Optimization of chemical batch reactors using temperature control

Jérémy Rouot

EPF, France

joint work with B. Bonnard (INRIA & UBFC)

Chemical Networks with mass action kinetics

Graph Model :

Species $\{X_1, \ldots, X_m\}$.

Notations : $\mathscr{R}$ is the set of reactions of the form :

$$\sum_{i=1}^{m} \alpha_i X_i \longrightarrow \sum_{i=1}^{m} \beta_i X_i$$

α_i, β_i are stochiometric coefficients.

Feinberg-Horn-Jackson graph

- Vertices : $\mathbf{y} = (\alpha_1, \ldots, \alpha_m)^\top$, $\mathbf{y}' = (\beta_1, \ldots, \beta_m)^\top$
- Orientation : $\mathbf{y} \to \mathbf{y}'$

$$\begin{tikzcd} A \arrow[r, shift left] & B \arrow[l, shift left] \arrow[r] & C \arrow[ll, bend left] \end{tikzcd} \tag{1}$$

Rate dynamics $\mathbf{y} \to \mathbf{y}'$ (Mass kinetics)

$$K(\mathbf{y} \to \mathbf{y}') = k(T)\, c^{\mathbf{y}}$$

- $k(T) = A \exp(-\frac{E}{RT})$: Arrhenius law
  E, A parameters, T temperature and R is the gas constant
- $c = (\mathbf{c_1}, \ldots, c_m)^\intercal$
  c_i : concentrations of the species X_i with

$$c^{\mathbf{y}} = \mathbf{c_1}^{\alpha_1} \ldots c_m^{\alpha_m}$$

$\Rightarrow K(\mathbf{y} \to \mathbf{y}')$ **depends only on** $\mathbf{y}$.

Dynamics for the network

$$\dot{\mathbf{c}}(\mathbf{t}) = F(\mathbf{c}(\mathbf{t}), T) = \sum_{\mathbf{y}\to\mathbf{y}'\in\mathscr{R}} K(\mathbf{y}\to\mathbf{y}')\,(\mathbf{y}'-\mathbf{y})$$

The dynamics is defined by the graph.

More explicit representation of the dynamics.

- **Stochiometric subspace**

$$S = \mathrm{span}\left\{\mathbf{y}' - \mathbf{y},\ \mathbf{y}\to\mathbf{y}' \in \mathscr{R}\right\}$$

- **Positive class** (strict if > 0)

$$(\mathbf{c}(\mathbf{0}) + S) \cap \mathbb{R}^m_{\geq 0}$$

Lemma

The class $(\mathbf{c}(\mathbf{0}) + S) \cap \mathbb{R}^m_{>0}$ *is* **invariant** *for the dynamics.*

Notations

- **Complex matrix :** $Y = (y_1, \ldots, y_n)$ (n : number of complexes).
- **Incidence connectivity matrix :** $\boldsymbol{A = (a_{ij})_{ij}}$
  with for instance $a_{21} = k_1$ indicating a reaction with constant k_1 from the first node of the graph to the second.
- **Laplacian matrix :**

$$\tilde{A} = A - \mathrm{diag}\left(\sum_{i=1}^{n} a_{i1}, \ldots, \ldots, \sum_{i=1}^{n} a_{in}\right)$$

One has

$$\dot{\mathbf{c}}(\mathbf{t}) = f(\mathbf{c}(\mathbf{t}), T) = Y\,\tilde{A}\,c^{Y}$$

where $c^{Y} = (c^{y_1}, \ldots, c^{y_n})^{\mathsf{T}}$.

