Process intensification Course 2006 – 2007, DCT - TU Delft

Exercise to analyse trade-off between size and entropy production rate in a process unit.

By Prof. Johan Grievink. D.d. 26/Nov/2006

Analysis of trade-off between volume size and entropy production rate
Impact of intensification on entropy production rate and exergy losses

Example:
Isothermal, single chemical reaction in a well- mixed continuous flow reactor
Two different situations are considered (due to new catalyst with a higher activity <= intensification)

System:
　　　　Feed S into product P in CSTR by means of one reversible reaction: S => P.
　　　　Production rate of p is fixed

Production target and operational policy for reactor:
R_{target}　= F [p]
R_{target}　= r .V
R_{target}　= F {$[s]_{in}$ – [s] }

F　　　　molar flow rate through the reactor
[p]　　　molar fraction of product species P
[s]　　　molar fraction of reactant species S
r　　　　molar reaction rate per unit volume [$kmol/(m^3 s)$]
R_{target}　molar production rate of product P to be formed in reactor [kmol P/s]
V　　　　reactor volume

Operational policy:
　　1)　　R_{target}　　　kept constant
　　2)　　$[s]_{in}$　　　kept constant

F, [p] and [s] may be varied in order to optimise the design.

Relation driving force affinity (A) and reaction rate r:
Rate of the reversible reaction:

$r = k_f [s]^{vs} – k_b .[p]^{vp}$　with　　　　　　　　K　　= k_f / k_b　　= exp (- ΔG^0_r /RT)

Free energy change in reaction:　　　　ΔG^0_r　= $\sum_i v_i. \mu^0_i$ (T)
ν　　　stoichiometric coefficient
μ　　　chemical potential of species i:　　$\mu(T, x) = \mu^0_i(T) + RT. \ln[x_i]$
x　　　molar fraction of species i

Introduce affinity of reaction: $\qquad A \quad = \; - \Delta G_r \,(T,x) \; = - \sum_i \nu_i . \, \mu_i \,(T,x)$

Note that if any of the product species is not present, $[x_i] = 0$, the affinity goes to infinity (the reverse reaction does not run. The reaction is in equilibrium when $A = 0$, corresponding with the familiar equilibrium condition: $K = [p]_e^{\nu p} / [s]_e^{\nu s}$
So, A can vary between zero and infinity (when no product P is present).

Re-arrange reaction rate in terms of affinity:
$r \qquad = k_f \,[s]^{\nu s} \{\; 1 - .[p]^{\nu p} . \, [s]^{-\nu s} / K \; \} \qquad = \qquad k_f \,[s]^{\nu s} . \{1 - \exp(-A/RT) \}$
$\mathbf{r} \qquad \mathbf{= r_f \{1 - \exp(-A/RT) \}} \qquad\qquad \text{with}$
$r_f \qquad = \; k_f \,[s]^{\nu s} \qquad\qquad\qquad\qquad \text{(maximum forward rate)}$
The maximum forward rate r_f is determined by catalyst effectiveness (k_f) only.

There is a consistent link with Non-Equilibrium Thermodynamics:
For small affinity A the reaction rate is *linear* with affinity:
$r \qquad \sim r_f . \, A / (R.T) \qquad \text{with } r=0 \text{ for } A=o$

Computation of reactor volume
Fix the production rate R_{target} and the driving force $A([s])$ by means of the exit concentration of reactant s. Then, one can compute: Flow F, reaction rate $r(A)$, and the required volume

Make a plot how the volume varies as function of the affinity:
The plot is a hyperbolic one with two asymptotes:
        Vertical asymptote: for affinity to zero   ➔ Volume goes to infinity
        Horizontal asymptote: for large affinity   => Volume goes to a minimum.

Here is room to draw the plot { V vs A vs σ_{Siir} }

Entropy production rate [σ_{iir} in kJ/ (K.s)] :

$$T * \sigma_{Siir} = V * r (A) *A$$

σ_{Siir} Total entropy production rate (kW/K)
T   Reactor temperature

Note that this expression can be rewritten as:

$$T * \sigma_{Siir} = R_{target} *A$$

The plot the entropy production rate as function of the affinity A is a linear one.

Trade-off:
Large affinity is good for smaller volume (low investment) but worse for entropy production rate.

Note that improving the catalyst and so increasing the reaction rate coefficient does lead to smaller volume. As long as the same the same amount of product is produced the entropy production rate does NOT change. Also, the trade-off pattern does not change.

The gain obtained by means of the catalytic intensification of the reaction rate can be allocated in a distributed way. It is possible to reduce size of the reactor to the fullest extend, keeping the driving at the same level as for the conventional case. But one can also decide not use the full extent of size reduction and to choose for a smaller size reduction while reducing the driving force and the associated entropy production rate as well.

Part B: This case can be extended to cover the heat removal system.

Extended entropy production rate [σ_{iir} in kW/ K] :

$$T * \sigma_{Siir} = V * r (A) *A + X. J_q. (T-T_c)$$

X   Heat exchange surface
J_q Heat transfer rate per unit area
T   Reactor temperature
T_c Coolant temperature

Heat flux equation as a function of the driving force :

$$J_q = \lambda . (T-T_c)$$

λ heat transfer / conductivity coefficient

The energy balance is set up to keep constant reactor temperature.

I.e., the heat removal rate is coupled with production rate.

X. J_q $= \Delta H_r . r(A). V$

Using the standard production rate specification: $r(A) . V = R_{target}$,
one gets a simple entropy production function, linear in both driving forces.

$T * \sigma_{Siir} = R_{target} . \{A + \Delta H_r . (T-T_c)\}$

Conclusion: entropy production rate is proportional with driving forces

Small temperature difference is beneficial for entropy production but leads to larger area X because of smaller heat flux J_q.

Make a plot of heat exchange area X versus the driving force, ΔT. The plot can also show the linear relationship of the entropy production rate with the driving force for heat transfer.

Plot $\{X$ vs ΔT vs $\sigma_{Siir}\}$

Conclusion:
This example shows the potential reduction of total volume and/or area obtained by PI can be deliberately given away to reduce driving forces and to achieve a lower entropy production rate in the process, enhancing economy and ecology at the same time.