (2Q) for normal(NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying reactants' ratio: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



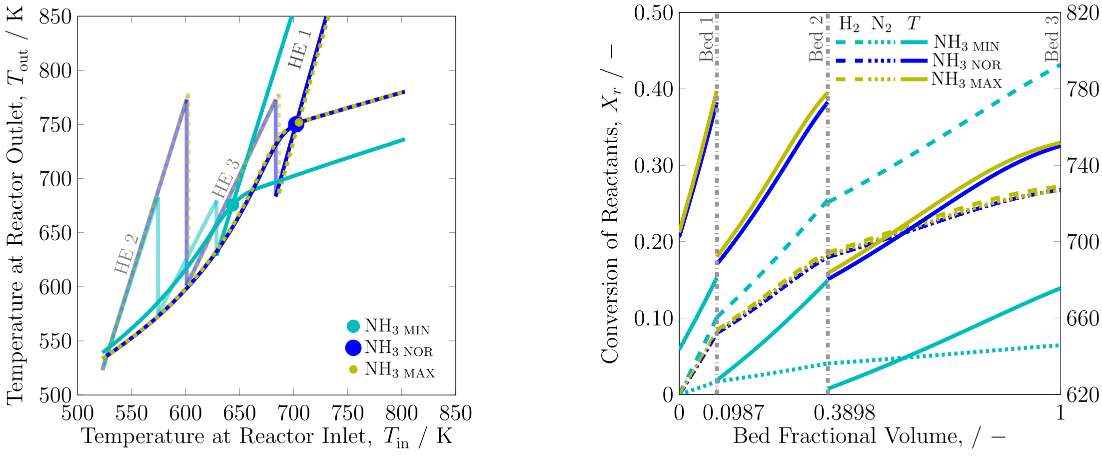
(a) (b)

Figure S9. Combination of indirect and direct cooling reactor system (HQ) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying reactants' ratio (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



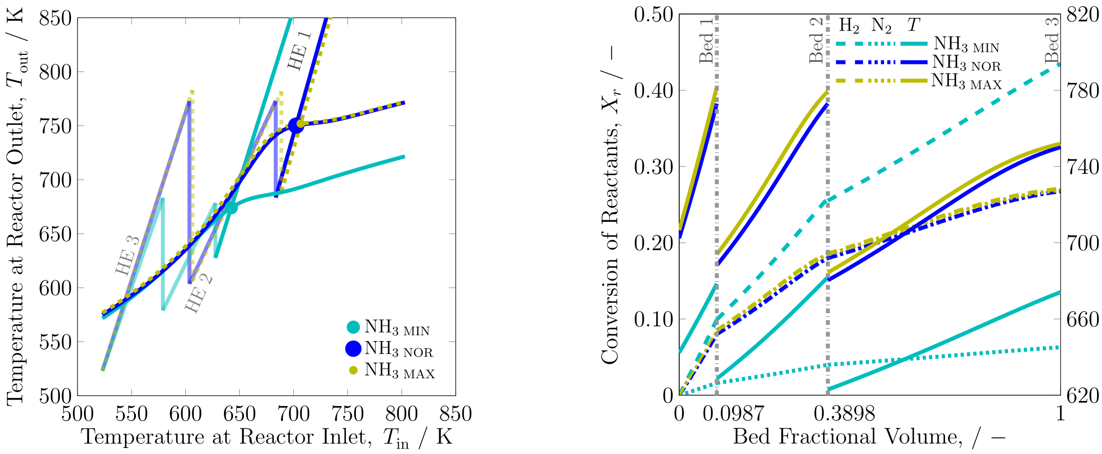
(a) (b)

Figure S10. Combination of direct and indirect cooling reactor system (QH) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying reactants' ratio: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



(a) **(b)**

Figure S11. Indirect cooling by inter-stage heat exchangers (with process feed exchanging heat first in HE 2) reactor system (2H-2) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying reactants' ratio: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.



(a) **(b)**

Figure S12. Indirect cooling by inter-stage heat exchangers (with process feed exchanging heat first in HE 3) reactor system (2H-3) for normal (NOR), minimum (MIN) and maximum (MAX) NH_3 production by varying reactants' ratio: (a) steady-state characteristics and (b) reactants conversion and temperature profiles.

Nomenclature

List of Symbols

A	Constant for heat capacity / -
a	Activity / -
A_{HE}	Surface area for heat transfer / m^2
B	Constant for heat capacity / -
C	Constant for heat capacity / -
C^*	Heat capacity rate ratio / -
C_p	Specific heat capacity / kJ kg^{-1} K^{-1}
D	Constant for heat capacity / -
E_a	Activation energy / kJ $kmol^{-1}$
f	Fugacity / -
ΔH	Heat of reaction / kJ $kmol^{-1}$
K	Equilibrium constant / bar^{-2}
k	Reaction rate constant / kmol m^{-3} h^{-1}
k_0	Frequency factor / kmol m^{-3} h^{-1}
M	Molecular weight / kg $kmol^{-1}$
$\dot{m}$	Mass flow rate / kg h^{-1}
NTU	Number of transfer units / -
P	Pressure / bar
R_{NH3}	Rate of reaction / kmol m^{-3} h^{-1}
U	Overall heat transfer coefficient / W m^{-2} K^{-1}
y	Mole fraction / -
T	Temperature / K
X	Conversion of reactant / -
R	Universal gas constant / 8.314 kJ $kmol^{-1}$ K^{-1}

Greek Symbols

α	Constant / 0.5
ϕ	Fugacity coefficient / -
ε	Heat exchanger effectiveness / -
ν	Stoichiometric coefficient / -

Superscripts

$*$	At a particular arbitrarily chosen standard state
o	At temperature and pressure of system

Subscripts

2	Reverse reaction
c	Component
r	Reactant
in	Inlet
MAX	Maximum
MIN	Minimum
mix	Gas mixture
NOR	Normal

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