Zero deficiency theorem

Definition (Deficiency)

Feinberg and Horn-Jackson : articles in Archive Rational Mechanics
Graph concept : *deficiency :* $\boldsymbol{\delta = n - l - s}$ *where*

- n *: number of vertices*
- l *: number of connecting components*
- s *: dimension of the stochiometric subspace*

Definition

The network is **weakly reversible** *if* $\forall$ *vertices* (i, j) *such that* $\exists$ *oriented path joining* i *to* j*, there exists an oriented path joining* j *to* i*.*

Assumption $\boldsymbol{\delta = 0}$ *(Zero deficiency assumption)*

Theorem

1. *If the network is* **not weakly reversible** *then for arbitrary kinetics, the differential equation* **cannot have a positive equilibrium nor a positive periodic trajectory.**
2. *If the network is* **weakly reversible**, *there exists within each strictly positive compatibility class precisely* **one equilibrium** c^*, *this equilibrium is locally asymptotically stable with (pseudo-Helmholtz) Lyapunov function* $V(c, c^*) = \sum_i \left[c_i (\ln(c_i) - \ln(c_i^*) - 1) + c_i^* \right]$.
Moreover there is non trivial periodic orbit.

Application : Test bed cases :

case 1 : $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ $\qquad \delta = 3 - 1 - 2 = 0$: not weakly reversible

case 2 : (**McKeithan network**)

$$\begin{tikzcd} A \arrow[r, "k_1"] \arrow[r, leftarrow, bend right, "k_3"'] & B \arrow[r, "k_2"] & C \arrow[ll, bend left, "k_4"] \end{tikzcd}$$

$\delta = 3 - 1 - 2 = 0$: one single equilibirum globally asymptotically stable

Equilibrium for the McKeithan network

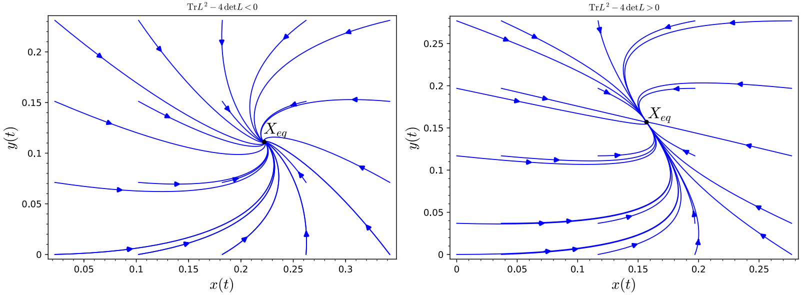


FIGURE – Phase portrait for the McKeithan model. (left) Focus ; (right) Node.

Geometric Optimal Control

Optimal Control Problem

$$\frac{\mathrm{d}\mathbf{c}}{\mathrm{d}t} = f(\mathbf{c}, T), \quad \frac{\mathrm{d}T}{\mathrm{d}t} = u, \quad u \in [u_-, u_+]$$

$u(\cdot)$ tracked the derivative of the temperature (related to the Goh Transformation).

Single input C^ω-control system :

$$\begin{cases} \dot{\mathbf{q}} = F(\mathbf{q}) + u\,G(\mathbf{q}), \quad |u| \leq 1, \\ \mathbf{q} = (\mathbf{c}, T) \in \mathbb{R}^n \end{cases}$$

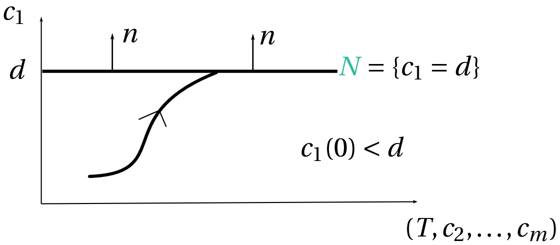
Formulation :

$$\max \mathbf{c_1}(t_f) \quad t_f : \text{ time batch duration}$$

Formulated as

$$\begin{cases} \min\ t_f, & |u| \le 1 \\ \mathbf{c_1}(t_f) = d \text{ is a desired quantity} \end{cases}$$

$\mathbf{N}$: terminal manifold of codimension 1.



Necessary optimality conditions Pontryagin Maximum Principle (1956)

Statement :

$$\begin{cases} \dot{\mathbf{q}} = F(\mathbf{q}) + u\,G(\mathbf{q}), \quad |u| \leq 1, \\ \min\ t_f, \quad \mathbf{q}(t_f) \in \mathbf{N} \end{cases}$$

- $H(\mathbf{q}, p, u) = p \cdot (F(\mathbf{q}) + u\,G(\mathbf{q})),\ p \in \mathbb{R}^n \setminus \{0\}$: adjoint vector
- H : pseudo-Hamiltonian and the maximized Hamiltonian is

$$M(\mathbf{q}, p) = \max_{|u| \leq 1} H(\mathbf{q}, p, u), \qquad \mathbf{q}, p \text{ are fixed}$$

Theorem

Assume $(q^*(\cdot), p^*(\cdot))$ *is a time minimal solution on* $[0, t_f^*]$ *then there exists* $p^*(\cdot)$ *such that a.e. on* $[0, t_f^*]$ *:*

$$\dot{q}^*(\cdot) = \frac{\partial H}{\partial p}(q^*(t), p^*(t), u^*(t)), \quad \dot{p}^*(\cdot) = -\frac{\partial H}{\partial q}(q^*(t), p^*(t), u^*(t)) \qquad (2)$$

the maximization condition is satisfied

$$H(q^*(t), p^*(t), u^*(t)) = M(q^*(t), p^*(t)).$$

Moreover

- $t \mapsto M(q^*(t), p^*(t))$ is constant and ≥ 0 and at the final time one has the *transversality condition* :

$$p^*(t_f) \perp T_{q^*(t_f)}\mathbf{N} \qquad (3)$$

Extremals are solutions of (2). BC-extremal : transversality condition (4) satisfied.

Maximization condition

- *regular :*

  $$u(t) = \mathrm{sign}\, p(t) \cdot G(\mathbf{q(t)}) \text{ a.e.}$$

  Finite number of switches : **Bang-Bang**

- *singular :*

  $$p(t) \cdot G(\mathbf{q(t)}) = 0 \quad \forall t$$

Exceptional extremals : $M = 0$.

Moreover

- $t \mapsto M(q^*(t), p^*(t))$ is **constant** and $\geq \mathbf{0}$.
- *Transversality condition* :

$$p^*(t_f) \perp T_{q^*(t_f)}\mathbf{N} \tag{4}$$

Extremals are solutions of (2). BC-extremal : transversality condition (4) satisfied.

Maximization condition

- *regular :*

$$u(t) = \operatorname{sign} p(t) \cdot G(\mathbf{q}(\mathbf{t})) \text{ a.e.}$$

  Finite number of switches : **Bang-Bang**

- *singular :*

$$p(t) \cdot G(\mathbf{q}(\mathbf{t})) = 0 \quad \forall\, t$$

Exceptional extremals : $M = 0$.

Computations of singular extremals and properties

Notation : X, Y : two vector fields on $\mathbb{R}^n$

Lie bracket :

$$[X,Y](q) = \frac{\partial X}{\partial q} Y(q) - \frac{\partial Y}{\partial q} X(q)$$

$z = (q,p)$ $H_X(z) = p \cdot X(q)$

Poisson bracket :

$$\{H_X, H_Y\}(z) = p \cdot [X,Y](q)$$

Computations $H_G(z) = p \cdot G(q) = 0$

Differentiating twice w.r.t. time gives the two equations

$$\frac{\mathrm{d}}{\mathrm{d}t} H_G(z) = \mathrm{d}H_G \cdot \dot{z} = \{H_G, H_F + u\, H_G\} = \mathbf{\{H_G, H_F\} = 0}$$

$$\mathbf{\{\{H_G, H_F\}, H_F\}(z) + u\,\{\{H_G, H_F\}, H_G\}(z) = 0}$$

Then if $\{\{H_G, H_F\}, H_G\}(z) \neq 0$ then we compute $\hat{u}$ and plug it in H to obtain the *true Hamiltonian*.

Generalized Legendre-Clebsch condition

$$\{\{H_G, H_F\}, H_F\}(z) \geq 0$$

$\Rightarrow$ necessary optimality condition (High Order Maximum Principle, Krener).

Strict Legendre-Clebsch condition

$$\{\{H_G, H_F\}, H_F\}(z) > 0$$

Classification of singular extremals

$M = H_F$: constant value

- $M = 0$: **Exceptional case**
- $M > 0$: $\{\{H_G, H_F\}, H_G\}(z) > 0$: **Hyperbolic case** (**fast**)
- $M > 0$: $\{\{H_G, H_F\}, H_G\}(z) < 0$: **Elliptic case** (**slow**)

Classification of regular extremals (Ekeland - IHES, Kupka - TAMS)

Denote :

- σ_+ : bang arc with $u = +1$
- σ_- : bang arc with $u = -1$
- σ_s : singular arc $u = u_s \in]-1, 1[$

$\sigma_1\sigma_2$ is the arc σ_1 followed by σ_2.

Switching surface :

- $\Sigma : \{p \cdot G(q) = 0\}$

$\Phi(t) = p(t) \cdot G(\mathbf{q(t)})$ is the **switching function**.

$\dot{\Phi}(t) = p(t) \cdot [G, F](\mathbf{q(t)})$

$\ddot{\Phi}(t) = p(t) \cdot \big([[G, F], F](\mathbf{q(t)}) + u(t)\,[[G, F], G](\mathbf{q(t)})\big)$

Ordinary Switching time : $t \in]0, t_f[$ such that $\Phi(t) = 0$ and $\dot{\Phi}(t) \neq 0$

Lemma

Near $z(t)$ every extremal solution projects onto $\sigma_+\sigma_-$ if $\dot{\Phi}(t) < 0$ and $\sigma_-\sigma_+$ if $\dot{\Phi}(t) > 0$

Fold case : If $\Phi(t) = \dot{\Phi}(t) = 0$ then $z(t) \in \Sigma'$

$\ddot{\Phi}_\varepsilon(z(t)) = p(t) \cdot \big([[G,F],F](\mathbf{q(t)}) + \varepsilon\, [[G,F],G](\mathbf{q(t)})\big), \quad \varepsilon = \pm 1$

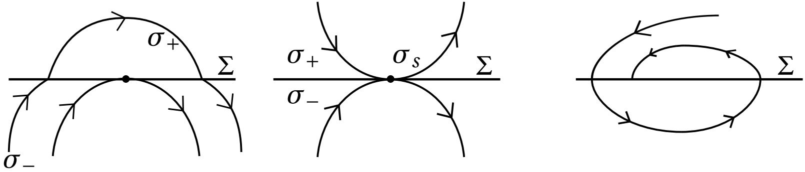
Assumption : Σ' : surface of codimension two, $\ddot{\Phi}_\varepsilon(z(t)) \neq 0$ for $\varepsilon = \pm 1$.

$z(t)$: fold point

- Case 1 : **parabolic case** $\quad \ddot{\Phi}_+(t)\ddot{\Phi}_-(t) > 0$
- Case 2 : **hyperbolic case** $\quad \ddot{\Phi}_+(t) > 0$ and $\ddot{\Phi}_-(t) < 0$
- Case 3 : **elliptic case** $\quad \ddot{\Phi}_+(t) < 0$ and $\ddot{\Phi}_-(t) > 0$

u_s is the singular control defined by

$$p(t) \cdot \big([[G,F],F](\mathbf{q(t)}) + u_s(t)\, [[G,F],G](\mathbf{q(t)})\big) = 0$$



Fold case

In the parabolic case $|u_0| > 1$ and the singular arc is not admissible.

Theorem

Kupka TAMS In the neighborhood of $z(t)$ every extremals projects onto :

- *Parabolic case : $\sigma_+\sigma_-\sigma_+$ or $\sigma_-\sigma_+\sigma_-$*
- *Hyperbolic case : $\sigma_\pm\sigma_s\sigma_\pm$*
- *Elliptic case : every extremal is of the form $\sigma_+\sigma_-\sigma_+\sigma_-\dots$ (Bang-Bang) but the number of switches is not uniformly bounded.*

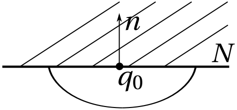
Application to Chemical Networks

Time minimal synthesis for chemical systems

$$\begin{cases} \min \ t_f \qquad |u| \leq 1 \\ \dot{\mathbf{q}} = F(\mathbf{q}) + u\, G(\mathbf{q}) \\ \mathbf{c_1}(t_f) \in \mathbf{N} = \{\mathbf{c_1} = d\} \end{cases}$$

Methods : Two steps :

1. Calculation of the time minimal syntheses near the terminal manifold
2. Bounds on the number of switches

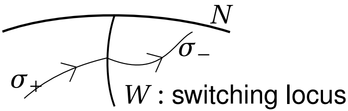


`Step 1`: Take $q_0 \in \mathbf{N}$, $z_0 = (q_0, n(q_0))$ where $n(q_0)$ is the normal vector of $\mathbf{N}$ at q_0.
Find, in a small neighborhood U of q_0, the time minimal closed loop control $u^*(q)$ to reach $\mathbf{N}$ starting from $\mathbf{q}$ in minimal time.

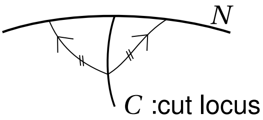
Computations : $\dot{\mathbf{q}} = F(\mathbf{q}) + u\,G(\mathbf{q}),\ q(t_f) \in \mathbf{N}$

Synthesis : $u^*(\mathbf{q})$ means

- determine the **switching locus**
  Ex. :



- determine the **splitting locus** or the **cut locus** C where two distinct optimal trajectories occur.
  Ex. :



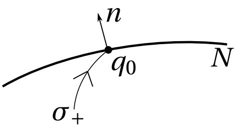
Tools : Singularity theory $\mathbf{N} = \{f^{-1}(0)\}$

- *expand* at q_0 with Taylor series : jet spaces.
- *compute :* Normal form to estimate W, C near q_0. The tools are simple but the classification is complicated.

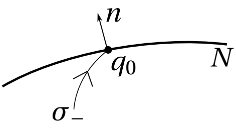
Tools : Singularity theory $\mathbf{N} = \{f^{-1}(0)\}$

- *expand* at q_0 with Taylor series : jet spaces.
- *compute :* Normal form to estimate W, C near q_0. The tools are simple but the classification is complicated.

Ex. : *Two reactions only*. $(C, T) \in \mathbb{R}^3$ $\dot{\mathbf{q}} = F + u\,G$ and $\mathbf{N} = f^{-1}(0)$.
Generic case $z_0 = (q_0, n(q_0))$.
***G* is tangent to $\mathbf{N}$** : Then $p \cdot G = 0$ so p is normal to $\mathbf{N}$.
Using classification of extremals at a point such that $p \cdot G(\mathbf{q}) = 0$, $p \cdot [G, F](\mathbf{q}) \neq 0$:



or



depending on the sign of $p \cdot [G, F](q_0)$.
... but there are more complicated situations

Define :

$\mathcal{S}$ the singular locus : $\{\mathbf{q} \in \mathbf{N};\ n \cdot [G,F](\mathbf{q}) = 0\}$

$\mathcal{E}$ the exceptional locus : $\{\mathbf{q} \in \mathbf{N};\ n \cdot F(\mathbf{q}) = 0\}$

For $\mathcal{S}$: from the classification near a fold point one has :

- *Hyperbolic* case
- **Elliptic** case
- *Parabolic* case

To make the analysis we construct a semi-normal form : $\mathbf{q} = (x,y,z)$ near 0

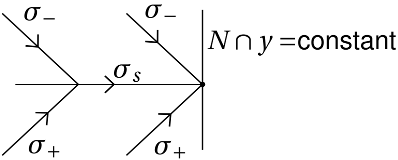
$$\begin{cases} \dot{x} = 1 + a(x)\,z^2 + 2b(x)\,yz + c(x)\,y^2 + \dots \\ \dot{y} = d(x)\,y + e(0) + \dots \\ \dot{z} = (u - \hat{u}(x)) + f(x)\,y + g(0)\,z + \dots \end{cases}$$

with

- $\mathbf{N}$ is identified to $x = 0$
- the singular arc is identified to $\sigma_s : t \to (t,0,0)$ with singular control $\hat{u}$.
- $a(0) < 0$ hyperbolic if $|\hat{u}| < 1$.
- $a(0) > 0$: elliptic if $|\hat{u}| < 1$.
- parabolic if $|\hat{u}| > 1$.

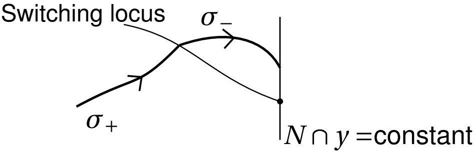
Synthesis : There exists a C^0-foliation by planes such that in each plane the synthesis is :

Case : Hyperbolic.



Note that the synthesis is $\sigma_+\sigma_s\sigma_-$ hence the temperature is not constant.

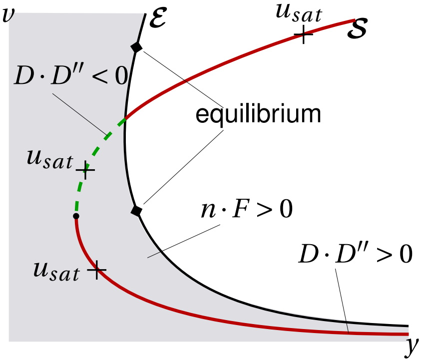
Case : Parabolic. For instance, a synthesis is



The McKeithan network

$$\begin{tikzcd} T+M \arrow[r, "k_1"] & B \arrow[r, "k_2"] \arrow[l, bend left, "k_3"] & C \arrow[ll, bend left, "k_4"] \end{tikzcd}$$

Stratification of the terminal manifold :



Bridge phenomenon

Local (planar) simplified model (inspired from the saturation problem in Magnetic Resonance Imaging) :

$$\min_{u(\cdot)} t_f \qquad \dot{q}(t) = F(q(t)) + u\, G(q(t)), \quad t \in [0, t_f]$$

where

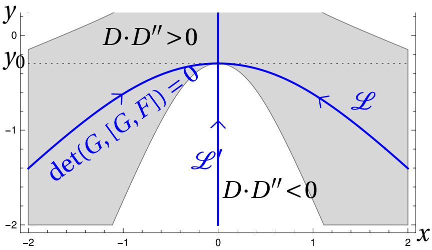
$$q = (x, y), \quad F = (1 - x^2 y)\frac{\partial}{\partial y}, \quad G = -(y-1)\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}.$$

Singular lines $\mathscr{L}$: $\det(G, [G, F])(q) = 0$

- **fast** if $D(q) \cdot D''(q) > 0$
- **slow** if $D(q) \cdot D''(q) < 0$

where $D(q) = \det(G(q), [G, F](q), [[G, F], G](q))$
and $D'(q) = \det(G(q), [G, F](q), [[G, F], F](q))$

Singular sets

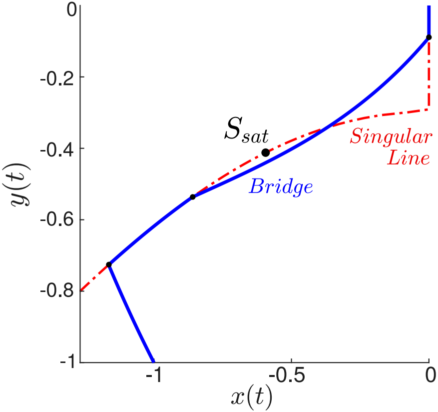


The **Singular control** along $\mathscr{L}$ is

$$u_s(q) = -\frac{D'(q)}{D(q)}$$

and is not bounded.

Trajectories : bridge



Bridge connecting two switching points of the singular set.

Conclusion

General techniques to handle complicated networks :

Geometric approach : Find coordinates to analyze the syntheses

→ applicable to general networks

Details :

T. Bakir, B. Bonnard, J. Rouot *Geometric Optimal Control Techniques to Optimize the Production of Chemical Reactors using Temperature Control* (submitted 2019)

B. Bonnard, G. Launay, M. Pelletier,
Classification générique de synthèses temps minimales avec cible de codimension un et applications,
Annales de l'I.H.P. Analyse non linéaire **14** no.1 (1997) 55–102.

Even a simple network $A \to B \to C$ can give complex optimal solution : work in progress on the *McKeithan network*.